Instability and Patterning of Thin polymer films

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Lecture Number # 29

Intermolecular Forces between Particles and Surfaces - III

Welcome back, we continue our discussion on intermolecular interaction forces. We talked in the previous class about the total interaction, total potential energy of interaction between two blocks of materials one and two with thicknesses is d1 and d2, where the interaction is only due to the attractive London forces and this is the expression we have obtained, which let us rewrite because we will be building our concepts based on this. Let me just caution you A12 and this 12 has nothing to do in common, this 12 is a numerical pre-factor which comes from the integration and A12 is essentially the Hamaker constant between blocks of material 1 and 2.

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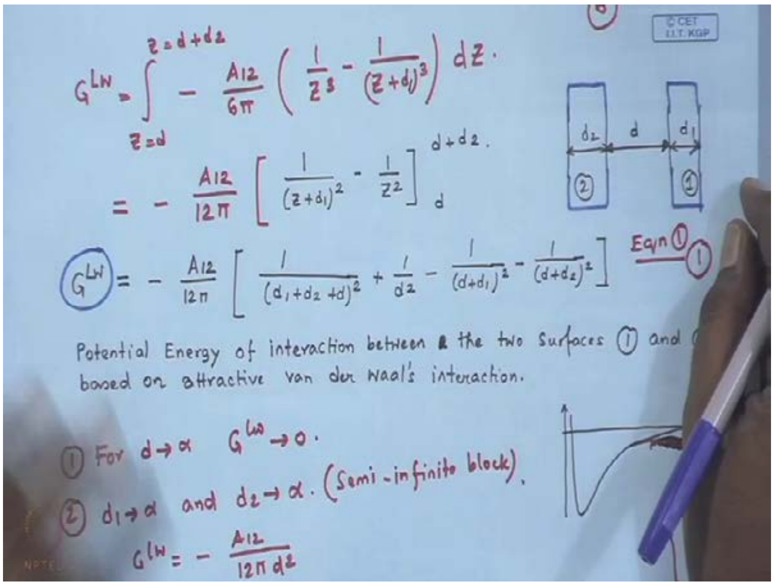

$$G^{LW} = \int_{z=d}^{z=d+d_2} -\frac{A_{12}}{6\pi}\left(\frac{1}{z^3}-\frac{1}{(z+d_1)^3}\right)dz.$$

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

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

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

① For $d \to \alpha$ $G^{LW} \to 0$.

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

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

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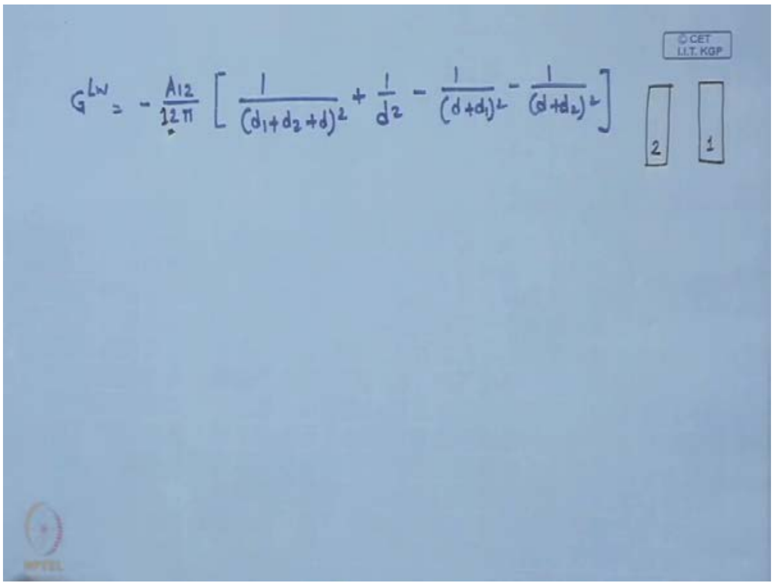

$$G^{LW} = -\frac{A_{12}}{12\pi}\left[\frac{1}{(d_1+d_2+d)^2} + \frac{1}{d^2} - \frac{1}{(d+d_1)^2} - \frac{1}{(d+d_2)^2}\right]$$

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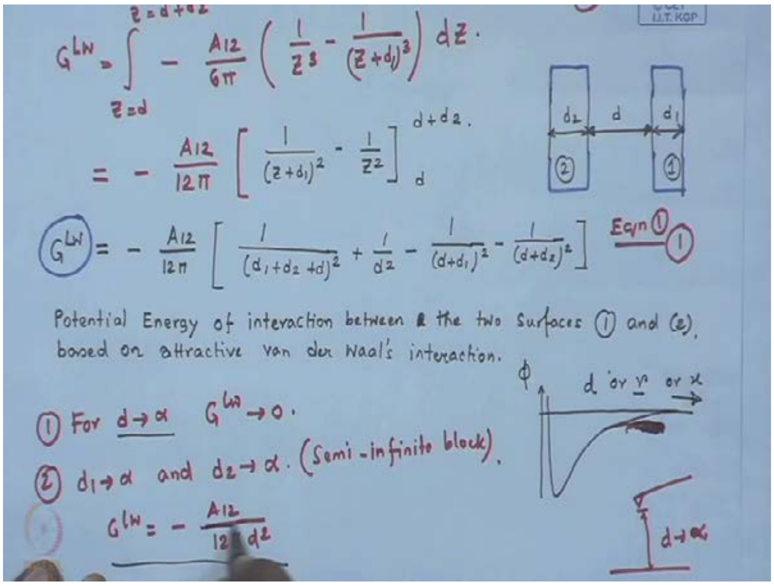

$$G^{LW} = \int_{z=d}^{z=d+d_2} -\frac{A_{12}}{6\pi}\left(\frac{1}{z^3} - \frac{1}{(z+d_1)^3}\right) dz.$$

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

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

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

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

And we also talked about certain limiting cases for example, if the separation distance between these two blocks is infinity that is d tending to infinity in that case GLW tends to 0 or there is no vander waals interaction, because you are in this part of the force curve.

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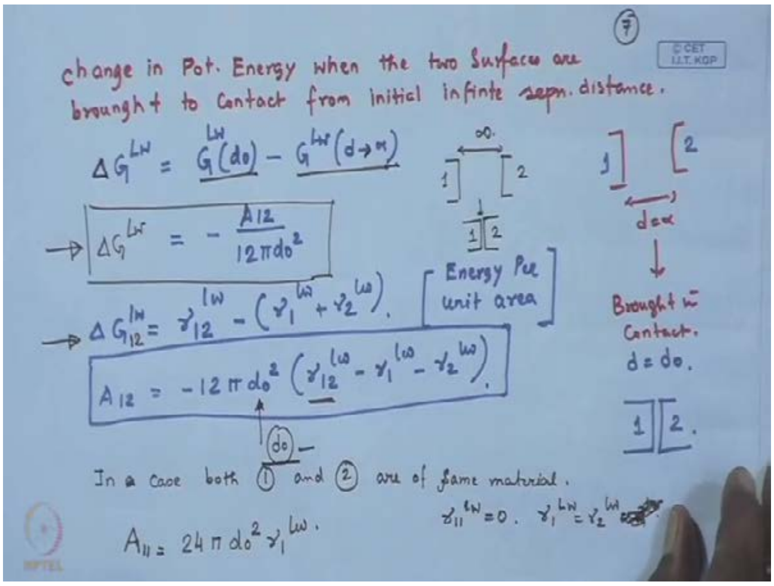

change in Pot. Energy when the two Surfaces are brounght to Contact from initial infinte sepn. distance.

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

$\rightarrow \boxed{\Delta G^{LW} = -\frac{A_{12}}{12\pi d_0^2}}$

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

[Energy Per unit area]

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

$\uparrow \textcircled{d_0}$ –

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

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

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

Similarly, if d1 and d2 both are very, very thick I mean, you are talking about the interaction between two semi infinitely thick blocks then of course, you get GLW to be equal to minus A12 divided by 12 phi d square. Further, we talked that we could calculate the change in the potential energy, when the two surfaces are brought in contact from initial infinite separation and essentially what we do? We look at G at d0 that is at contact and look at the change in energetic of the system that is the delta GLW, when G is at d0 that is at contact minus the initial condition that is GLW d tending to infinity and it turns out that the delta GLW is minus A12 divided by 12 phi d0 square. We also understand that this delta GLW 12 if you want to be more accurate, that is two surfaces of 1 and 2, which were initially at infinite separation distance, they are brought in contact.

So, we know from macroscopic surface tension, this can be considered as gamma 1 12w minus gamma 1 plus gamma 2 both the LW components. The situations match, if there is no other interaction; so in that case one gets A12 is equal to this.

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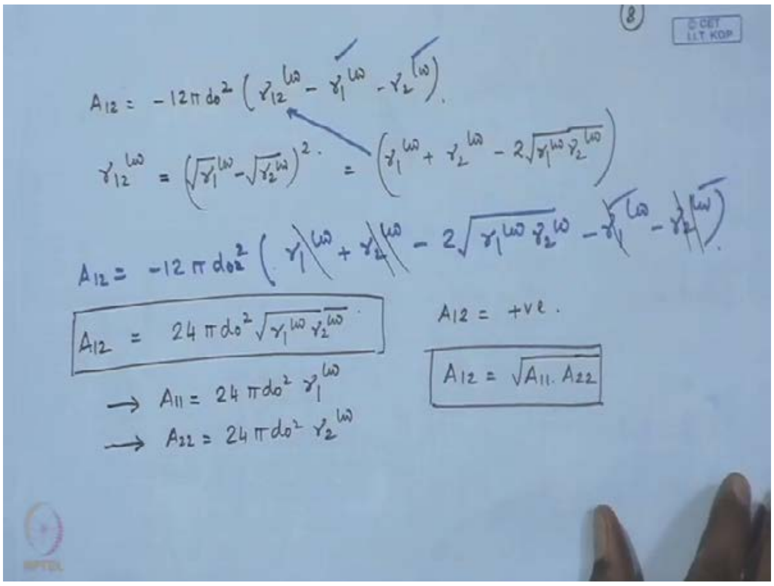

$A_{12} = -12\pi d_0^2 \left(\gamma_{12}^{LW} - \gamma_1^{LW} - \gamma_2^{LW}\right)$.

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

$A_{12} = -12\pi d_{0}^2 \left(\cancel{\gamma_1^{LW}} + \cancel{\gamma_2^{LW}} - 2\sqrt{\gamma_1^{LW}\gamma_2^{LW}} - \cancel{\gamma_1^{LW}} - \cancel{\gamma_2^{LW}}\right)$.

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

$A_{12} = +ve$.

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

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

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

So, if d0 is somehow can be measured, then everything else can be macroscopically measured. We also showed that A12 can sort of take this functional form these are some of the expressions, which we will be need and A11 and A22 have these functional forms and of course, one can show that A12 is under root of A11 into A22.

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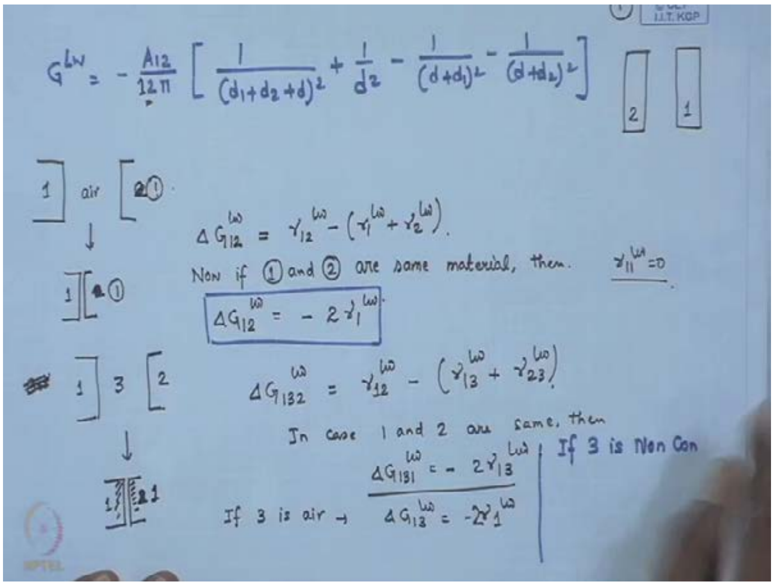

$G^{LW} = -\frac{A_{12}}{12\pi}\left[\frac{1}{(d_1+d_2+d)^2} + \frac{1}{d^2} - \frac{1}{(d+d_1)^2} - \frac{1}{(d+d_2)^2}\right]$

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

Now if ① and ② are same material, then.

$\gamma_{11}^{LW} = 0$.

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

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

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 Con

Well, we start to build our concepts from this point. So, what we need to understand is that, this if you now look relook take a relook at this scenario you have 1 and 2, and they are in air and you bring them in contact we have no problem in understanding that G12.

If you consider only the LW component it is fine it is equal to gamma 12 LW minus gamma 1LW plus gamma 2LW. Now, if 1 and 2 are same material, then we have gamma 12 LW is equal to minus 2 gamma 1LW, because gamma 11LW is equal to 0.

So, in that case the situation gets transferred to something like this now think of the other scenario, if you have both 1 and 2 now, let us think of a scenario, where 1 and 2 are initially dispersed in a medium or dispersed in a medium 3 and then they come in contact.

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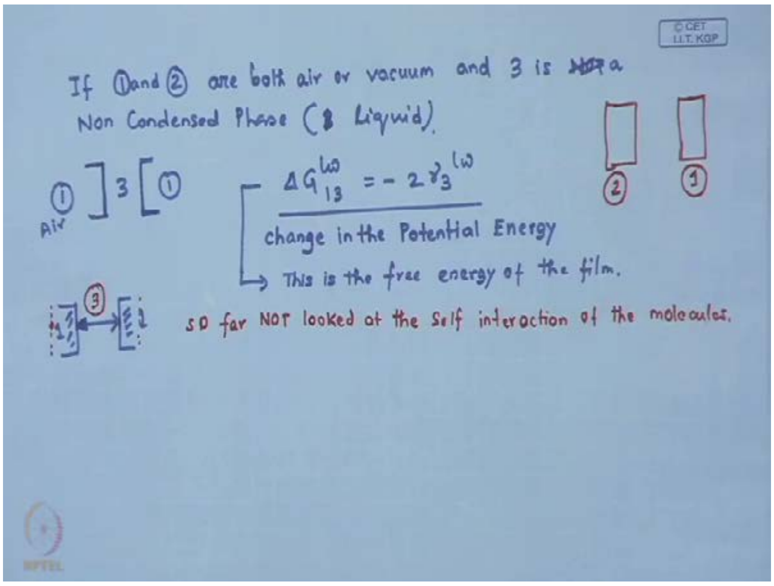

If ① and ② are both air or vacuum and 3 is a Non Condensed Phase (Liquid).

$\Delta G_{13}^{LW} = -2\gamma_3^{LW}$

change in the Potential Energy

→ This is the free energy of the film.

so far NOT looked at the Self interaction of the molecules.

So, here also what happens is delta G132 is initially the finally, it will be gamma 12 minus gamma 13LW plus gamma 23LW. Here, also if 1and 2 are the same material then we will be left with. So, this whatever is the change in this potential energy is due to interaction of two condensed phases or 2 blocks of 1, due to vander waals interaction. Now, think of a scenario that the other thing can be that if 3 is air then of course, we get to GA gamma 13LW and this gets back to gamma 1 its identical to these scenarios, but now think of in other setting it is the opposite setting of this that if 3 is non condensed phase ok I use a fresh sheet.

If 1 and 2 are both air or vacuum and 3 is not a 3 is non condensed phase. Let us, say liquid so, what you have which is air therefore, the gamma delta GLW in this case again turns out to be minus 2, but gamma 3 in this case. What is this is essentially the change in the potential energy due to the presence due to this film so, this is essentially the free energy of the film per unit area or in other words unlike this situation where if A one was a non-condensed phase.

We talked about the interaction of molecules across these two phases. So, we talked about the interaction of all the molecules over here with all the molecules over here, but what we did not talked is that if three, is a non condensed phase irrespective of whether 1 is a condensed phase or not or for every non condensed phase, we have so far not looked at the self interaction of the molecules.

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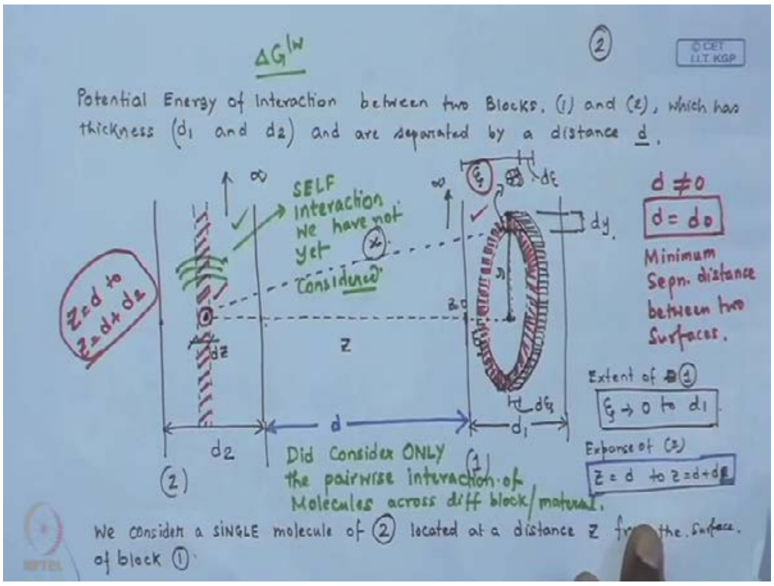

ΔG^{LW}

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.

SELF interaction we have not yet considered

Did Consider ONLY the pairwise interaction of Molecules across diff block/material.

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

That is we have taken to put it in simple terms we have taken 2 blocks we go back to the previous derivation which we have understood in great detail. We have taken 2 blocks and the way we did our derivation, we talked about the possible vander waals interaction of all the molecules of this phase or this block with all the molecules of this block.

So, we did consider only the pair wise interaction of molecules across different block or material. We never talked or considered the self interaction that is how the molecules of a single block or a single material or a single object are interacting so, the self interaction we have not yet considered. So, the only thing we have considered that there will be an excess potential energy that will be generated or excess potential energy that is delta GLW since, we have considered the vander waals component of interaction only if the 2 blocks are at infinite distance and they are brought to some finite distance each so, that we can consider or we understand now. But so far, we have not considered the self energy so, the self interaction energy which we are going to do now.

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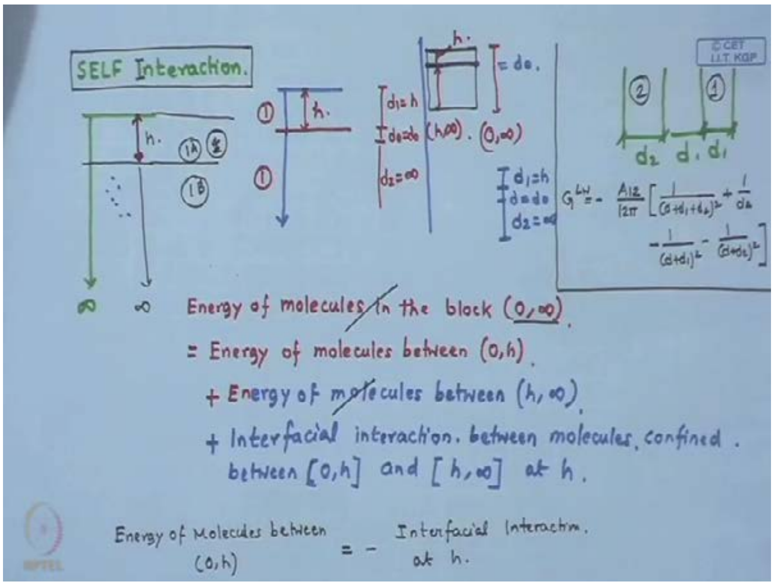

SELF Interaction.

Energy of molecules in the block $(0,\infty)$.

= Energy of molecules between $(0,h)$.

+ Energy of molecules between (h,∞).

+ Interfacial interaction. between molecules, confined. between $[0,h]$ and $[h,\infty]$ at h.

Energy of Molecules between $(0,h)$ = − Interfacial Interaction. at h.

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

So, let us look at the self interaction of the molecules so, we look at the self interaction let us say we have a semi infinite block of material one we would also. I would also like you to keep this figure in tact in your mind and the expression corresponding expression for the delta G or the GLW. Let us, write it down we will be need it so that expression this is something I would like you to keep in mind. Now, coming back to here as try to identify the component of self interaction let us, say that we have a semi infinite block of material 1 we generated an interface over here at a finite thickness each and it stretches to infinity.

So, it is like you have a block like this, which can be a block of wood a block of butter whatever, it is you sort of cut it here generate an interface and it remains over there itself, but what happens now this has a finite thickness h this anyway tends to from earlier the expanse was from 0 to infinity now the expanse is from Y equal to h to infinity, but what you need to understand that this is now at interface so, though the same material is at contact this interface now there is a finite separation distance and that is d0.

This picture now in away sort of gets transferred to d1 equal h d equal to d0 and d2 equal to infinity and you can immediately draw a comparison between this and this. So, I will repeat what I have done I have taken a block of let us say material one, which is semi infinite and at a distance h. I have created an interface so, I have applied some energy so, the question to ask is let us say you have taken this is something we have talked in one of the earlier classes when we were talking about surface tension. So, you can just look back to those lectures and find out I give you an example that if you have taken a block of butter and then you just cut it you are supplying some energy from outside.

Now, you are neither you are creating any butter nor you are destroying any butter mast conserved so, the why you need to supply this extra energy well you need to essentially supply this extra energy to create this additional interfaces we get generated by cutting now suppose we do the same thing, we cut it cut this block of material over here at a distance h let us that from the top and we keep it placed over there. So, that is all what we have done it is the same material. Let us say this is material 1, but of course in order to create this interface you have to supply some external energy that something you should not forget and the other thing is so, earlier the expanse was from 0 to infinity now, the first block is at the thin layer is between let us say 0 to h and the second layer is from h to infinity and since, you have created an interface the interface we understand that the minimum separation distance that an interface can assume is d 0.

So, we sort of can have a mental image of the system as d1 equal to h d equal to d0 and d2 equal to infinity so, that is what we have so, now let us say we talk of energy of molecules in the block. In the range 0 to infinity is equal to molecules between 0 to h plus h to infinity plus interfacial interaction between molecules confined between 0, h and h infinity at h.

So, all we have done we have considered we have just written in simple words the total energy of interaction of the molecules present with in this block that is now. We are talking about the self energy of interaction. When in the earlier lectures, we were defining the intermolecular forces we never mentioned that intermolecular forces have to act across different blocks or different material that we have never mentioned. So, there is no reason to consider that these intermolecular forces which can span few tens of nanometer across vacuum area, there will be no interaction between neighboring molecules, so that is present and that is what we are identifying or referring towards the self interaction of the molecules.

So, what we have done we have considered the self interactive we are now trying to identify some expression for the self interaction of these molecules and in order to do so, we have just taken a block which is a semi infinite block and we have sort of cut a thin layer of thickness h at the top and we have placed it back left it back on the surface.

So, now in simple terms we are looking at the total energy of interaction of the molecules, which was confined between 0 to infinity and we identify that after we have created the interface this energy of molecules between 0 to infinity it is now splitting to sort of three parts. The first one is energy of molecules between 0 to h, then energy of molecules between h to infinity and interfacial interaction between the molecules confined between 0 to h that is this block, which now, let us say becomes the block 1 and the remaining part of the block.

So, I would not confuse you with by saying that it is 1 and 2, I would probably say 1A and 1B, because of the fact that the key difference between here is these two are dissimilar material which under specific case can be a similar material, but here they are definitely similar material. Now, we understand that since this is semi infinite shows the total energy of interactional molecules between 0 to infinity and h to infinity they are sort of both infinite and they sort of cancel out.

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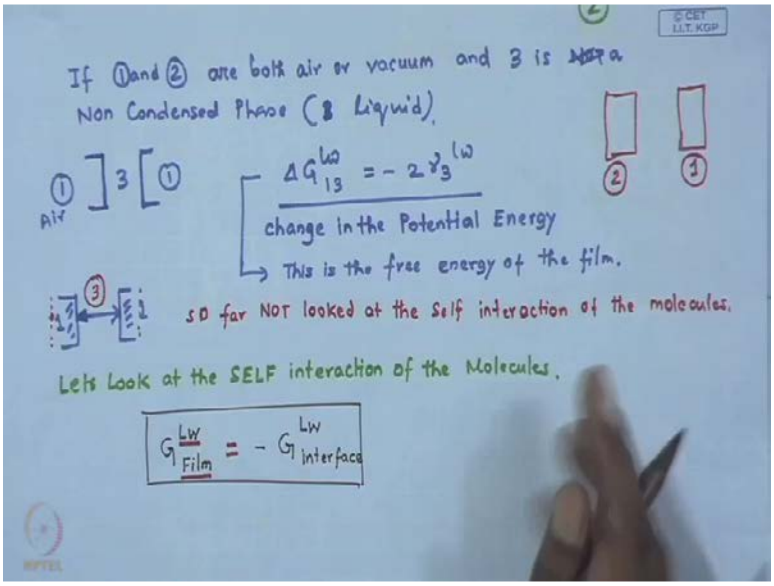

If ① and ② are both air or vacuum and 3 is ~~NOT~~ a Non Condensed Phase (Liquid).

$$\Delta G_{13}^{LW} = -2\gamma_3^{LW}$$

change in the Potential Energy

This is the free energy of the film.

so far NOT looked at the Self interaction of the molecules.

Lets Look at the SELF interaction of the Molecules.

$$\boxed{G_{\underline{Film}}^{\underline{LW}} = -G_{interface}^{LW}}$$

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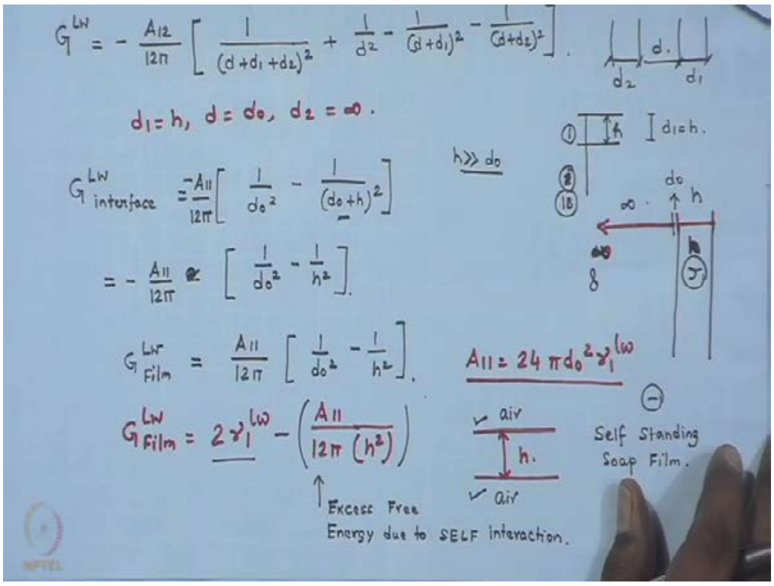

$$G^{LW} = -\frac{A_{12}}{12\pi}\left[\frac{1}{(d+d_1+d_2)^2} + \frac{1}{d^2} - \frac{1}{(d+d_1)^2} - \frac{1}{(d+d_2)^2}\right].$$

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

$h \gg d_0$

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

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

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

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

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

$\uparrow$ Excess Free Energy due to SELF interaction.

Self Standing Soap Film.

Therefore, what you have left to it is energy of molecules 0 to h is equal to minus interfacial interaction at h or simply one can write the GLW the potential energy of interaction of the film based on vander waals interaction. So, GLW film is equal to minus GLW interface this one can write now. I have already told you that we have the GLW interface the expression is already available to us interfacial interaction based on vander waal's forces and that is we know that it can be written as or the expression is and this is for this particular setting two blocks of material 1 and 2 which has separated by d. In our case we have created the interface over here. So, this is our first block this is now, the 1B or the remaining part of the block.

So, this thickness is h here is the interface. So, we can write sort of d1 is equal to h if you just turn this picture by 90 degree then it sort of becomes as if this is h and this is semi infinite block with an interface over here. So, this is the same thing we had this is what we have created so, this stretches up to infinity same material of 1 this is the figure we have drawn here. So, I am just trying to give you an analogue this is what we have done. So, we just rotate it like this and then map it onto this figure we already know this is h this is d0 and this is now infinity. So, in other words if you plug in d1 equal to h d equal to d0 and d2 equal to infinity into this expression, then that will give you the GLW at the interface, which turns out to be 1 by d0 square minus 1 by d0 plus h square and one may also argue that h is much larger than d0 so therefore, this second term can be approximated as 1 by h square so this is 1 by d0 square minus 1 by h square.

Now, we have GLW of the inter film is equal to minus of GLW of the interface and we now have an expression for the GLW at the interface to be equal to, I am sorry I just missed it out, it is A11 divided by 12 phi, I just missed out the numerical pre-factor with the minus sign. So, it is we now have an expression for the GLW at the interface which is minus A11 divided by 12 phi multiplied by 1 by d0 square minus 1 by h square for a geometry like this. So, this is h this stretches all the way up to infinity and this is the same material therefore we have A11. Therefore, since we are now able to find out an expression for GLW at interface therefore, we get GLW of the film to be equal to A11 divided by 12 phi into 1 by d0 square minus 1 by h square and now. We also have A11 in one of our previous slides we have found out that A11 turns out to be equal to 24 phi d0 square gamma 1 LW.

So, if you substitute that we get the GLW of the film to be equal to 2 gamma 1LW minus A11 divided by 12 phi into h squares so, this is a situation where we have a scenario like we have a film of thickness h and which is surrounded by air on both sides.

It is more like a self standing soap film type of a thing. Now the total energy of the film one can see is a summation of the surface tension term that is corresponding to 2 gamma 1 comes from this side as well as from this side and then there is a term which is an excess term. So, A11 divided by 12 phi h square is sort of an excess free energy due to self interaction and you do not have to consider anything to say that well the total energy ascribed to the interfaces is 2 gamma 1 for a film like this. But what you see here that the total free energy of the film is not 2 gamma 1 LW, but it has an additional term the more interesting term. So, which arises out of the self interaction of the molecule because, we have now considered self interaction of the molecule and more importantly this excess free energy sort of tends to 0 as the film becomes thicker.

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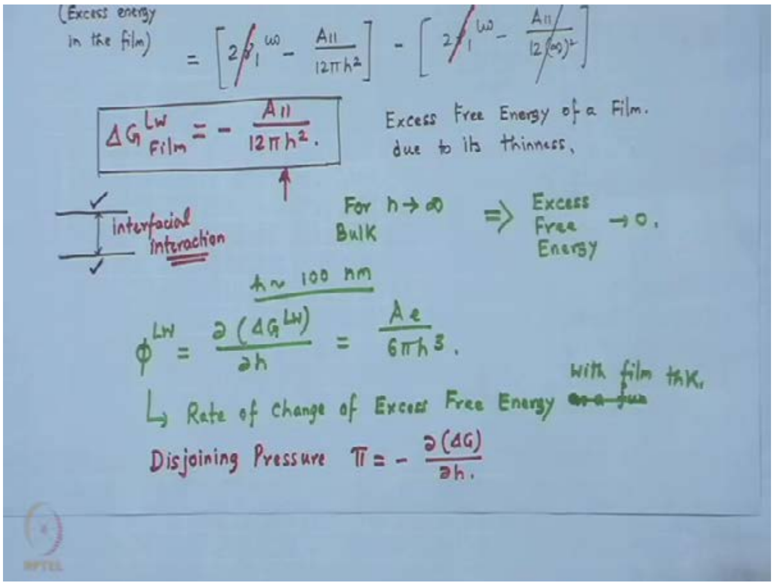

(Excess energy in the film) $= \left[\cancel{2\gamma_1^{LW}} - \frac{A_{11}}{12\pi h^2}\right] - \left[\cancel{2\gamma_1^{LW}} - \cancel{\frac{A_{11}}{12(\infty)^2}}\right]$

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

Excess Free Energy of a Film. due to its thinness.

Interfacial interaction

For $h \to \infty$ Bulk $\Rightarrow$ Excess Free Energy $\to 0$.

h ~ 100 nm

$$\phi^{LW} = \frac{\partial(\Delta G^{LW})}{\partial h} = \frac{A_e}{6\pi h^3}.$$

↳ Rate of change of Excess Free Energy ~~as a fun~~ with film thk.

Disjoining Pressure $\Pi = -\frac{\partial(\Delta G)}{\partial h}.$

So, one can now try to identify the excess free energy in a film by seeing that will might show or that is the excess energy in the film. This is for a film the energy of film corresponding to a finite thickness h minus the energy of film had it been infinitely thick. So, you see the first term will be 2 gamma 1 LW minus A11 divided by 12 phi h square in the first case and in the second case the term will be 2 gamma 1LW minus A11 divided by 12 into you substitute infinity here so, this term tends to 0 and now as you perform this subtraction this term also cancels out so, you are left with this excess free energy to be equal to minus A11 divided by 12 phi h square.

This is the excess free energy of a film due to its thinness. I would say because the moment h tends to higher values this term delta GLW of a film goes to 0 or in other words so, this is a very important concept. So, if you have a thin film then what happens is that because of the interfacial interaction that is the self energy of the interactions a self energy of the molecules you can visualize it like that or due to the interfacial interaction the interaction. So, here again you have two interfaces or two surfaces which are separated by a finite distance. So, due to the interfacial interaction there is an excess amount of energy which is manifested like this and we will later see that this excess interfacial energy is key to many settings or many unique properties of a thin film as compared to a bulk block laid.

So, the same instead of a thin film if there a now, the layer is very key you got it is a bulk we consider then what will happen h will tend to infinity and the immediate consequences the excess free energy tends to 0. So, the other way nice way or nice convention of identifying a thin film would be a system where the excess interfacial free energy is finite it is non 0 so one can look into it like that.

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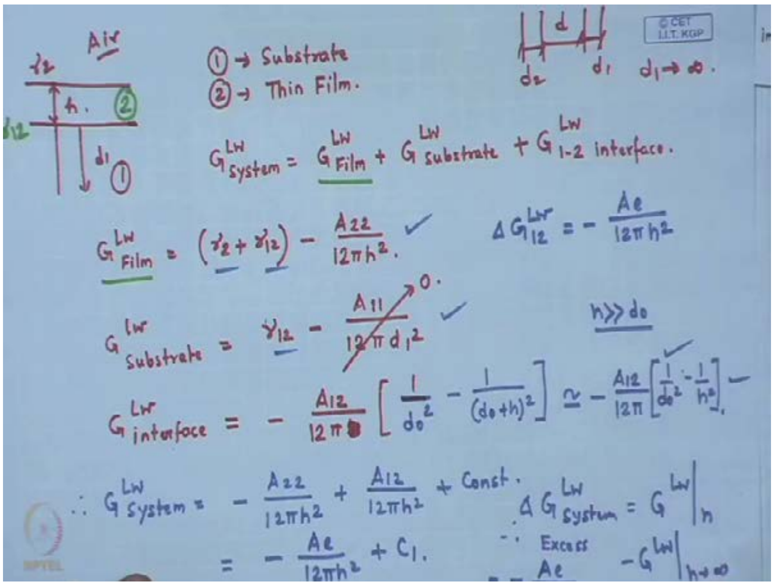

So, physically this term sort of becomes significant for ranges of h varying between up to let us say maximum of 100 nanometer certainly, not more than that effective interface potential a phi LW is defined as rate of change of this excess energy as a function of film thickness which turns out to be Ae divided by 6 phi h cube. So, it is the derivative of excess free energy with respect to the thickness that the rate of change of the excess with film thickness. We define the disjoining pressure phi as the negative of this term, the negative of the effective interface potential which is known as the disjoining pressure. We will look into how a system gets affected based on the disjoining pressure or when we will talk about the stability of a thin film later, but let us continue our discussion with this self interaction or whatever self interaction.

So, earlier we considered a system in which we sort of had a thin layer of h and then it was placed on a block of the same material but more realistic is a setting where you have a thin layer of let us say material 2 on a semi infinite block of material 1. We have talked about for example, spin coating so, this is exactly what you are likely to create. So, in that case 1 becomes your substrate and 2 is your thin film so in this case if you look at the GLW of the system what you get is GLW of the film the substrate plus GLW the interface. GLW of the film you now have two interfaces one is the surface with air let us, say which has surface energy of gamma 2 this is now an interface between 1 and 2. Therefore the total energy ascribed at the interface per unit area is gamma 2 plus gamma 12 and the excess free energy which is A22 divided by 12 phi h square.

So, this corresponds to the first term GLW of the film g l GLW of the substrate it is a semi infinite substrate so, only one of the interfaces are available so, it is gamma 12 minus A11 divided by 12 phi d1 square. So, let us say this is d1 we would again like to draw this figure here d1 tends to infinity so, therefore, this term is cancelled and the interfacial GLW at the interface is minus A12 divided by 12 phi into, we have already talked about the expression for the interfacial energy which is the GLW at the interface is minus A11 divided by 12 phi into 1 by d0 square minus 1 by d0 plus h square.

Of course; here it was earlier case it was an interface between 1 and ne1 therefore, it was A11 here it is an interface between 1 and 2 therefore, the term gets replaced with A12, but other terms remains the same. So, interfacial width is d0 square minus d0 plus h square d1 tends to infinity therefore, all other terms tend to infinity and this one we are good that h is much larger than d0 therefore, this term can be subsequently written as A122 divided by 12 phi into 1 by h zero square therefore, the total GLW of the system if you add up all these three terms you find that this this this as well as this term they are constant. So, only terms which are non-constants are you will find that it is A22 minus A2 2 divided by 12 phi h square plus A12 divided by 12 phi h square plus all constants.

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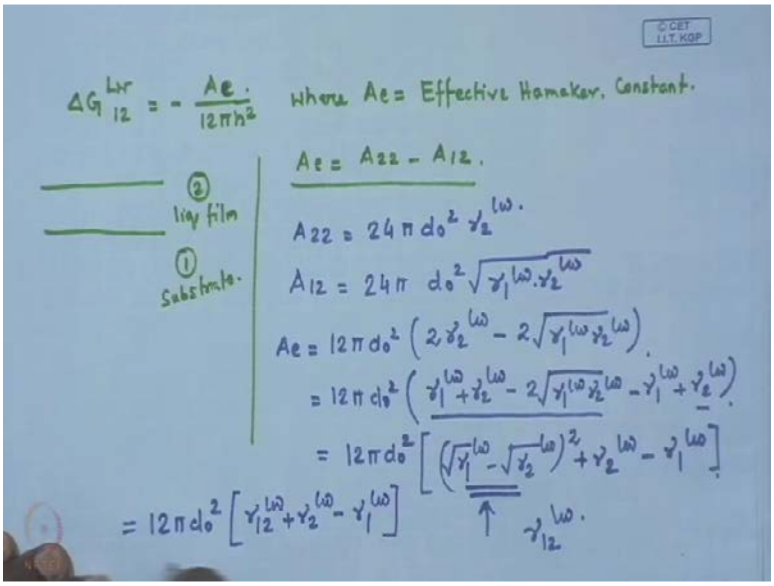

$$\Delta G_{12}^{LW} = -\frac{A_e}{12\pi h^2}$$ where A_e = Effective Hamaker. Constant.

$$A_e = A_{22} - A_{12}.$$

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

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

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

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

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

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

So, this one is minus Ae divided by 12 phi h square plus C1 therefore, GLW of the system the excess is GLW at h minus GLW at h tending to infinity. Therefore, if you do the subtraction you get minus Ae divided by 12 phi h square because of the fact that if you do the subtraction from here to here these terms the constants cancel out. Therefore, the excess free energy of the system is given as the minus Ae divided by 12 phi h square where, alright I will write it down here for this particular system where it is the effective Hamaker constant and is in this particular case Ae is equal to A22 minus A12.

Now, we will soon see that lay if one so, this is the condition we had considered that we have a film of 2 on a substrate of 1. So, we will soon see that whether if a liquid film of 2 on substrate of 1 remains stable or not will depend largely on the effective Hamaker constant. We also know that A22 can be written as and A12 can be written as I would request you to look into the previous lectures to get to these expressions.

Therefore, Ae is can be written as 12 phi d0 square into 2 gamma 2LW minus 2 under root of gamma 1LW into gamma 2LW and one can do a little bit of algebraic manipulation of the form add and subtract gamma 1LW and a 1 gamma 2LW comes here anyway from here. So, this you have 2 gamma once so, what you have is and these three in combined will give you under root gamma 1LW minus under root gamma 2 LW whole square minus plus gamma 2LW minus gamma 1LW and this we know from a our previous lectures we have done this is actually gamma 12 LW. So, the expression finally, turns to phi d0 square into gamma 12LW plus gamma 2LW minus gamma 1LW.

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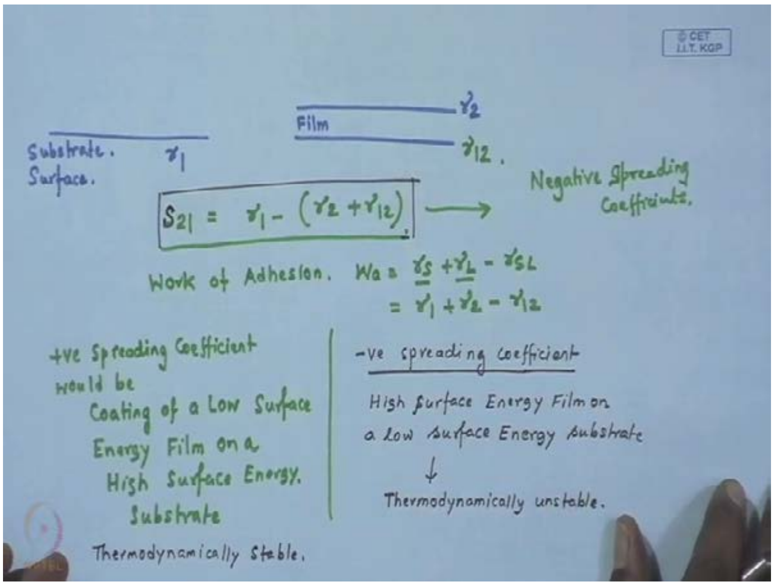

Film γ_2

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.

-ve spreading coefficient
High Surface Energy Film on a Low Surface Energy Substrate
↓
Thermodynamically unstable.

So, this is the final expression for a e in terms of the hum surface tension and interfacial tension now, here I would like to introduce the concept of what is known as the spreading coefficient let me just do it. In very simple terms suppose you have a surface, a bare surface which has a surface energy of gamma 1 and you coat a film on top of it of material 2. So, this is the film this has a surface energy of gamma 2 now, but the substrate surface which had an energy of gamma 1 now, gets replaced with interfacial energy gamma 12 so, the total energy before was gamma 1 while the total energy after coating is gamma 12 So, the spreading coefficient S21 is defined as the initial energy minus final energy.

So, if you now look carefully what you have got in the previous expression is nothing, but the negative of spreading coefficient 21 the LW component of spreading coefficient 21. Therefore, we can write look at the expression again the very simple concept there is another parameter that can be defined that is known as the work of Adhesion also based on similar concepts, which is Wa, which is gamma S plus gamma L minus gamma SL or in this case it will be gamma 1 plus gamma 2 solid liquid and the interfacial tension. So, this is the work of adhesion so, which can be sort of regarded as the adhesion of the total surface energy is minus the interfacial energy but, the spreading coefficient is defined as the energy per unit area before minus the energy of unit area after you have coated.

So, in simple terms let us see what it means that if you have a from simple physical understanding you can immediately say about the stability of a film. So, what does a negative spreading coefficient mean? Negative spreading coefficient means that you had a surface bare surface which was having a surface energy of gamma 1 per unit area and by coating a film you have replaced that surface with two energy components now; one is the surface energy or the surface of the liquid and the interface between the substrate and the film. So, a spreading coefficient a negative spreading coefficient implies is that by way of coating you have actually increased the energy. So, whatever was the total energy before you coated the film and the total energy after you have coated the film the right hand side is actually higher so, you have in the process created more energy by coating this film.

We know that every natural process sort of has a tendency to go towards the energy minimization. So, this of course, by way of coating this particular film which results in a negative spreading coefficient you have actually increased the total energy. Therefore, a film that corresponds to a negative spreading coefficient is thermodynamically unstable without going into any mathematical derivation you can immediately say this, but please do not forget that here we consider only the effect of the surface and interfacial energies. So, what is missing here is the self interaction or the thicknesses effects are missing we will come to those aspects in couple of lectures time.

In contrast if there is a situation where the spreading coefficient is positive that is by coating the film you that implies that by coating the film you actually reduced the total energy of the system. So, such type of films are thermodynamically stable because by way of coating of the film that there is a reduction of the energy. So, example of a positive spreading coefficient would be coating of a low surface energy film on a high surface energy substrate. Ideally this type of a film is thermodynamically stable we will see there are other parameters also, then we discuss thin film instability. In contrast, if you coat a high surface energy film substrate, then it becomes the spreading coefficient becomes negative and the film becomes thermodynamically unstable.

The other thing is that the expression of spreading coefficient of course, here the way we have derived is we have sort of this correlates to the vander waal's component of spreading coefficient, but important thing to note the spreading coefficient is not limited the definition of spreading coefficient is not limited to vander waal's interaction. So, you can have thus total spreading coefficient based on considering all the components of surface and interfacial tension of course, you can consider one of the components independently and can get individual components of spreading coefficient.

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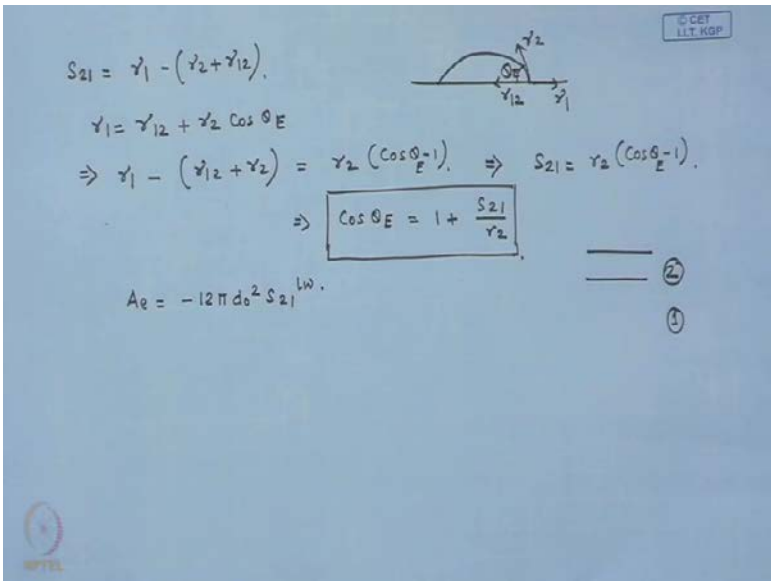

$$S_{21} = \gamma_1 - (\gamma_2 + \gamma_{12}).$$

$$\gamma_1 = \gamma_{12} + \gamma_2 \cos\theta_E$$

$$\Rightarrow \gamma_1 - (\gamma_{12} + \gamma_2) = \gamma_2 (\cos\theta_E - 1). \Rightarrow S_{21} = \gamma_2 (\cos\theta_E - 1).$$

$$\Rightarrow \boxed{\cos\theta_E = 1 + \frac{S_{21}}{\gamma_2}}.$$

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

I would just like to show you how spreading coefficient can also be correlated to the equilibrium contact angle. So, this is what we have the definition of spreading coefficient. Now, for a liquid which is making a finite contact angle on a solid surface 1 let us, say we have from young's equation therefore, one can write. Therefore, one gets an expression for S21 is equal to r2 theta minus 1 or I will write cos theta E this is the equilibrium contact angle or one can correlate the equilibrium contact angle as this and we have already said that we have been able to correlate the effective Hamaker constant for a system, in which is film of layer 2 has been coated on a substrate of layer 1 as minus 12 phi d0 square into S21LW.

Now, in case for the liquid and the solid both are a polar and there is no other components of surface and interfacial tension then of course, S21 is equal to S21LW and then one can write that Ae is equal to minus 12 phi d square into S21LW. So, we already understand a little bit based on the sign of the based on basic physics that how a positive or a negative value of spreading coefficient is going to sort of dictate the stability of your of a film or sort of influences the stability of a film. We will see that subsequently an in terms of how the sign of so, that that implies now, that we have already considered here that a positive value of spreading coefficient would result in a thermodynamically stable film.

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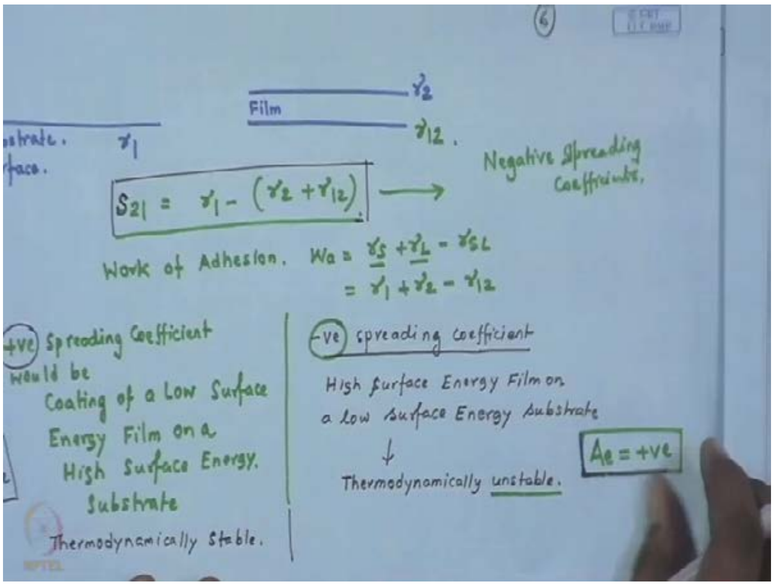

$$\boxed{S_{21} = \gamma_1 - (\gamma_2 + \gamma_{12})} \longrightarrow$$

Negative Spreading Coefficients.

Work of Adhesion. $W_a = \underline{\gamma_S} + \underline{\gamma_L} - \gamma_{SL}$
$= \gamma_1 + \gamma_2 - \gamma_{12}$

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

(-ve) spreading coefficient
High surface Energy Film on a low surface Energy substrate
↓
Thermodynamically unstable.

$$\boxed{A_e = +ve}$$

So, if we have the entire spreading coefficient is contributed by vander waal’s forces. It implies that the necessary condition for stable film is Ae equal to negative or the effective Hamaker constant for a system has to be negative. In contrast we have seen that based on basic thermodynamic consideration that a negative value of spreading coefficient is likely to result in a thermodynamically unstable film. Therefore, a negative value of spreading coefficient would result in a positive value of effective Hamaker constant. So, we will revisit some of these concepts in greater detail based on certain other considerations in the subsequent class; thank you.