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**Lecture - 32**  
**VdW Interaction Between Two Surfaces**

Welcome back, we sort of take a quick detour not exactly a detour one of the necessary conditions what you have seen for this dewetting spontaneous dewetting to take place, was there has to be an active inter facial interaction between the two interfaces of the film and we argued qualitatively that this happens only if the film is very thin and the nature of Van Der Waals interaction is attractive.

It is time that we look in to this aspect in bit more detail. I also sort of you have trusted me so far by allowing me to tell that the interaction between two surfaces, Van Der Waals interaction between two surfaces the scaling is no longer one by r to the power 6, but scaling is must by d square. So, it is time we look in to those aspects.

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**vdW Interaction between two Particles**

The potential energy of interaction between two molecules or atoms due to van der Waal's force which is attractive, and mathematically is given as

$$\psi(x)_a = \psi'_a = -\beta x^{-6}$$

$x$  is the separation distance between two particles  
 $\beta$  is a material specific property which determines the precise magnitude of the long range inter-molecular attraction and  
 $\psi'_a$  represents the potential energy of interaction between two molecules in case of attraction

When the two particles are in very close proximity, the electrons in the outer orbital overlap, resulting in stiff Born repulsion, which has a faster decay as compared to the attractive interaction and is given as

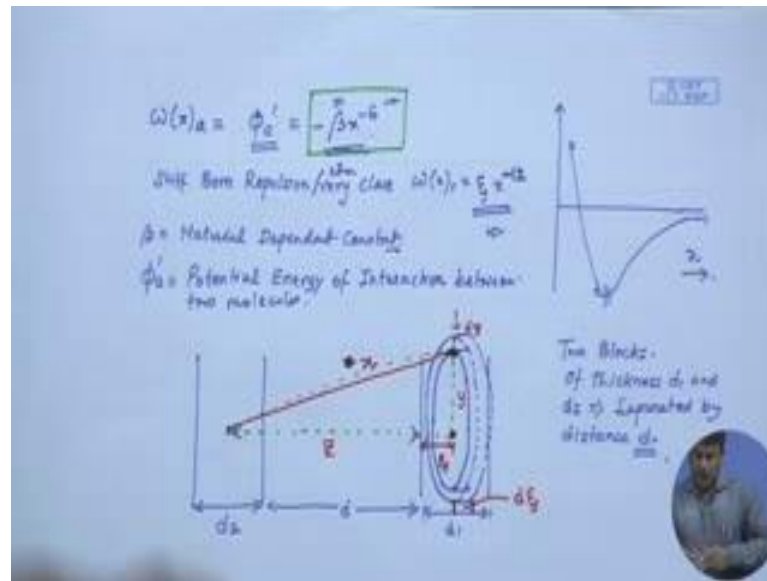
$$\psi(x)_r = \psi'_r = \zeta x^{-12}$$

**Typical L-J Potential Curve**

The slide features a graph of potential energy  $\psi(x)$  versus separation distance  $x$ . The curve shows a steep repulsive wall at small  $x$  (labeled 'Repulsive  $\psi'_r$ ') and a deeper attractive well at larger  $x$  (labeled 'Attractive  $\psi'_a$ '). A minimum point is marked with a red dot. Above the graph, two spheres representing particles are shown with overlapping outer orbitals, illustrating the cause of the repulsive force.

So, let us start from this expression, which is the potential energy of interaction between two molecules due to Van Der Waals interaction is; I am just replacing  $r$  with  $x$ .

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So, this is  $x$  now which is find; in fact this expression does not even capture the repulsive part, typically there is a stiff born repulsion this is called the born repulsion this part very close to the when the two surfaces are very close and it is sort of given by some  $\zeta x$  to the power minus 12. So, you see that the scaling is even sort of the exponent is even higher at the denominator. So, when  $x$  is very small this term dominates when  $x$  is bit higher this term becomes small and this term dominates and when  $x$  becomes bigger macroscopic scale does not even need to be macroscopic few micron onwards both the terms go to zero, so and there is no Van Der Waals source.

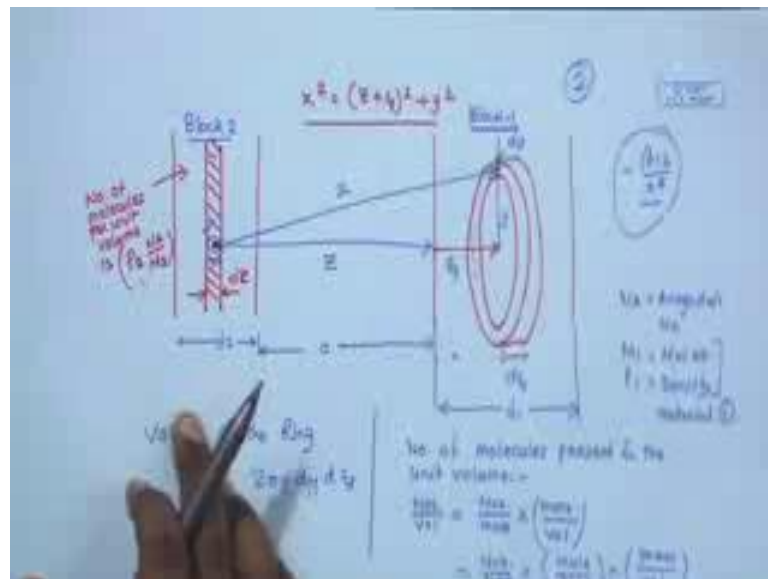
So, any way  $\beta$  of course, is a material dependent constant and however, the generic nature remains the same and this  $\phi_0'$  a sort of represents the potential energy of interaction between two molecules, we would like to take; look into the interaction let us try to understand the figure first between two blocks of materials  $d_1$  and  $d_2$ , which are separated by a distance  $d$ .

So, these are the two surfaces, two blocks of thickness  $d_1$  and  $d_2$ , which as separated by distance  $d$ . So, there we go; we consider a single molecule. So, what we know; we know the potential energy of interaction between two single molecules. So, idea is that we will try to find out two molecules present in within these two blocks, we know the expression for the interaction between them and then we will try to integrate in such a way so that our formulation covers the interaction of all molecules present in block 2 with all

molecules present in block 1, that in other words it is the interaction between the two blocks.

So, let us say we identify these two molecules whose has a separation distance of let us say  $x$ , we also draw a horizontal line from here drop apart and identify this is the point, we draw a circular ring within the material or block 1; look in to the construction carefully of course, you get a very neat version of construction in the ppt. So, what we have? From here to here it is  $Z$  this as I already pointed out is  $x$  and this is  $\zeta$  of course, the width of this block is  $d$   $\zeta$  this is  $y$  from the center to this.

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And the width of this block this is the thickness of this ring is  $dy$  I will just quickly redraw this part of the picture. So, you have ring; so center of which is at a distance  $\zeta$ , the width is  $d \zeta$ , this point is  $y$ , the width or the thickness is  $d y$  and this point we have identify the molecule we have identified in block 2 is at a distance  $Z$  from the surface of block 1 and this particular molecule we have identified in block 1 the direct separation distance is  $x$ .

So, I hope now the picture is clear; you can again have a look of the picture here in the PPT but I just wanted to give you a flavor of how it is constructed because I always feel that that gives a better idea of course, I will put up all these scan copies available to make it available to you.

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**vdW Interaction between two Surfaces**

Consider a ring like volume of material 1:

The volume is  $dV = 2\pi y dz$

Number of molecules present in unit volume of material 1:

$$N_1 = \frac{N_A}{M_1} \rho_1$$

Where:

- $N_A$  is number of molecules per unit mole of A (Avogadro Number)
- $M_1$  is molecular weight of 1
- $\rho_1$  is the density of material 1

Number of molecules present in the ring of volume  $dV$  is  $\left(\frac{N_A}{M_1} \rho_1\right) (2\pi y dz)$

Based on the assumption of additivity, the net interaction energy between 1 of phase 2 with all molecules of phase 1 in the ring:

$$d\phi = \left(\frac{N_A}{M_1} \rho_1\right) (2\pi y dz) \left(-\frac{B_1}{z^6}\right)$$

So, now let us see what we can do. So, what is the volume of the ring it is ring not to the rime you just learned in dewetting; volume of the ring is  $d \times 2\pi y \times dz$ . Now what is the number of molecules present within this ring? So, let us find out the number of molecules present in the unit volume, one can easily calculate it from Avogadro's number, but I will show it in the most simple way so that you all understand and you can remember.

So, it is essentially numbers per volume, but we are going to find out and this is something that is known number per mole is known that is Avogadro's number mole per unit volume of course, you can just write it like you multiply the numerator and denominator with mole. So, it is become like this; so this becomes Avogadro's number and this part again you can split up numbers per mole of course, it remains as it is; mole per mass and this term have to be the molecular weight and further you can split it as mass per volume.

So, what is it? It turns out  $N_A M_1^{-1} \rho_1$ , where  $N_A$  is Avogadro number  $M_1$  and  $\rho_1$  are molecular weight and density of material 1.

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No. of molecules present within the Ring  $\omega$

$$\left(\frac{N_A}{M_1} \rho_1\right) (2\pi y dy dz)$$

Net Interaction Energy Between  $\omega$  as a single molecule of Block 2 with all molecules of Block 1 within the Ring  $\omega$

$$d\phi^* = \left(\rho_1 \frac{N_A}{M_1}\right) (2\pi y dy dz) \left(-\frac{\beta_{12}}{x^6}\right)$$

We can now find out the Interaction Energy of  $\omega$  molecule in Block 2 with all molecules of Block 1

$$\phi^* = \int_{z=0}^{z=2a} \int_{y=0}^{y=2a} -\frac{\beta_{12}}{x^6} \rho_1 \frac{N_A}{M_1} \cdot 2\pi y dy dz$$

So, this is known. Then number of molecules present within the ring is  $N_A$  by  $M_1$  into  $\rho_1$  into  $2\pi y dy dz$ , based on the figure and the construction we have made right. Now what we have is the essentially it is assumption of additivity that the total inter. So, what we find out at this point is the interaction of one molecule, this is this molecule present in block 2 with all molecules of block 1 present within the ring right and what is the total interaction is based on the concept of additivity, that a net interaction energy between one molecule of phase 2 or block 2 with all molecules of block 1 within the ring is you do not even use a symbol we will talk about it later; see what has been done is very simple you know the strength of Van Der Waals interaction between two molecules of 1 and 2 is this  $\beta_{12}$  divided by  $x$  to the power 6, you have identified.

So, what you have done is that you are now looking into so in other words let me just try to take a minute to explain this the strength of interaction of this molecule of 2 with one molecule of material 1 is given by this. So, it has the same strength of interaction with all the other molecules present in the ring right, we assuming that all the molecules present in the ring are at a distance of  $x$  to the power 6  $x$  to the power minus (Refer Time: 13:54) are at a distance of  $x$  from this particular molecule.

So, what is the total interaction energy of one molecule of 2, that is this molecule with all molecules of 1 that is present with in the ring, you simply calculate the number of

molecules present in the ring multiply with this and the you see that is exactly what we have done this part corresponds the ring volume, this is the a number of molecules present per unit volume you multiply that so these two, product in fact, gives you number of molecules present with in the ring element and this is what you have.

So, now based on this what you can do is you can now find out the identified molecule in block 2 with all molecules of block 1 and how can one do that one can simply do that by integrating this expression within suitable limits and what are the expanses of block 1; zeta stretches from zero to d 1 and y stretches from zero to infinity. So, you simply perform this integral; I think the detail steps are given here.

So, all we need to do but I will are given in the PPT, but I will do it in front of you eyes so, that you can follow it clearly all we need to do is to invoke the Pythagorean Theorem where we find based on the geometry that x square is in fact, Z plus zeta whole square plus y square this is some simple Pythagoras Theorem.

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$$\omega(d) = - \frac{2 \rho_1 N_A \pi \beta_{12}}{M_1} \int_{z=0}^{z=d_1} \int_{y=0}^{y=\infty} \int_{x=0}^{x=\infty} \frac{y dz dx}{[(z+y)^2 + y^2]^3}$$

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

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

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

Replaced  $x$  in terms of  $z$  and  $y$  using Pythagoras Theorem.

Energy of Interaction of a single molecule of  $\ominus$  with all molecules of  $\oplus$ .

So, what we have is this let us write this as some w d not the phi double dash exactly. So, you see this expression for phi double dash. in fact, you can write minus rho 1 N A pi beta 1 2 by M 1 those are in fact, nothing but the constants they are coming out.

So, where has this come; in fact, this comes from the expression of 2 y d y you get this that is why the 2 comes in and you substitute x in terms of these right. So, this is simpler

algebra do it yourself now you first look into this part of the integral and this gives you in fact, again if you perform this definite integral and integrating; so, this integral now if you integrate the expression that you have got here you will get an expression like this I just suggest that you sit with it once and just do it.

So, this  $y \, dy$  is there all you have done is see this part is already there in the expression all you have done is you have replaced here how you are got it if you still have doubt; replaced  $x$  in terms of  $y$ ,  $Z$  and  $\zeta$  using Pythagoras theorem. I, to some of you I am going too slowly, but it is just for your all other friends to catch up and I always teach like this these steps often tend to drive away people, but this nothing to be scared you should understand every step.

So, the total; the expression of  $\phi''$  at this stage which is not exactly  $\phi''$  let us write  $w$  because this is  $\phi''$  will be using for interaction of all molecules of 2 with 1 so I will just replace this as  $w$  turns out to be minus  $\rho N A \pi \beta \frac{1}{2}$  divided by  $6 M_1$  this. So, what is this? In fact, this gives the energy of interaction of a single molecule of all molecules of 1.

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**vdW Interaction between two Surfaces**

Upon integrating the equation, it gives the total interaction of all molecules in the ring with a single molecule residing at a distance  $z$  from surface of material 1.

Net interaction energy of a molecule at a distance  $z$  from the surface of Phase 1 with all molecules of Phase 1 is given as

$$w(z) = \int_{-\pi/2}^{\pi/2} \int_0^{2\pi a} -\frac{C_6}{r^6} (2\pi a y \, dy) \, d\theta$$

Applying Pythagoras theorem in figure, we get  $r^2 = (z + \zeta)^2 + y^2$

Consequently, the integral now becomes

$$w(z) = \frac{-2\pi a N_1 \beta_1 \pi}{M_1} \int_{-\pi/2}^{\pi/2} \int_0^{2\pi a} \frac{(y \, dy) \, d\theta}{[(z + \zeta)^2 + y^2]^3}$$

And eventually yields

$$w(z) = w'' = \frac{-\rho_1 N_1 \beta_1 \pi}{6 M_1} \left[ \frac{1}{z^3} - \frac{1}{(z + d)^3} \right]$$

So, now what do we do we simply do that we just look in to this figure. So, what we have is for this block as well just like this formula this expression not even a formula this is the expression we derived. So, number of molecules per unit volume is simply what we do is we identify a region cross section is  $A$  and the thickness is  $d$   $Z$ . So, we now

know the strength of interaction of all interaction energy of this particular molecule with all molecules of 1.

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$$dG^{LW} = \left( \rho_2 \frac{NA}{M_2} \right) w(d) dZ$$

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

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

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

$$G^{LW}(d) = -\frac{A_{12}}{12\pi d^3} \left[ \frac{1}{\left( \frac{d_1+d_2+d}{d} \right)^2} + 1 - \frac{1}{\left( \frac{d+d_2}{d} \right)^2} - \frac{1}{\left( \frac{d_2}{d} \right)^2} \right]$$

So, what we can do is we can find out the energy of interaction of all molecules present within this thin strip with that of 1 very easily and that turns out to be take a fresh page and write it here what is this, this is simply you actually need to multiply. So, let us take a minute to write it down; A is let us say the cross sectional area. This particular term is the number of molecules present within this fate, but what we do is we look at the interaction per unit area they were. Therefore, we divide it by A and that that gives us an expression for G L W. So, what is the expression for G L W; the expression turns out to be now you see the limits of Z vary from d to d plus d 2.

The limits of Z this is how Z is defined in fact, Z starts from here. So, the limits of Z varies from d that is here to d plus d 2 you simply integrate to get the G L W that is the energy of interaction between two surfaces due to Van Der Waals forces and this turns out to be; my suggestion would be what I suggest also when I teach this particular stuff in a class that, do the derivation once; it is very easy, but if you do it you will feel scared and you will also mess up you will never understand how the terms are coming. So, you can look into what I have done more than welcome to see it and then please do the derivation once.



So, we take out a constant which is  $A_1^2$  this part we take out; in fact, this  $\pi$  square is not coming in fact, you have deliberately added made it  $\pi$  square to look it symmetric with  $N A$  square and one  $\pi$  in fact, goes in the denominator and this is what is known as the Hamaker constant. So,  $A_1^2$  is a Hamaker constant that depends on the densities of the two of the molecular weight and the densities of the two blocks we are talking about. So, the expression that we get after you perform this integral is  $d G L W$  as a function of the separation distance is minus  $A_1^2$  divided by  $12 \pi$ .

Please remember this  $12$  comes from integral it has nothing to do with  $1^2$  we are writing here and that gives you  $d_1$  plus  $d_2$  plus  $d$  whole square it is a simple integration, but please do it;  $d$  plus  $d_1$  whole square minus  $d$  plus  $d_2$  whole square. So, that is the expression of the Van Der Waals interaction between two surfaces. I have said that the interaction skills is  $1$  by  $d$  square well it is in fact true; what we have done is you have considered two surfaces of finite thickness. If you now consider that the two blocks are very wide; that both  $d_1$  and  $d_2$  tends to infinity then you will find that  $G L W$   $d$  between two surfaces only the two surfaces actually becomes  $A_1^2$  divided by  $12 \pi d$  square at the denominator.

So, here you see one thing I have proven it is a case like this, this stretches to infinity in this direction this stretches to infinity in this direction and what you get is the Van Der Waals interaction between two surfaces scales as  $1$  by  $d$  square, but this expression that we have derived it might takes some time for you to get use to this expression; I honestly request that you do the derivation once so that you that agree upon what we have done and you understand it very very well actually (Refer Time: 27:12) something more interesting because we have considered finite thickness, so we can in fact plug in the thickness of a film here. And we can get an expression of disjoining pressure that something that I will take up in the next class.

Thank you.