Soft Nano Technology
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Lecture - 34
Interaction Between Two Surfaces – 3

Welcome back to this 34th lecture now. We will continue our discussion on what we have been discussing for the last 2 lectures and we started this in the context of understanding, spontaneous instability in ultra thin films and what we realize there that the situation becomes completely different for a film if it is thinner than let us around 100 nano meter or a thick neck critical thickness below which there is active interfacial interaction between it is 2 interfaces due to Van Der Waals interaction.

And therefore, we decided to look in more detail in to the expression for Van Der Waals interaction. What we have done so far? We will do a quick recapitulation of that.

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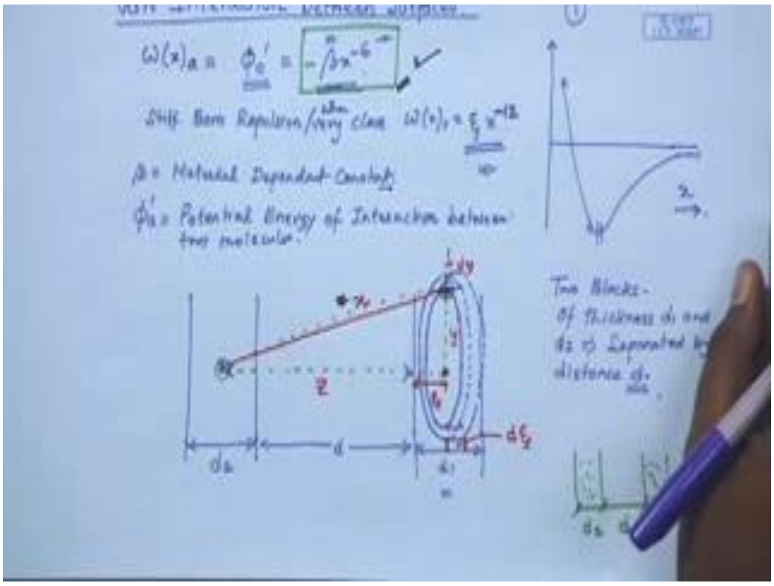

We have looked into started by looking at the normal 6, 12 potential, the attractive part of the 6, 12 potential, that is the pure Van Der Waals attraction between two molecules. Let say which has a scaling of x to the power minus 6. We considered or we decided to look into the interaction between thin, 2 thin blocks of materials 1 and material 2 of thicknesses d 1 and d 2, which has separated by a separation distance of d right and what did we consider? We considered 1 molecule of 1 and 1 specific molecule of 2 and we simply started off by looking at the potential energy of interaction between these 2 molecules is known to us.

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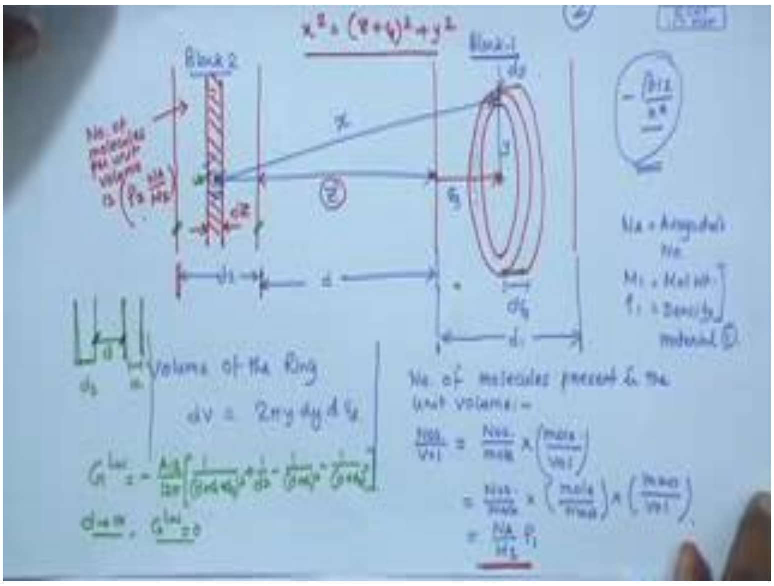

Therefore, based on that what we try to do was based on the assumption of additive interaction, that we decided to figure out the total energy of interaction of this particular molecule of 2, with all molecules of 1 and for that we actually choose a geometry and infinite a decimal element which is a ring like element, I have discuss it adequately.

Therefore we first figured out what is the number of molecules, present number of molecules of body of material 1 within this ring and then we looked in to the total interaction of this molecule with all the molecules within the ring and the expressions are here.

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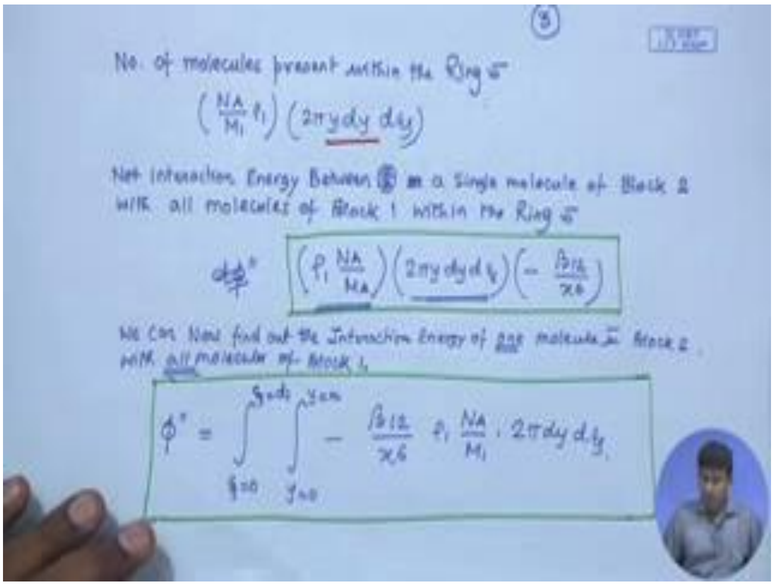

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No. of molecules present within the Ring =

$$\left(\frac{N_A}{M_1}\rho_1\right)\left(2\pi \underline{y\,dy}\,d\zeta\right)$$

Net interaction Energy Between a single molecule of Block 2 with all molecules of Block 1 within the Ring =

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

We can Now find out the Interaction Energy of one molecule in Block 2 with all molecules of Block 1.

$$\boxed{\phi^{*} = \int_{\zeta=0}^{\zeta=d_1}\int_{y=0}^{y=\infty} -\frac{\beta_{12}}{x^6}\,\rho_1\frac{N_A}{M_1}\,.\,2\pi y\,dy\,d\zeta}$$

Then we decided to integrate this expression suitably under appropriate geometry and the limits are the way the construction was taken for d zeta varies between 0 and d 1 and y varies between 0 to infinity to essentially find out the interaction of 1 molecule of material 2 with all molecules, of the block or the strip 1. After we did that we numerically did the expression and we obtained an expression for this, which is something like this. Then what we did was we looked into the strip of material 2 over here, figure out the total number of molecules present in the strip per unit area, multiplied the expression we have got by that and then integrated by this from Z varying to d to Z varying into d plus d 2.

And finally, the expression we got is the expression for interaction Van Der Waals interaction, the free energy of Van Der Waals interaction or free energy of interaction of two blocks of thickness this is d 1 and d 2, separation separated by distance d.

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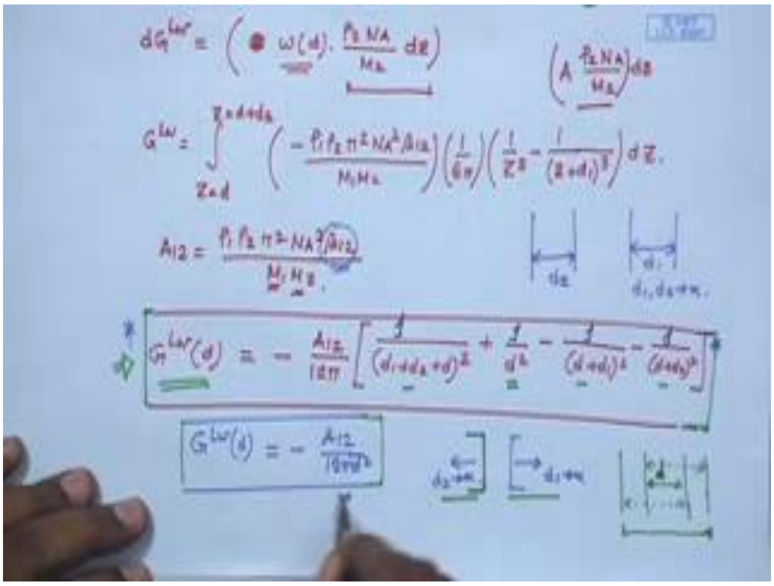

The nature of interaction is of course P only Van Der Waals and then what we did was we look into certain limiting cases. For example if we look at the interaction between two semi infinite blocks, we find the GLW is given by this particular expression.

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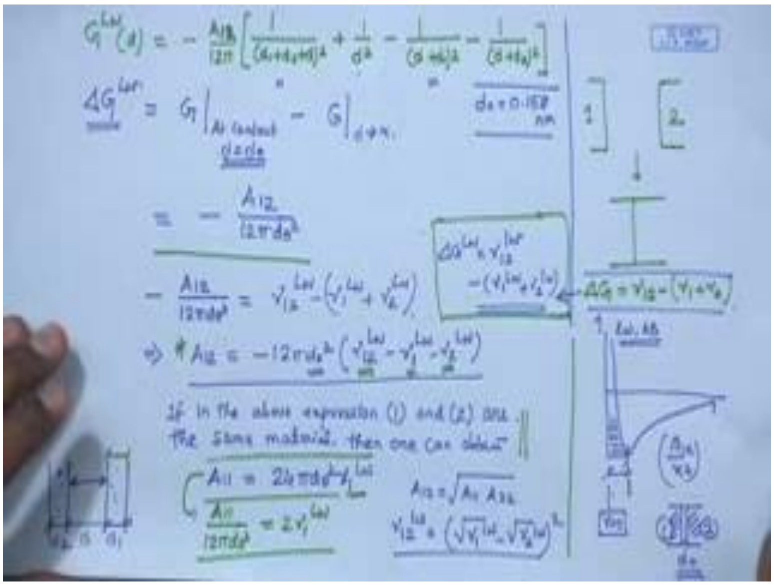

We also made an assumption that at contact d is not going to 0 because our expression we have considered does not go down to 0. So, there is going to be an equilibrium separation distance d 0 and based on that one can calculate the delta G LW which is like when the 2 surfaces are infinitely apart purses they are brought in contact and one gets an expression like this. However, from even more simpler understanding one can get an expression delta GLW which is like this and then one can equate these two to get a very interesting expression of haymaker constant which contains the surface and interfacial energy components Van Der Waals components of a surface and interfacial energies of the 2 materials and d 0. One can now do a clever twisting and one can simply assume the 2 materials to be made of the same thin and then one can obtain the expression for A1 1 also. I think the discussion up to this point is pretty simple, excepting are many few take some to look in to the expression and the derivation.

What we have done beyond this point is essentially to identify. So, what did we understand? We understood that if we have two blocks let say that has just (Refer Time: 05:51) draw a figure again. So, what we understood was it is better to draw a figure. Sorry I should have done it before. That if you have 2 blocks, which are close by right, then there is some interaction; there is some free energy of interaction. I will probably do a better job by writing the whole expression again.

If you see several things, if you see the d is very high, the d is very large, the 2 blocks are very far away then d tending to infinity irrespective of whether individual blocks are thick or thin. Once is GLW tends to 0 right. So, when the two interfaces are close to each other then only there is some interaction, but then we also see, that there will be some additional terms if d 1 and d 2 are thin, if d 1 and d 2 also very thick, then there is no interaction.

So, all that is fine, but what we realized that when we talked about the derivation of this interaction which is absolutely fine or up to this point we have not considered any self interaction of the molecules right, because we have consider Van Der Waals interactions. So, we know that Van Der Waals interaction is Omni present based on that logic we have considered interaction eventually of all molecules of 2 with all molecules of 1 which is also fine but what about the self interaction of the molecules.

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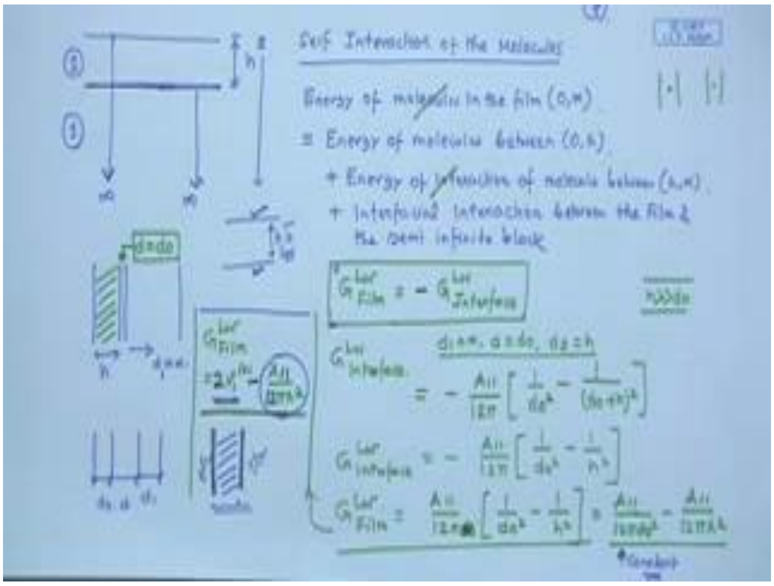

Self Interaction of the Molecules

Energy of molecules in the film (0,∞)

= Energy of molecules between (0,h)

+ Energy of interaction of molecules between (h,∞)

+ Interfacial interaction between the film & the semi infinite block

$\boxed{G^{LW}_{Film} = -G^{LW}_{Interface}}$

$d_1=\infty,\ d=d_0,\ d_2=h$

$G^{LW}_{Interface} = -\frac{A_{11}}{12\pi}\left[\frac{1}{d_0^2}-\frac{1}{(d_0+h)^2}\right]$

$G^{LW}_{Interface} = -\frac{A_{11}}{12\pi}\left[\frac{1}{d_0^2}-\frac{1}{h^2}\right]$

$G^{LW}_{Film} = \frac{A_{11}}{12\pi}\left[\frac{1}{d_0^2}-\frac{1}{h^2}\right] = \frac{A_{11}}{12\pi d_0^2} - \frac{A_{11}}{12\pi h^2}$

$h \gg d_0$

$G^{LW}_{Film} = 2\gamma_1^{LW} - \frac{A_{11}}{12\pi h^2}$

So, we decided to look into that in a bit abstract way. So, what we did was we took a strip of it and placed it back on the substrate and that gives us this expression from which we obtain that GLW of the film the free energy of the film in fact, is negative of the free energy at the interface. And for a system like this one can always find the interfacial energy of interaction based on this expression and for from that one gets an expression for the free energy of a film of a thin film.

Of course, the free energy if you look at the full expression of the thin free energy of a film, this particular case in fact of the film dares like a so film. Therefore 1 finds 2 gamma 1. Which corresponds to the energy at the two surfaces and it has an additional term and you see that the free energy of the film in fact, becomes 2 gamma 1 if h is large.

So, if h is thick, of course you have a film and simply the energy interfacial energy is the 2 surface energies, but if the film is thin enough if h is low and there is in fact one can the easiest way to understand, there is interfacial interaction due to Van Der Waals forces and that leads to this excess free energy.

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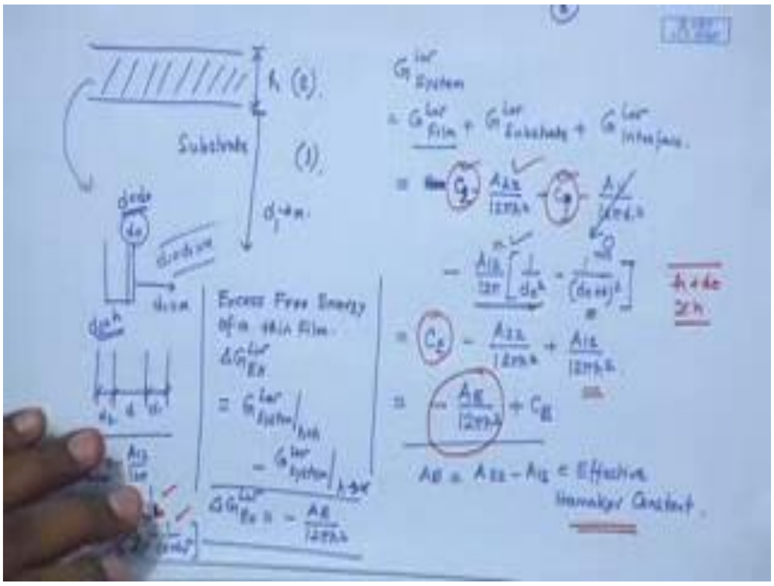

So, one can in fact use this concept to look into very practical situation not an abstract situation any more that, you have a film quoted on a substrate. So, all we did was to look into the GLW of the system and we understand that it has in fact 3 terms, GLW of the film, GLW of the substrate and the interfacial interaction again.

So, film is easy now, we have this expression already 2 gamma 1 minus a 1 1 divide by 12 pi h square, I have decided to write a constant C1 because 2 gamma 1 is constant it does not vary with the h. So, here the film is represented as 2. So, it is C1 minus A22 divided by 12 phi h square, substrate similarly is a C2 or if you want to match with 2 and 1, you can change this also no problem. C1 minus A11 divided by 12 pi d1 square, which is fine in fact, only cases is we know that often the substrates are semi infinite is very thick. In that case this particular term numerically tends to 0 and the interfacial interaction.

What has been done? You simply draw this picture. So, GLW interface you have as a minus A12 divided by 12 pi is apparently for writing it again and again, but I am sure some of your friends will be benefited from this repetition d plus d1 whole square minus d divided by d plus d2 whole square. Now you see for yourself what are the x terms that is remain in this term. See you all I have done are to rotate this figure by sort of anti clock wise by 90 degree. So, you find your d2 is equal to h, you can always even more than a welcome to write it like this d is equal to d0 and d 1 is equal to d1 is equal to infinity right.

So, the movement d1 tends to infinity what happens is this term goes to in 0 and this term also goes to 0. Now you are left with these 2 terms here you see d2 is h so that is fine and d plus d2, sorry this is d square, sorry this not d2 this is d square. So, d square is d zero square and this is d plus d2. So, that is h plus d0. All we are saying is h plus d0 is approximately equal to h right. So, that in fact, gives us and it turns out that you have a constant term. So, if you are looking at the free energy of the system of course, you need to evaluate the constants correctly, but that is not exactly our intention.

So this also is another constant. So, everything gets augmented as an effective constant and then you are left with this term. So, you are you get a minus A22 divided by 12 by h square plus A12 divided by 12 pi h square just use this assumption. So, you get an effective haymaker constant which is this. Depending on the complexity of the system the expression for the effective haymaker constant goes on changing.

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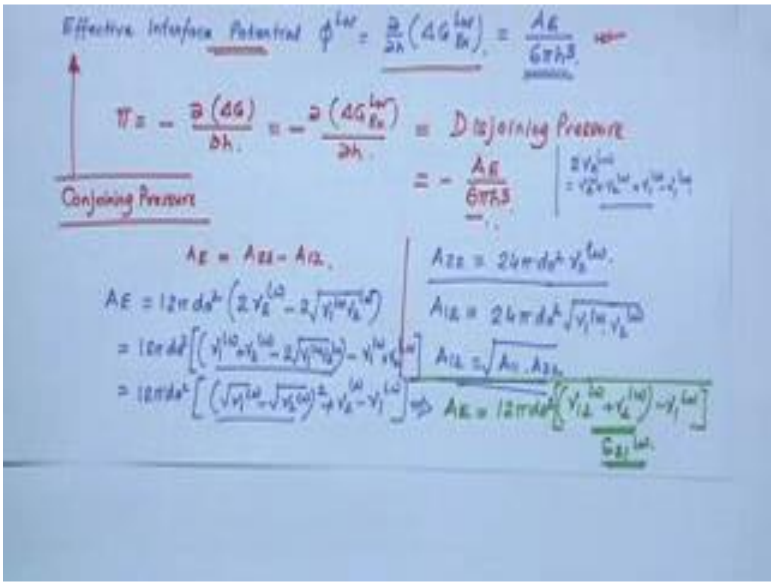

Effective Interface Potential $\phi^{LW} = \frac{\partial}{\partial h}(\Delta G^{LW}_{Ex}) = \frac{A_E}{6\pi h^3}$

$\Pi = -\frac{\partial(\Delta G)}{\partial h} = -\frac{\partial(\Delta G^{LW}_{Ex})}{\partial h}$ = Disjoining Pressure

$= -\frac{A_E}{6\pi h^3}$

Conjoining Pressure

$2\gamma_2^{LW} = \gamma_2^{LW}+\gamma_2^{LW}+\gamma_1^{LW}-\gamma_1^{LW}$

$A_E = A_{22} - A_{12}$

$A_E = 12\pi d_0^2\left(2\gamma_2^{LW} - 2\sqrt{\gamma_1^{LW}\gamma_2^{LW}}\right)$

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

$= 12\pi d_0^2\left[\left(\sqrt{\gamma_1^{LW}}-\sqrt{\gamma_2^{LW}}\right)^2+\gamma_2^{LW}-\gamma_1^{LW}\right] \Rightarrow A_E = 12\pi d_0^2\left[\left(\gamma_{12}^{LW}+\gamma_2^{LW}\right)-\gamma_1^{LW}\right]$

G_{21}^{LW}

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

$A_{12} = 24\pi d_0^2\sqrt{\gamma_1^{LW}\gamma_2^{LW}}$

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

At this point so what we have? We have now found out or expressed the excess free energy of a thin film. So, this excess energy is arising because of the slenderness of the film that is it is very thin. So GLW excess is GLW of the system for h is equal to h when the film is thin, minus GLW of the system when h is very thick, that the there is h tending to infinity and it turns out that GLW excess is minus A divided by 12 pi h square. At this point we define another term interface effective potential, this is very important term which is how the excess free energy of the system changes how the excess free energy of the system changes with the film thickness and it is expression is A divided by 6 pi h cube.

So with this we proceed a bit further in fact, what we mentioned earlier, disjoining pressure is nothing, but negative of this effective interface potential. So, this is in fact, I will write very carefully LW component of excess free energy of a system how it varies with the h negative of that is known as the disjoining pressure and therefore it term it is expression is going to be minus A divided by 6 pi h cube.

Effective interface potential sometimes is also represented as conjoining pressure, that is interesting in fact, negative of disjoining pressure has a different name it is in fact conjoining pressure. So fine now what we do? We would like to correlate the film instability to this so called disjoining pressure or sign of this joining pressure. We can do it in several ways, one of the things we can do is to look in to the effective haymaker constant itself.

So, AE as we have already seen AE turns out to be A22 minus A12 and I would like to draw your attention that some slides back we have derived that A22 is equal to 24 pi d 0 square gamma 2 LW we did not derive it for A22 we derived it A11, but it is absolutely fine and A12 turns out to be 24 pi d0 square under root gamma 1 LW into gamma 2 LW is based on the fact that I told when this is something decided not to very simple is this.

So, what we have is AE turns out to be 12 pi d0 square 2 gamma 2 LW minus 2 under root gamma 1 LW, gamma 2 LW right and what we do is we split up we sort of add and subject a gamma 1 into the parenthesis. So, we split of this is bit of gimmickry 2 algebra gimmickry. So, this 2 gamma 2 LW we split up as gamma 2 plus gamma 2 all LW’s plus gamma 1 minus gamma 1, that is what you do and if you do that, you are left with 12 pi d0 square and this turns out to be this particular term is easy, does it remind you of anything. Considering the fact that this particular term is gamma 12 LW. So, I will write it here and what is it? It is nothing but should remember this now S21 LW spelling coefficient.

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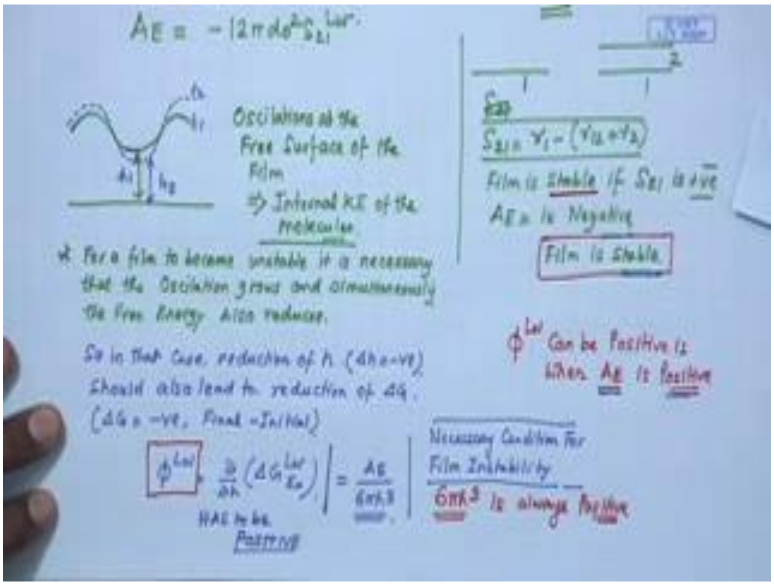

$A_E = -12\pi d_0^2 S_{21}^{LW}$

Oscillations at the Free Surface of the Film

⇒ Internal KE of the molecules

* For a film to become unstable it is necessary that the Oscillation grows and simultaneously the Free Energy also reduces.

So in that case, reduction of h ($\Delta h = -ve$) should also lead to reduction of ΔG. ($\Delta G = -ve$, Final − Initial)

$\boxed{\phi^{LW}} = \frac{\partial}{\partial h}\left(\Delta G^{LW}_{Ex}\right) = \frac{A_E}{6\pi h^3}$

HAS to be Positive

Necessary Condition for Film Instability

$6\pi h^3$ is always Positive

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

Film is Stable if S_{21} is +ve

A_E is Negative

Film is Stable

ϕ^{LW} Can be Positive is when A_E is Positive

Therefore based on this way, you can get AE is minus 12 pi d0 square is S21 LW. So, this is in fact easy, again you do you just do it yourself and you can get to these expressions. It is easy now, you can now co relate film stability in terms of you just write this as 1 and this as 2, instead of S and l what we have to been writing and the expression of h21 turns out to be gamma 1 minus gamma 12 plus gamma 2 that is all and we know that film is stable if S21 is positive; that means that AE is negative is a necessary condition for the film stability right. Negative means film is stable ok.

Now, one can look into it is from a slightly different perspective also. So bit qualitative, but it is very fascinating in fact from the stand point of this oscillation, because if you correlate it to back we started to do all this and we argued that there is oscillation and the film becomes unstable, this oscillations are attributed oscillations at the free surface of the film, this oscillations are attributed to the internal kinetic energy of the molecules, typically as soon as the surface oscillates it gives rise to Laplace pressure and surface tension tries to platinum, but in case the film thickness is small, that is there is one can now understand very clearly there is a excess free energy of interaction, what happens is they are might be. So, if the Van Der Waals interaction is attractive, then these oscillations have a reason now to grow right and therefore, there is a competition between the destabilizing Van Der Waals forces and the stabilizing Laplace pressure.

Now, let us examine under what condition this can happen? Now for film to become unstable, this is very critical and delicate concept. It is necessary that the oscillation grows and simultaneously the free energy also reduces because please do not forget we are talking about the spontaneous insatiability. So, until and unless the free energy reduces it will not evolve in that particular attention. So, in that case reduction of h is like this. You are looking at an unstable film. So, over these areas h is in fact reducing. Initially the thickness was h1 at this area at time t1, time t2 thickness is h2.

In case reduction of h; so delta h is negative, should also lead to reduction of delta G, that is delta G is also negative that is a final minus the initial configuration. So, for this to happen you see look at the expression. For this 2 happen delta h has become negative value I will write it down, effective interface potential for this to happen pi LW has to be positive. So, it turns out. So, if delta h is negative and delta G is also negative then pi LW which has an expression of AE divided by 6 pi hq has to be positive and this is the necessary condition for the film instability and must write has to be positive right and this is the necessary condition for film instability here we talked about the condition for stability. So, please do not confuse that.

So, this is the condition for instability now you see this term pi 6 pi hq is always positive. So, only way pi LW can be positive, is when AE is positive and that is exactly what we have told that AE negative is the condition for a stable film and here we get qualitatively the AE positive is the condition for an unstable film. Similarly one can argue. So, in other words one must have negative disjoining pressure to trigger film instability. A positive disjoining pressure implies a negative effective interface potential and that leads to a stable film.

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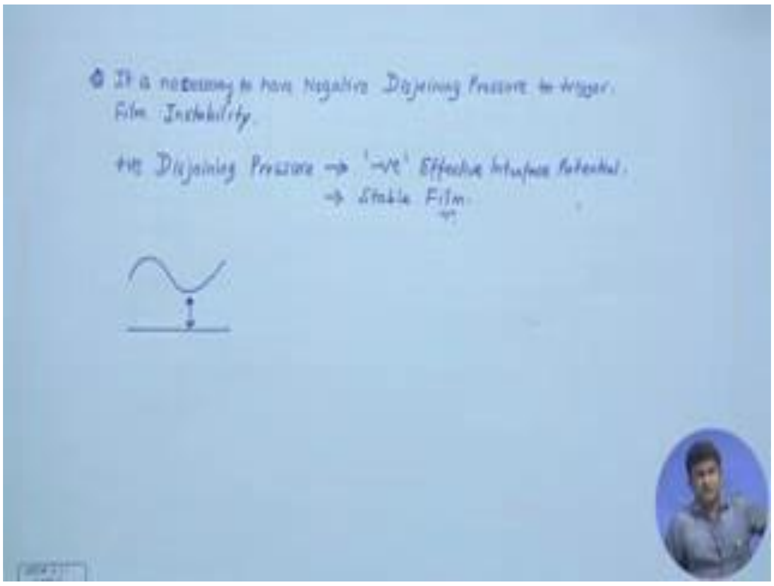

- It is necessary to have Negative Disjoining Pressure to trigger Film Instability.

+ve Disjoining Pressure → '-ve' Effective Interface Potential.
→ Stable Film.

So, now I hope you have a clearer picture of when a film can be stable or under what condition the film can be unstable. In fact, I post a question that stable film even when the film is thin. In fact, these areas the interaction the net interaction repulse, that is why not only Laplace pressure stabilizes the film, but also the positive disjoining pressure or the negative conjoining pressure also stabilizes the film. How is it possibly? It sort of implies that the effective Van Der Waals interaction between the 2 interfaces is repulsive, apparently Van Der Waals interaction what we consider is always attractive.

So, how is it possible? And it turns out that it is not the individual Van Der Waals interaction that matters, it is the effective Hamaker constant that matters and therefore, the relative magnitudes of A22 and A12 plays an important role depending on which it can be possible to have in effective, attractive or a repulsive Van Der Waals interfacial interaction, which is the key factor that governs the stability of the film.

There is a bit of more one can go in to with the theoretical detail with linear stability analysis. But that is something I will not do to avoid complication in this course. And next chapter next lecture we will go back to some qualitative discussion, but on a more complicated system that is on the dewetting not of a single layer. We will talk about certain aspects of dewetting again to get back our grove in to the experiment and studies and qualitative studies which we are doing, but we will also look in to the dewetting of a (Refer Time: 28:46).

Thank you.