Instability & Patterning of Thin Polymer Films
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Lecture No. # 30
Intermolecular Forces between Particles and Surfaces - IV

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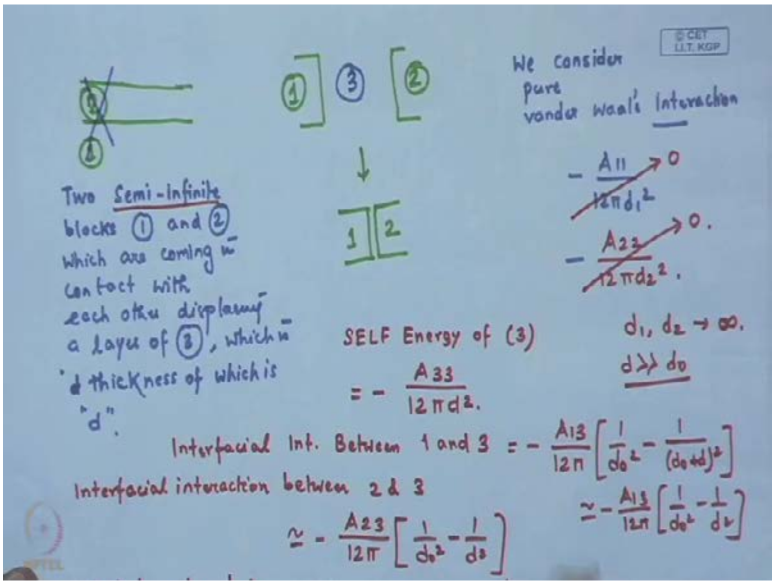

Two Semi-Infinite blocks ① and ② which are coming in contact with each other displacing a layer of ③, which is 'd thickness of which is "d".

We consider pure vander waal's Interaction

$-\cancelto{0}{\frac{A_{11}}{12\pi d_1^2}}$

$-\cancelto{0.}{\frac{A_{22}}{12\pi d_2^2}}.$

$d_1, d_2 \rightarrow \infty.$

$d \gg d_0$

SELF Energy of (3)

$= -\frac{A_{33}}{12\pi d^2}.$

Interfacial Int. Between 1 and 3 $= -\frac{A_{13}}{12\pi}\left[\frac{1}{d_0^2} - \frac{1}{(d_0+d)^2}\right]$

$\simeq -\frac{A_{13}}{12\pi}\left[\frac{1}{d_0^2} - \frac{1}{d^2}\right]$

Interfacial interaction between 2 & 3

$\simeq -\frac{A_{23}}{12\pi}\left[\frac{1}{d_0^2} - \frac{1}{d^2}\right]$

Welcome back, in the previous class we talked about self interaction energy within the film and based on that we derived an expression for the effective haymaker constant for a situation like this, where you have a film of let us say liquid 2 on a surface of liquid 1. Now, what we are going to do? We are going to look at the old problem of two blocks of 1 and 2 coming in contact with each other in a medium 3. And all we consider is both in terms of self energy as well, as interaction across different objects is we consider pure vander waal's interaction or the vender type interaction and we understand that the nature of this interaction is always attractive.

But we will see that in this particular system there can be situation where even based on pure vander waal's interaction you can have a effective repulsion between 1 and 2. So, let us identify the system unlike the previous system, we here we have two semi infinite blocks of 1 and 2, which are coming in contact with each other displacing a layer of 3, which is the thickness of which is d. So, the self energy of interaction of block 1 is A11 divided by whatever is its thickness 12 pi d1 square self energy of block 2 would be A22 divided by 12 pi d 2 square. Now, since both are semi infinite therefore, both d1 and d2 tend to infinity and therefore, both this term and this term tends to 0.

Self energy of 3 is off course minus A33 divided by 12 pi d square the interfacial interaction between 1 and 3 is minus A13 divided by 12 pi divided by 1 by d0 square minus 1 by d0 plus d square, which can be approximated as minus A13 divided by 12 pi d 0 square minus 1 by d square assumption is d is much larger than d0.

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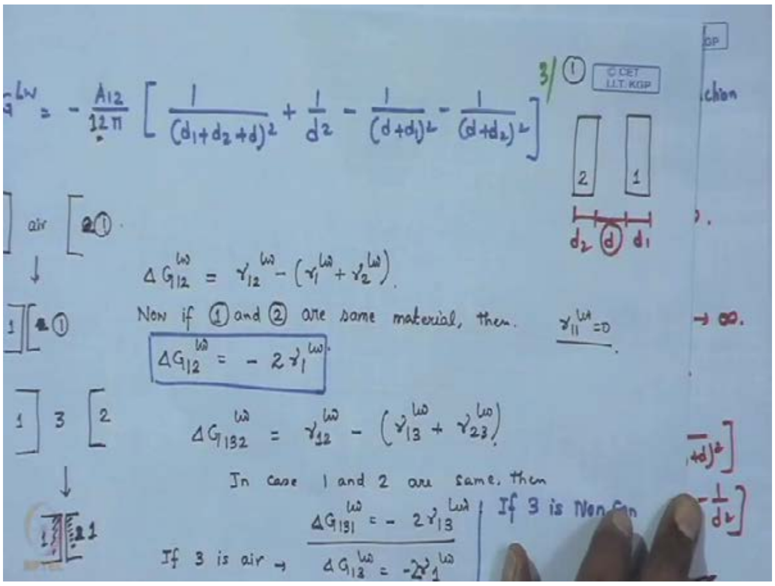

$$G^{LW} = -\frac{A_{12}}{12\pi}\left[\frac{1}{(d_1+d_2+d)^2} + \frac{1}{d^2} - \frac{1}{(d+d_1)^2} - \frac{1}{(d+d_2)^2}\right]$$

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

Now if ① and ② are same material, then. $\underline{\gamma_{11}^{LW} = 0}$.

$$\boxed{\Delta G_{12}^{LW} = -2\gamma_1^{LW}}$$

$$\Delta G_{132}^{LW} = \gamma_{12}^{LW} - (\gamma_{13}^{LW} + \gamma_{23}^{LW})$$

In case 1 and 2 are same, then

$$\Delta G_{131}^{LW} = -2\gamma_{13}^{LW}$$

If 3 is air → $\Delta G_{13}^{LW} = -2\gamma_1^{LW}$

If 3 is Non

Similarly, the interfacial interaction between 2 and 3 will lead to minus A23 divided by 12 pi divided by 1 by into 1 by d0 square minus 1 by d square and the interaction between 1 and 2 if you look at this term again between 1 and 2, so the minimum separation distance is d d1 tending to infinity d2 tending to infinity. So, that is given as minus A12 divided by 12 pi d square.

So, these are the four terms that remain active the self energy on interaction of 3 the interaction between the molecules 1 and 3, the interaction of between the molecules of 2 and 3, and the interaction between the molecules of 1 and 2 of course, you can immediately understand that if the layer the liquid layer 3 is very thick and wide, then two of the terms disappear that is the self energy of interaction of 3 tends to 0, because d is very large as well as the interaction the interfacial interaction of the interaction not exactly the interface. The interaction between the molecules of 1 and 2 also tends to 0 there will be only local interfacial interaction between 13 and 23, because these terms still remain active because de might be very high, but this d0 square this is a small this is a small so, this term remain active.

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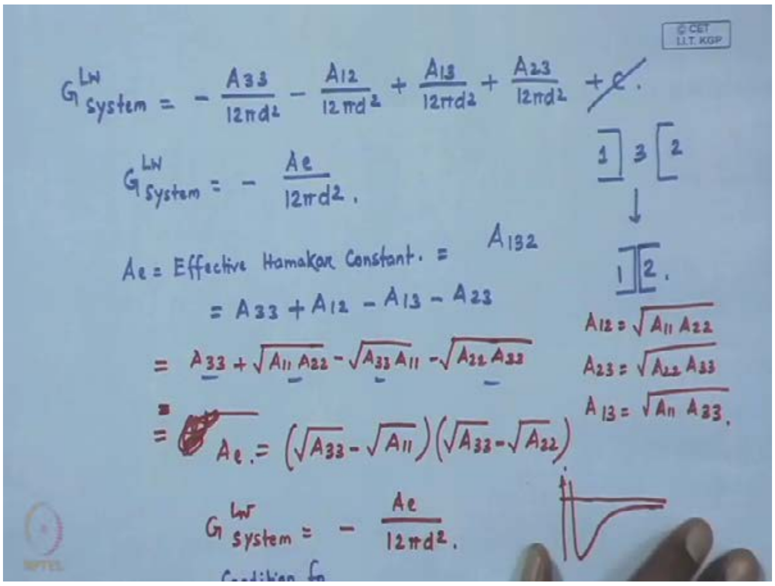

$$G^{LW}_{system} = -\frac{A_{33}}{12\pi d^2} - \frac{A_{12}}{12\pi d^2} + \frac{A_{13}}{12\pi d^2} + \frac{A_{23}}{12\pi d^2} + \cancel{c}.$$

$$G^{LW}_{system} = -\frac{A_e}{12\pi d^2}.$$

A_e = Effective Hamakar Constant. = A_{132}

$$= A_{33} + A_{12} - A_{13} - A_{23}$$

$$= A_{33} + \sqrt{A_{11}A_{22}} - \sqrt{A_{33}A_{11}} - \sqrt{A_{22}A_{33}}$$

$$= A_e = \left(\sqrt{A_{33}} - \sqrt{A_{11}}\right)\left(\sqrt{A_{33}} - \sqrt{A_{22}}\right)$$

$$G^{LW}_{system} = -\frac{A_e}{12\pi d^2}.$$

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

$A_{23} = \sqrt{A_{22}A_{33}}$

$A_{13} = \sqrt{A_{11}A_{33}}$.

Condition fo

So, considering this four interactions the GLW of the system turns out to be minus A33 divided by 12 pi d square minus A12 divided by plus the constant. So, we are interested in the change in energy and therefore the constant does not matter or we are interested in the change in energy as a function of d. So, the constant really does not matter, we can neglect it. So, therefore we can write the GLW of the system minus A e by d square, where A e is the haymaker constant and in this case as a expression of A33 plus A12 minus A13 minus A23.

We should not sort of confuse this haymaker constant the effective haymaker constant in the previous ones so, I guess we should be better to write something like this A132. We have talked about the convention of 132 before, where 1 and 2 coming contact with each other by dislodging the liquid 3. So, we can write that what we already know that A12 in one of our previous classes, we have shown that it is a A11 in to A22 A23 is similarly, we can written as A22 in to A33 and A13 once it can be written as a A11 in to A33. So, in that way what we can write here if you plug in this expression and do a little bit of algebraic manipulation, if just have to consider the first term third term club the first and third term together the second and the fourth term together. What you get is eventually if you do the simplification, you would be getting an expression (no audio from 9:20 to 9:35) like this the effective haymaker constant.

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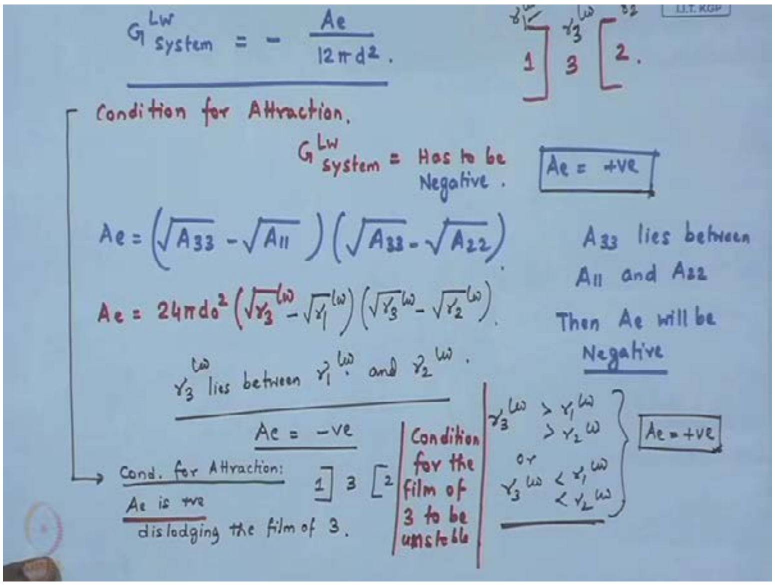

$G^{LW}_{system} = -\frac{A_e}{12\pi d^2}$.

γ_3^{LW}

1] 3 [2.

Condition for Attraction.

G^{LW}_{system} = Has to be Negative.

$\boxed{A_e = +ve}$

$A_e = \left(\sqrt{A_{33}} - \sqrt{A_{11}}\right)\left(\sqrt{A_{33}} - \sqrt{A_{22}}\right)$.

A_{33} lies between A_{11} and A_{22} Then Ae will be Negative

$A_e = 24\pi d_0^2 \left(\sqrt{\gamma_3^{LW}} - \sqrt{\gamma_1^{LW}}\right)\left(\sqrt{\gamma_3^{LW}} - \sqrt{\gamma_2^{LW}}\right)$.

γ_3^{LW} lies between γ_1^{LW} and γ_2^{LW}.

Ae = −ve

Cond. for Attraction: Ae is +ve dislodging the film of 3.

1] 3 [2

Condition for the film of 3 to be unstable

$\left.\begin{array}{l} \gamma_3^{LW} > \gamma_1^{LW} \\ \quad\;\; > \gamma_2^{LW} \\ \text{or} \\ \gamma_3^{LW} < \gamma_1^{LW} \\ \quad\;\; < \gamma_2^{LW} \end{array}\right\} \boxed{A_e = +ve}$

Now, we know that the GLW of the system is minus A e divided by 12 pi d square and we also know from the force curve that the any interaction is attractive as long as it remains negative. So, this interaction will remain attractive only when A e will be positive so, if we simple argue that the condition or let us write it down here in a fresh; and if we write down the condition for attraction, attraction between what? Condition of attraction between 1 and 2; so we are argue that since the interaction is vender weal's based on vender weal's interaction therefore, in a the interaction between A and 1 and 2 will be always be attractive. But now you have a liquid three, we are not considering any polar interaction or anything like that we are only considering the interaction, the vender weal's interaction, but the interaction between 13, 23 and 33. Now the condition of attraction between 1 and 2, remains that the GLW of the system has to be negative; or in other words therefore, A e has to be positive.

Now, you see the in this particular case the expression of A e is given as therefore, you can see that if A e or A33 lies between its simple mathematics. If A33 lies between A11 and A22 then A e will be negative. This can also be written in terms of the surface tenses as A e is equal to 24 pi d0 square into under root of gamma 3 LW of minus under root of gamma 1LW into gamma 3 gamma 2LW and the issued be if gamma 3 lies between gamma 1 or gamma 3LW lies between gamma 1LW and gamma 2 LW then you will have A e to be equal to negative. In the event that gamma 3LW is greater than both gamma 1LW and gamma 2LW or gamma 3LW is less then both gamma 1LW and gamma 2LW you will have a positive A e.

So, this is now you can see the depending on the relative magnitudes of the surface tension the vander waal’s component of surface tension you can have an interfacial attraction or repulsion between the two blocks 1 and 2 even though we are considering only the vander waal’s interaction. Other interesting thing is that we say the condition for attraction is a e as to be positive so, in that case 1 and 2 will get attracted to words each other. So, this is an important point. So, condition for attraction just read this one condition for attraction is A e is positive attraction between 1 and 2. So, they will coming in close contact with each other by dislodging the film of 3. So, in other words this though this is a condition for attraction between 1 and 2 this is also a condition for the film to be unstable.

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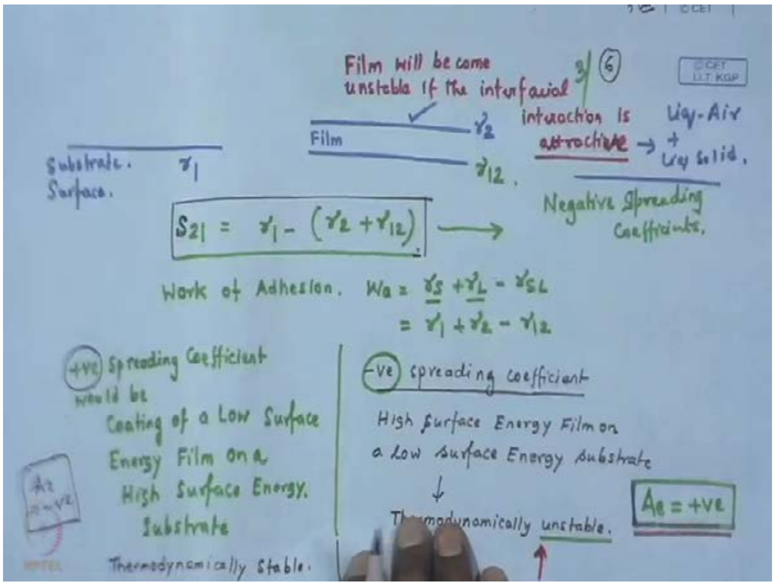

Film will be come unstable if the interfacial interaction is attractive → Liq-Air + Liq Solid.

3/⑥

Film γ_2

γ_{12}.

Substrate. Surface. γ_1

$$\boxed{S_{21} = \gamma_1 - (\gamma_2 + \gamma_{12})} \longrightarrow$$

Negative Spreading Coefficients.

Work of Adhesion. $W_a = \gamma_S + \gamma_L - \gamma_{SL}$

$= \gamma_1 + \gamma_2 - \gamma_{12}$

(+ve) Spreading Coefficient would be Coating of a Low Surface Energy Film on a High Surface Energy. Substrate

Thermodynamically Stable.

$A_e = -ve$

(-ve) spreading coefficient

High Surface Energy Film on a Low Surface Energy Substrate

↓

Thermodynamically unstable.

$\boxed{A_e = +ve}$

A positive value of A e will result in the film to become unstable and if you now, refer back to this old slide, which we prepared in the context of explaining to you spreading coefficient you find the exactly the same thing a positive value of A e refers to thermo dynamically unstable film. So, the film is essentially ruptures; so essentially we are talking about the same thing, same scenario only difference is here; we talked about a separate liquid film coated on a same scenario only rigid substrate. And here we are talking about a liquid film, which is sandwich between two solid surfaces, which try to sort of come in contact with or sort of disappear. So, the condition for instability here is manifested by an attractive interfacial interaction same thing is valid here a film will become unstable, if the interfacial interaction is attractive.

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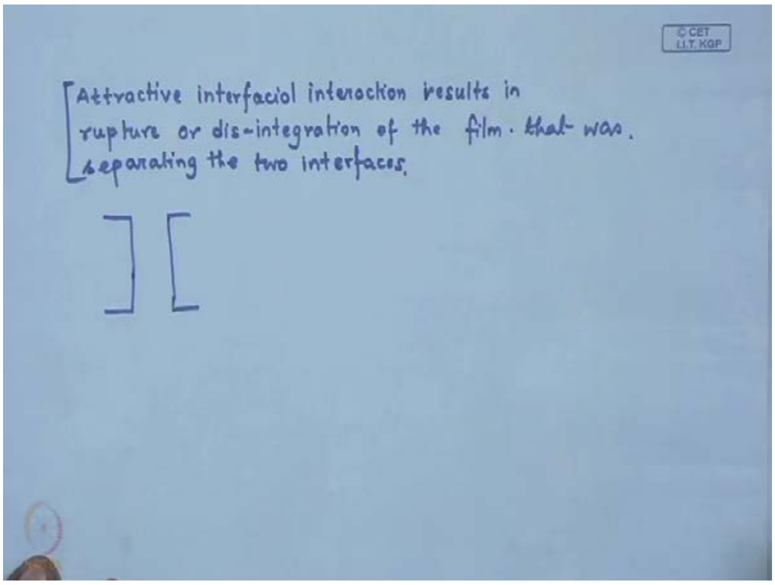

Attractive interfacial interaction results in
rupture or dis-integration of the film. that was.
separating the two interfaces.

What is the interfacial inter attractive? Here the interfacial interaction is the between this liquid air interface and the liquid solid interface. In contrast, here the interaction is between two liquid solid interfaces; so, the condition for attractive interfacial or in other words, attractive interfacial interaction in variably results in rupture or disintegration of the film that was separating the two interfaces.

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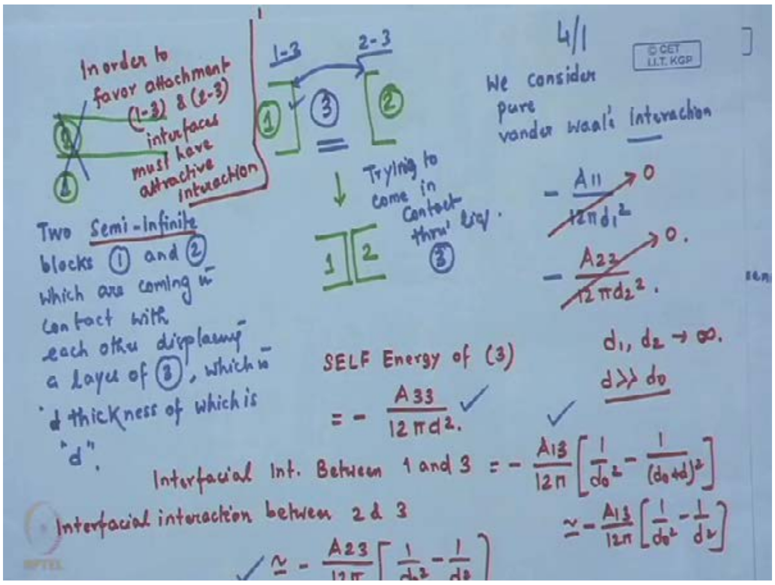

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In order to favor attachment (1-3) & (2-3) interfaces must have attractive interaction

1-3

2-3

① ③ ②

Trying to come in contact thru' liq. ③

1 2

Two Semi-Infinite blocks ① and ② which are coming in contact with each other displacing a layer of ③, which is thickness of which is "d".

We consider pure vander Waal's Interaction

$-\frac{A_{11}}{12\pi d_1^2} \to 0$

$-\frac{A_{22}}{12\pi d_2^2} \to 0.$

$d_1, d_2 \to \infty.$

$d \gg d_0$

SELF Energy of (3)

$= -\frac{A_{33}}{12\pi d^2}.$ ✓

Interfacial Int. Between 1 and 3 $= -\frac{A_{13}}{12\pi}\left[\frac{1}{d_0^2} - \frac{1}{(d_0+d)^2}\right]$ ✓

$\simeq -\frac{A_{13}}{12\pi}\left[\frac{1}{d_0^2} - \frac{1}{d^2}\right]$

Interfacial interaction between 2 & 3

✓ $\simeq -\frac{A_{23}}{12\pi}\left[\frac{1}{d_0^2} - \frac{1}{d^2}\right]$

We will understand this in greater detail but again let me just quickly tell you what the basic essence of this is. So, we are doing this apparently very simple calculation here trying to find out the condition, we are talking about two blocks 1 and 2, which are coming in contact or trying to coming in contact through liquid 3. And in order to do that if the 12 coming in contact liquid, there can be two ways to visualize it.

One of the possible way is to they are must be an attractive interfacial interaction between 1 and 2, but the other way of looking out is the film of three has to sort of disintegrate, because there is a layer of 3 which is between these two surfaces. And if this two surfaces once to come in contact, first thing is the two interfaces if you now, look at instead of looking at the two blocks, if you now look at from the stand point of this liquid layer its two interfaces of the 13 interface and the 23 interface. So, these two interfaces have to be attractive the 13 interface and the 23 interface, and these two interfaces in order to favor attachment the 13 and the 23 interfaces must be have attractive interaction. The moment these two attractive interaction of course, the blocks 1 and 2 would come in contact, but what will happen is that the film that was initially separating the two blocks 1 and 2 has to sort of disintegrate and disappear or rupture in favor of attachment of these two interfaces.

So, essentially the two separate interfaces the 13 and the 23 interfaces would like to merge for are new 12 interfaces at the cost of disintegration of the film 3, which was isolating the 13 and the 23 interfaces. One way of looking the condition at the condition film between the two as to be unstable or a film will be unstable, if there is an attractive interfacial interaction between its two interfaces exactly, the same thing happens when we are talking about a film, which is coated on a rigid surface.

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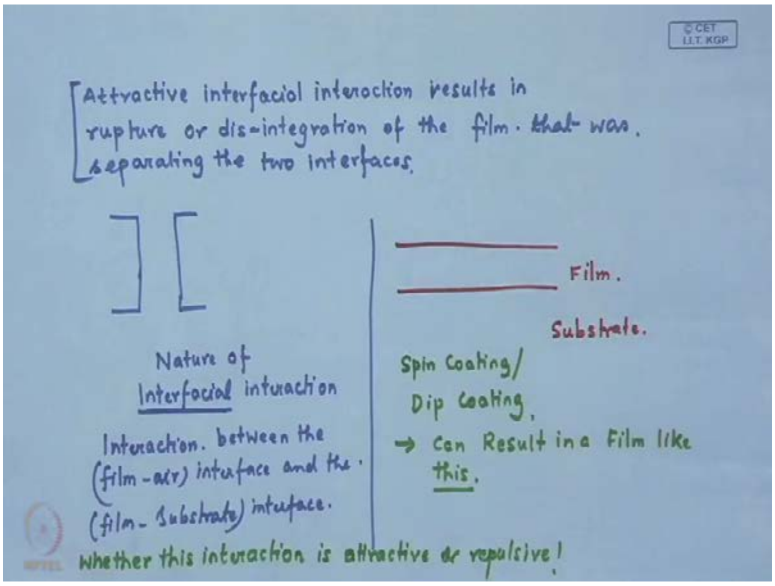

Attractive interfacial interaction results in rupture or dis-integration of the film. ~~that~~ was separating the two interfaces.

Nature of Interfacial interaction

Interaction. between the (film-air) interface and the (film-Substrate) interface.

Spin Coating/ Dip Coating.

→ Can Result in a Film like this.

Whether this interaction is attractive or repulsive!

So, let me write in a neat of sheet of paper, so that you do not confuse it. So, here we have a film, here we have a substrate and we have talked about discussed about adequate experimental techniques like spin coating dip coating, which can result in a film like this. Now, the question to ask is whether if film created like this remains stable over a prolong period of time or disintegrates? The answer to that is it depends to a large extent on the nature of interfacial interaction. What is meant by interfacial interaction? It is the whether the interaction between the film-air interface and the film substrate interface whether this interaction is attractive or repulsive depends on that. So, if the interaction is attractive of course, then these two interfaces will try to merge with each other exactly in the same fashion as here were the two interfaces try to merge with each other by preferentially draining of liquid film or by dislodging or disintegrating of the liquid film.

In contrast, if the interfacial attraction is repulsive, then the film layer remains impact exactly the same thing happens here the interfacial interaction is repulsive, then which we have also understood that it happens under a situation where so let us write it down somewhere.

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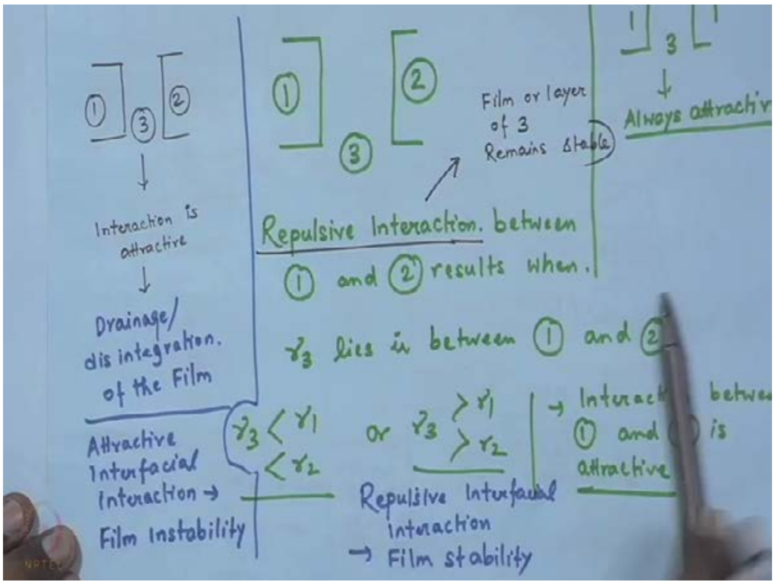

If repulsive interaction between 12 and 3 between 1 and 2 results, when we have seen that gamma 3 lies in between 1 and 2 if gamma 3 is less then both gamma 1 and gamma 2 or gamma 3 is greater than both gamma 1 and gamma 2. Then of course, the interaction between 1 and 2 is attractive. One can also explain in this way that this interaction irrespective of the magnitude of 1 and 3 will be always attractive as you cannot have a value of a gamma 3, which is between gamma 1 and gamma 1. So, it will either be gamma 3 will be higher than gamma 1 or it will lower then gamma 1 but irrespective of the case the interaction will be attractive. So, a repulsive attraction this is the necessary condition for a repulsive interaction so, the repulsive interaction also implies that the film or layer of three remains stable.

We are talking about instability or eventually, we will be talking about instability two things are getting attractive dislodging a liquid layer in between them its fine but that is also. So, here if they come in contact or the interaction is attractive, then 1 and 2 join up but this also leads to drainage or disintegration of the film. So, we can start developing our own rule of thumb based on our understanding which is of course, fundamental understanding any attractive interfacial interaction results in film instability.

In context, if you have a repulsive interfacial interaction like to have a film stability, we just given example the same thing is valid, when you have a film which is coated on a substrates repulsive interfacial interaction, what we have written here. So repulsive interaction interfacial interaction leads to film stability exactly over here the same thing these two interfaces repel each other so, the film remains stable.

So this concept, what we have written here remains valid irrespective of here setting it like this or like this. So, repulsive interfacial interaction will lead to film stability in contrast an attractive interfacial interaction will lead to a film instability. We will talk about this in greater detail, when we do the thin film equation, but right now we will talk little bit about another aspect of this attachment.

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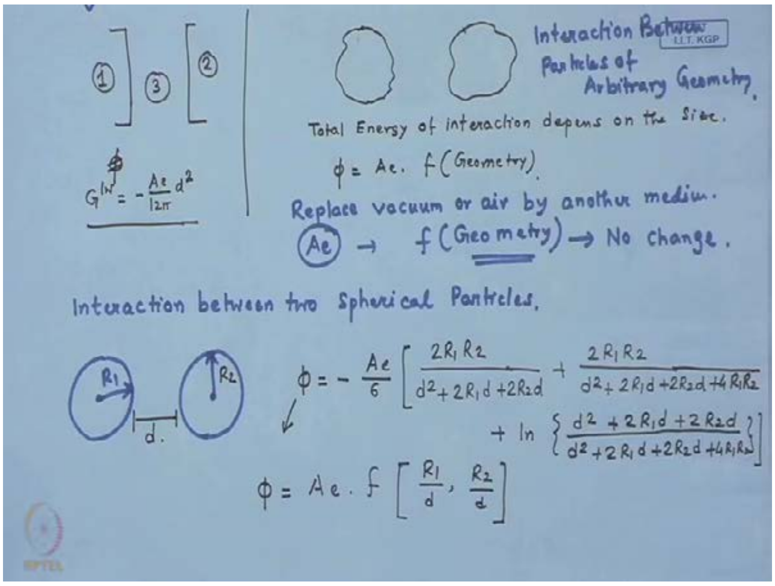

Interaction Between Particles of Arbitrary Geometry.

ϕ

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

Total Energy of interaction depens on the Size.

$\phi = A_e \cdot f(\text{Geometry})$.

Replace vacuum or air by another medium.

$\boxed{A_e} \rightarrow \quad f(\underline{\underline{\text{Geometry}}}) \rightarrow \text{No change}.$

Interaction between two Spherical Particles.

$$\phi = -\frac{A_e}{6}\left[\frac{2R_1R_2}{d^2+2R_1d+2R_2d} + \frac{2R_1R_2}{d^2+2R_1d+2R_2d+4R_1R_2} + \ln\left\{\frac{d^2+2R_1d+2R_2d}{d^2+2R_1d+2R_2d+4R_1R_2}\right\}\right]$$

$$\phi = A_e \cdot f\left[\frac{R_1}{d}, \frac{R_2}{d}\right]$$

What we have talk so far drawn so far is something like a geometry like this, where the surfaces are sort of flat and parallel and we have talked about their attachment or the condition of the attachment, but let us now try to understand or identify the condition or the what happens, when two surfaces of arbitrary geometry try to come in contact with each other. So, for this type of setting we now have the expression for pi or the GLW of the system in very clear terms, which is essentially minus A e 12 pi into whatever is the separation distance depending on d but between two surfaces of arbitrary geometry, what is the important thing or the important derivations.

Here the interfacial interaction per unit area is a function only of the separation distance what happens here the total energy of interaction depends on the size and effectively. So, pi becomes the function of effective haymaker constant into function of geometry. Now, if you we have seen from this system that whether you replace the vacuum or air by another medium only the magnitude of A e changes, but this geometric parameter remains unaltered, which for a definite geometry where of the form like this.

Whether you if you change the medium let us say plug in a liquid 3 over here, but will changes this one will change remains un altered. So, same thing is valid over here also between the interactions of between particles of arbitrary geometry. If we consider the interaction between two spherical particles let us say of radius R1 R2 and the separation distance is d, then one can get this derivation is beyond the scope one gets that A e equal to the pi equal to A e by 6 into 2 R1 R2 (no audio from 32:50 to 33:15), a little longest expression (no audio from 33:21 to 33:45) and important thing to notice this is not the unit area this is the total potential. Therefore, what we can write it becomes function of Ae into essentially there are three parameters R1 R2 and d but what can be seen it can be sort of resolve as function of R1 by d and R2 by d two geometric parameters.

So, these two are spherical particles. So, there is angular symmetry over there, but if you take any other type of particles even its cylindrical particles, these type of angular symmetry will missing, and there will be need to introduce more geometric parameters.

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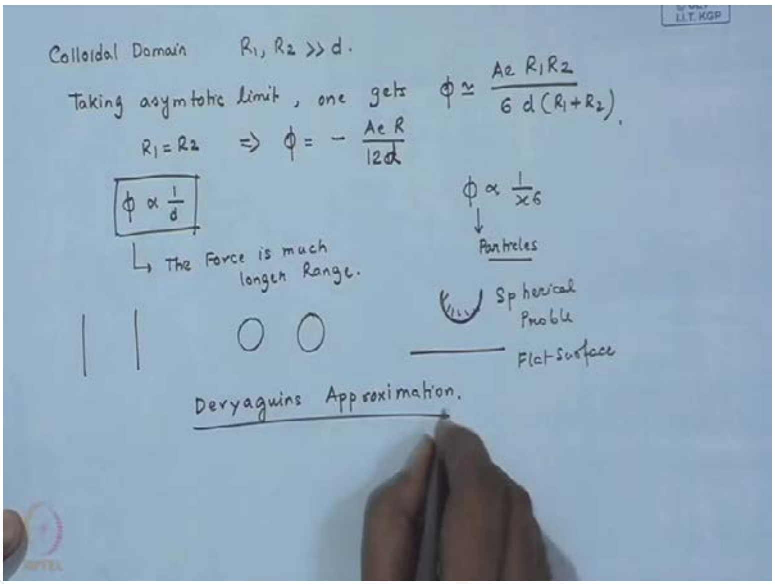

Colloidal Domain $R_1, R_2 >> d$.

Taking asymtotic limit, one gets $\phi \simeq \frac{A_e R_1 R_2}{6 d (R_1 + R_2)}$.

$R_1 = R_2 \Rightarrow \phi = -\frac{A_e R}{12 d}$

$\boxed{\phi \propto \frac{1}{d}}$

↳ The Force is much longer Range.

$\phi \propto \frac{1}{x^6}$

↓

Particles

Spherical Proble

Flat Surface

Deryaguins Approximation.

What is important to note or interesting to note that for spherical particles the vander waal’s forces scale up with R1 by d and R2 by d. So, if R increase by hundred times and d also increases by hundred times the sort of magnitude of vander waal’s forces or remains ruffle the same. So, in practical setting in colloidal domain, what we have R1 and R2 much larger then d. So, therefore taking asymptotic limit one gets and for the specific case R1 equal to R2 one also gets pi is equal to minus A e R divided by 12 d hence, the decay of vender weal’s force is with separation distance is 1 by d.

So, this is very interesting now we know that the decay was as 1 by X to the power 6 for particles or molecules or atoms for two parallel surfaces the decay sort of reduce to 1by X square 1 by d square. But now we see that the decay between two spherical surfaces, the decay of the non retarded vender weal’s force between two spherical surfaces as a function of 1 by d, which means that the decay is even more sluggish as compared to the particles or between two parallel surfaces or in other words the force here becomes much longer range for complicated geometry of course, we do not have expressions for the intermolecular interaction or for a b type interaction.

And therefore, when we talk we need to sort of identify or we need to identify the actual forces the force measurement module of the atomic microscope, which we talk comes in handy. But what we have is the geometries that we have understood are that it say that the we have an expression of interaction between two parallel plates and two spherical surfaces. But even if you are measuring the force between two surfaces using an atomic force microscopic colloidal probe, you are actually leading to this situation. So, you have a spherical probe and you have a flat surface. So, this force can be sort of quantified based on what is of course, based on an approach and withdraw you will generate a force curve. But in order to convert that force curve or extract the relevant information to convert that force in to the exact potential, you need to use what is known as the Deryaguins Approximations. This is a critical concept of soft condoms physics.

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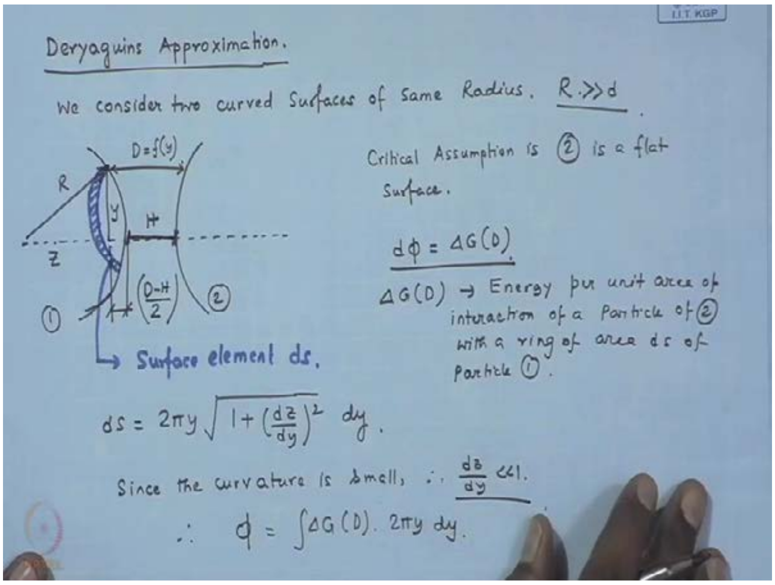

Deryaguins Approximation.

We consider two curved Surfaces of Same Radius. $R \gg d$.

Critical Assumption is ② is a flat Surface.

$$d\phi = \Delta G(D)$$

$\Delta G(D) \rightarrow$ Energy per unit area of interaction of a Particle of ② with a ring of area ds of Particle ①.

$$ds = 2\pi y \sqrt{1+\left(\frac{dz}{dy}\right)^2}\, dy.$$

Since the curvature is small, $\therefore \frac{dz}{dy} \ll 1.$

$$\therefore \quad \phi = \int \Delta G(D).\, 2\pi y\, dy.$$

I will cover it in very brief detail just it is important for you to know the existence of Deryaguins Approximation; even if you find understanding it little bit difficult does not really matter, you can refer to any standard text book or the internet for finding the what it means. So, it essentially in nut shell it talks about the interaction of two spherical surfaces of same radius of curvature, and then assumes one of them to be a having infinite radius of curvature; one of them to be flat and tries to develop an expression for this setting for expression for pi for the setting, and which if you now measure the force or greater force distance curve, use an atomic microscope matches exactly the situation, because eventually deryaguins approximation gives you how to measure the pi between one curve surface and one flat surface. And in an atomic force microscope, we have already talk, if you using a colloidal probe you exactly have that setting.

So, we consider two curve surfaces of same radius let us say R it is like this. And so, this is the axis (no audio from 40:44 to 41:10); these the gap between the two surfaces and R is much greater then d critical assumption is two is a flat surface. So, we consider thus the way we talked about surface element while deriving the expression for yang laplace equation for a symmetric surfaces. We consider a surface element DS and this particular zone if you look carefully this is nothing but D minus H by 2 this is H so, this is D minus H by 2 this particular zone, and what we have is d phi is delta d as a function of G the separation distance. Now, delta G D is the energy per unit area of interaction of a particle of 2 with a ring of area ds of particle 1 of particle of 2 with a particle of one which lies within the area ds; and you can also see from simple plane geometry that ds stands out to be 2 pi y into under root of 1 plus dz by dy whole square into dy.

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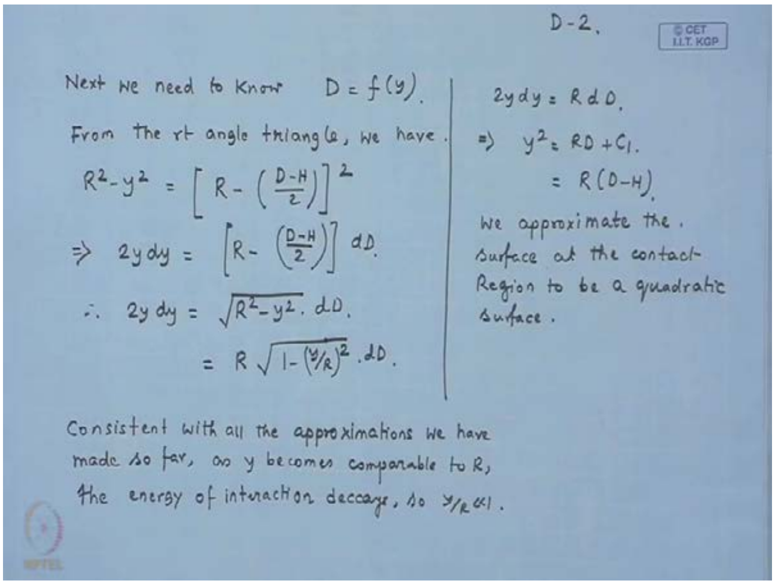

D-2.

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Next we need to know $D = f(y)$.

From the rt angle triangle, we have.

$$R^2 - y^2 = \left[R - \left(\frac{D-H}{2}\right)\right]^2$$

$$\Rightarrow 2y\,dy = \left[R - \left(\frac{D-H}{2}\right)\right] dD.$$

$$\therefore 2y\,dy = \sqrt{R^2 - y^2}\,.\,dD.$$

$$= R\sqrt{1 - (y/R)^2}\,.\,dD.$$

$$2y\,dy = R\,dD.$$

$$\Rightarrow y^2 = RD + C_1.$$

$$= R(D-H).$$

We approximate the surface at the contact Region to be a quadratic surface.

Consistent with all the approximations we have made so far, as y becomes comparable to R, the energy of interaction deccays, so $y/R \ll 1$.

Since, the curvature now since the is small therefore, dz dy can be divided much smaller then y and therefore, pi is delta GD into 2 pi y dy next, we need to know D as a function of y now, from the right angle triangle over here we know or we have R square minus y square equal to R minus D minus H by 2 whole square.

So, this is the R square is essentially y square plus this amount, which is R minus D minus H by so, this is Pythagoras Theorem. So, this plus y square equal to r square; so, if we differentiate from the both sides we get 2y dy is R minus D minus H by 2dD R is constant therefore, 2y dy is under root R square minus y square in to dD, which tends to be R into 1 minus y by R square dD. Now, consistently with all the approximations we have made so far as y becomes comparable to R the energy of interaction decays, so y by R becomes much smaller than 1. What we want to do is we would like to written the interaction in the vicinity of the minimum separation distance. So, the idea is that we take the assumption y by R much smaller than R.

We actually want to retain the interaction in the vicinity of the minimum separation distance interact and we neglect the interaction at greater distance, but the error as the interaction any where reduces with increase separation distance the error remains still small and in so therefore, what we have is 2y dy is equal to R d D or in other words we get y square equal to R D plus C1 we eventually an evaluate the constant R into D minus H. So, we approximate the surface at the contact region to be a quadratic surface the precise details of before we move on I mean, I think that we I need to quickly do a recap.

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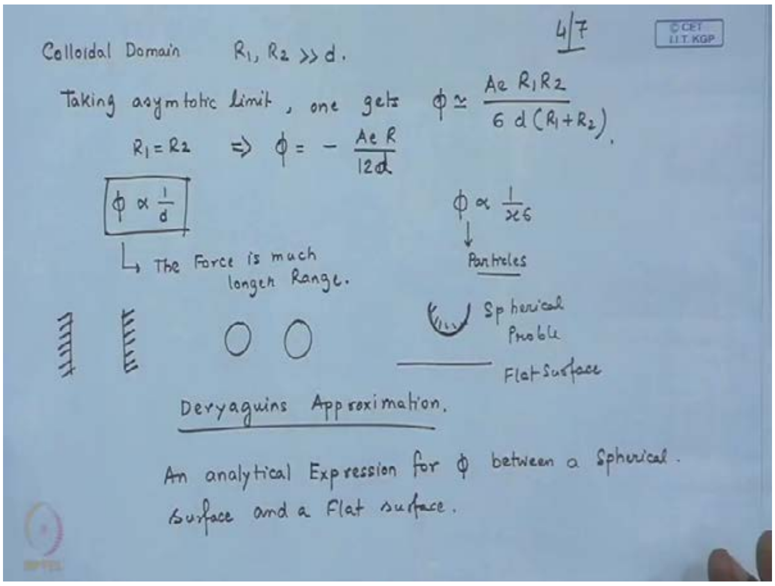

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Colloidal Domain $R_1, R_2 >> d$.

Taking asymtotic limit, one gets $\phi \simeq \frac{A_e R_1 R_2}{6 d (R_1+R_2)}$.

$R_1 = R_2 \Rightarrow \phi = - \frac{A_e R}{12 d}$

$\boxed{\phi \propto \frac{1}{d}}$

↳ The Force is much longer Range.

$\phi \propto \frac{1}{x^6}$

↓

Particles

Deryaguins Approximation.

An analytical Expression for ϕ between a Spherical. Surface and a Flat surface.

Deryaguins Approximation essentially is aimed at generating an expression for pi and analytical expression for phi between is a spherical surface and a flat surface why this because we have a expressions for interaction between two flat surfaces, and we have interactions available we did not do the detailed derivation does not real matter is not important, but is important for you to understand what are the expressions that already exists.

We have the expression of interaction between two flat surfaces, and we have the expression of the potential for interaction between two spherical surfaces. What is important that we would like to so, here we find that the interaction becomes the function of these geometric parameters and also the fact these are spheres. But more complicated geometric so, bringing need the normal geometric parameters increases, so it becomes difficult and probably one has to talk of think off the force measurement direct force measurement using an atomic force microscope or a surface force separators to measure the forces rather than getting an analytical expression.

But one of the critical one of the ways is to sort of find out an expression for pi between a spherical surface and a flat surface and that is what is done using, what is the objective of Deryaguins Approximation or that is how it works it is its sort of starts of by considering the interaction between the two curve surfaces of same radius and consider the surface element of ds on the first spherical surface.

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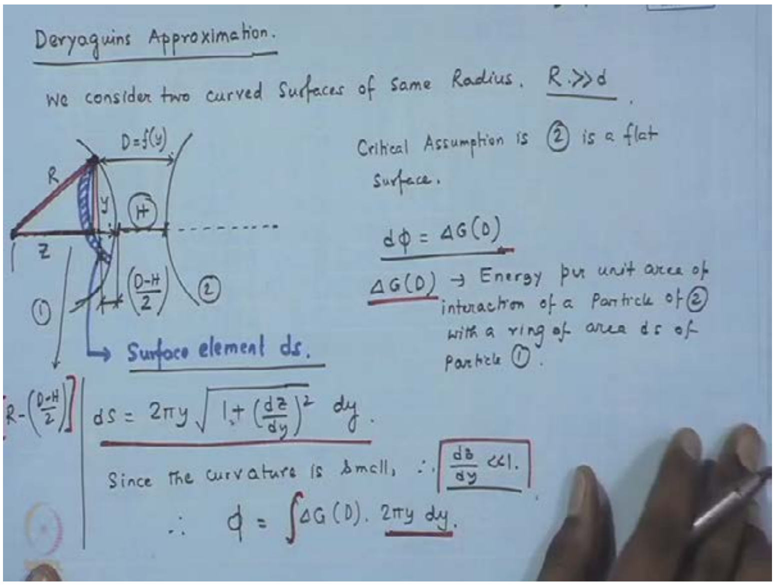

Deryaguins Approximation.

We consider two curved Surfaces of same Radius. $R >> d$.

Critical Assumption is ② is a flat Surface.

→ Surface element ds.

$d\phi = \Delta G(D)$

$\Delta G(D)$ → Energy per unit area of interaction of a Particle of ② with a ring of area ds of Particle ①.

$ds = 2\pi y \sqrt{1 + \left(\frac{dz}{dy}\right)^2}\, dy$.

Since the curvature is small, ∴ $\boxed{\frac{dz}{dy} << 1.}$

$\therefore \quad \phi = \int \Delta G(D).\, 2\pi y\, dy.$

So, this is the surface element, which is at distance y from the central line, which lies on the line, but the minimum point of contact is so, this is H this zone is since the two have the same radius of curvature. So, this zone is D minus as H by 2 this is y this is R this is center. So, here from this way this is also R and this distance will be R minus D minus H by 2 we will be using somewhere. So, it is important that we identify the Pythagoras Theorem for this particular triangle where we will find that R square we will use that R square in to this particular things square plus y square.

Now, this is the surface element I strongly recommend you to look at the derivation for the young laplace equation for an axis symmetric surface to get an expression for this one how this thing comes. Since, the curvature is small therefore, del z by del y is much smaller than 1 and del pi is equal to delta G of D as a function of delta GD.

Now, delta GD is the energy of energy per unit area of or energy per unit area of interaction of a particle of 2 with a ring with a particle, which is within the ring ds, I would say therefore, pi is equal to delta GD into 2 pi dy that is delta GD in to ds, which is 2 pi dy under the fact the curvature is small, and then we need to identify d as function of y and from the right angle triangle. We find that as you mention we consider this right angle triangle where R square is equal to R minus D minus H by 2 whole square plus pi square that exactly what we have written and from that we get 2y dy is equal to this particular expression.

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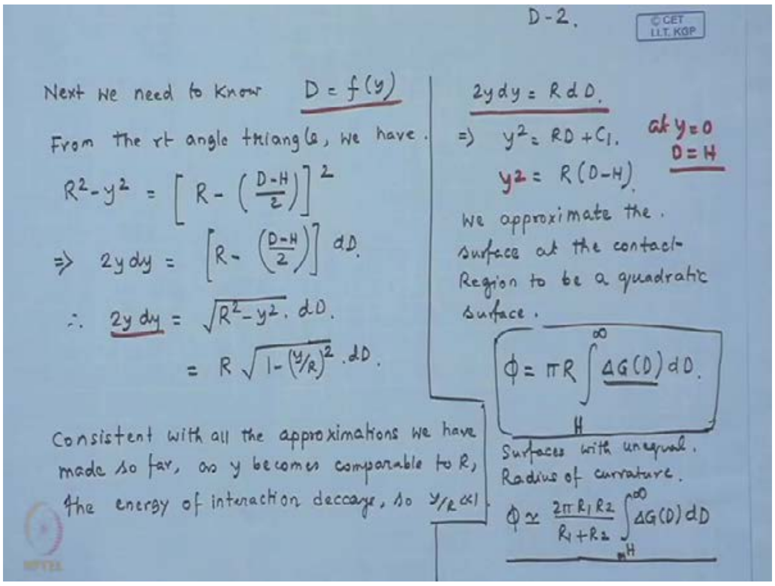

D-2.

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$$\therefore \quad \underline{2y\,dy} = \sqrt{R^2 - y^2}\,.\,dD.$$

$$= R\sqrt{1 - (y/R)^2}\,.\,dD.$$

Consistent with all the approximations we have made so far, as y becomes comparable to R, the energy of interaction deccays, so $y/R \ll 1$

$$\underline{2y\,dy = R\,dD.}$$

$$\Rightarrow \quad y^2 = RD + C_1. \qquad \text{at } y = 0$$

$$\underline{D = H}$$

$$y^2 = R(D-H).$$

We approximate the surface at the contact Region to be a quadratic surface.

$$\boxed{\phi = \pi R \int_H^\infty \underline{\Delta G(D)}\, dD.}$$

Surfaces with unequal. Radius of curvature.

$$\underline{\phi \simeq \frac{2\pi R_1 R_2}{R_1 + R_2} \int_H^\infty \Delta G(D)\, dD}$$

Now, consistently the approximations we have met so far we understand that y becomes compare as y becomes comparable to R, the energy of interaction D case that is far away from this point of minimum interaction y becomes comparable. R is large you are essentially talking about this zones for the interaction decays and therefore, we neglect this particular term and write that 2y dy is equal to R in to dD an upon integration and substitution of the constants of integration at y equal to 0, you just plug in that D equal to H. And therefore, you get this particular expression for y square, which gives you that the surface at the contact region that is this particular region of quadratic surface, which is perfectly find the pre size details of the surface is not that greatly important. What is important is the configuration of the surface near the vicinity of the point of contact; and therefore, we get pi equal to pi R integral each varying between D varying between H and infinity delta GD into dD. This is a general expression and which can be valid for all types of interaction not only limited to vender weal’s interaction, once you know the nature of delta G as a function of D.

So, and it can further be extended for surfaces with unequal radius of curvature, we can have pi is equal to 2 pi R1 R2 divided by R1 plus R2 integral of H to infinity delta GD dD. So, this is the Deryaguins Approximation, but this is more of an important conceptually to understand that identical expression, it is possible to find out an analytical expression for this particular setting that the interaction between the spherical surface and flat surface

So, with that we come to an end of this particular module which is on inter molecular forces between surfaces and particles we talked about the vender weal’s interaction between particles to start with then we talked about the parallel surfaces. Eventually we talked about the vender weal’s interaction or the total interaction between the surfaces with the geometry and we also talked about the interaction the self interaction of the molecules as well as interfacial interaction. Based on that, we tried to find out the condition under which a film becomes or for the first time we talked about condition in terms of the effective haymaker constant, that gives you an idea what can make a film stable or unstable; what is the condition, necessary condition for the interfacial interaction to be attractive or repulsive, even if you consider interfacial interaction only based on vender weal’s forces, thank you.

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