Soft Nano Technology
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Lecture - 07
Fundamental Concepts Related to Surface Tension – 4

Welcome back, continue our discussion with surface tension.

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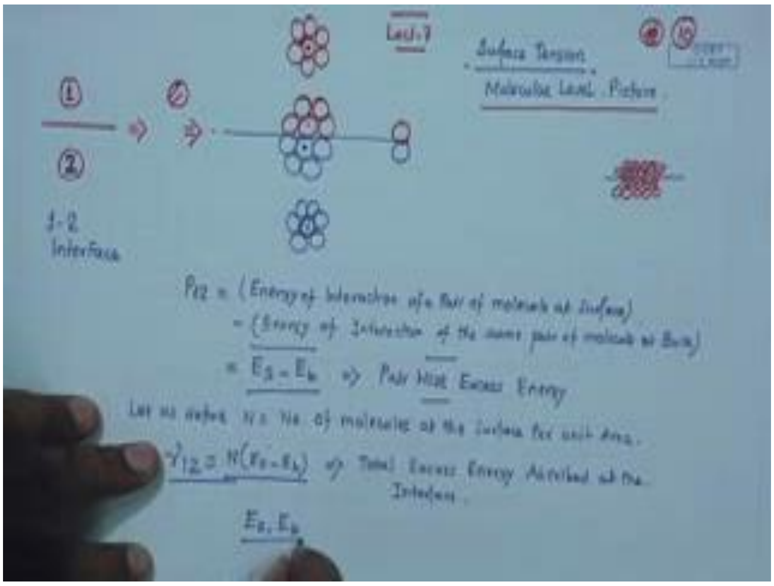

P_{12} = (Energy of interaction of a pair of molecule at Surface) − (Energy of interaction of the same pair of molecule at Bulk)

$= E_s - E_b \Rightarrow$ Pair Wise Excess Energy

Let us define N = No of molecules at the surface per unit Area.

$\gamma_{12} = N(E_s - E_b) \Rightarrow$ Total Excess Energy Ascribed at the Interface.

E_s, E_b

And what we now do, we have understood surface tension effects of a surface tension particularly in terms of hydrophobicity and hydrophilicity.

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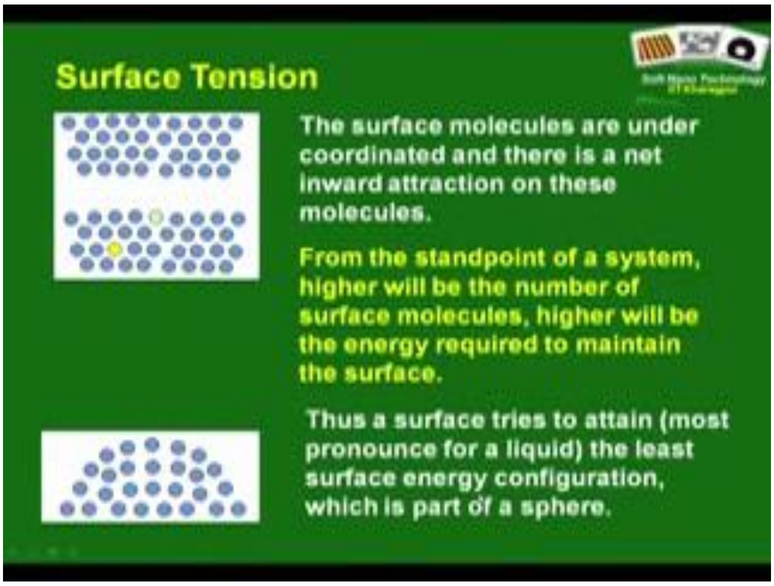

Surface Tension

The surface molecules are under coordinated and there is a net inward attraction on these molecules.

From the standpoint of a system, higher will be the number of surface molecules, higher will be the energy required to maintain the surface.

Thus a surface tries to attain (most pronounce for a liquid) the least surface energy configuration, which is part of a sphere.

In this particular lecture, we take a bit detail molecular level look of surface tension. We have already talked about, so this is let say you had a bulk and then you have created a surface. So, what happens is that you are essentially in order to create the surface; you are overcoming the interactions between the 2 between the molecules present on the both sides. So, let us say you have a bulk like this, you have these molecules, and you can create a surface let say you cut it out. So, you are in fact switching of the interaction between these molecules.

We have also seen that the coordination number, we already have understood that the surface molecules are under coordinated as compare to the bulk molecules. And therefore, there is a net inward force on these surface molecules which manifested in the surface energy or surface tension. In fact, the net inward force where the bulk is pulling the surface molecules in side is responsible for the term surface tension, why the surface molecules are suppose to always under tension. There pulled inward. And this is also responsible were if you have a finite volume of liquid resting on a solid surface it does not remain flat, but it in fact takes a hemispherical shape as we have already talk in the context of Young’s Laplace equations.

Now, what you are going to look here is let say we look into the interface between 2 condense phases 1 and 2. So, if we look that exemplify the picture a bit let say the red represents the molecules of 1, and green represents the molecules of 2. We identify 2 molecules let say this molecule and this molecule, what we do in order to get a expression of about the surface and interface tension. Suppose, what we do is we keep this molecules ones at the surface, and then we take them back into the bulk, or let say we have the same pair we have identified these 2 molecules we consider the total interaction they are undergoing when both of the molecules are at the bulk. And when these 2 molecule pair, so this is one molecule of one and one molecule 2 a specific molecule of one and a specific molecule two, when they are at bulk verses when they are brought to the interface.

Let us identify a term let say P 1 2, we define it as energy of interaction of a pair of molecule at surface minus energy of interaction of the same pair of molecule at bulk. Remember when at the surface these pair actually interacts with each other, it is this and this direct interaction between this and this. But when we take there is the respective molecules back to the bulk they are not interacting with themselves any more, but they are interacting with neighboring molecules within the respective faces. So, this molecule of one, when it was at the surface was interacting with some molecules of one some molecules of 2 and the chosen molecules of two. But when this is back to the bulk it is only interacting with certain molecules certain number of molecules of one the number of molecules a number is given by the coordination number.

Same is valid for these molecules of specific molecule of two, when it was at the surface it was interacting with the specific molecule of one and some molecules of 2 and some molecules of one, but when it is back to the bulk, it is only interacting with some molecules of two. So, we write this as E s minus E b, which is a pairwise excess energy. Why excess energy because we argue that the nature of interaction when the molecules where at the surface are going to be different than the nature of interaction when the molecule are at the bulk, so that is why sort of pairwise excess energy.

Now, let us define N equal to number of molecules at the surface per unit area. Therefore, simply what do you think this parameter is going to give, this parameter is nothing but total excess energy ascribed at the interface. And therefore simply this is inter facial energy this is the gamma 1 2 so, this is simple. So, this is the excess energy for pair and now know the number of molecules are number of pair resting on the surface you multiply this term with the number of molecules per unit area, you get the inter facial energy, fair enough. Now this is still a expression and if you want to evaluate it, what needs to be done we need expressions for E s and E b.

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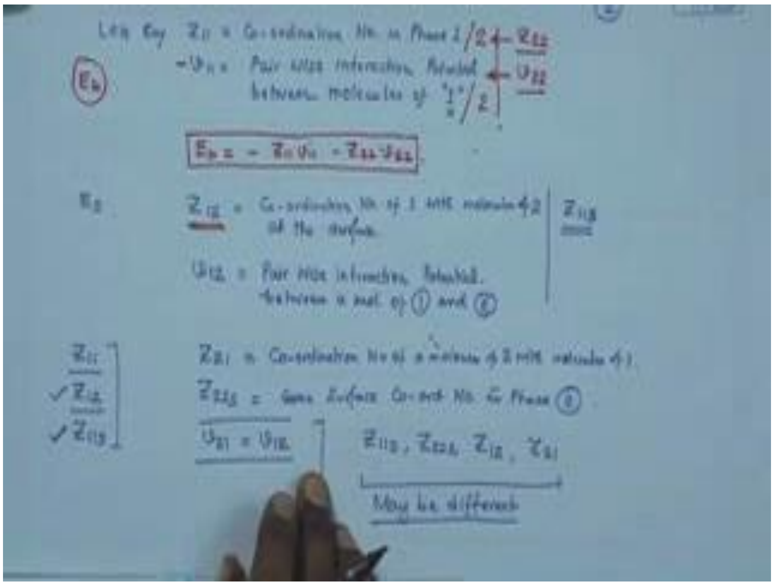

Let us try to do that; and for that, what we do. Let us say Z 1 1 is the coordination number in phase one and V 1 1 is the pairwise interaction potential between molecules of am deliberately writing it in front of you as if I using the black board in the class, I never gives this presentation in the form of a ppt. Because if you write the terms then you sort of tend to get a very clear idea what I will be talking about. So, essentially what Z 1 1 what gives is this particular coordination number, and individual interaction energy of interaction between these 2 molecules of phase one are given as V 1 1. Question to ask is what are the components of V 1 1.

Of course, now we know from our initial discussion Van der Waals forces must be present and then depending on the structure the nature of the material you can have the polar interaction also. You can have a particularly for long chin polymers, you can have some sort of steric interaction that is interaction due to the structure of the molecules. A simple example is that they are can be effects like entanglement.

Now, what is entanglement is like when you are having noodles let say and you try to have it with a fork, they are might be certain strings of noodles that might fall down from your fork and that is because that particular string of noodles is entangled with the bulk resting on your plate. This is some sort of a very simple example of what is entanglement, but when you are having rice with a spoon, this never happens whatever you pick up it actually gets transfer to your mouth, because these are now very small entities, rice as small as compare to threads of noodles, and therefore, there is no effect of entangle.

In principle for long chain molecules and they are can be some steric and interactions like entanglement effect, but then again these are research level topics; and for our discussion, we will keep our discussion limited to Van der Walls and polar interaction only. So, what I mean what is important coming back to context is that you have a coordination number Z 1 1 for phase one, and the interaction between to 2 molecules. So, that also should making think about what are the other parameters you need to fully defined in order to obtain expression for E b, because we while talking about E b, you are considering the interaction of this molecules here and this molecule here.

The other parameters that you need to write an expression for E b is Z 2 2 and V 2 2 that is the coordination number in phase, so I will use the same expression and above I writing. So, Z 1 1 is the coordination number in phase one, Z 2 2 in the coordination number in phase two. V 1 1 is the pair wise interaction potential between molecules of one and V 2 2 is a pair wise interaction potential between the molecules of two. So, in principle we just additionally consider that if we are considering an attraction is always negative. So, therefore, expression for E b terms out to be minus Z 1 1 V 1 1 minus Z 2 2 V 2 2.

Similarly, let me make you think, what are the parameters you need to define in order to get an expression for E s? And it turns out that the parameters you need to define are Z 1 2 that is coordination number of one with molecules of 2 at the surface. Similarly, you need to also define in a V 1 2 that is the pair wise interaction potential between a molecule of one and two. It is obvious that this interaction is possible only at the interface; it is not possible anywhere else. So, essentially what it talks about is the Z 1 2, so this is the coordination number or the number of molecules of 2 surrounding a surface molecule of one inter facial molecule, molecule that is molecule of one that is resting at the inter face. But that does not give you the full picture because you also need to consider the number of molecules of one that are surrounding this particular molecule of one and therefore you need to also define the surface coordination number in phase one.

I will take a minute for a sort of an informal discussion, please convince yourself if you understand the difference between these three terms clearly. So, Z 1 1 essentially you are talking about the coordination number here for a molecule surrounded entirely by molecules of one in the bulk. Z 1 2 is the coordination number with respect to one molecule of one, how many molecules of two, it is directly interacting with when the molecule of one is at the surface. But this molecule you can see is interacting with some molecules of two, the coordination number of which is given by Z 1 2, and some molecules of one the coordination number of which is given by Z 1 1 S.

Similarly, when you talk about this particular molecule of two, you again need to define 2 different coordination numbers and those are Z 2 1 and Z 2 2 S. So, this is the coordination number of a molecule of 2 with molecules of one. And this is coordination number surface coordination number in phase two. Only thing that you may want to look of course, you need a V 2 1 and it is very logical that V 1 2 is equal to V 2 1, but until and unless you assume something and that is exactly what you are going to assume next. I do not want to talk too much about it until and unless you assume there is no reason for Z 1 1 S, Z 2 2 S, Z 1 2 and Z 2 1 to be same, they may be different.

I will repeat we are taking about pairwise interaction a term we have define the term P 1 2, which is essentially the pair wise excess energy between molecules at bulk and at the surface. So, it is the energy of interaction of a pair of molecular at the surface minus the energy of the interaction of pair of molecule at bulk (Refer Time: 16:16) E s minus E b. Now if you know the number of molecules present at the surface which let says N you in fact get an expression for inter facial energy gamma 1 2 straight away as N times E s minus E b. But in order to evaluate, this you need to have expressions for E s and E b and were building concepts.

In order to have an expression for E b, where we essentially consider this interaction and this interaction only we need to know the bulk coordination number of in phase 1, and the pair wise interaction energy between molecules of one. Similarly the bulk coordination numbers of phase in phase 2 and the pairwise interaction potential or interaction energy between molecules of two. And if you define that appropriately you get an expression for E b as this.

Similarly, in order to obtain an expression for E s, we need to define the different coordination numbers like the cross coordination numbers I would say Z 1 2, Z 2 1, Z 1 1 S and Z 2 2 S. Of course, we just need to be define a V 1 2. This interaction energy is remain same these are same as V 1 1 and V 2 2, there is no change in that.

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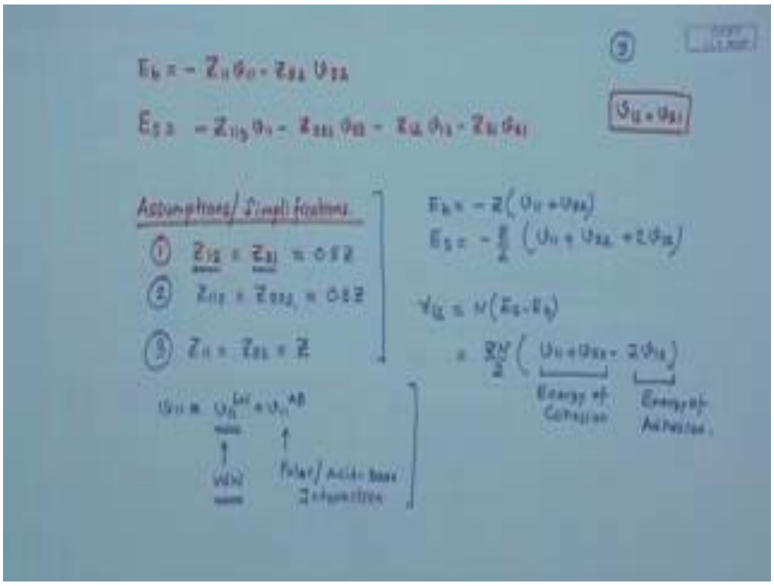

③

$E_b = -Z_{11}\upsilon_{11} - Z_{22}\upsilon_{22}$

$E_s = -Z_{11s}\upsilon_{11} - Z_{22s}\upsilon_{22} - Z_{12}\upsilon_{12} - Z_{21}\upsilon_{21}$

$\boxed{\upsilon_{12} = \upsilon_{21}}$

Assumptions/ Simplifications

① $Z_{12} = Z_{21} = 0.5Z$

② $Z_{11s} = Z_{22s} = 0.5Z$

③ $Z_{11} = Z_{22} = Z$

$E_b = -Z(\upsilon_{11} + \upsilon_{22})$

$E_s = -\frac{Z}{2}(\upsilon_{11} + \upsilon_{22} + 2\upsilon_{12})$

$\gamma_{12} = N(E_s - E_b)$

$= \frac{ZN}{2}(\underbrace{\upsilon_{11} + \upsilon_{22}}_{\text{Energy of Cohesion}} - \underbrace{2\upsilon_{12}}_{\text{Energy of Adhesion}})$

$\upsilon_{ii} = \underset{\text{vdW}}{\upsilon_{ii}^{LW}} + \underset{\text{Polar/ Acid-base Interaction}}{\upsilon_{ii}^{AB}}$

Let us write and expression for e s and you see if you can convince yourself. I will just rewrite we already have an expression for E b. And we are now writing an expression for E s. As you can figure out from the symbols we have defined E s is going to have four components and that is interaction of molecule this molecule with all molecules of 2 interaction of this molecule with all molecules of one, this molecule interaction which 2 and this molecules interaction with one. So, we are going to have four components in E s and the full expression is going to be Z 1 1 S, so of course, minus sign comes in because you are considering an attractive interaction; Z 1 1 S V 1 1, Z 2 2 S V 2 2 minus Z 1 2 V 1 2 and Z 1 1 V 2 1. Now of course, we will do some simplification, but among all the expressions the only real thing that obviously happens is V 1 2 is V 2 1.

Now, we do some approximations, and what we consider is that these are assumptions or simplifications. The first assumption that we make is Z 1 2 is equal to Z 2 1, the logical and you know when many of the derivations you need to have some simplifications which are quite ok. We also assume that Z 1 1 S is equal to Z 2 2 S. Third assumption, we make is the coordination number, the bulk coordination number in the 2 phase are same as something like Z. Once we get this and if you looking to the picture, it is so here the coordination number Z 1 1 has been assign consider to be same as Z 2 2 and both are equal to Z. It is sort of logical you can consider it to be logical or you can consider it to be some sort of a simplification that Z 2 1, Z 1 2 both are equal to half Z, and this also follows at the surface coordination number of Z 1 1 S and Z 2 2 S are also half Z.

These are simplifications, but if you draw any picture like the one have drawn over here you can pretty well convince yourself there is not too much of a problem. Of course, if you always consider that you have molecules of difference size, and therefore, the coordination numbers are different. And therefore, you have every logic every reason to consider that and the reason why we defined in fact 2 different variables Z 1 2 and Z 2 1, but let us say for simplification this is something that is valid.

If you consider that then what we get we get a simplified expression for E b as minus Z into V 1 1 plus V 2 2; and E s minus Z by 3 V 1 1 plus V 2 2 plus 2 V 1 2. See, we are not considering V 1 1 equal to V 2 2, because we understand that if the materials are different, the intermolecular interactions are going to be different. And as long as you do not assume that V 1 1 and V 2 2 are same you are quite you trust me you are quite. So, from this expressions you can get an expression from gamma 1 2 combining the fact that this is equal to N E s minus E b which turns out to be if you write the expressions here Z N by 2 V 1 1 plus V 2 2 minus 2 V 1 2.

Now, what is V 1 1, in fact V 1 1 and V 2 2 are the interaction energies within the bulk. These are sort of energy of cohesion and this is V 1 2, this is interface. So, this is the adhesive part of the energy. So, now we do some bit of, what is important that this V 1 1 or any V i j comprises of the Van der Waals interaction of course, and it may also might have polar interactions. So, it is something like V 1 1 l W plus V 1 1 A B, L W stands for the Van der Waals interaction A B is the polar interaction or as it is called the acid base interaction and something like that. So, we will consider it, but as we have already agreed that the Van der Waals interaction is a most general one. So, first we will only consider a case with Van der Waals interaction and then we will further add the concepts, but before that we do a some bit of additional maneuver with the equation which we have in our hand.

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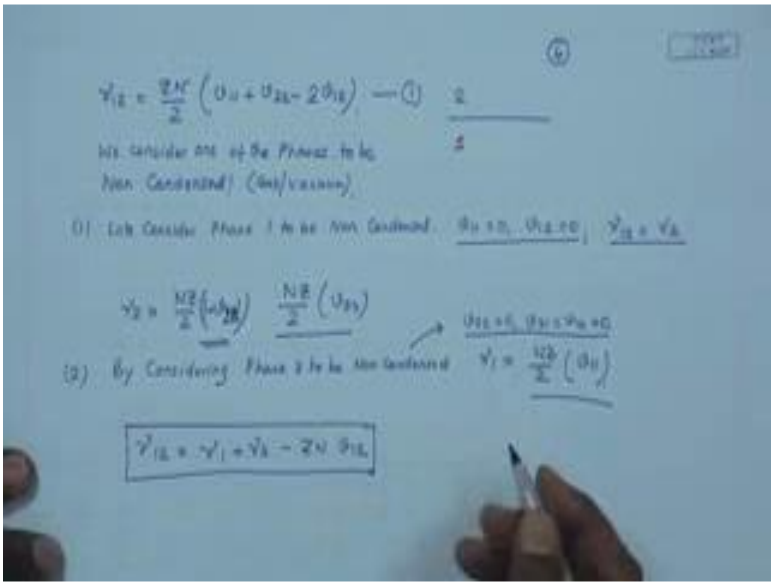

We have this now suppose we consider though we have started our consideration based on an interface between 2 non-condensed phases. Suppose, we consider that one of the phases is I am sorry we have started our discussion based on the interface between 2 condensed phases. Suppose, we consider one of the phases is non-condensed that is let me have the picture here also for our understanding let us consider one of the phases to be non-condensed, like it can be either a gas or a vacuum whatever.

Let us say one, let us first consider phase one non-condensed. What does it mean it means V 1 1 is going to 0; and V 1 2 is going to be also 0, because there not an adequate number of molecules present in this phase. For interacting the molecules of 2 and as I consequence this gamma 1 2 in the expression in fact changes to gamma 2. So, by a little clever manipulation, we get a expression of gamma 2, we consider this to be a negative interaction. So, we just take the modulus value just do not worry about because surface tension can never be negative.

Similarly, by considering phase 2 to be you can also not worry about this modulus value at all phase-two to be non-condensed. We actually get gamma one in that case what happens is V 2 2 become 0, and V 2 1 equal to be 1 2 becomes 0. So, again you get gamma 1 as I am sorry there is small mistake here this will become V 2 2, this comes out to be V 1 1. Now, if you substitute back these to equations in this equation, let say equation one what we get is gamma 1 2 is equal to gamma 1 plus gamma 2 minus Z N V

1 2. So, I will start further discussion from this point in the next class. And we will see, we will get an expression of inter facial components and then we will start it considering the Van der Waals interaction and the polar interaction.

Thank you.