Soft Nano Technology

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Lecture - 33
Interaction Between Two Surfaces – 2

Welcome back. We have been discussing now, we are trying to obtain a mathematical expression for the Van der Waals interaction between two surfaces.

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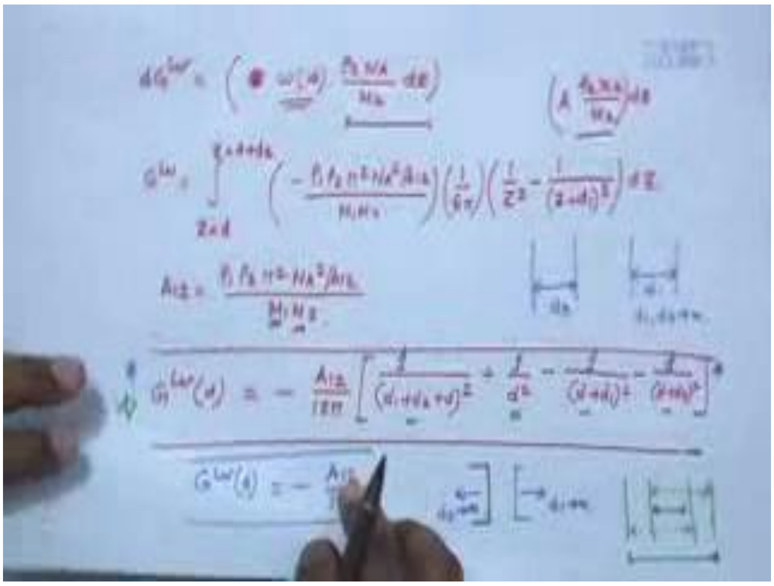

And in the previous lecture we have derived that it is say pretty lengthy expression I am afraid, but if you look carefully it is not that complicated. In fact, it not only looks or provides an expression for Van der Waals interaction between two surfaces; it talks about the Van der Waals interaction. This is a picture you should always remember. It talks about the Van der Waals interaction between two thin strips of material. So, what it means that each of these blocks is adequately thin.

And therefore, terms like one by d 1 square or one by d 2 square are non zero, because since the terms are in the denominator the movement either of d 1 or d 2 becomes very large that particular term that contains expression for either d 1 or d 2 we will gain to zero. And that is why what I have said from this expression that, if you would like to look in to the Van der Waals interaction between two surfaces of two semi-infinite blocks.

You can use this expression and simply plug in d 1 tending to infinity d 2 tend infinity that in facts makes all these three terms other than this particular term vanish and therefore the expression reduces to very simple expression. But I will not encourage you to simplify it is straight away, I will rather prefer that you remember this expression; it is in fact very very easy to remember. You see here is the total separation distance the far this interaction between the far this two interfaces, this is the interaction between the nearest to interfaces and here this on talks about interaction between this and this.

We will see how this particular expression can be used more effectively. Now, this expression can also be used to re create another setting that we have already talked about, I will write down this expression because we will need it several times in this particular lecture.

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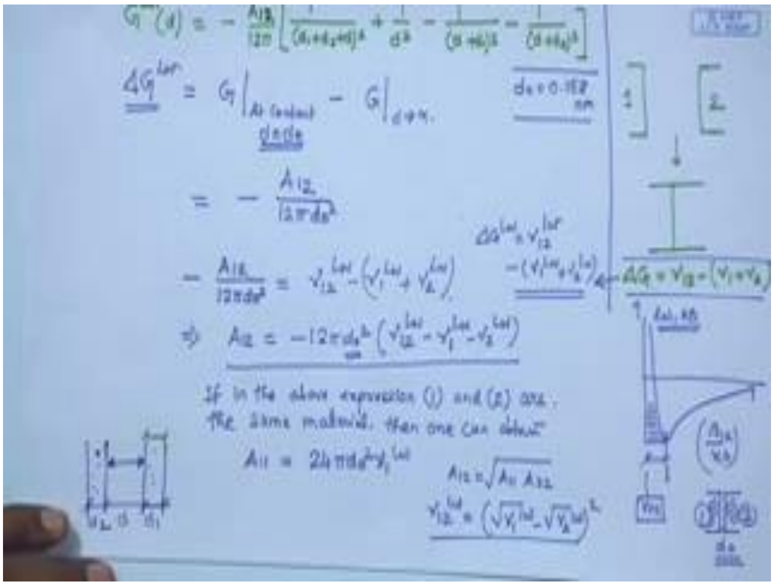

A quick reminder this A 12 divided by 12 phi has nothing to do with the coefficients. So, if it is a 23 please do not write 23 pi because I have seen people doing that mistake.

What we can easily do is that; one example we have discussed many times before is this particular example. We have two surfaces, which are initially far away and then they come in contact. Well, and for that we have written an expression delta G equal to gamma 12 minus gamma 1 plus gamma 2. Now you see this particular equation gives the expression of the free energy of the system. Therefore, one can in principle use this to calculate delta G of course, this is the Lw interaction only, and this is G at contact minus G of the system when d tends to infinity; the two blocks are far away.

There is a small catch here. What would you think would b the value of d at contact? And common logic tells in fact d should be zero, but if you plug in d equal to zero here the value of G goes to infinity. This is also logical because after all you have used and equation that is valid only up to this point, because you have started with the beta 12 beta 12 divided by x to the power 6 expression which is not valid for this particular region. Where, the two actually coming contact, it is here where r is equal to zero.

This particular expression is valid not for r equal to zero, but for the point where the two molecules sought of contact to each other not when the nucleons the distance between their nucleons goes to zero. So same thing is valid, I mean this expression is valid for a regime where there is no strip bond repulsion. And therefore it can sound a bit artificial, but this is how it is always considered. That when two surfaces come in contact following this particular approach the separation distance at contact is always consider to be d equal to d 0, which is all also referred to as the equilibrium separation distance. And this turn certain experiments it is almost considered to be constant irrespective of the material which is valued at 1.58 angstrom 158 nanometers.

So if you consider that, of course we are assuming that d 1 and d 2 are both infinite therefore you can get an expression which is because, here d tends to infinity therefore all the terms goes to infinity a goes to zero. And here again d 1 and d 2 are very large therefore all the terms are zero. So therefore, only one term you can alive.

However, you can compare the expression of delta G Lw that is the free energy change as you bringing the two blocks from infinity to contact. That is what is delta G Lw. G Lw is the free energy of the system. Please understand delta G Lw is the change in the free energy as you bring the two blocks from infinite distance to contact. But this delta G Lw you can also obtain an expression from here, of course you cannot compare delta G because delta G might be comprising of a Lw and AB component, but you can always get an expression for delta G Lw, if the all the materials are polar then there is absolutely no problem, which is this is the same expression only the Lw components.

And now, you can compare these two and therefore what you get is this expression. What is the utility of this expression? Utility of this expression is that now you can obtain the magnitude of Hamaker constant. The only assumption that you require is the value of d 0, because all other parameters you can measure. And this is a far improved expression of Hamaker constant, let say in comparison to something like this where you need a parameter like beta 12 which is material dependent and we to find out every time

Well, so fair enough. One can further straight it and one can assume that if in the above expression 1 and 2 are the same material, then obtain A 11 gamma 11 of course goes to zero is equal to 24 phi d 0 square gamma 1 Lw right. So, these things one can do and one can also sort of show, maybe you can try to show this a clue is you start of from this expression. May be I will put this one of us one of the assignments.

So, now we look into one unique case. And that case is so far while we were talking about the interaction for this particular system. And let me again draw the picture. This is a picture that you will need again and again and again which is fine. You have considered the interaction between all molecules of this block with all molecules of this block right that is how we have derived. But what we have so far neglected or we have not explicitly talked above is there is interaction between the molecules of the same block also. But, in other words we are talking that there is interaction between these two interfaces because they are very close by, but if the thickness of the block or the width of the block is less then these two interfaces also very closed by.

Is there any interaction between these two interfaces? Well, let us have a look. One can look into it from two situations like, one can look into it from a situation from one can start simply from here and consider something like a so film, but even if you do not do that we can take a slightly more rigorous approach, and let see what where we approach.

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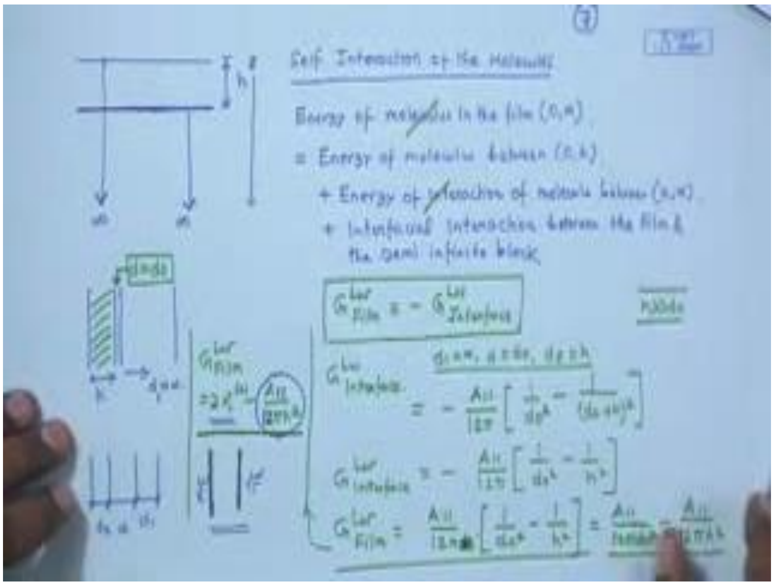

So, what we do is we take a block of a semi infinite block of a material and then we cut it. Take out a thin strip of it, this is a thought experiment please understand that. Take out a thin strip of the material, whose thickness is h, we sort of so we create an interface. This is a slightly I mean I would not say this is a complicated issue but please understand between in this way, we create an interface therefore we spend some amount of energy and then we place it back. So, like you cut a chunk of something you keep it there, that is what we are doing. And therefore, this remains again semi infinite.

So, what we are looking at is the self interaction of the molecules. So, what we I simply write is that energy of all molecules; let say this is at 0 equal z equal to it is start from here. So, this is the initial energy of the molecules, of course we want not talking about nuclear reaction therefore the total energy remains constant right. If you do that now you have created this interface and you have cut out this thin film and then you have created this interface. So, this equals energy of interaction of molecules between 0 and h plus the interfacial interaction between the film and the semi infinite block.

So if you invert it you actually get back your earlier picture. This is the earlier picture we have the original picture. What you have is lecture this is the substrate height a substrate width this tends to infinity. You have checked out thin film of thickness h and you have replaced it back, therefore here d is equal to d 0.

Now you can further do a simplification in this expression by saying that well after no one knows were exactly infinity is therefore the this term and this term cancels out. So, what you get energy of interaction a molecules between 0 and h is equal to negative of interfacial interaction between these two. Or in other words G Lw, this is a bit abstract I would say you cut it and place it and then you are one hand saying gamma 11 is always 0, but then here we are assuming I am just high lighting what are the limitations; that you are high lighting that though you keep the block of the same material over here or strip of same material over a block of it there is this separation distance d 0 comes in.

Anyway, but from this picture you can easily calculate this G Lw interface by simply taking this expression, this is an expression that will be needing again and again and again. And all you need to do plug in d 1 equal to infinity d equal to d 0. So, plug in d 1 equal to infinity d equal to d 0 and d 2 equal to h. As you do that what you get is G Lw interface turns out to be minus A 11 because blocks are of the same material divided by 12 pi 1 by d 0 square plus minus sorry, d 0 plus h square. In fact, one can further simplify that h is much higher than d 0. So, h is in the typically in the range of nanometer d 0 is one not a less than nanometer angstrom.

So, one can further simplify it that is G Lw interface equal to minus A 11 by 12 pi 1 by h square. Therefore, the G Lw of the film. Now what is this energy? I mean I like to draw your attention toward say particular term and you can expand this. And I would like to also draw your attention from here using this expression you can calculate A 11 divide by 12 pi d 0 square you simply turns out to be 2 gamma 1 Lw. So, I just write it down. Again telling it is a bit abstract, but it explains lot of things very nicely. So, that is what it tells. And this is the film we are talking about.

So, as if this behaves like a self standing so film; so what are the energies? Of course, it has, so this is the film sorry I will use a different color. This is the film, so it of course has two interfaces or two surfaces which correspond to gamma 1 and gamma 1, if we consider only the Lw components we are considering here. So, that is where the 2 Lw 2 gamma 1 comes in of the film. Now you see you have an extra term which scales us the h 2 the power minus 2. What does it mean? It means that if the film thickness is lays is very very small then there is some extra energy comes in to the system, that extra energy comes in to the system where extra can be plus or minus whatever the energy is different that only at that abstract only at the surfaces because of the interfacial interaction between each two interfaces.

So, this is the effect of self interaction of the molecules. We will understand it in a even better way. And we pick up a more realistic situation rather than a talking about cutting thin strip of film and then placing it back on it. This is more of a as I mentioned it is an abstract experiment because where the materials are identical.

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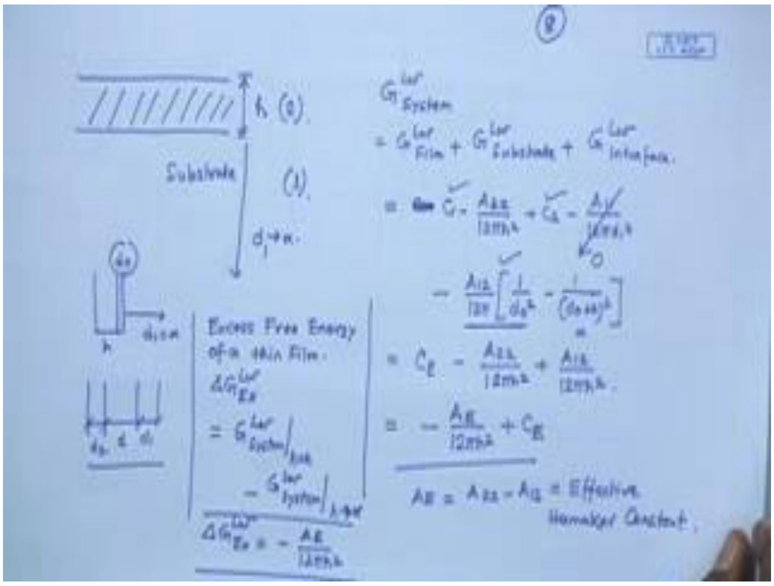

But we have already learnt about spin coating and therefore I am sure you will no problem in considering a system like this which is 1. So, we again consider often subtract like silicon wafer or glass whatever you take is much thicker as compared to the thickness of the film. So, what we again take? We take G Lw of the system is G Lw of the film, G Lw of the substrate plus G Lw at the interface. And here you see it is again if you tilt it, it is roughly the same picture as we have talked. So, you coat a film according to this picture, there is a finite contact separation d 0 even if you coat the film. And this is identical the semantic the basic system we have consider.

Now you have an expression for G Lw of the film which is 2 gamma 1 Lw minus A 11 into 12 pi h square so we used that. In fact, it turns out these are constants so it does not really matter; because you are going to look in to the change of G has a function of h. So, it really does not matter, but any way you can write the full term. So, let us write like constants because what will happen I do not want to the get into the details.

So, this film we showed it 2 gamma 1 minus A 11 divided by 12 pi h square, this arising out of the interfacial interaction. Here it will be not 2 gamma 1 because you have one free surface and one interface, so let us not over complicate the things. So, what we have is constants that is say C 1 minus A 22 is the film divided by pi h square for the substrate again we have C 2 minus A 11 divided by 12 pi d 1 square, and it turns out the this term is 0 because of the substrate d 1 tends to infinity and minus only the terms that will be alive will be A 12 divided by 12 pi which terms will be alive; the terms that does not contain d 1, so this term goes to 0 this term also goes to 0, so d is d 0 which is simple. And this particular case d 2 is actually h, so it is say h plus d 0 you can write.

So, the terms will be 1 by d 0 square divided by 1 divided by d 0 plus h square again this term 1 can simplify. So, this turns out to be some effective constant C E minus A 22 and this term also gets augmented to the constant, so this is a constant, this is a constant, this is a constant. A 22 divide by 12 pi h square plus A 12 divided by 12 pi h square and what we get is minus A E divide by 12 pi h square plus C 1 or C E as a effective constant. Where, A E is nothing but A 22 minus A 12 and is termed as the effective Hamaker constant. So, what do we get? We get that we are getting a term of the G Lw of the system to be this.

One can in fact use this to identify the excess free energy of a thin film. And what is the excess free they free energy? One can write it as delta G Lw excess is equal to G Lw of the system when film is thickness is h minus G Lw of the system when h tends to infinity. This way also you can write it down it makes perfect sense. So, then as you subtract these two terms in this particular case even this term goes to 0. The constant gets cancelled out and therefore the expression for delta G Lw excess is simply minus A E divided by 12 pi h square.

Now this is a very important consideration why you can sort of co related to spreading co efficient and stuff like that which I will do in the next class, but I will just introduce you to a term that we talk about and that is.

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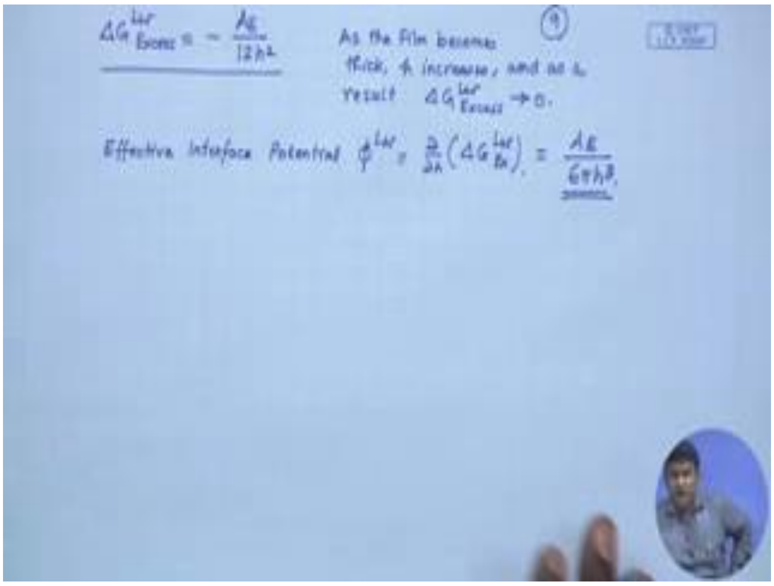

So, we now have an idea about the excess free energy of a system or of a film. And this excess free energy arises because of the thinness of the film. So, you can see as the film becomes thick h increases and as a result delta G Lw excess tends to 0.

One can also define a term called effective, now this is a bit tough as compare to what we have been a taking so far but therefore, I will revise it again in the next lecture so that it becomes more appropriate and palatable to you. But I will stop here just by defining the there is an another term one can write has effective interface potential which one can write us phi Lw and which is the rate of change of this excess free energy with the film thickness. And one can see it is the expression turns out to be A E divided by 6 pi h cube.

So, the previous lecture we looked in to the interaction between the two surfaces and it is effect when we talked about the self energy. Something we will continue our discussion even in the next class.

Thank you.