Instability and Pattering of Thin Polymer Films
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Lecture No # 28
Intermolecular Forces between Particles and Surfaces – II

Welcome back. In the previous lecture we talk about the different types of interaction forces or intermolecular interaction forces. As we told that in this particular lecture and probably in the subsequent one, we will continue talking about these interaction forces between two charge neutral polar surfaces.

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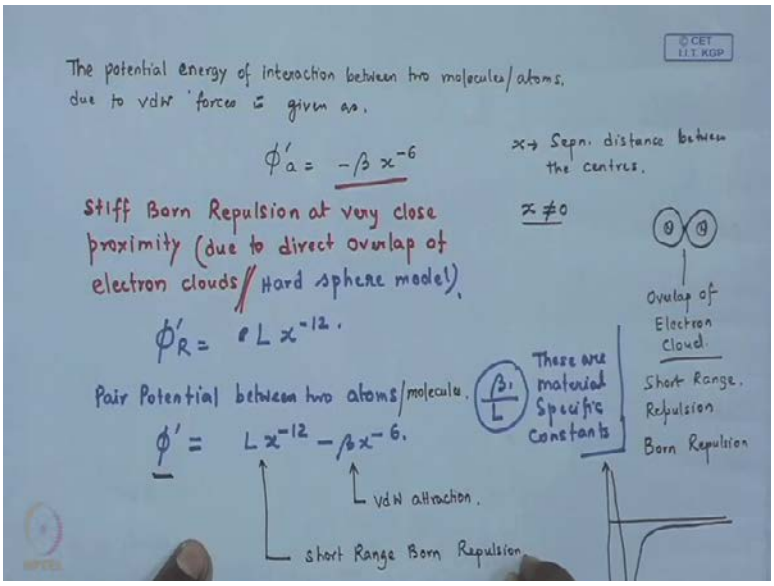

The potential energy of interaction between two molecules/atoms, due to vdW forces is given as.

$$\phi'_a = \underline{-\beta x^{-6}}$$

$x \rightarrow$ Sepn. distance between the centres.

$\underline{x \neq 0}$

Stiff Born Repulsion at very close proximity (due to direct overlap of electron clouds// Hard sphere model).

$$\phi'_R = L x^{-12}.$$

Pair Potential between two atoms/molecule.

$$\underline{\phi'} = L x^{-12} - \beta x^{-6}.$$

$\uparrow$ Short Range Born Repulsion

$\uparrow$ vdW attraction.

$\boxed{\frac{\beta,}{L}}$ These are material Specific Constants

Overlap of Electron Cloud.

Short Range. Repulsion

Born Repulsion

So, we get started with the fact that the potential energy of interaction between two molecules or atoms due to induced dipole type or the dispersion force type Vander Waals forces is given as x is sort of you can regard as the separation distance, between the centers. And therefore, one has to understand that when these two molecules or atoms come in direct contact x will not be zero, because of the fact that if there are the separation distance between the centers. So as they come closer, their electron clouds first sort of start overlapping, which gives rise to short range repulsion, which is also known as the born repulsion. And this essentially we understand this corresponds to this part of the curve. Because, have there been no repulsive component at extending to 0 following this relation the interaction would have tend to minus infinity, which does not happen.

So we also consider, stiff born repulsion at very close proximity, which is due to direct overlap of electron cloud or this is also, sometimes referred to as the so called Hard Sphere model. Anyway so the phi dash r the repulsion of the component the potential energy one can write as let us, say use the prefactor l x to the power beta. So therefore, the pair wise potential or as we will be referring as pair potential between two atoms is given as l. We use the term phi dash.

So let us, try to understand this is the pair wise potential energy of interaction. So, this is the pair wise potential energy of interaction between two molecules or atoms. And, whether the atoms or the molecules are of the all of the same species or they are of the different species. Even, if they are the same species by depending on a species to species, how the properties of individual atoms, individual molecules their molecular rate coming? That comes in through these two constant beta and l. So, these are materials specific constants. However, the generic nature of interaction remains unaltered irrespective of the exact system.

So, that is important. So, let me just again repeat. So, this is the pair wise potential energy of interaction between to atoms or molecules. And this refers to the Vander Waals interaction. And this refers to the short range born repulsion.

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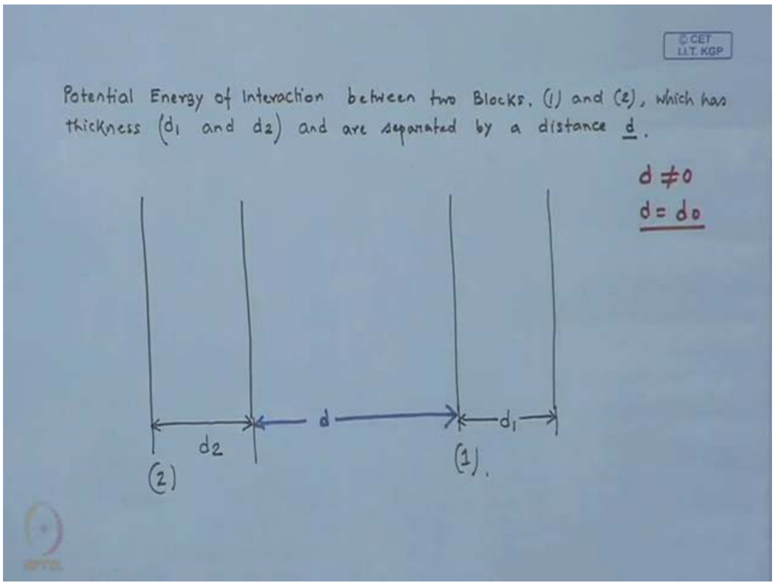

Potential Energy of Interaction between two Blocks, (1) and (2), which has thickness (d_1 and d_2) and are separated by a distance $\underline{d}$.

$d \neq 0$

$\underline{d = d_0}$

Now, we will be interested to look at the interaction, the potential energy of interaction between two blocks. Let us say, 1 and 2 which has thickness d 1 and d 2 respectively and are separated by a distance d. So, this is very, very simple. So, you have a block this is block 2; this is block 1. The thickness of this block is d 2. The thickness of this block is d 1 and these two blocks are separated by a distance d.

We are interested to find out the total potential energy of interaction between these two blocks. And for that, we will be assuming only the attractive or we will consider, only the attractive part of the Vander Waals interaction; so will be considering this. With the fact that, these two blocks the nearest they can come is when they come in contact.

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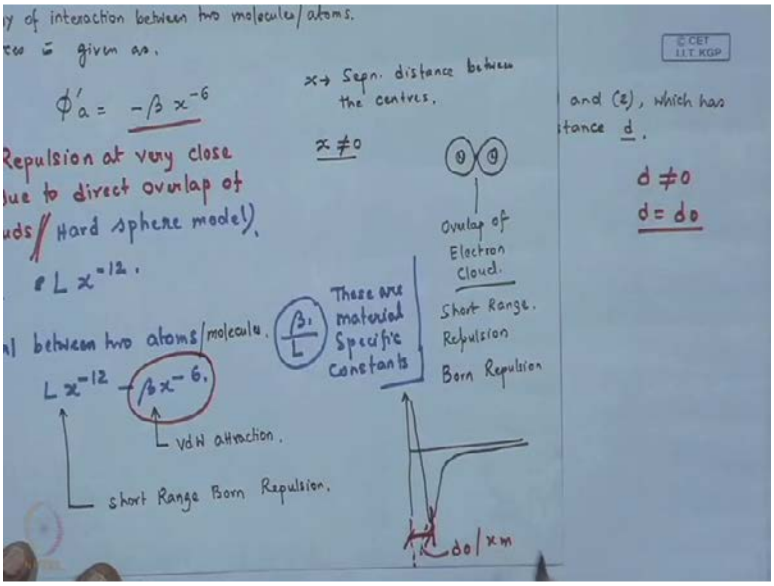

But in that case we will assume that d is not going to equal to 0, but it will be some d 0 which essentially corresponds to this point. So, this point is the minimum distance at which it can come. So, since it cannot come to distance below this let us say, d 0 or x m or whatever. Therefore, there is these two blocks can never be subject to the repulsive interaction and it is perfectly justified to consider these attractive interactions only.

So, one can also from this particular relation sorry I just forget to mention. One can from this particular relation, one can set del phi del x is equal to or del phi del x is equal to 0 to obtain a value of x m, which turns out to be equal to 2 l by beta raise to the power one sixth. So, this gives you the minimum in the potential curve and from that you can find out the minimum distance, where the two atoms or molecules can sort of come in contact.

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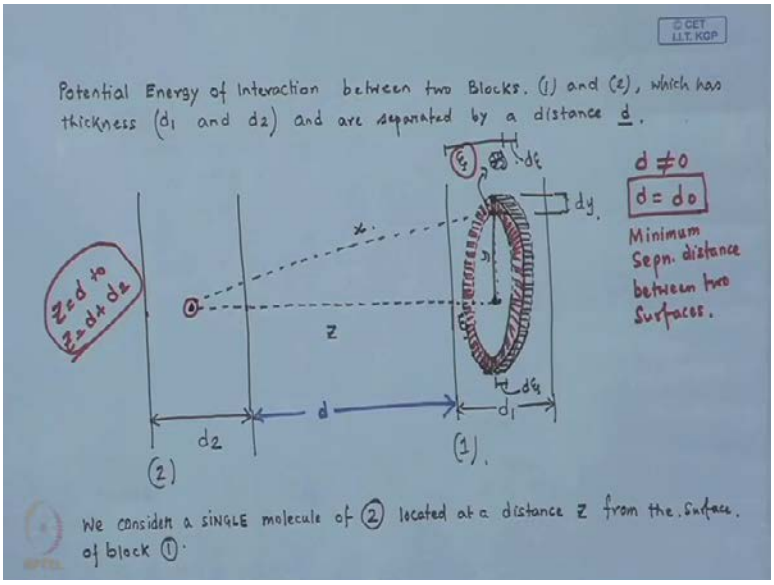

Potential Energy of Interaction between two Blocks. (1) and (2), which has thickness (d_1 and d_2) and are separated by a distance $\underline{d}$.

We consider a SINGLE molecule of ② located at a distance z from the surface of block ①.

So, there they this d zero we consider is essentially an equivalent of that between two surfaces. So, this is let us, point it out minimum separation distance between two surfaces. So, now in order to find out the interaction between these two blocks, what we do? Is we consider, a single molecule of 2 located at a distance z from the surface of block one. So let us, say this is one molecule which we consider and this distance is z.

Now, we identify a location. Let us say, which is at a distance zeta away from the top surface. It is inside the block and we consider a annular ring over here. A thin ring of width del zeta, if you follow the construction, should be able to understand it very clearly. So, this is d g, this is y. And let us say, the width of the ring is del y.

So, this is the thickness of the ring this is del z. And let us say, this is the width of the ring. Sorry for the slightly poor construction. This is del y. So, this d y, this is d z, this is a annular ring which we have considered, this is the center. The center is at a distance zeta away from the surface, the width is d zee, this is the thickness del y and this is y. We will be eventually doing a construction later, so I will just attach it. This line and this we mark as the distance as x.

Now, I will repeat. We have picked up one molecule of material 2 and we have identified a zone of this nature a annular ring. The centre of this ring is over here, which is at a distance eta from the centre from the top surface of block 1. And the point or the particle which we have identified is at a distance z from the top surface of block one. So, this particle can lie within the limits of z equal to d to z equal to d plus d 2. That is the bounds over which the particle can lie. So, this is the z equal to d the particle can be here or at any location down all the way up to here. So, this is d 2 d plus d 2. For material one we have identified an annular volume like this

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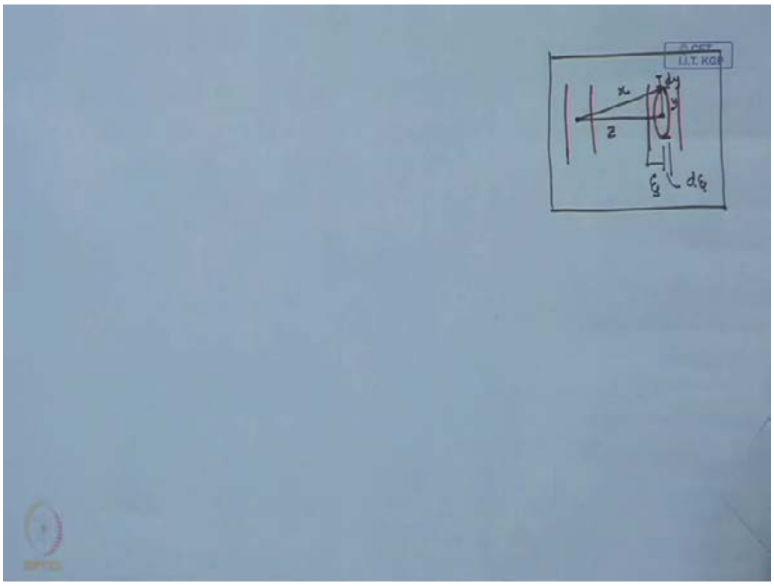

Now, the volume of this ring like thing, you have to keep this in your mind for a while. Or maybe we will have a quick smaller version of the picture over here. So, this is the location, this is z, this is eta, this is delta eta, this is y, this is delta y and this you join up to get x. So, this is the sort of the shortened version of picture which we will carry in our subsequent slides.

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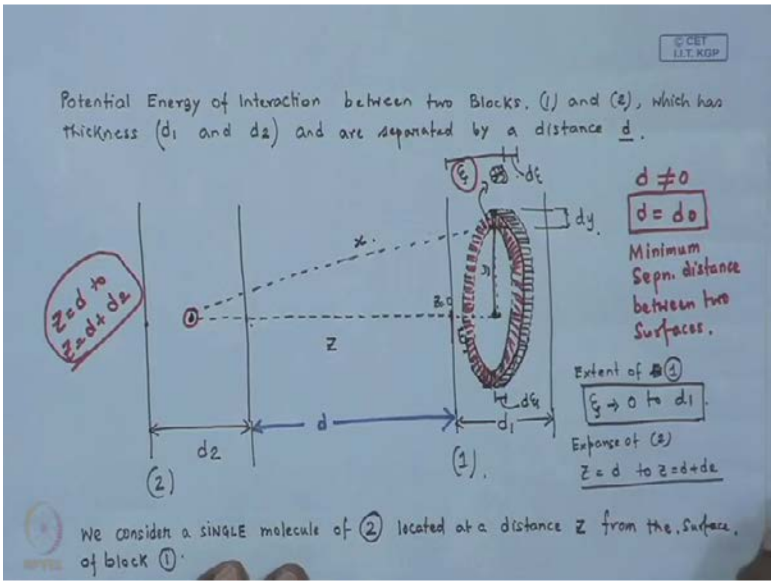

Potential Energy of Interaction between two Blocks, (1) and (2), which has thickness (d_1 and d_2) and are separated by a distance d.

We consider a SINGLE molecule of ② located at a distance z from the Surface of block ①.

When in a class room I teach these this thing, I typically have this picture in one corner of a big black board, but that much amount of leverage you have to give me in a video lecture. So, I guess this picture you once again have a detail look two blocks of width or thickness d 1 and d 2 and they are separated by at a distance d look at the origin of sets. So, here is z equal to zero and it increases in this direction. Here z is equal to d, here z is equal to d plus d 2.

And, you have considered a ring like annular a space, which is at a distance zeta inwards from the, inward in the block one. So, the limit of zeta is essentially 0 to d 1, and that is the extent of the first object; extent of the second object, block 1. The expanse of block 2 is: z equal to d to z equal to d plus d 2. And we have considered an annual a ring width is del zee, height is it is the inner radius or inner perimeter is at a distance y, outer perimeter is at distance y plus delta y. And here is a shorten are a miniaturized version of the picture.

Now, we calculate the volume of the ring element, d v which is 2 pi y del y into del zeta. You can find that out easily. So, this is (Refer Slide Time: 09:52) 2 pi y is the perimeter into del y, it talks about this face multiplied by the width del zeta. So, this is the volume.

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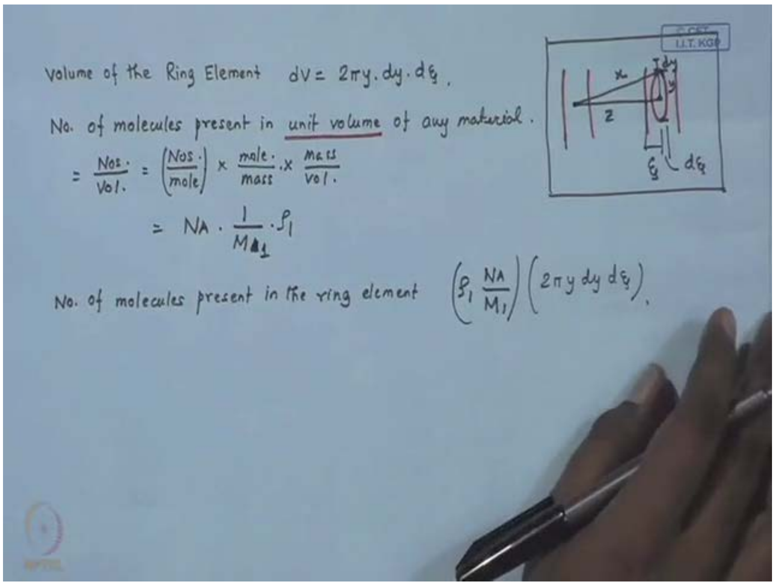

Volume of the Ring Element $dV = 2\pi y . dy . d\xi$.

No. of molecules present in unit volume of any material.

$$= \frac{Nos.}{Vol.} = \left(\frac{Nos.}{mole}\right) \times \frac{mole.}{mass} . \times \frac{mass}{Vol.}$$

$$= N_A . \frac{1}{M_1} . \rho_1$$

No. of molecules present in the ring element $\left(\rho_1 \frac{N_A}{M_1}\right)\left(2\pi y \, dy \, d\xi\right)$.

So, number of molecules present in unit volume of any material, this is eleventh standard science is equal to numbers. I am doing it in the simplest possible way divided by volume. Which you can convert to numbers per mole into mole per mass into mass per volume. So, this is nothing, but Avogadro’s number. Mass per mole is essentially the molecular weight.

So, if we are talking about material one and material a or whatever and volume per mass per volume is nothing but density. So, number of molecules present is in this ring. Ring element is this is per number of molecules present per unit volume. So, you just multiple this along with this volume of the ring. So, that turns out to be rho 1 N A by M 1, I will change this to 1 multiplied by 2 pi y d y d eta.

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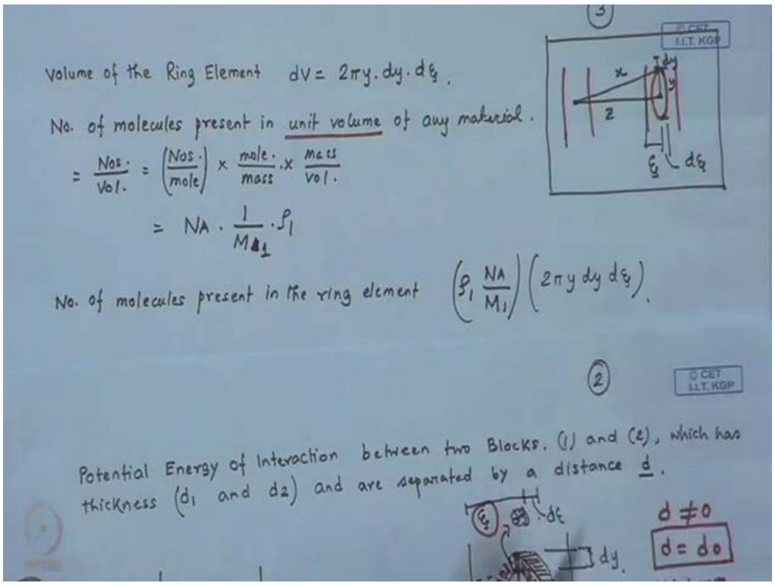

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Potential Energy of Interaction between two Blocks. (1) and (2), which has thickness (d_1 and d_2) and are separated by a distance d.

Now we have, we know that the interaction or the attractive interaction (Refer Slide Time: 08:20) between two molecules is beta into x to the power of minus 6. So, here the separation distance we have considered is x. So, any molecule we consider, which is which belongs to this ring is at a separation distance of x.

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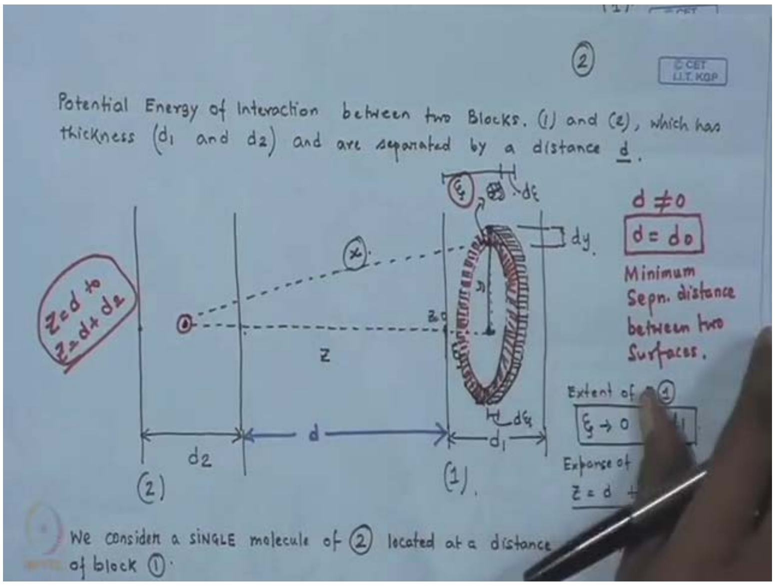

Potential Energy of Interaction between two Blocks. (1) and (2), which has thickness (d_1 and d_2) and are separated by a distance d.

We consider a SINGLE molecule of ② located at a distance

of block ①.

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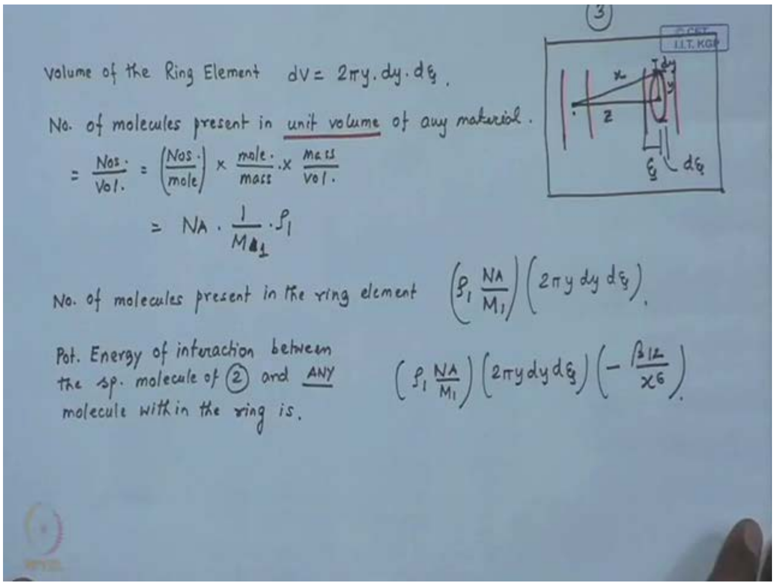
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No. of molecules present in the ring element $\left(\rho_1 \frac{N_A}{M_1}\right)\left(2\pi y\, dy\, d\xi\right)$.

Pot. Energy of interaction between the sp. molecule of ② and ANY molecule with in the ring is. $\left(\rho_1 \frac{N_A}{M_1}\right)\left(2\pi y\, dy\, d\xi\right)\left(-\frac{\beta_{12}}{x^6}\right)$.

So, the potential energy of interaction between this molecule, this particular molecule and any molecule present in this ring is, I will write it down without using any symbol. Between the specific molecule of two and any molecule present in the ring is, rho 1 minus beta 1 2 divided by x to the power 6.

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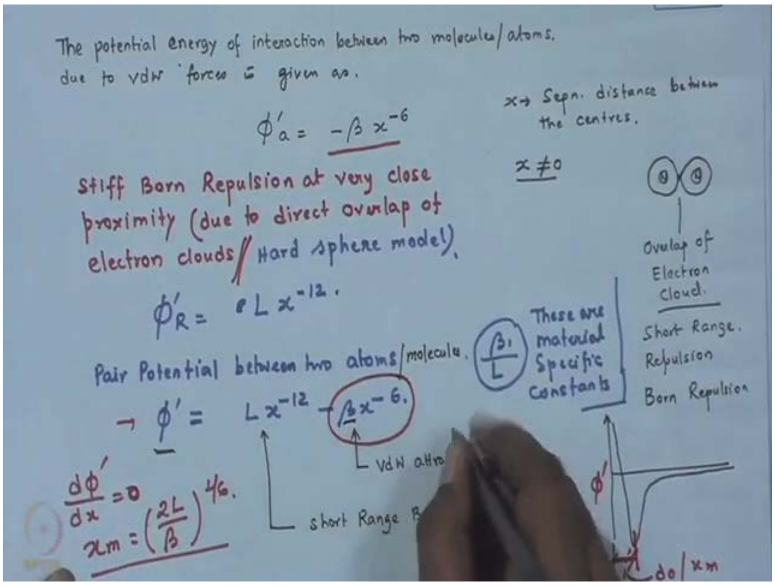
The potential energy of interaction between two molecules/atoms. due to vdW forces is given as.

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$x \rightarrow$ Sepn. distance between the centres.

$x \neq 0$

Stiff Born Repulsion at very close proximity (due to direct overlap of electron clouds / Hard sphere model).

$$\phi'_R = L x^{-12}.$$

Pair Potential between two atoms/molecules.

$$\rightarrow \phi' = L x^{-12} - \boxed{\beta x^{-6}}.$$

$\boxed{\beta, L}$ These are material Specific constants

$$\frac{d\phi'}{dx} = 0$$

$$x_m = \left(\frac{2L}{\beta}\right)^{1/6}.$$

So, beta 1 2 is the material specific property we talked about since we have two materials over here.

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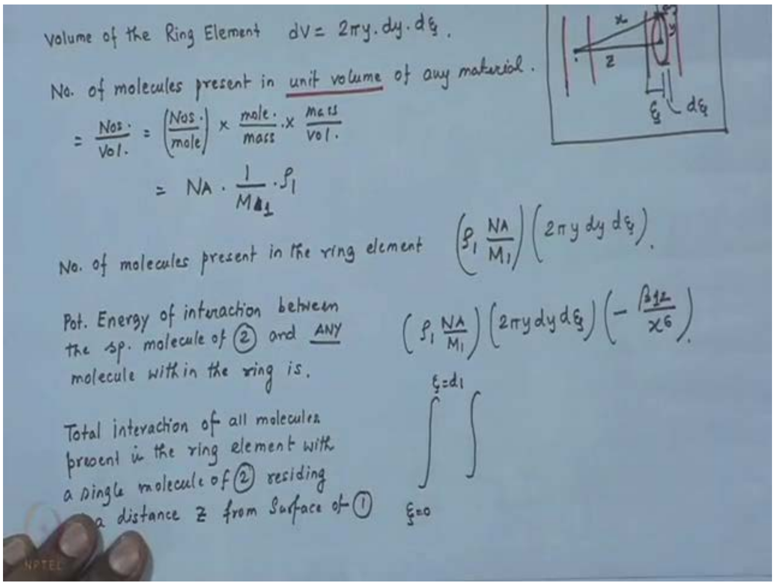

Volume of the Ring Element $dV = 2\pi y . dy . d\xi$.

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No. of molecules present in the ring element $\left(\rho_1 \frac{N_A}{M_1}\right)\left(2\pi y\, dy\, d\xi\right)$.

Pot. Energy of interaction between the sp. molecule of ② and ANY molecule with in the ring is. $\left(\rho_1 \frac{N_A}{M_1}\right)\left(2\pi y\, dy\, d\xi\right)\left(-\frac{\beta_{12}}{x^6}\right)$.

Total interaction of all molecules present in the ring element with a single molecule of ② residing a distance z from Surface of ① $\int_{\xi=0}^{\xi=d_1}\int$

1 and 2 therefore, we have use the suffix beta 1 2. Therefore total interaction of all molecules in the ring, element with a single molecule of 2 z distance z from surface of one is given as zeta, we have already identified the extent of zeta (Refer Slide Time: 09:52) is from extent of one or the expanse of one is from zeta equal to zero to d 1.

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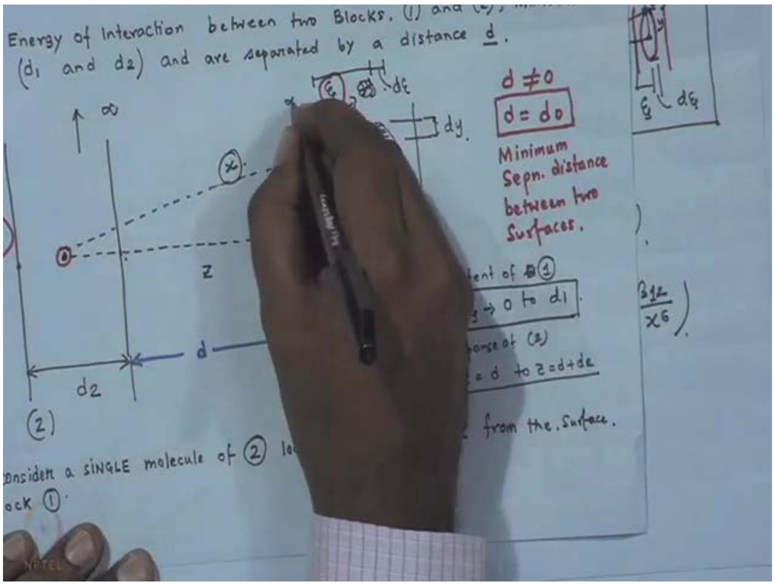

Energy of Interaction between two Blocks, (1) and (2),

(d₁ and d₂) and are separated by a distance d.

$d \neq 0$

$\boxed{d = d_0}$

Minimum Sepn. distance between two Surfaces.

tent of ①

$\boxed{\rightarrow 0 \text{ to } d_1}$.

panse of (2)

$= d \text{ to } z = d + dz$

from the Surface.

onsider a SINGLE molecule of ② lo

ock ①.

So, we integrate between zeta equal to 0 to zeta equal to d 1, y varies from so what we assume that both the object sort of stretch to infinity in this direction.

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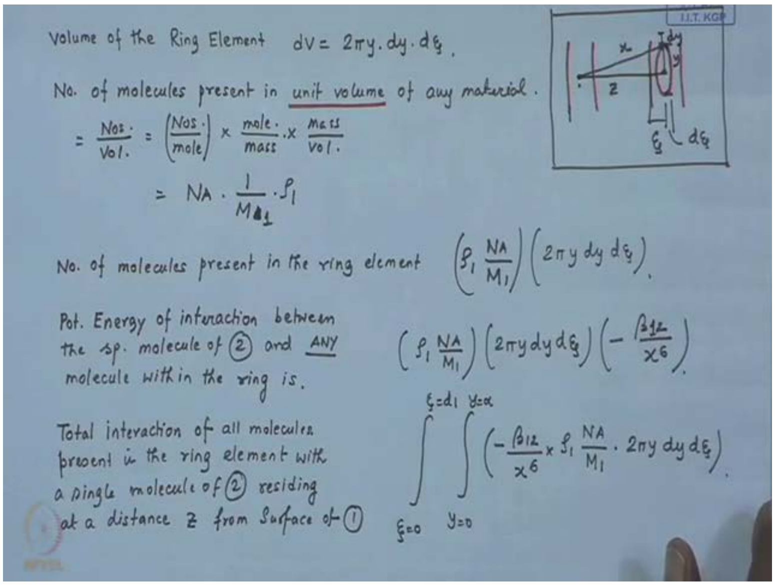

Volume of the Ring Element $dV = 2\pi y . dy . d\xi$.

No. of molecules present in unit volume of any material.

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$= N_A . \frac{1}{M_1} . \rho_1$

No. of molecules present in the ring element $\left(\rho_1 \frac{N_A}{M_1}\right)\left(2\pi y\, dy\, d\xi\right)$.

Pot. Energy of interaction between the sp. molecule of ② and ANY molecule with in the ring is. $\left(\rho_1 \frac{N_A}{M_1}\right)\left(2\pi y\, dy\, d\xi\right)\left(-\frac{\beta_{12}}{x^6}\right)$.

Total interaction of all molecules present in the ring element with a single molecule of ② residing at a distance z from Surface of ① $\int_{\xi=0}^{\xi=d_1}\int_{y=0}^{y=\alpha}\left(-\frac{\beta_{12}}{x^6} \times \rho_1 \frac{N_A}{M_1} . 2\pi y\, dy\, d\xi\right)$.

So, y varies from zero to infinity and the integral is on minus beta 1 2 divided by x to the power 6 into rho 1 N A M 1 into 2 pi y del y del zeta.

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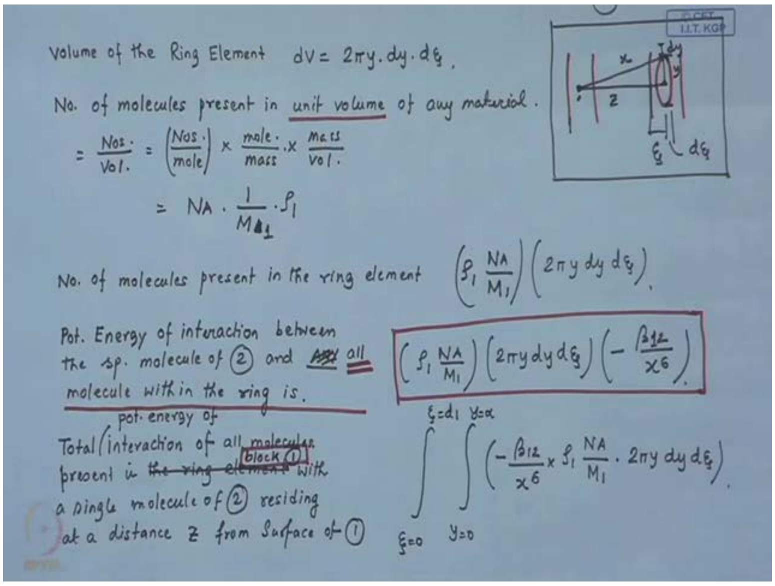

Volume of the Ring Element $dV = 2\pi y . dy . d\xi$.

No. of molecules present in unit volume of any material.

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$= N_A . \frac{1}{M_1} . \rho_1$

No. of molecules present in the ring element $\left(\rho_1 \frac{N_A}{M_1}\right)\left(2\pi y\, dy\, d\xi\right)$.

Pot. Energy of interaction between the sp. molecule of ② and ~~ANY~~ all molecule with in the ring is. $\boxed{\left(\rho_1 \frac{N_A}{M_1}\right)\left(2\pi y\, dy\, d\xi\right)\left(-\frac{\beta_{12}}{x^6}\right)}$.

Total (pot. energy of interaction of all ~~molecules~~ block ① present in ~~the ring element~~ with a single molecule of ② residing at a distance z from Surface of ① $\int_{\xi=0}^{\xi=d_1}\int_{y=0}^{y=\alpha}\left(-\frac{\beta_{12}}{x^6} \times \rho_1 \frac{N_A}{M_1} . 2\pi y\, dy\, d\xi\right)$.

Now, what we have from so, this is the expression of the total energy of interaction. The potential energy of all molecules present in the ring element with a single molecule of 2 residing at a distance zee. So, this is all molecules I am a little sorry, this is not the total energy of interaction of all molecules present in the ring element, but total energy of interaction present in of all molecules present in block 1.

That is why we do the integral so, the inner product, this is what is the potential energy of interaction between the specific molecule 2 and all molecules present within the ring element. That is why you multiple with the volume. So, if you do not multiply with the volume, the specific interaction between one molecule over here and one molecule in the ring element is given by: minus beta 1 2 i x to the power 6, where x is the separation distance. You multiply it by the total number of molecules present within the ring.

So, that is the expression, which gives you the total potential energy of interaction between the specific molecule you are talking over here and all molecules. I am a little sorry I just messed up a little bit. All molecules within the ring is given by this. And therefore, the total potential energy of interaction, of all molecules present in the block 1, with a single molecule of 2 residing at distance z from the surface of 1, that is this particular molecule, is you do the integration in terms of y and eta for the entire expanse of the block 1. And this is the expression.

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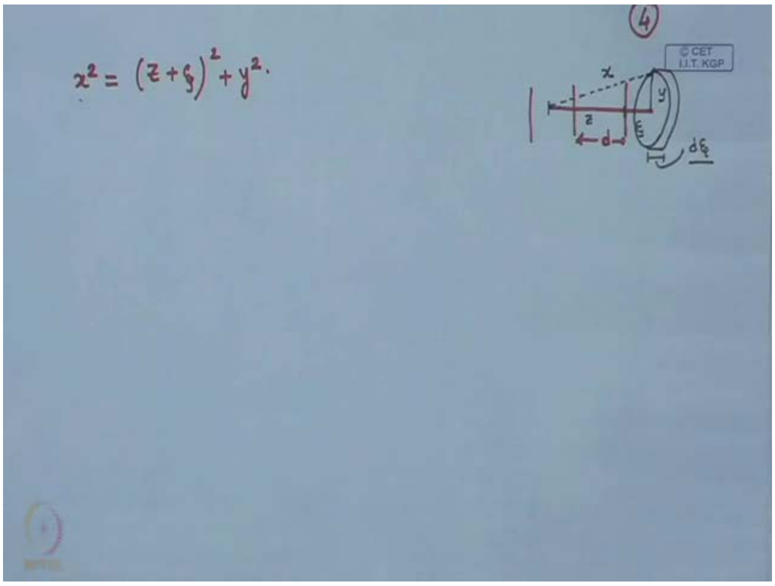

$$x^2 = (z+\zeta)^2 + y^2.$$

So, we now have to perform this integral. What we have looking again at the geometry, is that we have, x square from Pythagoras theorem is z plus zeta whole square plus y square. This you can write because the way we have defined our coordinate system this is the boundary of one, this is the boundary of two, this is d, this distance is z, this is eta, this is y, this is x. So, we have from Pythagoras theorem and this is here where you have the ring, it is del zeta and from Pythagoras theorem you have this.

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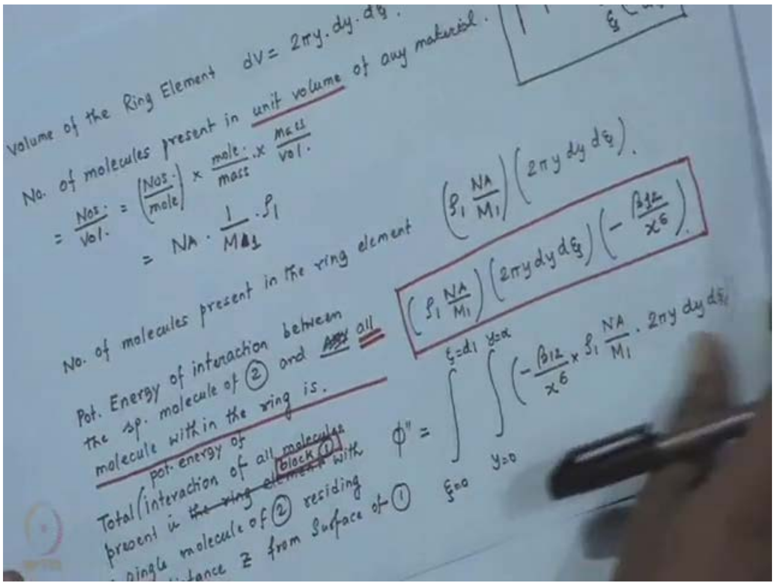

Volume of the Ring Element $dV = 2\pi y \cdot dy \cdot d\xi$.

No. of molecules present in unit volume of any material.

$= \frac{Nos.}{Vol.} = \left(\frac{Nos.}{mole}\right) \times \frac{mole}{mass} \times \frac{mass}{Vol.}$

$= N_A \cdot \frac{1}{M_1} \cdot \rho_1$

No. of molecules present in the ring element $\left(\rho_1 \frac{N_A}{M_1}\right)\left(2\pi y\, dy\, d\xi\right)$.

Pot. Energy of interaction between the sp. molecule of ② and ~~any~~ all molecule with in the ring is. $\boxed{\left(\rho_1 \frac{N_A}{M_1}\right)\left(2\pi y\, dy\, d\xi\right)\left(-\frac{\beta_{12}}{x^6}\right)}$.

Total (pot. energy of interaction of all molecules block ① ~~present in the ring element~~ with single molecule of ② residing distance z from Surface of ①

$\phi'' = \int_{\xi=0}^{\xi=d_1}\int_{y=0}^{y=\alpha}\left(-\frac{\beta_{12}}{x^6}\times\rho_1\frac{N_A}{M_1}\cdot 2\pi y\, dy\, d\xi\right.$

Therefore, so if we mark this as the phi double dash.

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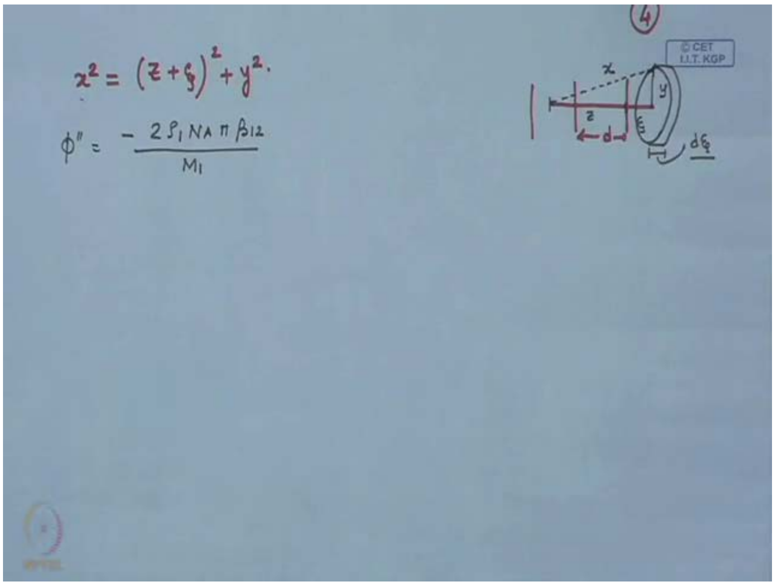

$x^2 = (z+\xi)^2 + y^2.$

$\phi'' = -\frac{2\rho_1 N_A \pi \beta_{12}}{M_1}$

So, phi double dash turns out to be this all these are constants. The minus sign originates from the fact that, we are talking about the attractive part of Vander Waals interaction which is always negative.

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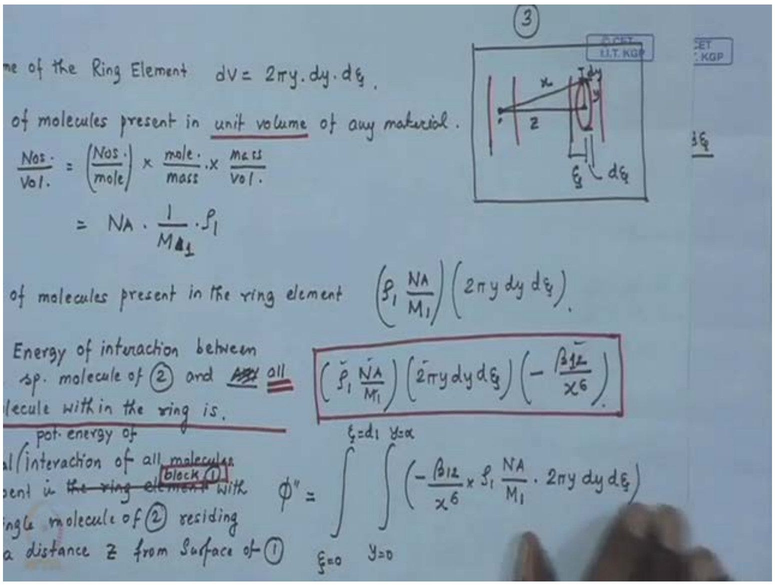


ne of the Ring Element $dV = 2\pi y . dy . d\xi$.

of molecules present in unit volume of any material.

$$\frac{Nos.}{Vol.} = \left(\frac{Nos.}{mole}\right) \times \frac{mole.}{mass} \times \frac{mass}{Vol.}$$

$$= N_A \cdot \frac{1}{M_1} \cdot \rho_1$$

of molecules present in the ring element $\left(\rho_1 \frac{N_A}{M_1}\right)\left(2\pi y\, dy\, d\xi\right)$.

Energy of interaction between sp. molecule of ② and ~~any~~ all lecule with in the ring is.

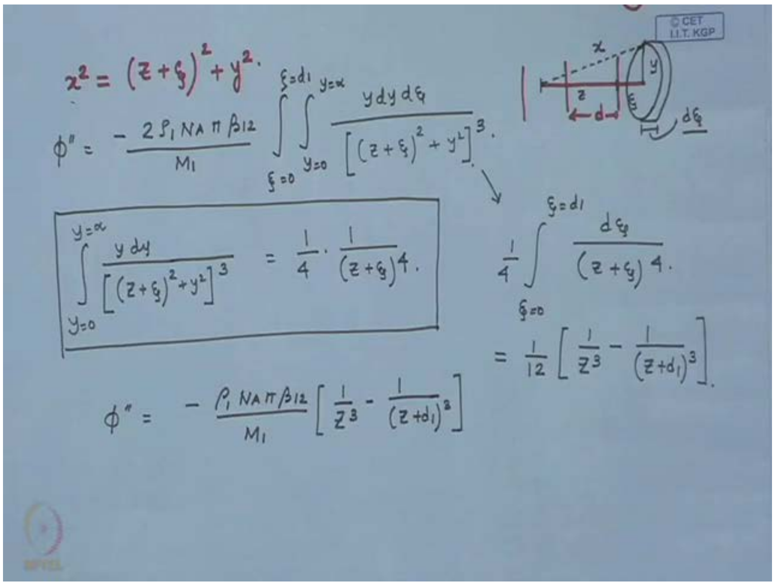
$$\boxed{\left(\rho_1 \frac{N_A}{M_1}\right)\left(2\pi y\, dy\, d\xi\right)\left(-\frac{\beta_{12}}{x^6}\right)}$$

l (pot. energy of interaction of all molecules ent in ~~the ring element~~ block ① with ngle molecule of ② residing a distance z from Surface of ①

$$\phi'' = \int_{\xi=0}^{\xi=d_1}\int_{y=0}^{y=\alpha}\left(-\frac{\beta_{12}}{x^6}\times \rho_1 \frac{N_A}{M_1} \cdot 2\pi y\, dy\, d\xi\right)$$

So, the interaction itself contains this minus term minus beta 1 2 divided by x to the power 6. So, you can see that, other than y d y d zee everything else this this this this, as well as beta, they are all constants and therefore, they have be taken out of the integral.

(Refer Slide Time: 27:42)



$$x^2 = (z+\xi)^2 + y^2.$$

$$\phi'' = -\frac{2\rho_1 N_A \pi \beta_{12}}{M_1}\int_{\xi=0}^{\xi=d_1}\int_{y=0}^{y=\alpha}\frac{y\, dy\, d\xi}{\left[(z+\xi)^2+y^2\right]^3}.$$

$$\boxed{\int_{y=0}^{y=\alpha}\frac{y\, dy}{\left[(z+\xi)^2+y^2\right]^3} = \frac{1}{4}\cdot\frac{1}{(z+\xi)^4}.}$$

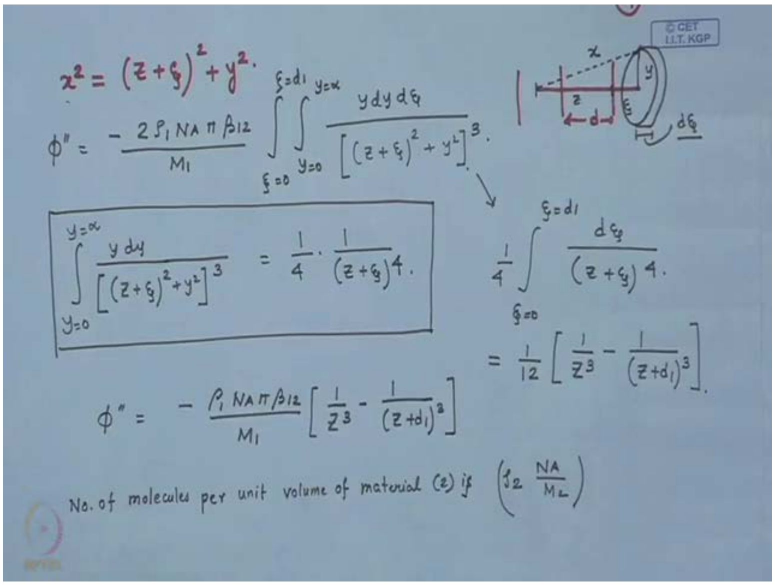
$$\frac{1}{4}\int_{\xi=0}^{\xi=d_1}\frac{d\xi}{(z+\xi)^4}.$$

$$= \frac{1}{12}\left[\frac{1}{z^3} - \frac{1}{(z+d_1)^3}\right].$$

$$\phi'' = -\frac{\rho_1 N_A \pi \beta_{12}}{M_1}\left[\frac{1}{z^3} - \frac{1}{(z+d_1)^3}\right]$$

And the integral is now, reduces to this form. And which turns out to be, if you do the first integration or let us, break it up without, if you look only at this integral it turns out to be one fourth of you are encouraged to try it out. Therefore, the overall integral now takes the shape of, using the results of this. What you get is this is now one fourth integrating between eta equal to zero. So, this is what you get. So, this is the integral. So, the potential energy of interaction between one single molecule of block two residing at a distance z from the surface and the entire, the all the molecules present within the block 1, which sort of stretches up to infinity in this particular direction.

(Refer Slide Time: 30:44)



$$x^2 = (z+\xi)^2 + y^2.$$

$$\phi'' = -\frac{2\rho_1 N_A \pi \beta_{12}}{M_1} \int_{\xi=0}^{\xi=d_1}\int_{y=0}^{y=\infty} \frac{y\,dy\,d\xi}{\left[(z+\xi)^2+y^2\right]^3}.$$

$$\boxed{\int_{y=0}^{y=\infty} \frac{y\,dy}{\left[(z+\xi)^2+y^2\right]^3} = \frac{1}{4}\cdot\frac{1}{(z+\xi)^4}.}$$

$$\frac{1}{4}\int_{\xi=0}^{\xi=d_1} \frac{d\xi}{(z+\xi)^4}.$$

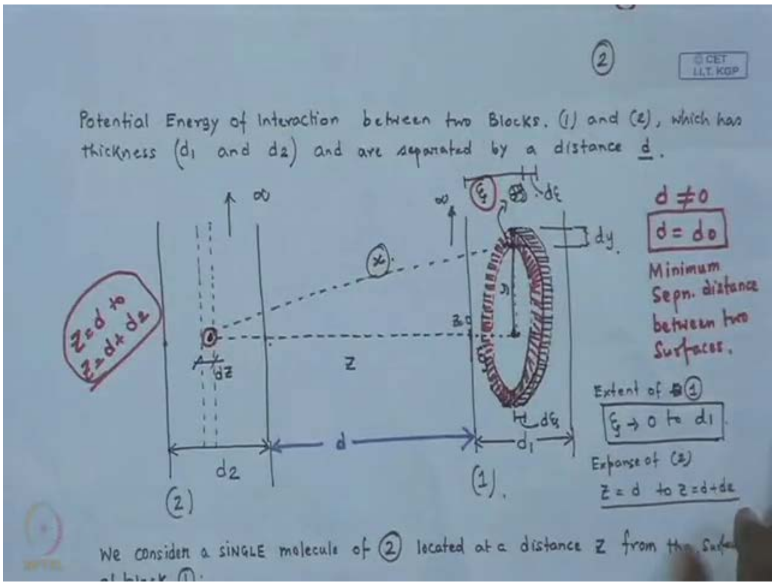
$$= \frac{1}{12}\left[\frac{1}{z^3} - \frac{1}{(z+d_1)^3}\right].$$

$$\phi'' = -\frac{\rho_1 N_A \pi \beta_{12}}{M_1}\left[\frac{1}{z^3} - \frac{1}{(z+d_1)^3}\right]$$

No. of molecules per unit volume of material (2) is $\left(\rho_2 \frac{N_A}{M_2}\right)$

So, beta 1 2 we have already mentioned, it is the coefficient which determines the strength of Vander Waals interaction and is a material dependent property. Now, the number of molecules per unit volume of material two, two is of course rho 2 n a by m 2.

(Refer Slide Time: 31:18)



②

Potential Energy of Interaction between two Blocks. (1) and (2), which has thickness (d_1 and d_2) and are separated by a distance d.

$d \neq 0$

$\boxed{d = d_0}$

Minimum Sepn. distance between two Surfaces.

Extent of ①

$\boxed{\xi \to 0 \text{ to } d_1}$

Expanse of (2)

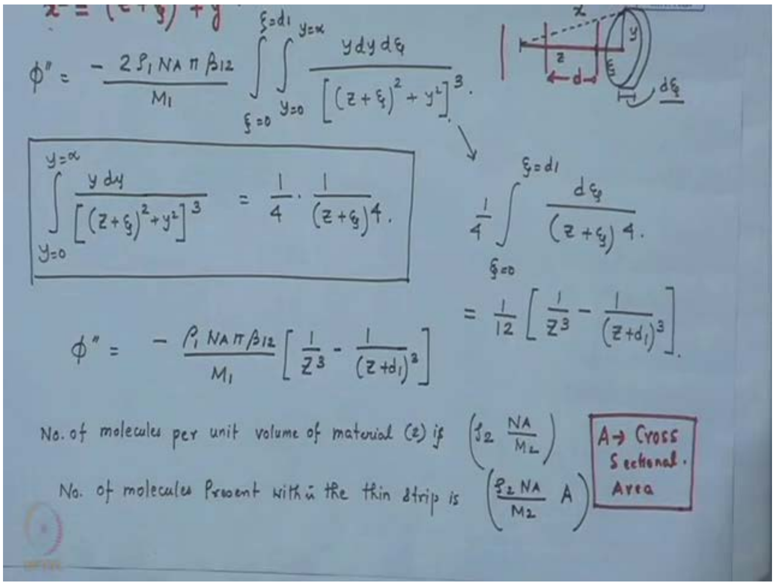
$z = d$ to $z = d + d_2$

$z = d$ to $z = d + d_2$

We consider a SINGLE molecule of ② located at a distance z from the Sur

Now we consider a thin strip of material 2 of width delta z, which contains the molecule we have been talking about. Therefore, the number of molecules present within this thin strip is, rho 2 N A M 2 into a where A is the, cross sectional area, which is this cross sectional area perpendicular to the deduction of this; so the total energy of interaction.

(Refer Slide time: 32:23)



$$\phi'' = -\frac{2\rho_1 N_A \pi \beta_{12}}{M_1} \int_{\xi=0}^{\xi=d_1} \int_{y=0}^{y=\infty} \frac{y\,dy\,d\xi}{\left[(z+\xi)^2 + y^2\right]^3}.$$

$$\boxed{\int_{y=0}^{y=\infty} \frac{y\,dy}{\left[(z+\xi)^2+y^2\right]^3} = \frac{1}{4}\cdot\frac{1}{(z+\xi)^4}.}$$

$$\frac{1}{4}\int_{\xi=0}^{\xi=d_1} \frac{d\xi}{(z+\xi)^4}.$$

$$= \frac{1}{12}\left[\frac{1}{z^3} - \frac{1}{(z+d_1)^3}\right].$$

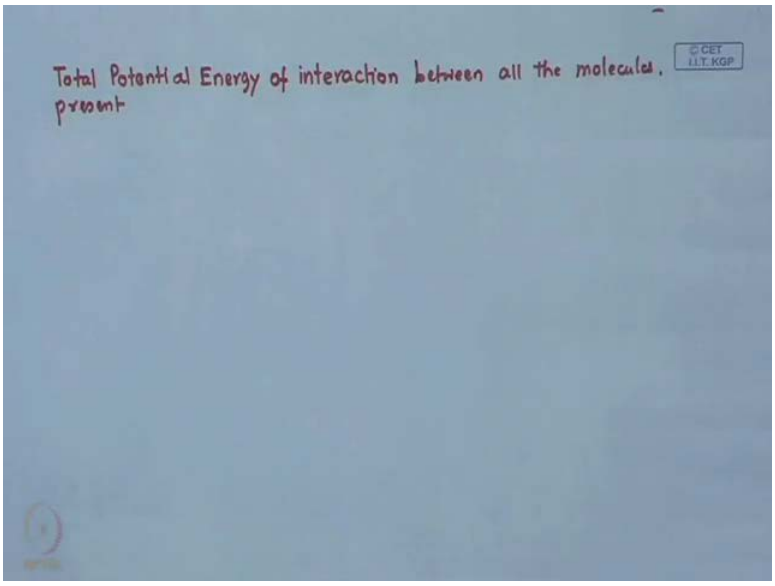
$$\phi'' = -\frac{\rho_1 N_A \pi \beta_{12}}{M_1}\left[\frac{1}{z^3} - \frac{1}{(z+d_1)^3}\right]$$

No. of molecules per unit volume of material (2) is $\left(\rho_2 \frac{N_A}{M_2}\right)$

No. of molecules Present within the thin strip is $\left(\frac{\rho_2 N_A}{M_2} A\right)$

A → Cross Sectional. Area

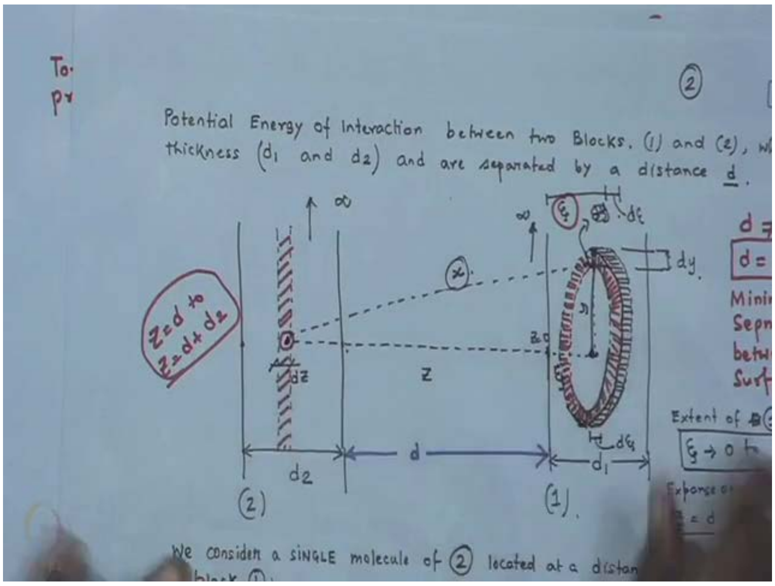
(Refer slide Time: 32:49)



Total Potential Energy of interaction between all the molecules, present

So, the total potential energy between all the molecules, present in this shaded zone.

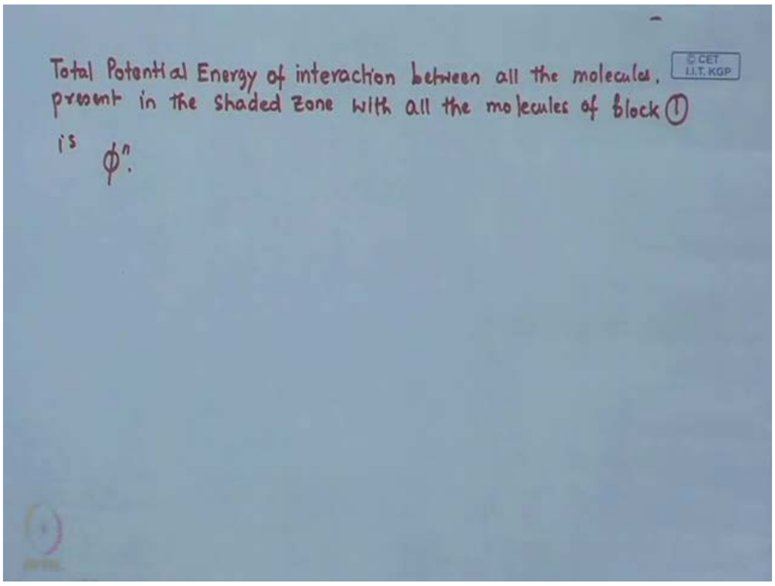
(Refer Slide Time: 33:22)



Potential Energy of Interaction between two Blocks, (1) and (2), w
thickness (d_1 and d_2) and are separated by a distance d.

We consider a SINGLE molecule of ② located at a distan
block ①.

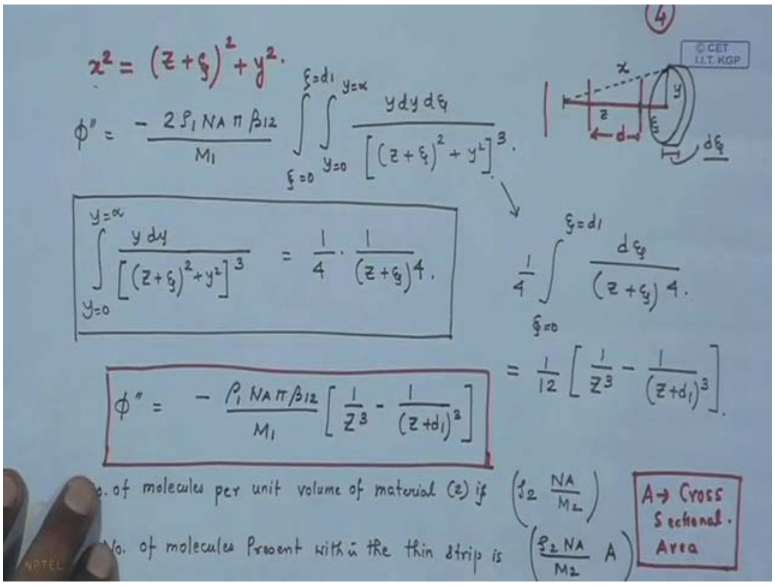
(Refer Slide Time: 33:30)



Total Potential Energy of interaction between all the molecules, present in the Shaded Zone with all the molecules of block ①
is ϕ''.

With all the molecules, of block one is phi double dash which is the expression we have obtain for interaction, of one specific molecule.

(Refer Slide Time: 33:58)



$$x^2 = (z+\xi)^2 + y^2.$$

$$\phi'' = -\frac{2\rho_1 N_A \pi \beta_{12}}{M_1}\int_{\xi=0}^{\xi=d_1}\int_{y=0}^{y=\infty}\frac{y\,dy\,d\xi}{[(z+\xi)^2+y^2]^3}.$$

$$\boxed{\int_{y=0}^{y=\infty}\frac{y\,dy}{[(z+\xi)^2+y^2]^3} = \frac{1}{4}\cdot\frac{1}{(z+\xi)^4}.}$$

$$\frac{1}{4}\int_{\xi=0}^{\xi=d_1}\frac{d\xi}{(z+\xi)^4}. = \frac{1}{12}\left[\frac{1}{z^3}-\frac{1}{(z+d_1)^3}\right].$$

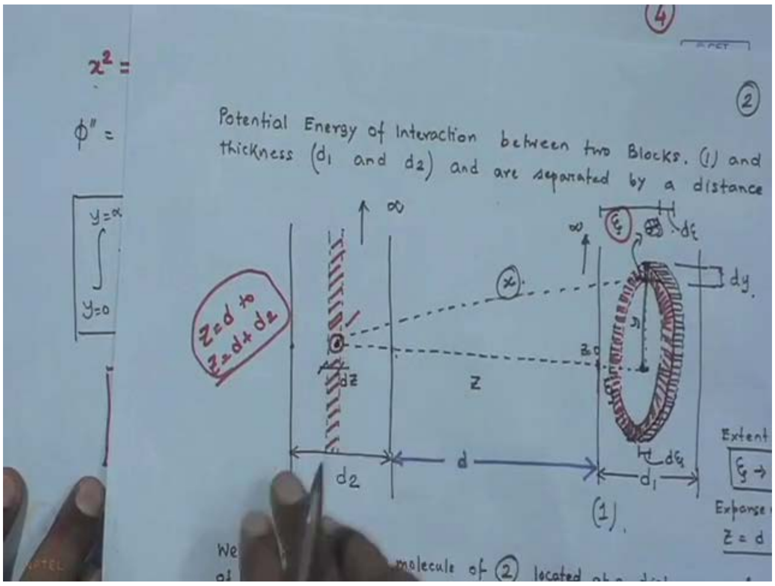
$$\boxed{\phi'' = -\frac{\rho_1 N_A \pi \beta_{12}}{M_1}\left[\frac{1}{z^3}-\frac{1}{(z+d_1)^3}\right]}$$

o. of molecules per unit volume of material (2) is $\left(\rho_2 \frac{N_A}{M_2}\right)$

o. of molecules Present within the thin strip is $\left(\frac{\rho_2 N_A}{M_2} A\right)$

A → Cross Sectional. Area

(Refer Slide Time: 34:08)



(2)

Potential Energy of Interaction between two Blocks. (1) and thickness (d_1 and d_2) and are separated by a distance

Extent

ξ →

Expanse

z = d

We

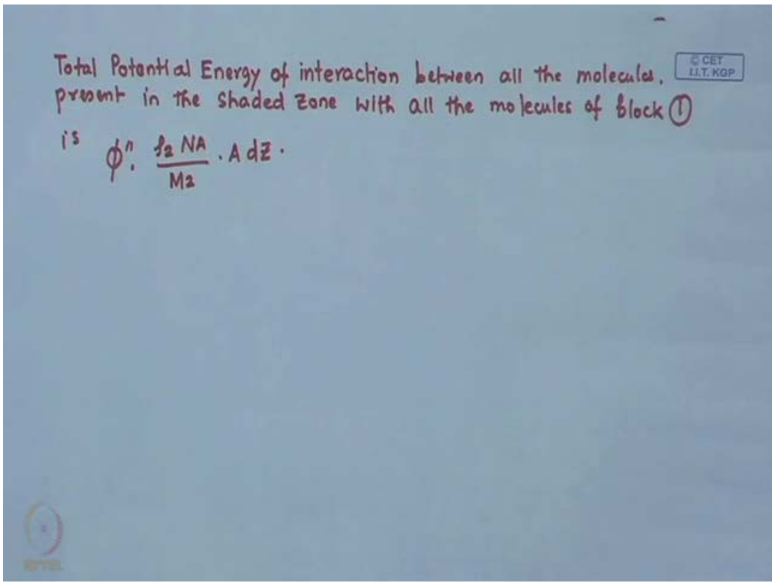
molecule of (2) located

We have talked about, with all the molecules present in the block one.

(Refer slide Time: 33:58)

So now we have two look into we consider, the all the molecules present within this,(Refer Slide Time:34:08) shaded region.

(Refer Slide Time: 34:26)

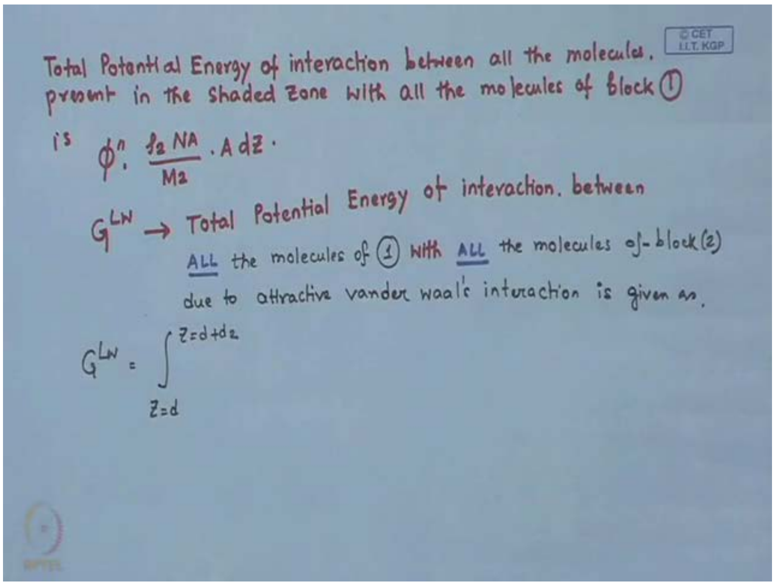


Total Potential Energy of interaction between all the molecules, present in the shaded zone with all the molecules of block ①

is $\phi^n \cdot \frac{\rho_2 N_A}{M_2} \cdot A\,dz$ ·

So, it is phi multiplied by rho 2 N A by M to A d Z. This is, the number of molecules that is present, because volume of the element is A d Z, which is present in the theme of strip.

(Refer Slide time: 34:54)



Total Potential Energy of interaction between all the molecules, present in the shaded zone with all the molecules of block ①

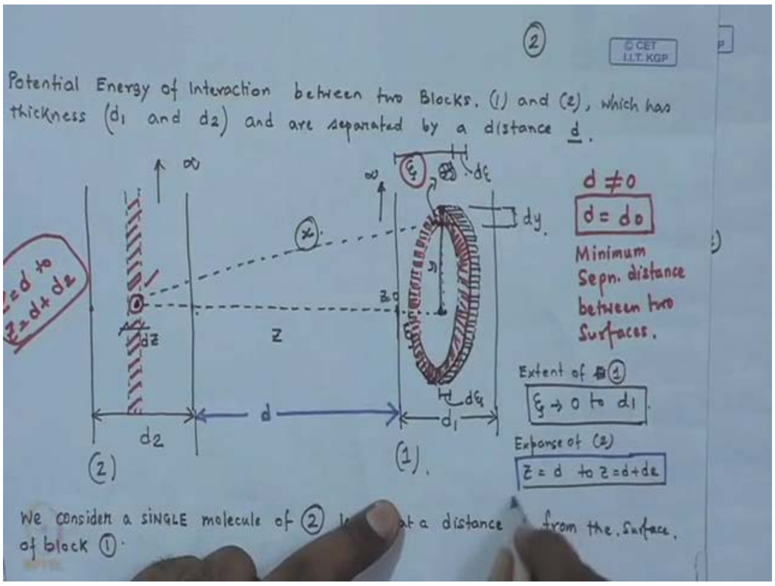
is $\phi^n \cdot \frac{\rho_2 N_A}{M_2} \cdot A\,dz$ ·

$G^{LW} \rightarrow$ Total Potential Energy of interaction, between ALL the molecules of ① with ALL the molecules of block (2) due to attractive vander waal's interaction is given as.

$$G^{LW} = \int_{z=d}^{z=d+d_2}$$

Therefore, the total potential energy of interaction now, if you calculate, it is the total potential energy of, interaction between all the molecules of 1 with all the molecules of block 2 due to attractive interaction is given as, G l w equal to: that is the expanse of the block 2 as we have already identified.

(Refer slide Time: 36:31)



②

Potential Energy of Interaction between two Blocks. (1) and (2), which has thickness (d_1 and d_2) and are separated by a distance $\underline{d}$.

$d \neq 0$

$\boxed{d = d_0}$

Minimum Sepn. distance between two Surfaces.

Extent of ①

$\boxed{\xi \to 0 \text{ to } d_1}$

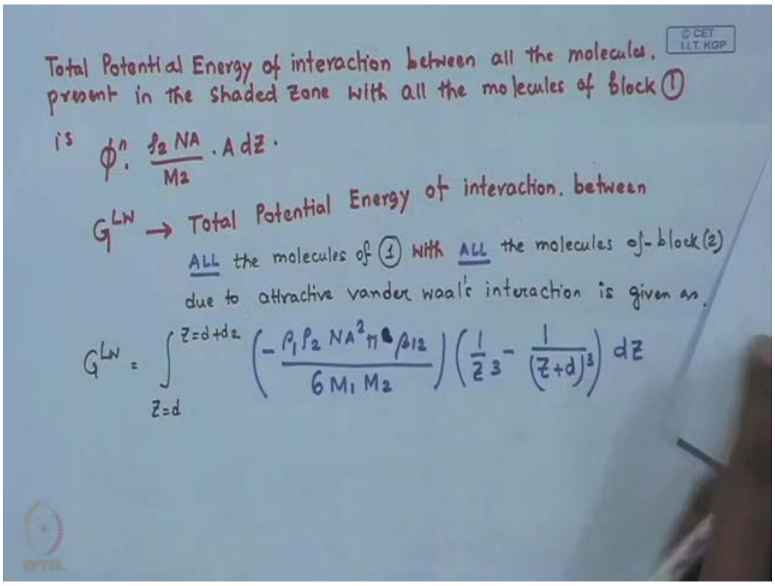
Expanse of (2)

$\boxed{Z = d \text{ to } Z = d + d_2}$

We consider a SINGLE molecule of ② [illegible] at a distance from the Surface of block ①.

So, expanse of 2 is in terms of Z equal is to d to Z is equal to d plus d 2.

(Refer Slide Time: 36:42)



Total Potential Energy of interaction between all the molecules present in the Shaded Zone with all the molecules of block ①

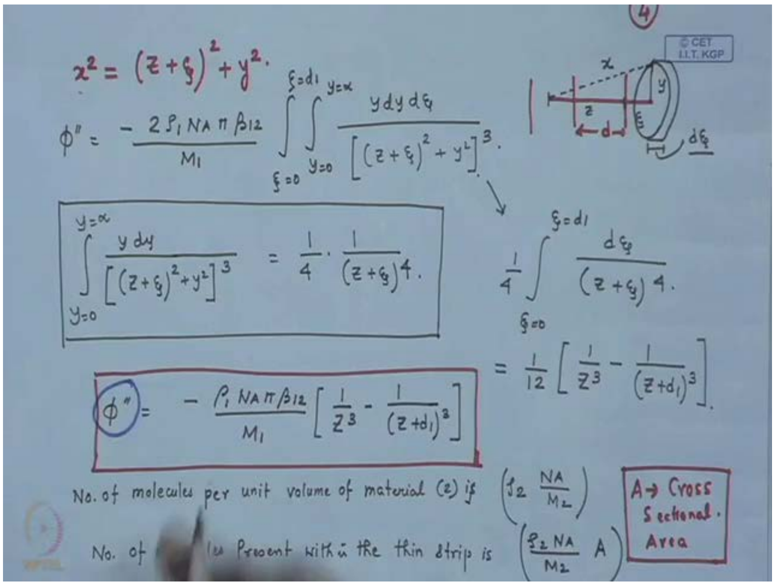
is $\phi^n_1 \cdot \frac{\rho_2 N_A}{M_2} \cdot A\, dZ$.

$G^{LW} \rightarrow$ Total Potential Energy of interaction between ALL the molecules of ① with ALL the molecules of block (2) due to attractive vander waal's interaction is given as.

$$G^{LW} = \int_{Z=d}^{Z=d+d_2} \left(- \frac{\rho_1 \rho_2 N_A^2 \pi \beta_{12}}{6 M_1 M_2} \right) \left(\frac{1}{Z^3} - \frac{1}{(Z+d)^3} \right) dZ$$

And so, this turns out to be minus rho 1, rho 2 N A square pi square beta 1 2 divided by M 1 M 2 into 6 over here, this is pi 1 by Z cube minus 1 by Z plus d whole cube d Z.

(Refer Slide Time: 37:42)



$$x^2 = (z+\xi)^2 + y^2.$$

$$\phi'' = -\frac{2\rho_1 N_A \pi \beta_{12}}{M_1}\int_{\xi=0}^{\xi=d_1}\int_{y=0}^{y=\infty}\frac{y\,dy\,d\xi}{\left[(z+\xi)^2+y^2\right]^3}.$$

$$\boxed{\int_{y=0}^{y=\infty}\frac{y\,dy}{\left[(z+\xi)^2+y^2\right]^3} = \frac{1}{4}\cdot\frac{1}{(z+\xi)^4}.}$$

$$\frac{1}{4}\int_{\xi=0}^{\xi=d_1}\frac{d\xi}{(z+\xi)^4}.$$

$$= \frac{1}{12}\left[\frac{1}{z^3}-\frac{1}{(z+d_1)^3}\right].$$

$$\boxed{\phi'' = -\frac{\rho_1 N_A \pi \beta_{12}}{M_1}\left[\frac{1}{z^3}-\frac{1}{(z+d_1)^3}\right]}$$

No. of molecules per unit volume of material (2) is $\left(\rho_2 \frac{N_A}{M_2}\right)$

No. of [illegible] les Present within the thin strip is $\left(\frac{\rho_2 N_A}{M_2} A\right)$

A → Cross Sectional. Area

So this is, phi double dash the expression of that we have multiplied by the number of molecules present within this thin strip.

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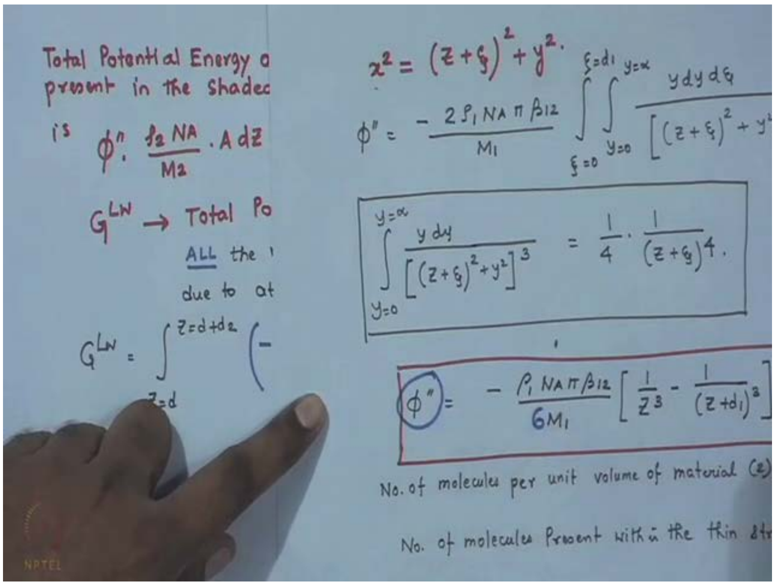


Total Potential Energy o
present in the Shadec
is $\phi''\cdot\frac{\rho_2 N_A}{M_2}\cdot A\,dz$

G^{LW} → Total Po
ALL the
due to at

$$G^{LW} = \int_{z=d}^{z=d+d_2}\Big(-$$

$$x^2 = (z+\xi)^2 + y^2.$$

$$\phi'' = -\frac{2\rho_1 N_A \pi \beta_{12}}{M_1}\int_{\xi=0}^{\xi=d_1}\int_{y=0}^{y=\infty}\frac{y\,dy\,d\xi}{\left[(z+\xi)^2+y^2\right.}$$

$$\boxed{\int_{y=0}^{y=\infty}\frac{y\,dy}{\left[(z+\xi)^2+y^2\right]^3} = \frac{1}{4}\cdot\frac{1}{(z+\xi)^4}.}$$

$$\boxed{\phi'' = -\frac{\rho_1 N_A \pi \beta_{12}}{6M_1}\left[\frac{1}{z^3}-\frac{1}{(z+d_1)^3}\right]}$$

No. of molecules per unit volume of material (2)

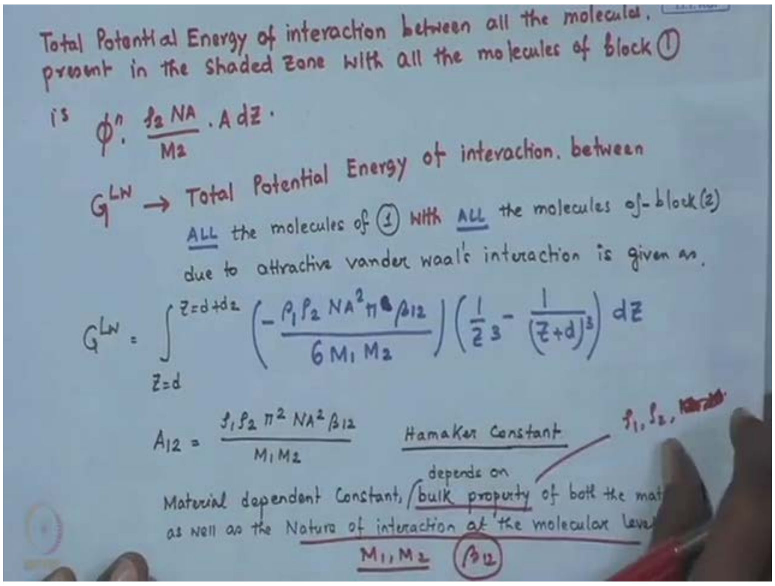
No. of molecules Present within the thin st

So, you see this rho 1 was there. So, this gets multiplied by rho 2 as well as rho 1 rho 2 N A was here N A comes from here as well. So, you have N A square you had pi over here. So, it is setting this pi. You had beta 1 2, so beta 1 2 is also there. You had a sorry I just missed out this multiplier 6.

(Refer Slide time: 37:41)

Because you have a 12 over here, performing the integral; and you had a 2 in the prefactor, numerical prefactor. So, over all the expression 6 and just get it corrected, I just missed this 6 out, and this.

(Refer Slide time: 38:51)



Total Potential Energy of interaction between all the molecules present in the shaded zone with all the molecules of block ①

is $\phi^n \cdot \frac{\rho_2 NA}{M_2} \cdot A\,dZ \cdot$

G^{LW} → Total Potential Energy of interaction. between ALL the molecules of ① with ALL the molecules of block (2) due to attractive vander waal's interaction is given as.

$$G^{LW} = \int_{Z=d}^{Z=d+dz} \left(-\frac{\rho_1 \rho_2 NA^2 \pi^2 \beta_{12}}{6 M_1 M_2}\right)\left(\frac{1}{Z^3} - \frac{1}{(Z+d)^3}\right) dZ$$

$$A_{12} = \frac{\rho_1 \rho_2 \pi^2 NA^2 \beta_{12}}{M_1 M_2}$$

Hamaker Constant

$\rho_1, \rho_2,$

Material dependent Constant, depends on bulk property of both the mat as well as the Nature of interaction at the molecular leve

M_1, M_2 β_{12}

So this 6 also comes in and you are left with this particular integral 6. So, if you now do the integration, you are left with or before we do the integral, let us, define A 1 2 which takes care of all the constants essentially rho 1 rho 2 pi square N A square beta 1 2 divided by M 1 M 2 and this is what is known as the Hamaker constant.

This is the Hamaker constant between 1 and 2. So, this is a material dependent constant, property of which depends on bulk properties of materials both the materials as well as the nature of interaction, at the molecular level. You can see the bulk properties that effect is the so, we talk about the bulk property, which is rho 1 rho 2 and the molecular weights or the rho 1 and rho 2.

The molecular weights are coming in as, function or effects the functionality as well as beta 1 2, which text care about the nature of interaction at the molecular level. So, this is Hamaker constant. So, if you replace the expression of Hamaker constant in this integral, what happens is you have a pi square over there. So, a pi comes in denominator.

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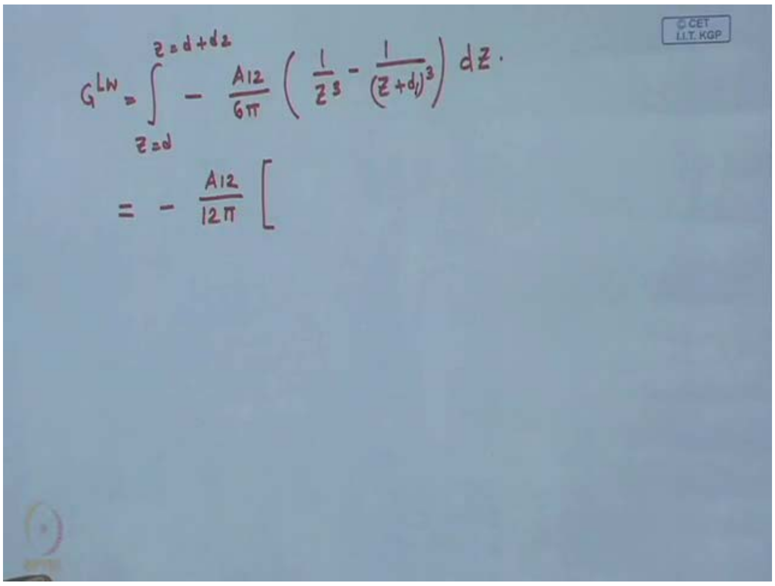

$$G^{LW} = \int_{z=d}^{z=d+d_1} -\frac{A_{12}}{6\pi}\left(\frac{1}{z^3} - \frac{1}{(z+d_1)^3}\right) dz.$$

$$= -\frac{A_{12}}{12\pi}\Big[$$

So, your expression for G l w now, reduces to 6 pi into 1 by and if you now perform the integral, what you will find is that it is sort of turns out to be, this will be d 1 I am sorry. This is d 1. So, be careful.

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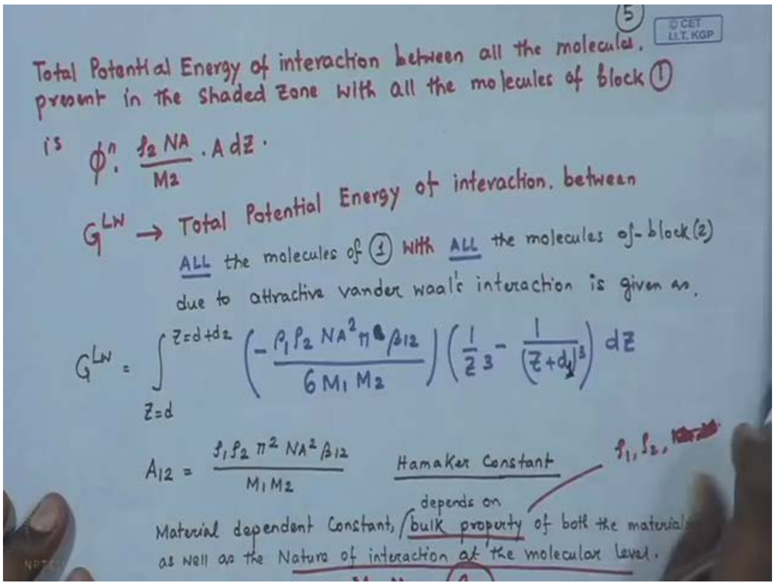


⑤

Total Potential Energy of interaction between all the molecules present in the shaded zone with all the molecules of block ①

is $\phi^n \cdot \frac{\rho_2 N_A}{M_2} \cdot A\,dz.$

$G^{LW} \rightarrow$ Total Potential Energy of interaction. between ALL the molecules of ① with ALL the molecules of block (2) due to attractive vander waal's interaction is given as.

$$G^{LW} = \int_{z=d}^{z=d+d_1} \left(-\frac{\rho_1 \rho_2 N_A^2 \pi^2 \beta_{12}}{6 M_1 M_2}\right)\left(\frac{1}{z^3} - \frac{1}{(z+d_1)^3}\right) dz$$

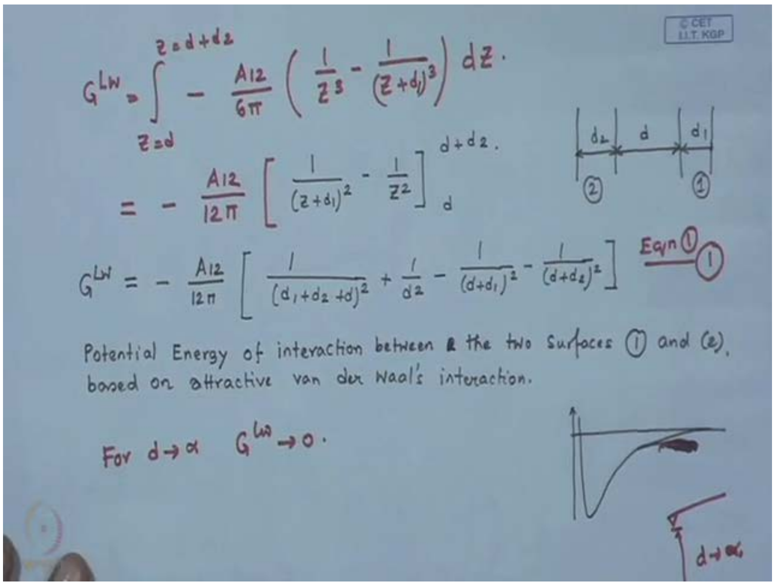
$$A_{12} = \frac{\rho_1 \rho_2 \pi^2 N_A^2 \beta_{12}}{M_1 M_2}$$ Hamaker Constant

$\rho_1, \rho_2,$

Material dependent Constant, / depends on bulk property of both the materials as well as the Nature of interaction at the molecular level.

This is d 1 square, yeah just get it corrected. We missed out this d 1 and yeah.

(Refer Slide Time: 42: 43)



$$G^{LW} = \int_{z=d}^{z=d+d_2} -\frac{A_{12}}{6\pi}\left(\frac{1}{z^3} - \frac{1}{(z+d_1)^3}\right) dz.$$

$$= -\frac{A_{12}}{12\pi}\left[\frac{1}{(z+d_1)^2} - \frac{1}{z^2}\right]_d^{d+d_2}.$$

$$G^{LW} = -\frac{A_{12}}{12\pi}\left[\frac{1}{(d_1+d_2+d)^2} + \frac{1}{d^2} - \frac{1}{(d+d_1)^2} - \frac{1}{(d+d_2)^2}\right] \quad \text{Eqn ①}$$

Potential Energy of interaction between the two surfaces ① and (2), based on attractive van der Waal's interaction.

For $d \to \alpha$ $G^{LW} \to 0$.

So, if you do that integral it will be, so the final expression for G l w is minus A 1 2. So, this is the energy of interaction due to, between the two surfaces. So this is 1, this is 2 and so, the potential energy of a interaction is the potential energy of interaction between the two surfaces considering, (Refer Slide Time: 21:24) the attractive Vander Waals interaction.

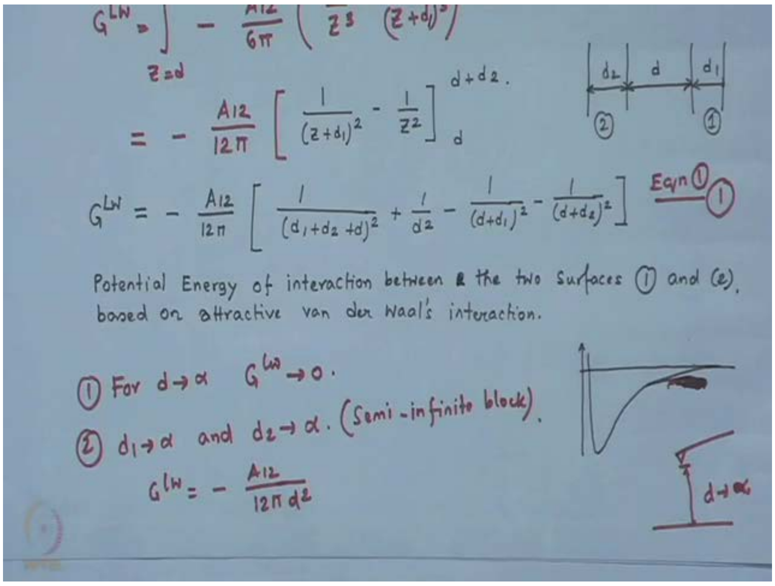
So, now you see that it depends, this potential energy of interaction depends on several parameters. That is, the separation distance, as well as the finite size of these two blocks. So, couple of things you can see immediately from the expression. That is firstly, we go on telling we have been talking that, this interaction of this Vander Waal interaction sort of becomes tends to 0, as the separation distance increases.

We argued, particularly if you now, compare or try to remember what we had talked about while talking about the atomic force microscope its approach. And withdrawal that when the separation distances are very very far. So, this is your tip and this is where your scanning surface is, there is no effective interaction between these two due to Vander Waals forces.

Well, what would that mean? That would essentially means that you set d tending to infinity. The separation distance between the two is 0. And now, if you substitute d tending to infinity so, please do not forget what is d, d is the sort of the separation distance between the two surfaces. The moment you substitute d is equal to infinity in the expression for the G w G l w let us, say we mark that as equation 1, you find that d is there in the denominator of all the terms.

So, for the first case is for d tending to infinity, G l w tends to 0. So there is no Vander Waals driven force, when the separation distance is very, very high. The second thing that you may want to find out, if that we are talking about the interaction between two semi infinite blocks let us, say. So, what would be the condition for semi infinite blocks?

(Refer Slide Time: 47:03)



$$G^{LW} = \int_{z=d} - \frac{A_{12}}{6\pi} \left(z^3 \quad (z+d_1)^3 \right)$$

$$= - \frac{A_{12}}{12\pi} \left[\frac{1}{(z+d_1)^2} - \frac{1}{z^2} \right]_{d}^{d+d_2}.$$

$$G^{LW} = - \frac{A_{12}}{12\pi} \left[\frac{1}{(d_1+d_2+d)^2} + \frac{1}{d^2} - \frac{1}{(d+d_1)^2} - \frac{1}{(d+d_2)^2} \right] \quad \underline{\text{Eqn ①}} \; ①$$

Potential Energy of interaction between the two surfaces ① and ②, based on attractive van der Waal's interaction.

① For $d \to \alpha$ $G^{LW} \to 0$.

② $d_1 \to \alpha$ and $d_2 \to \alpha$. (Semi-infinite block).

$$G^{LW} = - \frac{A_{12}}{12\pi d^2}$$

The condition would be, d 1 tending to infinity and d 2 tending to infinity. So, this is the condition for semi infinite block. And then in that case you can see that, G l w is minus a 1 2 divided by 12 pi d square, because d 1 and d 2 either of them are present in the all the other three terms in the denominator. So, for d 1 tending to infinity and for d 2 tending to infinity all these terms tends to 0. And therefore, this is the potential energy of interaction.

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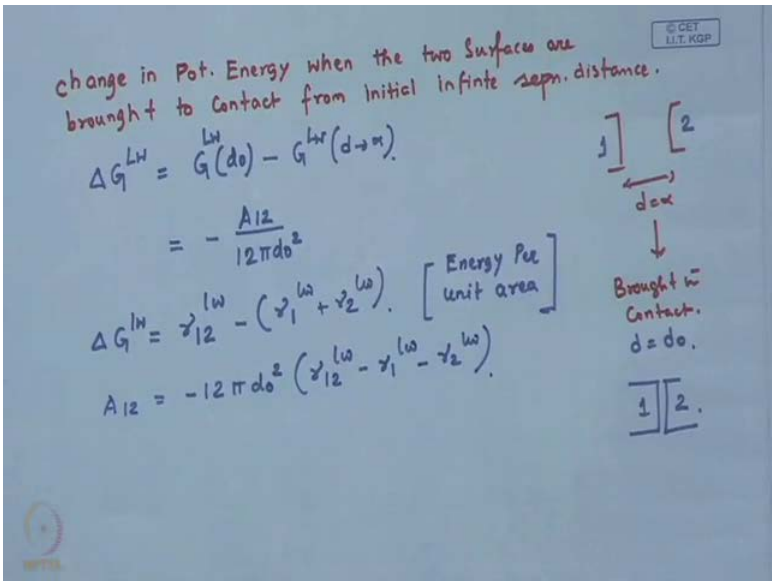

change in Pot. Energy when the two Surfaces are brought to Contact from Initial infinte sepn. distance.

$$\Delta G^{LW} = G^{LW}(d_0) - G^{LW}(d \to \infty).$$

$$= -\frac{A_{12}}{12\pi d_0^2}$$

$$\Delta G^{lw} = \gamma_{12}^{lw} - (\gamma_1^{lw} + \gamma_2^{lw}).$$ [Energy Per unit area]

$$A_{12} = -12\pi d_0^2 (\gamma_{12}^{lw} - \gamma_1^{lw} - \gamma_2^{lw}).$$

$d = \infty$

Brought in Contact.

$d = d_0$.

Now if we consider, the if you would like to find out the change in the force, when the two surfaces are brought to contact from initially infinite separation distance. So let us, say we talk about two semi infinite blocks which are initially at infinite separation and then they are brought in contact. So, based on the discussion we have already had, we understand that, these two are brought in contact this corresponds to d equal to d 0.

Therefore, we are talking about the change in the potential energy. So, we are talking about the delta G l w which corresponds to the final G l w at contact and the initial one was d tending to infinity. And this gives you the delta G l w is minus A 1 2 divided by 12 pi d zero square.

Now incidentally, if you remember so, these are the two blocks and now, these two are in contact. So, this is also a situation where in one of our earlier lectures we have identified that, this delta G l w can be represented as, gamma 1 2 l w minus gamma 1 l w plus gamma 2 l w. This is the energy per unit area of course. Therefore, what we can get is that, we can now, correlate A 1 2 in terms of 12 pi d 0 square gamma 1 2 l w minus gamma 1 l w minus gamma 2 l w. So, the biggest advantage now is that, the expression of A 1 2 which we had, was in terms of beta 1 2.

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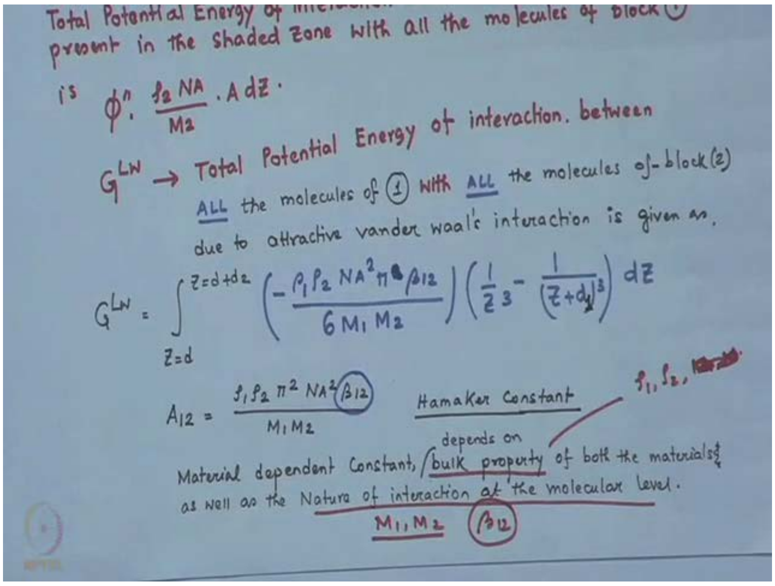

Total Potential Energy of
present in the shaded zone with all the molecules of block ①
is $\phi^n \cdot \frac{\rho_2 N_A}{M_2} \cdot A\,dz$.

$G^{LW} \rightarrow$ Total Potential Energy of interaction between ALL the molecules of ① with ALL the molecules of block (2) due to attractive vander waal's interaction is given as.

$$G^{LW} = \int_{z=d}^{z=d+dz} \left(-\frac{\rho_1 \rho_2 N_A^2 \pi^2 \beta_{12}}{6 M_1 M_2}\right)\left(\frac{1}{z^3} - \frac{1}{(z+d)^3}\right) dz$$

$$A_{12} = \frac{\rho_1 \rho_2 \pi^2 N_A^2 \boxed{\beta_{12}}}{M_1 M_2}$$

Hamaker Constant

$\rho_1, \rho_2,$

Material dependent Constant, depends on bulk property of both the materials & as well as the Nature of interaction at the molecular level.

M_1, M_2 $\boxed{\beta_{12}}$

Other parameters are all known, Avogadro’s number, density and the molecular weights are all known. But this beta 1 2 which sort of was signifying or was representing the strength of Vander Waals interaction was sort of a parameter which has to be experimentally determined or may be spectroscopically and determination of this parameter is slightly difficult.

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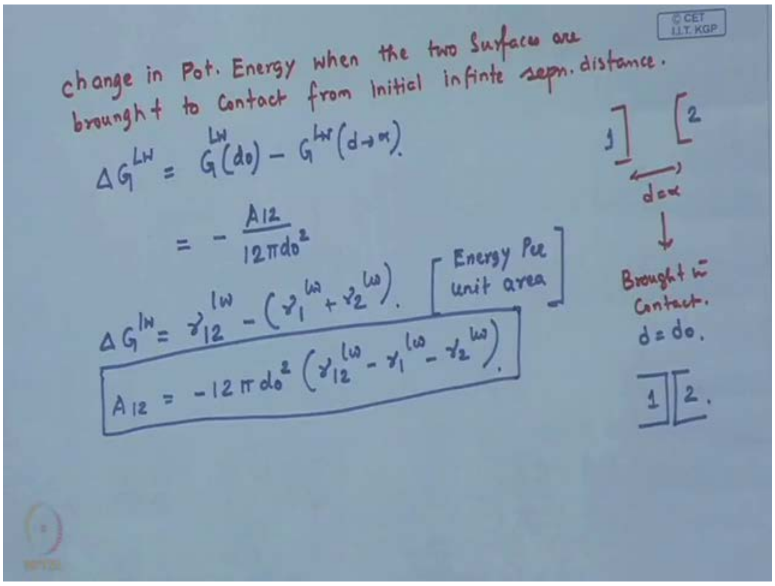

change in Pot. Energy when the two Surfaces are brought to Contact from Initial infinte sepn. distance.

$$\Delta G^{LW} = G^{LW}(d_0) - G^{LW}(d \to \infty)$$

$$= -\frac{A_{12}}{12\pi d_0^2}$$

$$\Delta G^{LW} = \gamma_{12}^{LW} - (\gamma_1^{LW} + \gamma_2^{LW}).$$

[Energy Per unit area]

$$\boxed{A_{12} = -12\pi d_0^2 (\gamma_{12}^{LW} - \gamma_1^{LW} - \gamma_2^{LW}).}$$

Now in contrast, now you have an expression for A 1 2 which is, in terms of parameters, which can be microscopically measured. Because, we have talked in while talking about the different components of surface tension that, the different individual components of surface tension can be easily found out or interfacial tension can be found out using contact angle goniometry, using appropriate probing liquids. The only thing that still cannot be physically determined and you have to rely on some model is this d 0.

Once you have and in many cases they are some standard numbers which are available. So, if you have d 0 now. Depending on the values of gamma 1 gamma 2 and gamma 1 2 they are l w components, you can easily determine the strength of the Vander Waals or the effective Hamaker constant.

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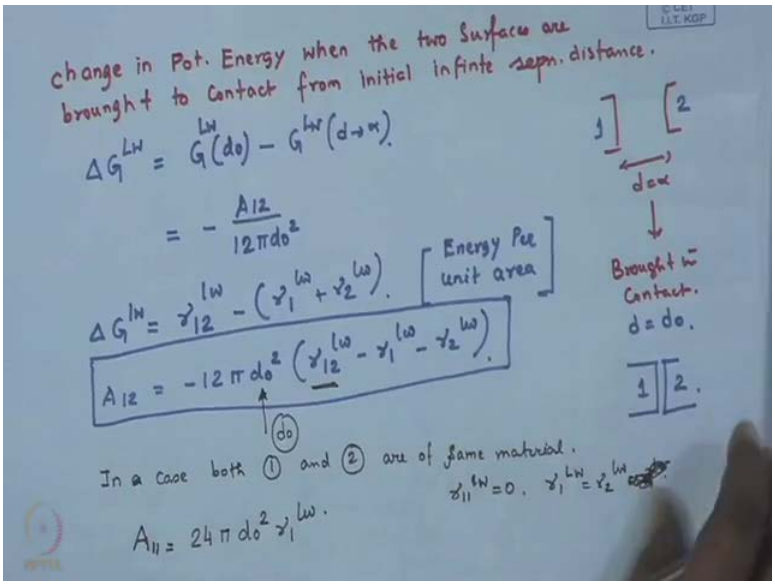

change in Pot. Energy when the two Surfaces are brounght to Contact from initial infinte sepn. distance.

$$\Delta G^{LW} = G^{LW}(d_0) - G^{LW}(d \to \infty).$$

$$= -\frac{A_{12}}{12\pi d_0^2}$$

$$\Delta G^{lW} = \gamma_{12}^{lW} - (\gamma_1^{lW} + \gamma_2^{lW}).$$

[Energy Per unit area]

$$\boxed{A_{12} = -12\pi \overset{\uparrow}{d_0^2}\,(\underline{\gamma_{12}^{lW}} - \gamma_1^{lW} - \gamma_2^{lW}).}$$

d_0

In a Case both ① and ② are of same material.

$\gamma_{11}^{lW} = 0.$ $\gamma_1^{LW} = \gamma_2^{LW}$

$$A_{11} = 24\pi d_0^2 \gamma_1^{LW}.$$

Now in case, in another special case, in case both 1 and 2 are of same material. Then what happens is, we essentially get a 1 1 l w is equal to 0, gamma 1 sorry gamma 1 1 l w equals to 0 gamma 1 l w equals to gamma 2 l w is equal to gamma 1 l w let us, say or gamma 1 l w is equal to gamma 2 l w. And then in that case A 1 2 gets replaced with A 1 1. So, this allows us to get an expression for A 1 1 as 24 pi d 0 square gamma 1 l w.

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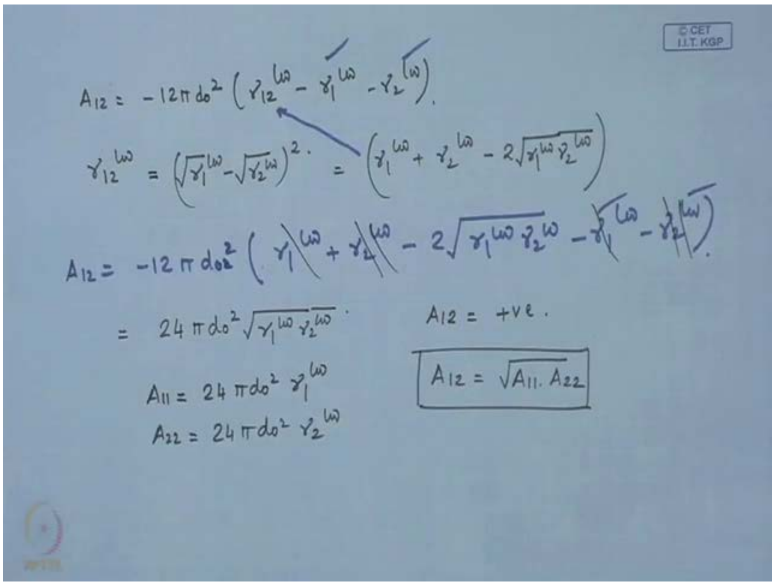

$$A_{12} = -12\pi d_0^2 \left(\gamma_{12}^{LW} - \gamma_1^{LW} - \gamma_2^{LW}\right).$$

$$\gamma_{12}^{LW} = \left(\sqrt{\gamma_1^{LW}} - \sqrt{\gamma_2^{LW}}\right)^2 = \left(\gamma_1^{LW} + \gamma_2^{LW} - 2\sqrt{\gamma_1^{LW}\gamma_2^{LW}}\right)$$

$$A_{12} = -12\pi d_0^2 \left(\cancel{\gamma_1^{LW}} + \cancel{\gamma_2^{LW}} - 2\sqrt{\gamma_1^{LW}\gamma_2^{LW}} - \cancel{\gamma_1^{LW}} - \cancel{\gamma_2^{LW}}\right).$$

$$= 24\pi d_0^2 \sqrt{\gamma_1^{LW}\gamma_2^{LW}}.$$

$$A_{12} = +ve.$$

$$A_{11} = 24\pi d_0^2 \gamma_1^{LW}$$

$$A_{22} = 24\pi d_0^2 \gamma_2^{LW}$$

$$\boxed{A_{12} = \sqrt{A_{11}.A_{22}}}$$

The other important thing is that, from this expression of A 1 2, we have minus 12 pi d 0 square gamma 1 2 l w minus gamma 1 l w minus gamma 2 l w. We know that, for Vander Waals pure Vander Waals interaction, gamma 1 2 l w is always it can represented as gamma 1 l w minus under root of gamma 2 l w whole square.

So, if you expand that, you get gamma 1 l w plus gamma 2 l w minus two gamma 1 l w into gamma 2 l w. So, if you substitute this back over here now, this whole expression gets substituted back here, 1 is left with so, 1 gets A 1 2 is equal to minus 12 pi d 0 square into gamma 1 l w plus gamma 2 l w minus 2 under root gamma 1 l w gamma 2 l w minus gamma 1 l w minus gamma 2 l w, because of these this and this.

So, these two terms cancels out and you are left with the fact that, it is 24 pi d 0 square into gamma 1 l w into gamma 2 l w. Which gives that, A 1 2 is always positive and also considering the fact that the expression of A 1 is 24 pi d 0 square, gamma 1 l w. Similarly, the expression of A 2 will be 24 pi d 0 square gamma 2 l w, one can get A 1 2 is equal to under root of A 1 1 into A 2 2. We will start our subsequent discussion from this point, thank you.