Instability and Patterning of Thin Polymer Films

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Module No. # 01
Lecture No. # 04
Surface Tension (in terms of molecular interactions)

Welcome back we have some discussion on surface tension particularly on issues related to hydrophobicity and hydrophilicity. I guess now understand what is structural super hydrophobicity and we just talked about the gaseous state (( )) and what exactly you define as a super hydrophobic surface. Now, you can all imagine that most of the stuff is a manifestation of the surface tension of the individual materials. Here, in this particular case the liquid and the solid substrate involved. So, it is important that we understand the nature of surface tension in greater detail.

If you remember in one of our previous classes, we had a discussion about the dispersion forces or the induced dipole induced dipole type of interaction, where we also talked about the bond formation of the permanent dipole, permanent dipole type of interaction. So, it is essentially what you see as a microscopic manifestation in terms of surface tension and interfacial tension it results from these molecular level interaction and what we will discuss in somewhat detail today with some simplest view. With that you will understand certain basic issues like whether how can you create a stable dispersion or agglomeration can occur in a liquid medium.

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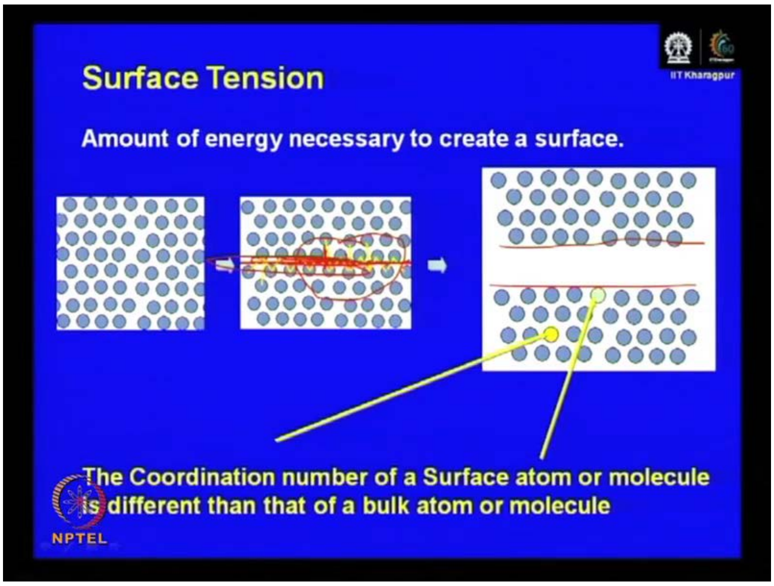

Surface Tension

Amount of energy necessary to create a surface.

The Coordination number of a Surface atom or molecule is different than that of a bulk atom or molecule

in one of our previous classes, we have talked about what surface tension is so we defined it in terms of the amount of energy necessary to create a particular surface. So, essentially we considered block of material and which was this essentially we wanted to create another surface, so you have to supply the amount of energy that is necessary to sustain this surface and this surface.

We also talked about the under coordination of the surface molecules, which means that the coordination number of the molecules present at the surface are different from the coordination numbers present inside the bulk, which results in some sort of imbalance in the interaction of these molecules, which manifests as some sort of a total energy penalty. In other words, see you sort of have to overcome the energy penalties or overcome all the permanent the interactions that are along this particular line, so eventually that is where that is the penalty you have to in order to create a particular new surface.

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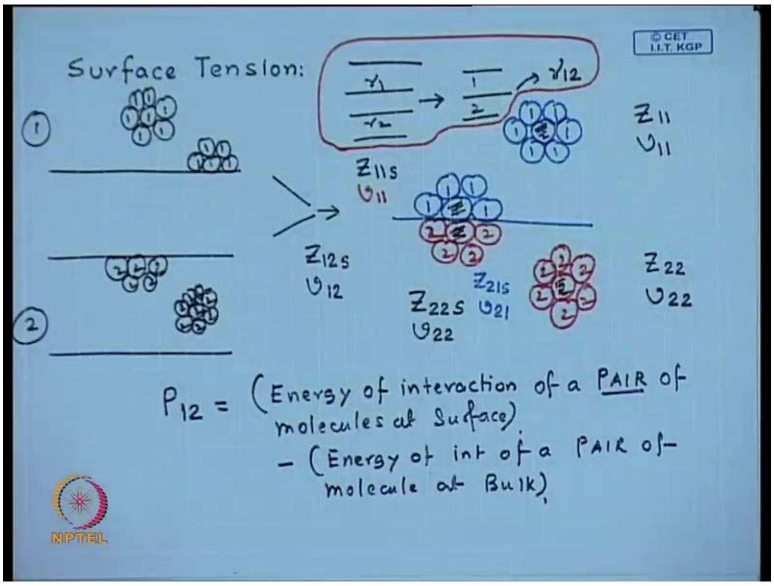

P_{12} = (Energy of interaction of a PAIR of molecules at Surface) − (Energy of int of a PAIR of molecule at Bulk)

So, today we will look at the reverse problem. Suppose we have a block of two materials. Let us say one is one, and the other is two, so you have molecules of one lined up here. Also, there are surface molecules and you have molecules of 2 present, so you have their corresponding bulk coordination and the surface coordination. Now, suppose we want to bring these 2 surfaces in contact, so what will happen is a scenario like this. You have molecules of 1 at the surface, here you have the bulk molecules, here you have the molecules of 2 and you have the bulk molecules as well.

Now, for the calculation of the energy of the interaction, so essentially what happens here is you have two blocks. Let us say this surface has a surface energy of gamma 1, this has a surface energy of gamma 2, and you bring them in contact. Now, you have a composite block of this and you know based on whatever discussion we have, it is no longer the surface tension of the individual molecules, but this as an interface between material one and material two and what you have the associated energy is gamma 1 2 or the interfacial tension.

Now, let us consider, in order, to calculate the interfacial energy, we proceed considering the pair wise interaction of the molecules. Let us say, we define P 1 2 as the energy of interaction of a PAIR of molecule. This is important and I will discuss what it means, pair of molecule at surface minus energy of interaction of a PAIR of molecule at bulk. So, essentially the P 1 2 sort of shows the difference in the energy level between a pair wise interaction at the surface and that at the bulk. So, let us consider that we sort of look at 2 molecules. We considered a pair of molecules of 1 and molecule of 2. Let us identify these two are the molecules, so when these two molecules are at the bulk, they are not interacting with each other, but the molecule 1 is interacting with all these.

This particular molecule of 1 is interacting with all the neighbouring molecules of 1, so you have a So, what are the individual components, individual components will be there, is going to be a coordination number. Let us say Z 1 1, I am coming to all that in detail. Let us say this is the V 1 1, we define as the pair wise interaction potential for interaction between the molecules of 1. Similarly, for a molecule in the bulk of two, we have something let us a called Z 2 2, which is the coordination number for the molecules of 2 in the bulk, you have corresponding V 2 2 pair wise interaction potential. Now, suppose here is a pair. This molecule and this molecule, let us say these two are pair and these two are now at the bulk, so if we calculate they interact and total interaction is based on these parameters, which we will do immediately. We will get the second term of the expression what we have written.

Now, let us consider that the same sets of molecules are brought to surface. Now, here what sort of interaction this molecule is subject to? This molecule is subjected to still subject to interaction with some number of molecules of 1. However, the number of molecules of 1 surrounding this particular molecule of 1 is less than that compared at the bulk. So, here you have a surface coordination number within one, let say which we term as Z 1 1 s, but the pair wise interaction potential or the interaction energy, between the molecules of 1 remains the same. So, that remains same as d 1 1, but simultaneously this molecule also interacts with some number of molecules of 2 at the surface.

So, on this side you can see it is interacting with the molecules of 1 only, but on this side it is interacting with some molecules of 2. So, these for let us say has a coordination number Z 1 2 s and of course, the pair wise interaction is V 1 2. Similarly, for a molecule or for the molecule of 2, which is sitting on the surface, it is still interacting with some molecules of 2. The corresponding coordination number, let us say it is Z 2 2 s, the interaction remains the same at V 2 2. In addition to that, what it will have it will have a coordination number of Z 2 1 s and V 2 1. So, these are the eight parameters we will be having. Let us have a clearer picture.

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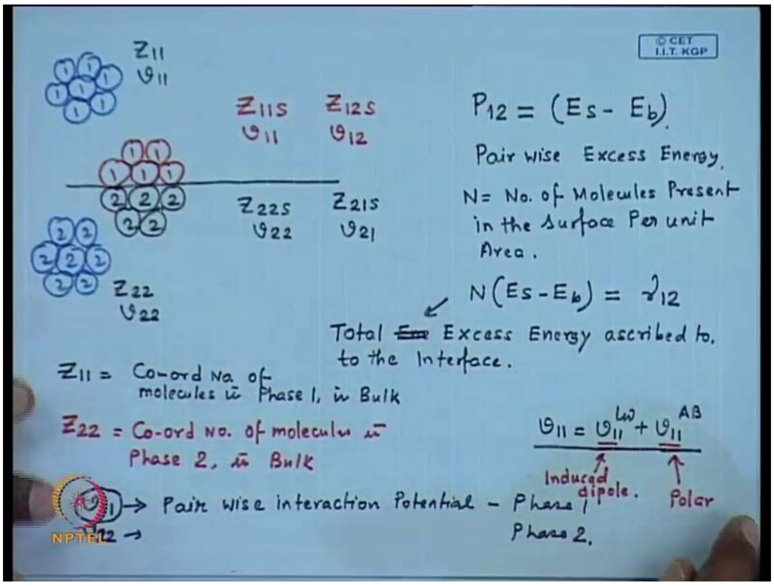

Z_{11} ϑ_{11}

Z_{11s} ϑ_{11} Z_{12s} ϑ_{12}

Z_{22s} ϑ_{22} Z_{21s} ϑ_{21}

Z_{22} ϑ_{22}

$P_{12} = (E_s - E_b)$.

Pair wise Excess Energy.

N= No. of Molecules Present in the Surface Per unit Area.

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

Total ~~En~~ Excess Energy ascribed to. to the Interface.

Z_{11} = Co-ord No. of molecules in Phase 1, in Bulk

Z_{22} = Co-ord No. of molecules in Phase 2, in Bulk

$\vartheta_{11} \rightarrow$ Pair wise interaction Potential – Phase 1

$\vartheta_{22} \rightarrow$ Phase 2.

$$\vartheta_{11} = \underset{\substack{\uparrow \\ \text{Induced dipole.}}}{\underline{\vartheta_{11}^{LW}}} + \underset{\substack{\uparrow \\ \text{Polar}}}{\underline{\vartheta_{11}^{AB}}}$$

So, we have molecules of 2 over here at the surface. We have molecules of 1 over here at the surface. So, when we talk about the pair wise interaction between this molecule of 1 and this molecule of 2, it depends several parameters, it depends on Z 1 1 s, which is the surface coordination number of the molecules of 1 at the surface. It depends on V 1 1; it depends on Z 1 2 s and it depends on V 1 2. Correspondingly, in the phase 2 we have Z 2 2 s we have V 2 2 we have Z 2 1 s and we have V 2 1. Now, correspondingly, if you simultaneously also consider the molecules, which are present at the bulk, then we will be having the parameters Z 1 1, V 1 1, Z 2 2 and V 2 2.

We have so essentially in our by the way we have define P 1 2, it turns out to be something like let us say E s minus E b. In other words; it is sort of the pair wise excess energy. Now, let us say that N is the number of molecules present in the surface per unit area. In that case, the total energy ascribe to the interface turns out to be N of E s minus E b. So, E s minus E b is the sort of excess energy ascribe at the interface of for a pair wise molecule, interaction of a pair of molecules. Now, if we have N number of molecule, which are present at the interface, then what is the total energy, total excess energy is N times E s minus E b. what is this parameter? This parameter is nothing but, the interfacial energy gamma 1 2.

So, this is the total energy or total excess energy, let us put it, and ascribed to the interface. In other words, this is the energy that is necessary to create the interface or so if you want to cut the block you can look it from the other prospective, this is the energy that is necessary to create the interface. Now, let us look into these parameters which we have defined in a little more detail. So, we have already define that Z 1 1 is the coordination number of molecules in phase 1 in bulk. So, obviously you can get an idea about what Z 2 2 stands for. It is the coordination number of molecules in phase, in the second phase in bulk. Therefore, if we assume that V 1 1, not an assumption, we have talked already about it. V 1 1 is the pair wise interaction potential, similarly, is V 2 2. This is in phase 1 and this is in phase 2. Now, we have already talked about the dispersion forces or the induced dipole, induced dipole type of interaction, the permanent dipole permanent type of dipole type of interaction.

Now, this V 1 1 is made up, the constituents of this V 1 1 will be essentially those different types of interaction. So, we will eventually have V 1 1, to be an additive summation of let say terms like we will come to it in get detail later. So, V 1 1 will be, let say V 1 1 LW plus V 1 1 AB, where LW is the Lifshitz-Van der Walls forces of the dispersion forces, which refers to the induced dipole, induced dipole type of interaction and AB is acid base type of the polar interaction. So, this is going to be the polar interaction, this is the neutral of the induced dipole interaction. So, we will look into it at the different constituents of the interaction potential but, as of now, let us carry it in the form of a clubbed or lumped interaction potential

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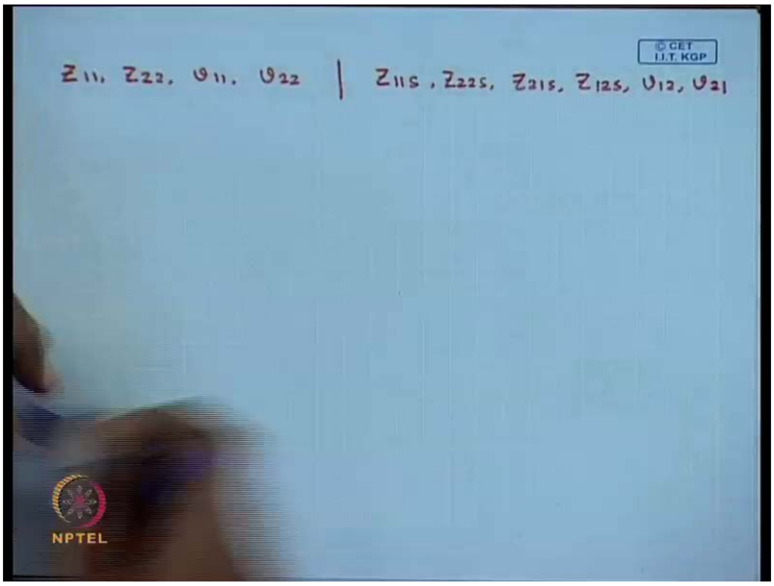

$Z_{11}, Z_{22}, v_{11}, v_{22}$ | $Z_{11s}, Z_{22s}, Z_{21s}, Z_{12s}, v_{12}, v_{21}$

So, if we now have a proper definition for Z 1 1, Z 2 2, V 1 1, V 2 2, and you can also probably make out what Z 1 1 s means, Z 2 2 s, Z 2 1 s, Z 1 2 s ,V 1 2 and V 2 1. So, these are essentially the surface Z 1 1 s, for example, is the surface coordination number of a molecule in phase 1 sitting at the surface. Z 2 2 is the surface coordination number of a molecule of 2 sitting at the surface, Z 2 1 is sort of the coordination number or the number of molecules of 2 that surrounds a molecule of 1 at the surface. Similarly, Z 1 2 s is the number of molecules of 1 that surrounds a molecule at the surface.

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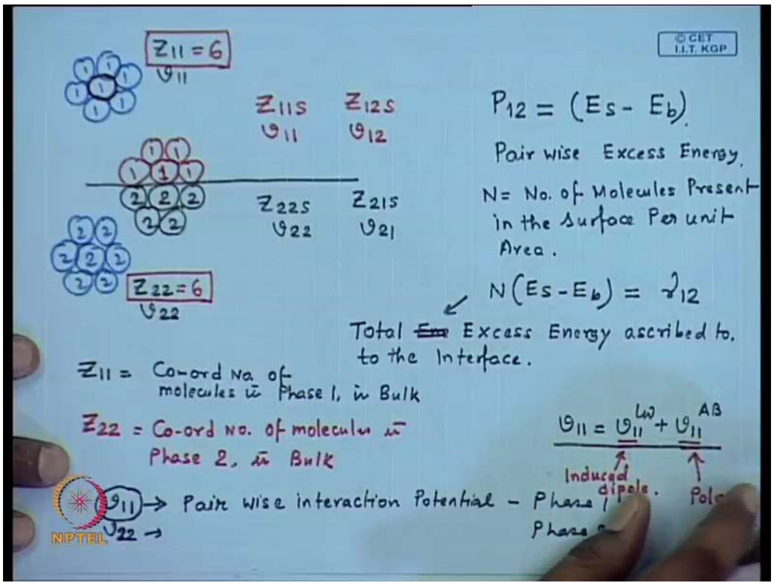

$Z_{11} = 6$

ϑ_{11}

Z_{11s} ϑ_{11} Z_{12s} ϑ_{12}

Z_{22s} ϑ_{22} Z_{21s} ϑ_{21}

$Z_{22} = 6$

ϑ_{22}

$P_{12} = (E_s - E_b)$.

Pair wise Excess Energy.

N= No. of Molecules Present in the surface Per unit Area.

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

Total ~~Em~~ Excess Energy ascribed to. to the Interface.

Z_{11} = Co-ord No. of molecules in Phase 1, in Bulk

Z_{22} = Co-ord no. of molecules in Phase 2, in Bulk

ϑ_{11} → Pair wise interaction Potential – Phase 1

ϑ_{22} → Phase

$\vartheta_{11} = \vartheta_{11}^{LW} + \vartheta_{11}^{AB}$

Induced dipole.

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So, this is essentially a molecule of 1, which is sitting at the surface. This here you see the 3 numbers, 3 numbers of molecules of 2 is interacting directly with this particular molecule of 1 sitting at the surface. So, in this particular case Z 1 2 s will be equal to 3 similarly, Z 2 1 s is also equal to 3; it may not be absolutely necessary that these 2 entities or numbers has to be same. Just for the sake of reference, so that things become easier for you. The way this particular figure is drawn, Z 1 1 turns out to be equal to six, the also the way the figure is drawn, Z 2 2 turns out also equal to six. So, I guess you have an idea clear idea about what Z 1 1, Z 2 2, Z 2 1, Z 2 1 s, etcetera means, but remember this whatever we have wrote in the form of 6 is just for an example or this turns out to be 3 is also, for an example.

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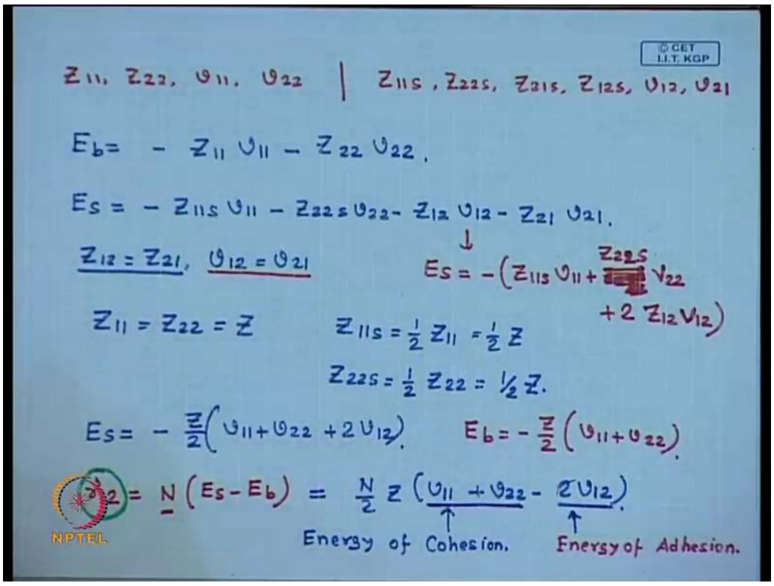

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$Z_{11}, Z_{22}, \upsilon_{11}, \upsilon_{22} \quad | \quad Z_{11s}, Z_{22s}, Z_{21s}, Z_{12s}, \upsilon_{12}, \upsilon_{21}$

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

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

$\underline{Z_{12} = Z_{21}}, \ \underline{\upsilon_{12} = \upsilon_{21}}$

$\downarrow$

$E_s = -(Z_{11s}\upsilon_{11} + Z_{22s}\upsilon_{22} + 2Z_{12}\upsilon_{12})$

$Z_{11} = Z_{22} = Z$

$Z_{11s} = \frac{1}{2}Z_{11} = \frac{1}{2}Z$

$Z_{22s} = \frac{1}{2}Z_{22} = \frac{1}{2}Z.$

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

$\gamma_{12} = \underline{N}(E_s - E_b) = \frac{N}{2}Z(\underline{\upsilon_{11} + \upsilon_{22}} - \underline{2\upsilon_{12}}).$

$\uparrow$ Energy of Cohesion. $\quad \uparrow$ Energy of Adhesion.

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So, if we have all these parameters, we understand all the parameters, then we can clearly write that E b turns out to be minus Z 1 1 V 1 1 minus Z 2 2 V 2 2, and E s turns out to be minus Z 1 1 s V 1 1 minus Z 2 2 s V 2 2 minus Z 1 2 V 1 2 minus Z 2 1 V 2 1. You might be wondering why I am writing this minus sign. Essentially, we are considering the V 1 1 to be negative, essentially, which means a negative interaction, essentially means an attractive interaction. We are assuming an attractive interaction, because of the simple fact that we have told that induced dipole induced dipole interaction or the dispersion force based interaction or Lifshitz-Van der Waals interactions is always attractive. It is more of a convention, you can write a positive sign and eventually if you solve the thing properly, the appropriate sign will come out, so that is nothing to really worry too much about it.

Now, if we look into this expression and start doing a little bit of simplification, if we assume or if we sort of consider that Z 1 2 is equal to Z 2 1 and which can be true or may not be true, but this is all most true at all cases that V 1 2 is equal to V 2 1. In that case the expression of E s get's simplified to minus Z 1 1 s V 1 1 say Z 2 2 s V 2 2 plus 2 Z 1 2 V 1 2. So, this is a Z 2 2 s. Now, let us do a little bit of simplification. We are doing these simplifications to understand or correlate surface and interfacial energies with the individual interaction parameters. Let us do a further simplification which can be correct in many cases. But, let us consider it, let us assume that Z 1 1 is equal to Z 2 2 equal to some sort of Z, and also let us say that Z 1 1 s is equal to half of Z 1 1, equal to half Z.

Of course, this can be possible, this may not be possible also, but for example, in the previous slide the way we drew the figure, it was matching.

So, let us also say that Z 2 2 s is equal to half of Z 2 2, which also turns out in that case to be half of Z. Therefore, in that case E s turns out to be minus Z by 2, V 1 1 V 2 2, plus 2 V 1 2, and E b turns out to be minus Z by 2 V 1 1 plus V 2 2. Therefore, based on these expressions, let us say what gamma 1 2 turns out to be; gamma 1 2, which is we have got it to be N multiplied by E s minus E b. I have a thing to point out. Please do not confuse this N with Avogadro's number in any way, because this is the number of molecules present at the surface per unit area. So, if plug in the expression for this turns out to be N by 2 Z V 1 1 plus V 2 2 minus 2 V 1 2. So, if you look at the expression, the first two terms; this represents the interaction the molecular level interaction of molecules within their respective phases and the second one sort of represents the interaction of molecules across phases.

So, it is this term, which actually contains the signature of the interactions between molecules of 1 and 2. While the summation of these two terms does not contain a signature of interaction between molecules across different phases, but it contains the interaction of the molecules, which are present in the bulk or it is essentially the self interaction rather than the dissimilar interaction. So, this part of the term is essentially refers is referring to the energy of cohesion rather and in contrast this part of the term refers to what is known as energy of adhesion.

So, you already see that we have been successful in representing gamma 1 2, which is the interfacial tension, in terms of molecular level interactions and what are these molecular level interactions? The molecular level interactions are the interactions between the molecules of 1, which are present in the bulk. The interaction of the molecules of 2, which are present in the bulk, which as collectively represents the energy of cohesion; the term corresponding to the energy of cohesion, as well as the interaction of molecules between the 2 phases. You must understand that is V 1 2 type of interaction occurs only at the interface molecules present say at the bulk deep into the bulk cannot so between this molecule and this molecule.

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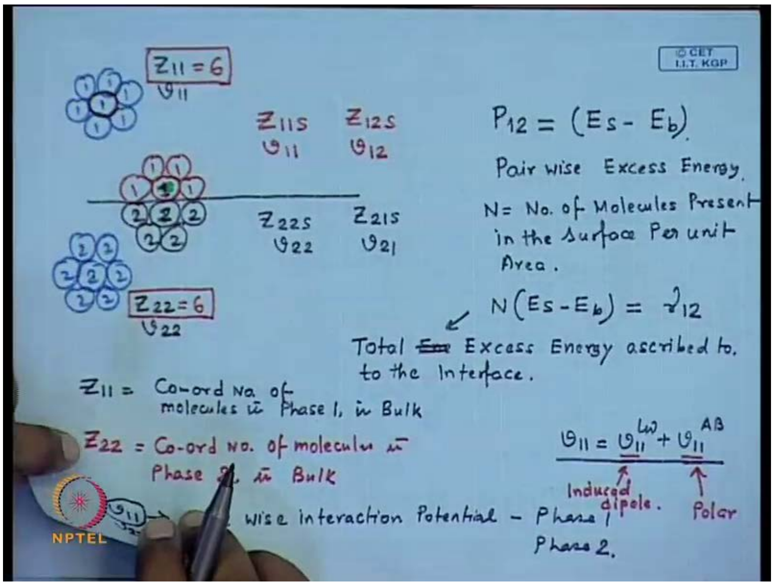

$\boxed{Z_{11} = 6}$ ϑ_{11}

Z_{11S} ϑ_{11} Z_{12S} ϑ_{12}

Z_{22S} ϑ_{22} Z_{21S} ϑ_{21}

$\boxed{Z_{22} = 6}$ ϑ_{22}

$P_{12} = (E_s - E_b)$.

Pair wise Excess Energy.

N = No. of Molecules Present in the Surface Per unit Area.

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

Total ~~En~~ Excess Energy ascribed to. to the Interface.

Z_{11} = Co-ord No. of molecules in Phase 1, in Bulk

Z_{22} = Co-ord No. of molecules in Phase 2. in Bulk

ϑ_{11} → wise interaction Potential – Phase 1 Phase 2.

$$\vartheta_{11} = \underset{\substack{\uparrow \\ \text{Induced dipole.}}}{\underline{\vartheta_{11}^{LW}}} + \underset{\substack{\uparrow \\ \text{Polar}}}{\underline{\vartheta_{11}^{AB}}}$$

Let say you cannot have a V 1 2. This molecule only has V 1 1, this molecule only has V 2 2. It is only these molecules, which are responsible for the interaction of the type V 2 1 or V 1 2, which is present at the surface and this is where the 2 surfaces are adhering. So, they correspond to the energy of adhesion, rather than the energy of cohesion, which is represented by the interaction V 1 1 and V 2 2.

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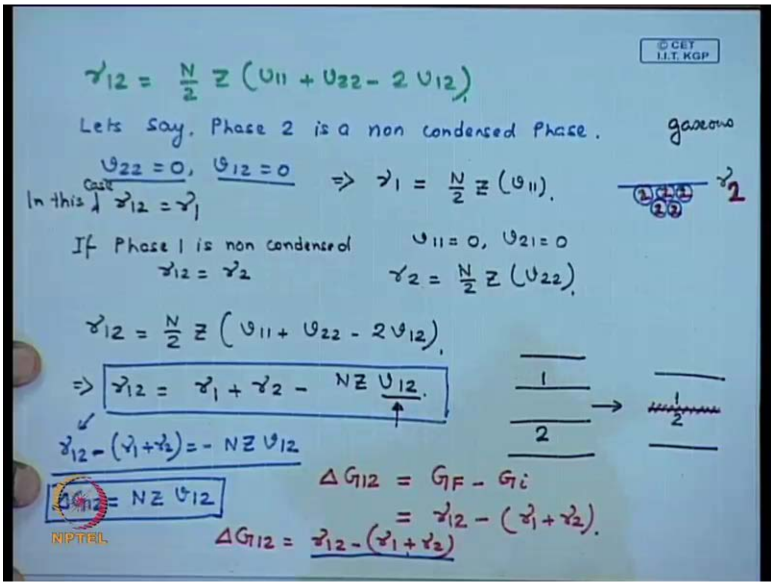

$$\gamma_{12} = \frac{N}{2} Z (\upsilon_{11} + \upsilon_{22} - 2\upsilon_{12})$$

Lets say. Phase 2 is a non condensed Phase.

$\underline{\vartheta_{22} = 0}$, $\underline{\vartheta_{12} = 0}$ $\Rightarrow \gamma_1 = \frac{N}{2} Z (\vartheta_{11})$.

In this case $\gamma_{12} = \gamma_1$

If Phase 1 is non condensed $\vartheta_{11} = 0$, $\vartheta_{21} = 0$

$\gamma_{12} = \gamma_2$ $\gamma_2 = \frac{N}{2} Z (\vartheta_{22})$.

$$\gamma_{12} = \frac{N}{2} Z (\vartheta_{11} + \vartheta_{22} - 2\vartheta_{12}).$$

$$\Rightarrow \boxed{\gamma_{12} = \gamma_1 + \gamma_2 - NZ\underline{\vartheta_{12}}.}$$

$$\underline{\gamma_{12} - (\gamma_1 + \gamma_2) = -NZ\vartheta_{12}}$$

$$\boxed{\Delta G_{12} = NZ\vartheta_{12}}$$

$$\Delta G_{12} = G_F - G_i = \gamma_{12} - (\gamma_1 + \gamma_2).$$

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

Now, so what we have so far is gamma 1 2 is N by 2 Z V 1 1 plus V 2 2 minus 2 V 1 2. Now, let say that is if 1 of the phases is a non-condensed phase, let say phase 2 is a non-condensed phase, which can be a gas or a vacuum. Then what eventually turns out is that V 2 2 is equal to 0, V 1 2 equal to 0. Now, is it an assumption or approximation? No it is not that. We understand from our school level understanding of physics that essentially the non-condensed phase like a gas for example, the molecules are far away apart and they are sort of randomly moving this direction. That is the reason gases do not have any specific shape in compare to in comparison to the gases the interaction is much higher in case of a liquid and if you go to a solid there is much more interaction, much tighter binding.

So, it essentially what it means in what we are discussing today that since the molecules are far apart there is virtually no cohesive interaction between these molecules, within the bulk of that non-condensed phase. Therefore, it is absolutely logical to regard V 2 2 be equal to 0. What about V 1 2? V 1 2 essentially refers to a case here, where you have a surface of one, but this is a non-condensed phase or a gaseous phase, let us say. So, there are hardly any molecules of 2 present with which a surface molecule of 1 can interact, though eventually V 1 2 is also equal to 0.

Therefore, these two are perfectly valid approximations, so what eventually comes out and in this particular case you do not have gamma 1 2, but all you have essentially the surface of one expose to a gaseous phase or a vacuum, so this is gamma 1. So, in this particular case gamma 1 2 is nothing, but gamma 1. Let me write it is in this case so from that we get an expression of gamma 1 which turns out to be N by 2 Z into V 1 1. Similarly, if we regard phase 2 to be a non-condensed and then phase 1 to b a non-condensed phase, what will happen? The obvious thing to happen is now we are considering of a scenario, where you have a surface of 2 interacting with a phase, which is gaseous, which is one.

So, within the phase the energy of interaction is almost equal to 0. Therefore, V 1 1 is conveniently equal to 0, also V 2 1 is 0, because there are hardly any molecules of 1 available at the interface to interact with a surface molecule of 2 and in this case gamma 1 2, essentially refers to gamma 2, so what you get is gamma 2 is N by 2 Z into V 2 2. So, with that what comes out is that if you now do a substitution in this particular equation, which we had already written that gamma 1 2 is N by 2 Z into V 1 1 plus V 2 2 minus 2 V 1 2, you will find that these two terms are now referring to essentially gamma 1 plus gamma 2.

So, based on whatever we have derived here, we can write or let me write the equation once more, so we had, now you can see that N by 2 Z into V 1 1 refers to gamma 1, N by 2 Z V 2 2 refers to gamma 2, therefore, we can conveniently write that gamma 1 2 is equal to gamma 1 plus gamma 2 minus N Z V 1 2. So, we still have to understand the nature of V 1 2, which we will take up in a minute. But, let us say that if we want to consider the process of attachment of the 2 surfaces, in terms of the change, in the free energy. So, here you had a surface of one, here you had a surface of 2. These 2 surfaces are now brought into contact, so thus two individual surfaces get's replaced with an 1 2 interface.

Now, if you look at the change in the free energy or delta G 1 2, which is the change in the free energy or the change in the excess energy because of the 2 surfaces have been brought in contact, which based on simple thermodynamics, you can write as G final minus G initial. So, this final into excess energy is nothing but, the interfacial tension and initial you have one surface here and one surface here, so it is gamma 1 plus gamma 2. So, in other words what you can write the delta G 1 2 is gamma 1 2 minus gamma 1 plus gamma 2. Now, you compare or look at this expression again. So, what you have already got, this you can nicely transpose to write gamma 1 2 minus gamma 1 plus gamma 2 is equal to minus N Z V 1 2. Now, you see that the left hand side here and the right hand side here are identical to each other. So, what you can write down is that your delta G 1 2, in such a case is essentially N Z V 1 2. So, the change in the free energy you can now see it can be correlated to the interaction of the pair wise interaction at the molecular level between the surface molecules.

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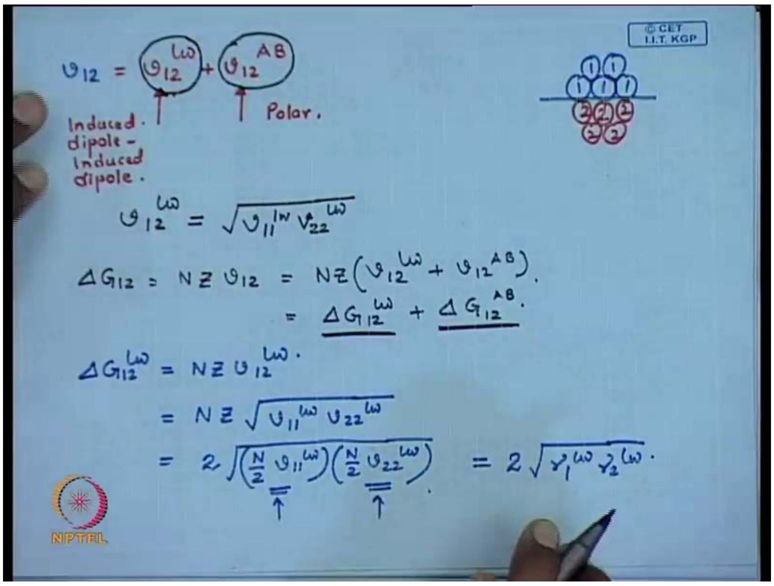


$$\vartheta_{12} = \boxed{\vartheta_{12}^{lw}} + \boxed{\vartheta_{12}^{AB}}$$

Induced dipole - Induced dipole.

Polar.

$$\vartheta_{12}^{lw} = \sqrt{\vartheta_{11}^{lw} \vartheta_{22}^{lw}}$$

$$\Delta G_{12} = N z \vartheta_{12} = N z \left(\vartheta_{12}^{lw} + \vartheta_{12}^{AB}\right).$$

$$= \underline{\Delta G_{12}^{lw}} + \underline{\Delta G_{12}^{AB}}.$$

$$\Delta G_{12}^{lw} = N z \vartheta_{12}^{lw}.$$

$$= N z \sqrt{\vartheta_{11}^{lw} \vartheta_{22}^{lw}}$$

$$= 2\sqrt{\left(\frac{N}{2}\vartheta_{11}^{lw}\right)\left(\frac{N}{2}\vartheta_{22}^{lw}\right)} = 2\sqrt{\gamma_1^{lw}\gamma_2^{lw}}.$$

Now, we need to consider the different interaction potentials. So, we have said that so I guess, we now understand what V 1 2 is? So, you have molecules of 1 present in the surface, you have molecules of 2 present in the surface, and V 1 2 V refer to the interaction between 2 molecules between a molecule of 1 with a molecule of 2. So, this one is an interaction of V 1 2, this is another interaction of V 1 2. The interaction energy is V 1 2, here the interaction energy is also V 1 2. At this point of time, we need to worry about what can be the lightly mechanisms, physical mechanisms of physical origins of these types of interactions. As we have told, we can have the most fundamental interaction is the induced dipole induced dipole type of interaction.

So, if you now consider these 2 set of molecules, you can probably get back to the simple picture, we had drawn in terms of the electronic cloud, the localization of the electronic cloud, which resulted in the induced dipole induced dipole type of interaction. You can think of it, so it is exactly same, now you have this molecule 1, there is a localization of the electronic cloud that induces a delta plus on 2, so there is a positive attractive interaction between these two. Exactly, same thing happens between all the adjacent molecules. So, this is the Lifshitz-Van der Waals, so the l w component of the interaction, but if the molecules are permanent dipole, there can be polar interaction which can lead to the so called polar interaction of the acid base type of interaction as we will be terming.

So, if we consider or restrict our discussion to these two major interactions, which are the most significant interactions, of course, I told that in terms of polymeric system there can be other types of interaction like some bit of entropic interaction or steric interaction or interaction resulting from the confirmation etcetera, but, which are much more specific and which are typically known and it is not necessary to include as a general discussion. So, we can simply understand that this V 1 2 is made up of at least two major terms or the two major contributing terms, which sort of gets added are the Van der Waals interaction or the induced dipole induced dipole type of interaction and the acid base or the polar interactions.

So, let us split it up in into V 1 2 equal to V l w plus V 1 2 AB, where this refers to the so called Van der Waals interaction, which is loosely called, but it is typically the dispersion forces, dispersion interaction, and this is the polar interaction, and this is the dipole type of interaction. Now, we need to sort of understand the individual constituents in greater detail. So, we understand what exactly is V 1 2 it is the Van der Waals interaction or the induced dipole induced dipole type of interaction between 2 molecules which are present at the surface. For Van der Waals forces, you can you can sort of apply a mixing rule that this is all most given; V 1 2 turns out to be. (Refer Slide Time: 32:53)

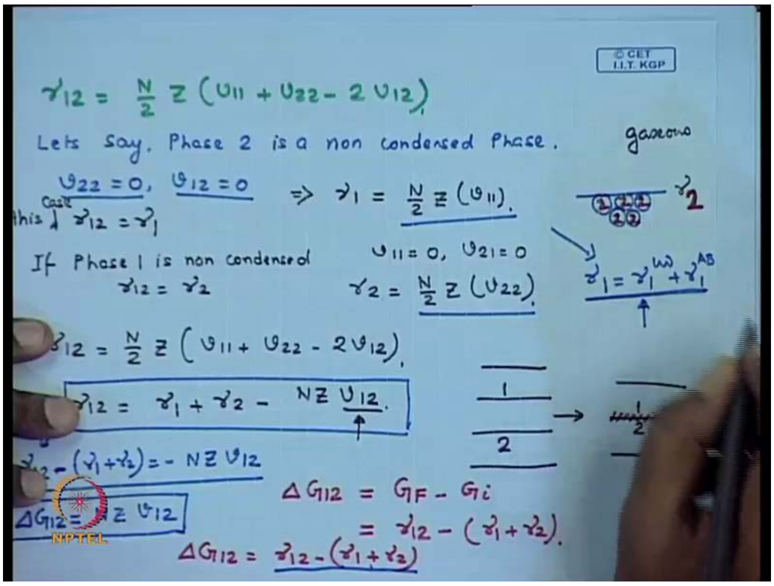
(No volume between: 32:54-33:55)

So, since you can split up V 1 2 in terms of V 1 2 l w and V 1 2 AB, you now have a look at the expression or relook up the expression of delta G 1 2 which turns out to be N Z V 1 2, which we can write as N Z V 1 2 l w plus V 1 2 AB, which essentially means that your delta G 1 2 also has two components. the delta G 1 2 based on the Van der Waals interaction or the induced dipole induced dipole type of interaction, as well as the delta G 1 2 based on the acid base or the polar interaction.

So, the expression for delta G 1 2 l w turns out to be N Z V 1 2 l w. Now, you see that you can substitute V 1 to l w in terms of this particular expression we have written, so this turns out to be N Z into under root V 1 1 l w plus V 2 2 l w. If you do a little bit of simplification, you can write this. Now, does this to individual term remind you of something? Well we just talked about these two terms in our previous slide (Refer Slide Time: 34:37)

Look at this, so they are essentially gamma 1 and gamma 2, but you are not talking of V 1 1 in totality, as we had done there, but we are talking of V 1 1 l w. Similarly, we are not talking of V 2 2 here but, we are talking of V 2 2 l w. So, going by this definition what this two refer to is essentially the Van der Waals component of surface tension of material 1 and material 2. So, this turns out to be under root 2 gamma 1 l w, gamma 2 l w. So, in other words what it means is just the way, the interaction, the interfacial interaction has different components in terms of the dispersion forces as well as the polar type of interaction.

(Refer Slide Time: 35:35)



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$\gamma_{12} = \frac{N}{2} z (v_{11} + v_{22} - 2 v_{12})$

Lets say. Phase 2 is a non condensed Phase. gaseous

$v_{22} = 0$, $v_{12} = 0$ $\Rightarrow$ $\gamma_1 = \frac{N}{2} z (v_{11})$.

this case $\gamma_{12} = \gamma_1$

If Phase 1 is non condensed $v_{11} = 0$, $v_{21} = 0$

$\gamma_{12} = \gamma_2$ $\gamma_2 = \frac{N}{2} z (v_{22})$.

$\gamma_1 = \gamma_1^{LW} + \gamma_1^{AB}$

$\gamma_{12} = \frac{N}{2} z (v_{11} + v_{22} - 2 v_{12})$.

$\boxed{\gamma_{12} = \gamma_1 + \gamma_2 - N z v_{12}.}$

$\gamma_{12} - (\gamma_1 + \gamma_2) = - N z v_{12}$

$\Delta G_{12} = z v_{12}$

$\Delta G_{12} = G_F - G_i$

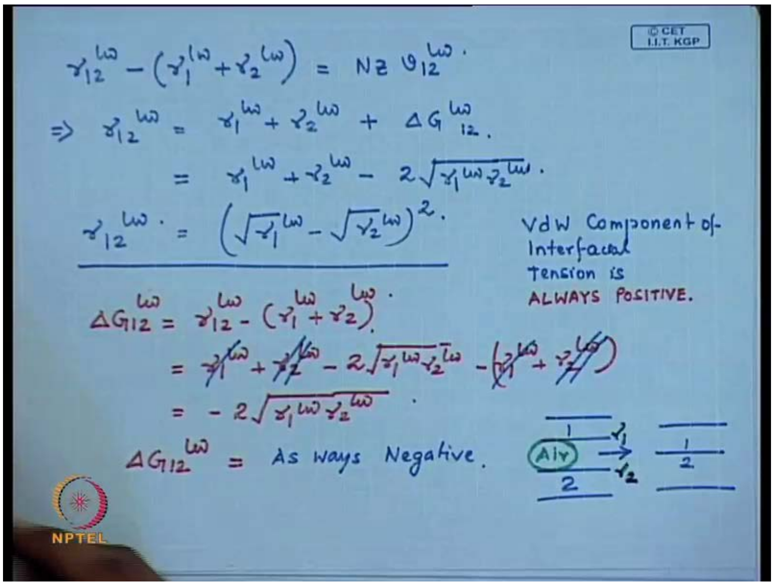
$= \gamma_{12} - (\gamma_1 + \gamma_2)$.

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

The surface tensions also, one can argue, one can clearly understand is made up of different components that is gamma 1 l w plus gamma 1 AB. So, that is the important message that comes out and essentially right at this movement, we have got an expression of delta G 1 2 l w in terms of gamma 1 l w and gamma 2 l w, which are essentially the Van der Waals component or the dispersion force base component of surface tension.

So, once we are there, so we can get in expression. I am sorry; this will come with a minus sign, because of the convention we are following. So, what we can write is that in one of the previous slides, just refer to this particular expression, where we have written gamma 1 2 in terms of this particular expression.

(Refer Slide Time: 36:34)



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$$\gamma_{12}^{LW} - (\gamma_1^{LW} + \gamma_2^{LW}) = Nz\,\vartheta_{12}^{LW}.$$

$$\Rightarrow \gamma_{12}^{LW} = \gamma_1^{LW} + \gamma_2^{LW} + \Delta G_{12}^{LW}.$$

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

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

VdW Component of Interfacial Tension is ALWAYS POSITIVE.

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

$$= \cancel{\gamma_1^{LW}} + \cancel{\gamma_2^{LW}} - 2\sqrt{\gamma_1^{LW}\gamma_2^{LW}} - (\cancel{\gamma_1^{LW}} + \cancel{\gamma_2^{LW}})$$

$$= -2\sqrt{\gamma_1^{LW}\gamma_2^{LW}}.$$

ΔG_{12}^{LW} = As ways Negative.

If we now consider only the Van der Waals component of the interaction, we can conveniently understand or write. if you just correlate look back to your notes and refer, this is obvious now and now what we have got is this or in other words we can write that gamma 1 2 l w is gamma 1 l w plus gamma 2 l w plus delta G l w 1 2. This turns out to be gamma 1 l w plus gamma 2 l w minus 2 under root gamma 1 l w into gamma 2 l w. So, this is now very simple, this is under root gamma 1 l w minus under root gamma 2 l w whole square. So, what does it mean? Gamma 1 2 l w is this is the expression, so gamma 1 2 l w and we know that gamma 1 and gamma 2 are real numbers.

So, gamma 1 2 l w is always positive right, so what it means that the Van der Waals component of interfacial tension is always positive. Now, that is a significant thing to emerge out, so which primarily means, now you look at the expression for delta G 1 2, which is gamma 1 2 minus gamma 1 plus gamma 2. If you look at the Van der Waals component of this delta G 1 2, you just expand this gamma 1 2 in terms of what we have derived here. So, this turns out to be gamma 1 l w plus gamma 2 l w minus 2 under root gamma 1 l w into gamma 2 l w minus gamma 1 l w plus gamma 2 l w. As these terms cancel out, you are left with minus 2 under root gamma 1 l w into gamma 2 l w.

So, what it means that the delta G 1 2, the Van der Waals component of delta G 1 2, is always negative. So, what does it mean, it means now what exactly is delta G 1 2 l w, Delta G 1 2 refers to 2 surfaces or the change in the free energy, when two surfaces are coming in contact. Now, where to what these two surfaces were expose to before. These two surfaces, we did not talk about it, but it is obvious that these two surfaces were exposed to either air or vacuum. So, these two were exposed to some non-condensed phase. Why, because we have assume the surface energies to be gamma 1 and gamma 2 conveniently. Had these two surfaces been exposed to a non-condensed phase like a liquid or a solid or something like that, you could not have considered the surface tensions to be gamma 1 2.

Had you had a non-condensed medium 3 of course, you had to consider interfacial tension gamma 1 3 and gamma 2 3 and things would have been complicated. So, essentially delta G gamma 1 2 refers to 2 surfaces, which were both expose to an non-condensed phase and are now coming in contact with each other and a negative expression of delta G 1 2. We know that all natural process tends towards minimization of energy. A negative sign for delta G 1 2 l w, shows that Van der Waals interaction in air or vacuum, will always lead to attachment of the two surfaces, which is perfectly in phase with whatever we have understood, based on the simple induced dipole induced dipole type of interaction, where we argued based on the physical mechanism that these forces are always attractive.

So, here you can see that particular occurrence itself that two surfaces both of which are expose to air or a vacuum, in other words, a non-condensed phase, based on Van der Waals interaction, their attachment is always favour or preferred. Now, we of course, we cannot have a system. There can be systems, where you have only in this type of induced dipole induced dipole type of interaction but, there can be always systems there are other types systems where there are other interactions as well.

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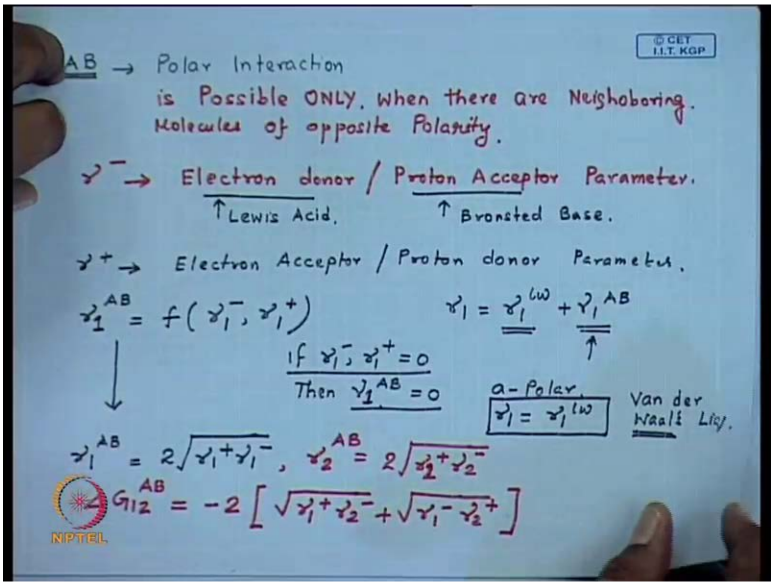

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AB → Polar Interaction is Possible ONLY. When there are Neighboring. Molecules of opposite Polarity.

$\gamma^- \rightarrow$ Electron donor / Proton Acceptor Parameter.

↑ Lewis Acid. ↑ Bronsted Base.

$\gamma^+ \rightarrow$ Electron Acceptor / Proton donor Parameter.

$$\gamma_1^{AB} = f(\gamma_1^-, \gamma_1^+)$$

$$\gamma_1 = \underline{\underline{\gamma_1^{LW}}} + \underset{\uparrow}{\underline{\underline{\gamma_1^{AB}}}}$$

$$\underline{\text{if } \gamma_1^-, \gamma_1^+ = 0}$$

$$\text{Then } \underline{\gamma_1^{AB} = 0}$$

a-Polar.

$$\boxed{\gamma_1 = \gamma_1^{LW}}$$

Van der $\underline{\underline{\text{Waals}}}$ Liq.

$$\gamma_1^{AB} = 2\sqrt{\gamma_1^+\gamma_1^-}, \quad \gamma_2^{AB} = 2\sqrt{\gamma_2^+\gamma_2^-}$$

$$G_{12}^{AB} = -2\left[\sqrt{\gamma_1^+\gamma_2^-} + \sqrt{\gamma_1^-\gamma_2^+}\right]$$

And one such interaction as we have already argued, are the AB type interaction and the polar interaction, which we will consider for the time being. Now, in order to understand the nature of the polar interaction, we need to understand that polar interaction is possible only when there are neighbouring molecules (No volume between: 42:16-42:29) of opposite polarity. We also need to define couple of empirical parameters to quantify the AB type interaction. One of them is gamma minus, which is essentially the parameter that corresponds to the electron donor, proton acceptor parameter.

If you refer to your or try to recall your basic chemistry, this is essentially in the electron donor is essentially one, which is known as the Lewis acid and a proton acceptor is a Bronsted base; it comes from the Bronsted-Lowry acid base theory. Similarly, we need to define a gamma plus, which is the conjugate property, which represents the electron acceptor, proton donor parameter. So, this is essentially a Lewis base Bronsted acid type of thing.

Now, in case of course, let us say for a material, so essentially gamma 1 AB or the polar interaction polar component of surface tension of material one, will be a function of gamma 1 minus and gamma 1 plus. What further we understand is that gamma 1 is a summation of gamma 1 l w plus gamma 1 AB. We have already understood what is gamma 1 l w, gamma 1 AB will be present if at least one of these, we will see it soon or in let me put it in the other way. If gamma 1 minus and gamma 1 plus are both zeroes then gamma 1 AB will be equal to 0. So, the material 1 is going to be a-polar material. If it is a liquid, it is a-polar material, and what it also means that it entire surface energy, a surface tension is composed of dispersion interaction or induced dipole induced dipole type of Van der Waals interaction.

In case, the one is a liquid having this type of a property where it is entire surface tension is contributed due to Van der Waals interaction. This is what is called a Van der Waals liquid. Probably, you have come across the name in your earlier thermodynamics courses. The functionality that goes is like this gamma 1 AB is twice under root of gamma 1 plus gamma 1 minus. Similarly, since we are in talking about the interaction of 1 and 2, gamma 2 AB is twice under root of gamma 2 plus gamma 2 minus. We also need to understand at this point of time that delta G 1 2 AB; what will be its physical nature?

Now, this particular term is going to be always negative or it is going to be always attractive, because of the fact that whenever a polar interaction between two materials, which are in contact with each other, is there, then there will be a bond formation. So, you have two sets of materials, which have opposite polarity, which are in contact with each other, there will be a physical bond formation. So, delta G 1 2 AB will always be negative, say because we are regarding that negative to be attraction. Then the expression goes something like this, gamma 1 plus under root of gamma 1 plus into gamma 2 minus gamma 1 minus into gamma 2 plus.

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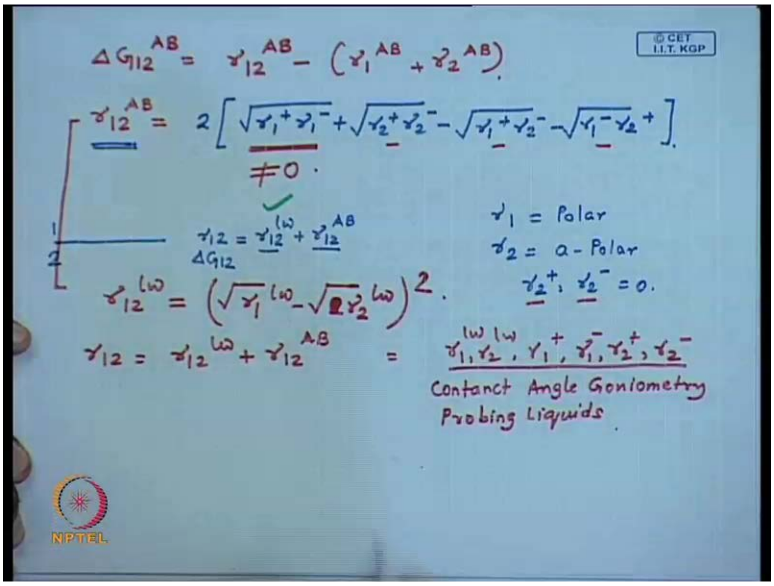


$\Delta G_{12}^{AB} = \gamma_{12}^{AB} - (\gamma_1^{AB} + \gamma_2^{AB})$.

$\underline{\gamma_{12}^{AB}} = 2\left[\underline{\sqrt{\gamma_1^+\gamma_1^-}} + \sqrt{\gamma_2^+\underline{\gamma_2^-}} - \sqrt{\underline{\gamma_1^+}\gamma_2^-} - \sqrt{\underline{\gamma_1^-}\gamma_2^+}\right]$.

$\neq 0$.

✓

$\gamma_{12} = \underline{\gamma_{12}^{LW}} + \underline{\gamma_{12}^{AB}}$

ΔG_{12}

γ_1 = Polar

γ_2 = a - Polar

$\underline{\gamma_2^+}, \underline{\gamma_2^-} = 0$.

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

$\gamma_{12} = \gamma_{12}^{LW} + \gamma_{12}^{AB} = \underline{\gamma_1^{LW}, \gamma_2^{LW}, \gamma_1^+, \gamma_1^-, \gamma_2^+, \gamma_2^-}$

Contanct Angle Goniometry

Probing Liquids.

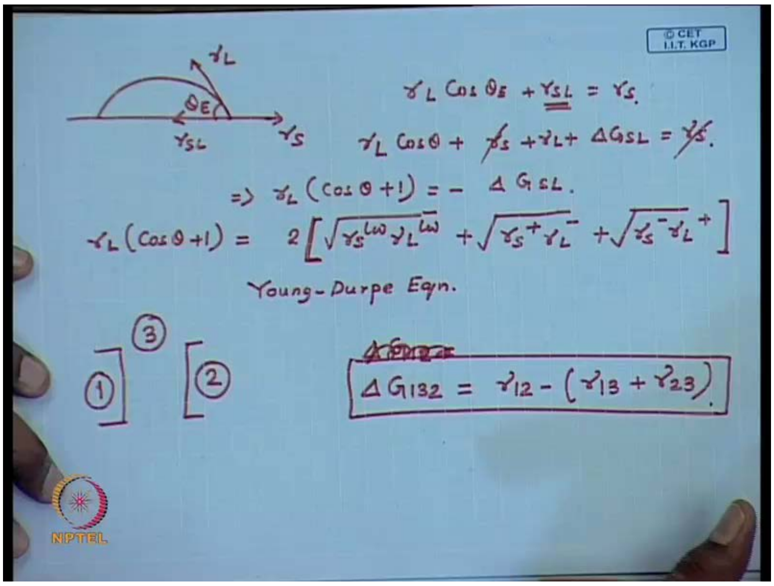
So, if you look at all these three expressions, now we already have that delta G 1 2 AB is gamma 1 2 AB minus gamma 1 AB plus gamma 2 AB. So, we have gamma 1 2 AB turning out to be twice gamma 1 plus gamma 1 minus plus gamma 2 plus, gamma 2 minus, minus gamma 1 plus, gamma 2 minus, minus gamma 1 minus, gamma 2 plus. We also have at this point. So, this is going to be the interfacial tension, the polar component of interfacial tension between 1 and 2. Now, interesting thing to note, so we revisit the problem again, we have two surfaces 1 and 2, which has formed an interface. We now understand that the interfacial tension or the interfacial interaction can be either. You can consider gamma 1 2 or you can consider delta G 1 2 is a function of the dispersion induced interaction as well as the polar induced interaction. This is the expression for the polar interaction.

Now, let us consider or let us try to think how general these interactions are. So, the moment you have two surfaces, we now understand that the dispersion induced interaction or the temporary dipole temporary dipole type of interaction is present in all classes of materials. So, whenever you have two surfaces which are in contact, your this term is always active. Now, we have told that polar interaction is possible only when you have surfaces of opposite polarity, which are adjacent to each other. Now, what is going to be the scenario where you have one surface, which is polar and one surface which is a polar, which is in contact.

So, let us say let us argue that is gamma 1 is polar gamma 2 is a-polar. So, if it is a polar what it means that gamma 2 plus and gamma 2 minus are both equal to 0. Does that mean that the gamma 1 2 AB is also going to be 0? If you now look into it carefully look into the expression carefully, because of the fact that gamma 2 plus and gamma 2 minus as 0, this term, this term and this term become 0. However, though gamma 2 plus is equal to 0 and gamma 1 is polar, you do have a nonzero gamma 1 to AB, because of the simple fact that this term is not equal to 0. So, we will understand with some specific examples.

However, at the moment, we have an expression for gamma 1 2, we also know the expression for gamma 1 2 l w, which turns out to be (( )). (No volume between: 51:00-51:11) Therefore, we can write the complete expression for gamma 1 2, as gamma 1 2, you can plug in the respective expression to get the complete expression for gamma 1 2 l w, in terms of gamma 1 l w, gamma 2 l w, gamma 1 plus. So, this is going to be; it contains six parameters and in one of the subsequent lectures, we will show that with the method of contact angle goniometry, and proper choice of, so the method of goniometry and proper choice of what is known as probing liquids, it becomes possible to find out that each individual parameter for an interacting system, if one of the system is particularly or at least one of the system is a liquid.

(Refer Slide Time: 52:21)



$$\gamma_L \cos\theta_E + \underline{\underline{\gamma_{SL}}} = \gamma_S.$$

$$\gamma_L \cos\theta + \cancel{\gamma_S} + \gamma_L + \Delta G_{SL} = \cancel{\gamma_S}.$$

$$\Rightarrow \gamma_L(\cos\theta + 1) = -\Delta G_{SL}.$$

$$\gamma_L(\cos\theta + 1) = 2\left[\sqrt{\gamma_S^{LW}\gamma_L^{LW}} + \sqrt{\gamma_S^{+}\gamma_L^{-}} + \sqrt{\gamma_S^{-}\gamma_L^{+}}\right]$$

Young-Durpe Eqn.

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

Now, if we come back or revisit our concept of the equilibrium contact angle what we had considered in the previous class is we had gamma L Cos theta E plus gamma s L equal to gamma s. you can now substitute gamma s L, which is essentially gamma 1 2 for a solid liquid system, gamma L Cos theta E plus gamma s plus gamma L plus delta G s L, equal to gamma s. If you cancel this out what you get gamma L Cos theta plus 1 equal to minus delta GSL. You have an expression for delta G 1 2 already, so we can get gamma s L, gamma L Cos theta plus 1 is twice gamma s l w, gamma L l w, plus gamma s plus gamma L minus, plus gamma s minus, gamma L plus. Here, you can see that if one of these, so if you know the individual interactions, you can find out Cos theta from here also. This is what is known as the form is known as the Young's equation. This is what is known as the Young-Durpe equation.

There can be other interesting settings where we can define the attachment or adhesion or whether in a liquid medium. If you have two surfaces now say, let us say 1 and 2, which are in a liquid medium 3, and they are trying to come in contact with each other. So, the thing becomes a little more complicated and it becomes essentially gamma 1 2 is sort of or the final interfacial tension or the delta G. It sort of changes to a system of delta G 1 3 2, which is gamma 1 2, because of the two surfaces comes in contact minus gamma 1 3 plus gamma 2 3. It becomes possible in one of the subsequent lectures, we will show depending on the relative magnitudes of 1 3 and 2 3, as well as the individual components, under what conditions attachment will be favoured or in what conditions the two surfaces 1 and 2 will sort of stay away from each other. Eventually, when there is an attachment in a liquid medium it is corresponds to the scenario of agglomeration. In the case where there is no attachment at the two surfaces, 1 and 2, sort of try to stay from away each other. It is a case of where you have a stable dispersion.

Thank you