Soft Nano Technology
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Lecture – 08
Components of Surface Tension – 1

Welcome back. Now on to the 8 Lecture, we have started to look into a sort of a detail picture about the surface and inter facial tensions. Where essentially continue our discussion on the components of surface tension and various aspects of inter facial energy. What we will do a quick recapitulation we now understand.

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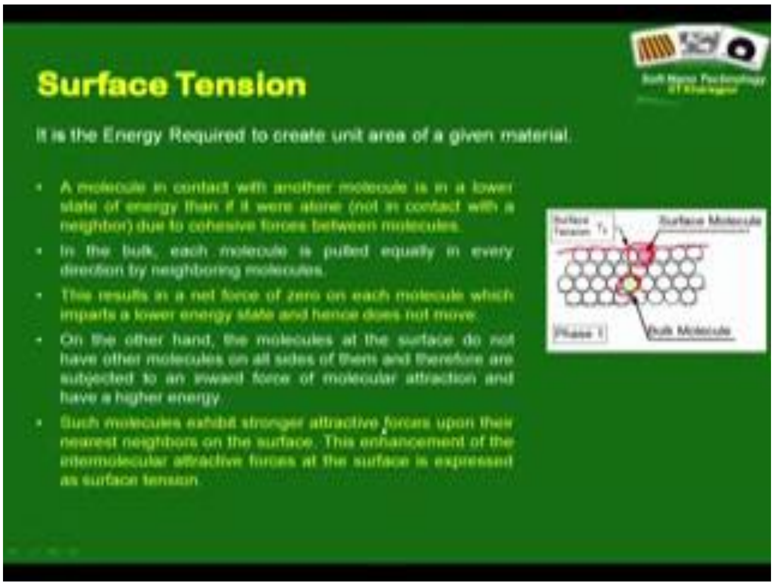

Surface Tension

It is the Energy Required to create unit area of a given material.

- A molecule in contact with another molecule is in a lower state of energy than if it were alone (not in contact with a neighbor) due to cohesive forces between molecules.
- In the bulk, each molecule is pulled equally in every direction by neighboring molecules.
- This results in a net force of zero on each molecule which imparts a lower energy state and hence does not move.
- On the other hand, the molecules at the surface do not have other molecules on all sides of them and therefore are subjected to an inward force of molecular attraction and have a higher energy.
- Such molecules exhibit stronger attractive forces upon their nearest neighbors on the surface. This enhancement of the intermolecular attractive forces at the surface is expressed as surface tension.

What is a surface and what is the fundamental difference between a surface molecule and a molecules. So, this is surface molecule; which has lower coordination number as compared to a bulk molecule.

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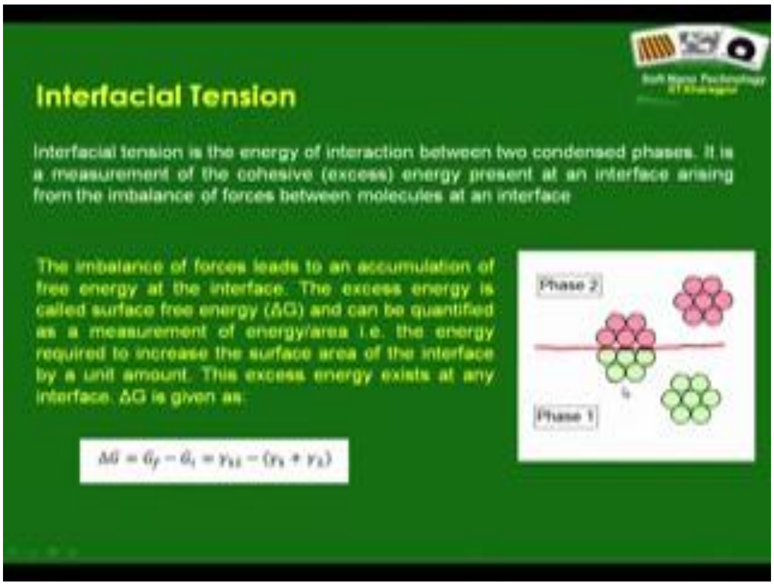

Interfacial Tension

Interfacial tension is the energy of interaction between two condensed phases. It is a measurement of the cohesive (excess) energy present at an interface arising from the imbalance of forces between molecules at an interface

The imbalance of forces leads to an accumulation of free energy at the interface. The excess energy is called surface free energy (ΔG) and can be quantified as a measurement of energy/area i.e. the energy required to increase the surface area of the interface by a unit amount. This excess energy exists at any interface. ΔG is given as:

$$\Delta G = G_f - G_i = \gamma_{12} - (\gamma_1 + \gamma_2)$$

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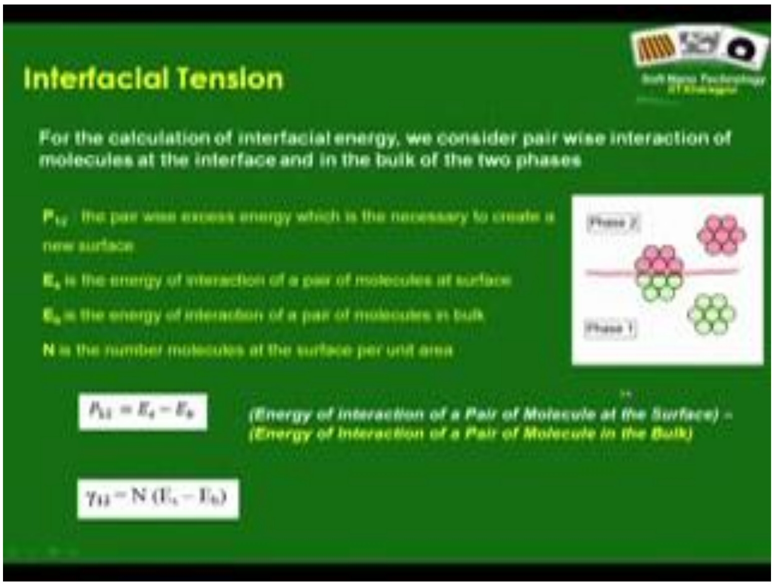

Interfacial Tension

For the calculation of interfacial energy, we consider pair wise interaction of molecules at the interface and in the bulk of the two phases

P_{12} : the pair wise excess energy which is the necessary to create a new surface

E_s is the energy of interaction of a pair of molecules at surface

E_b is the energy of interaction of a pair of molecules in bulk

N is the number molecules at the surface per unit area

$$P_{12} = E_s - E_b$$

(Energy of interaction of a Pair of Molecule at the Surface) – (Energy of Interaction of a Pair of Molecule in the Bulk)

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

We were considering the interaction; pair wise interaction between 2 molecules between 2 phases and for while doing that, we considered the interaction for the excess pair wise interaction pair wise excess interaction energy when the molecules.

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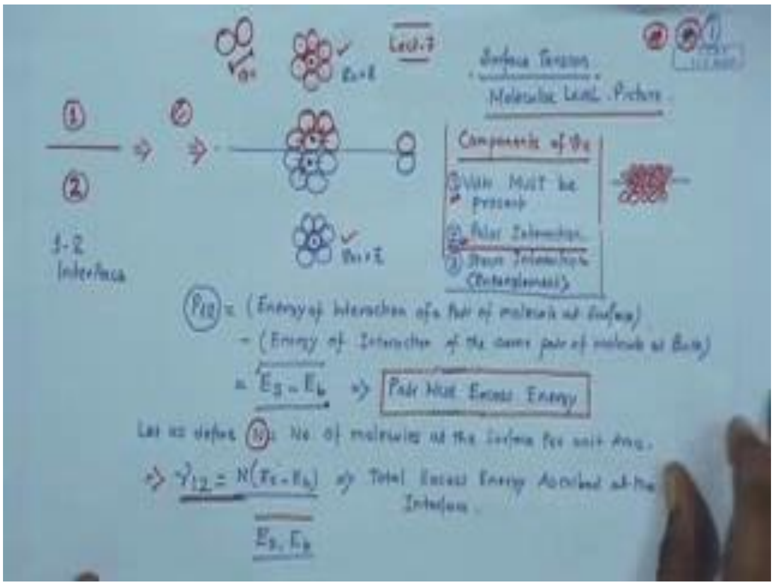

Were at the surface versus at the bulk and then we could correlate it to the surface tension, considering the total number of molecules present at the surface.

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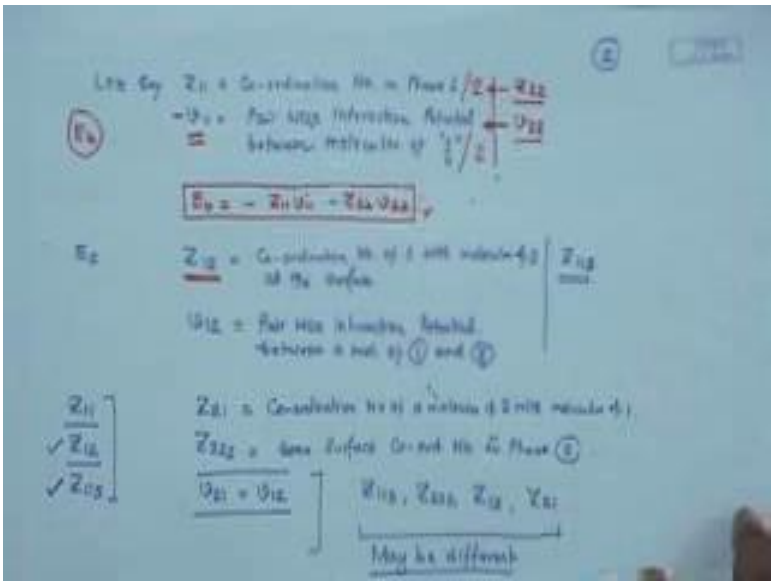

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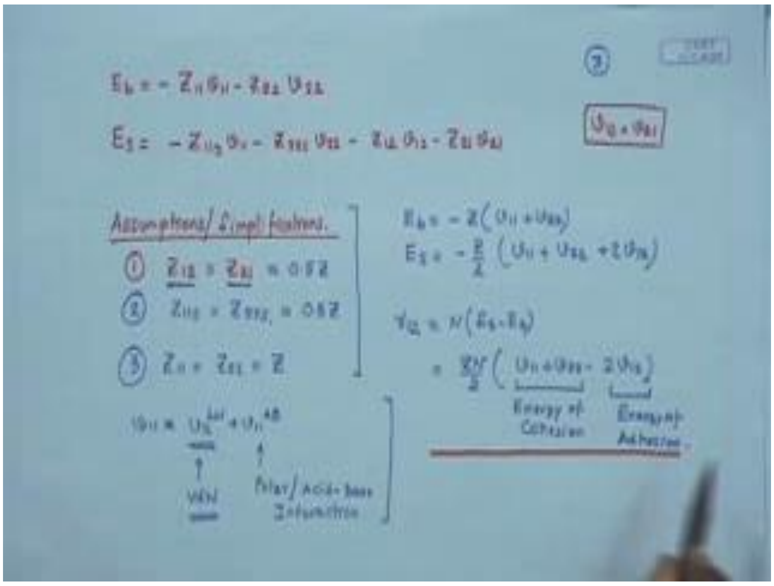

Eventually, we considered the interaction between individual molecules, defined the different coordination numbers and under certain assumptions; we could eventually get an expression like this for gamma12.

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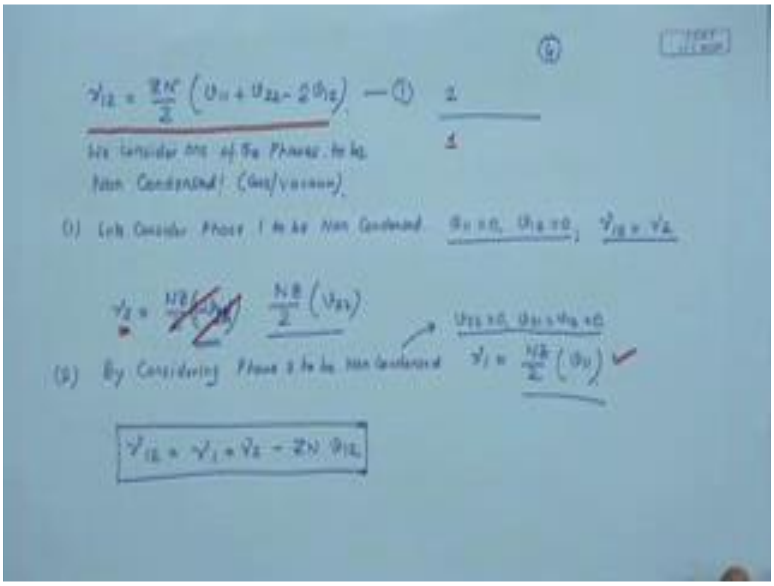

And with further approximation by considering that, one of the phases to be condense a non-condense ways or a gas or a vacuum.

We could get expressions for gamma 2 and similar expressions for this is wrong In fact, similar expressions for gamma 1 and that now gives us this particular expression.

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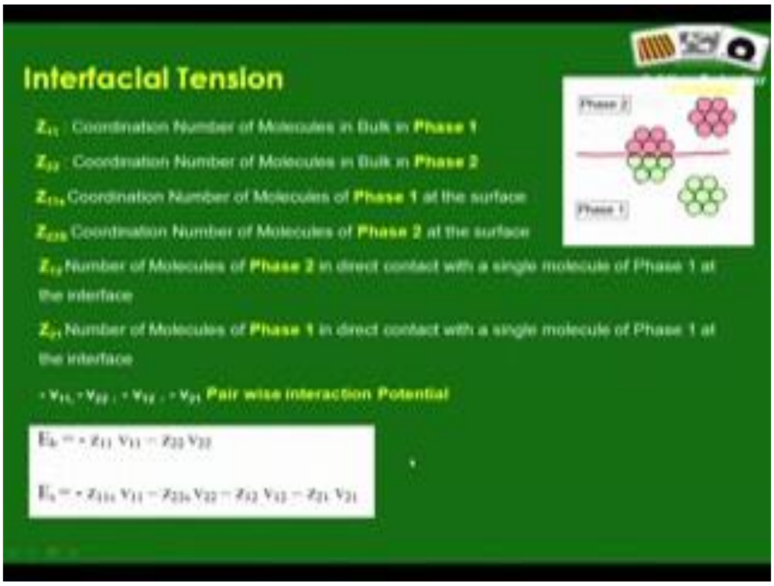

Interfacial Tension

Z_{11} : Coordination Number of Molecules in Bulk in **Phase 1**

Z_{22} : Coordination Number of Molecules in Bulk in **Phase 2**

Z_{11s} Coordination Number of Molecules of **Phase 1** at the surface

Z_{22s} Coordination Number of Molecules of **Phase 2** at the surface

Z_{12} Number of Molecules of **Phase 2** in direct contact with a single molecule of Phase 1 at the interface

Z_{21} Number of Molecules of **Phase 1** in direct contact with a single molecule of Phase 1 at the interface

$-v_{11}, -v_{22}, -v_{12}, -v_{21}$ **Pair wise interaction Potential**

$E_b = -z_{11}v_{11} - z_{22}v_{22}$

$E_s = -z_{11s}v_{11} - z_{22s}v_{22} - z_{12}v_{12} - z_{21}v_{21}$

Now we can also use this, so, we start our discussion which we already did up to this point and let us start our discussion from this particular step.

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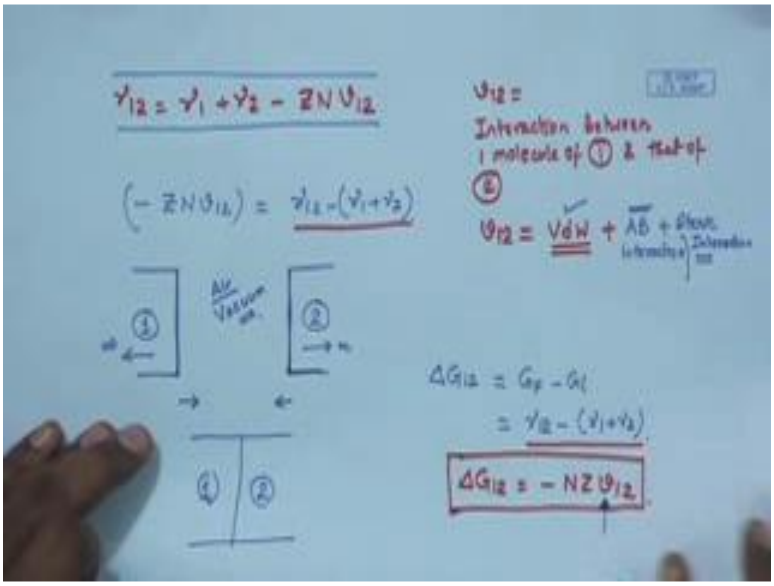

$\gamma_{12} = \gamma_1 + \gamma_2 - ZN\vartheta_{12}$

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

$\vartheta_{12} =$ Interaction between 1 molecule of ① & that of ②

$\vartheta_{12} = VdW + AB + Elect.$

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

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

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

What we have is, that is V1 2 is the interaction between 1 molecule of 1 and that of 2 and as we have already argued that, this V 12 includes the Van der Waals interactions of course, and might include other parameters like, the polar interaction, may be the static interaction, which we will we now understand, but we will not consider this in greater detail.

We will be happy to look into the Van der Waals interaction initially and then the polar interactions. We just reframe this equation in a slightly different format, to essentially what we get out of that is, we can write this as; which is fine. But now let us consider another picture suppose we have a surface 1 object 1. This can be semi infinite straight in this direction, but you consider an object of 1. So, this is a surface let us assume the surface areas as same, and let us also consider that they are initially infinitely separated away and we bring them together in contact.

This is the initial configuration and eventually this is the final configuration. So, now, if you look into, the change in the energy between the final state and initial state what we get is this. So, we look into the free energy at the final and the initial. The internal energy of each of the objects remains same, these are non-reacting system, and there is no change in size.

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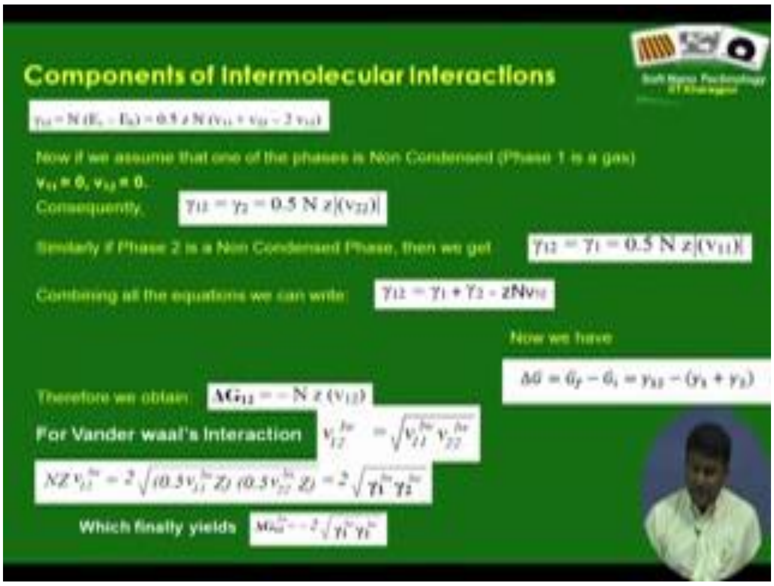

Components of Intermolecular Interactions

$\gamma_{12} = N(E_c - E_b) = 0.5\,z\,N\,(v_{11} + v_{22} - 2v_{12})$

Now if we assume that one of the phases is Non Condensed (Phase 1 is a gas)

$v_{11} = 0,\ v_{12} = 0.$

Consequently, $\gamma_{12} = \gamma_2 = 0.5\,N\,z\,|(v_{22})|$

Similarly if Phase 2 is a Non Condensed Phase, then we get $\gamma_{12} = \gamma_1 = 0.5\,N\,z\,|(v_{11})|$

Combining all the equations we can write: $\gamma_{12} = \gamma_1 + \gamma_2 - zNv_{12}$

Now we have $\Delta G = G_f - G_i = \gamma_{12} - (\gamma_1 + \gamma_2)$

Therefore we obtain $\Delta G_{12} = -N\,z\,(v_{12})$

For Vander waal's Interaction $v_{12}^{lw} = \sqrt{v_{11}^{lw}\,v_{22}^{lw}}$

$NZv_{12}^{lw} = 2\sqrt{(0.5v_{11}^{lw}Z)\,(0.5v_{22}^{lw}Z)} = 2\sqrt{\gamma_1^{lw}\gamma_2^{lw}}$

Which finally yields $\Delta G_{12}^{lw} = -2\sqrt{\gamma_1^{lw}\gamma_2^{lw}}$

All that changes is actually finally, these 2 objects are in contact and initially the total energy at the surface was this. Now if we compare these and this equation what we get is we straight away get an expression for delta G12 which turns out to be minus NZV12. So, this allows us to get an expression for the change in the free energy; when 2 objects come in contact with each other, but initially it must be understood that the 2 objects come in contact either in here or vacuum.

Now, let us consider or take a slightly detail look and look into the different components or different forces that contribute into thisV12. So, let us1st assume that as we have already told that Van der Waals interactions, is only present. So, let us first assume or consider only Van der Waals sources.

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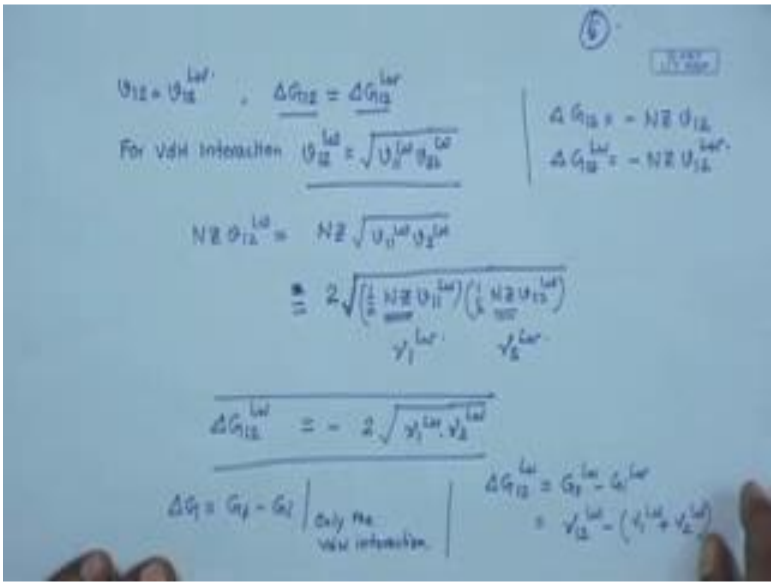

⑥

$v_{12} = v_{12}^{LW}$, $\Delta G_{12} = \Delta G_{12}^{LW}$

For VdW interaction $v_{12}^{LW} = \sqrt{v_{11}^{LW} v_{22}^{LW}}$

$\Delta G_{12} = -NZ v_{12}$

$\Delta G_{12}^{LW} = -NZ v_{12}^{LW}$

$$NZ v_{12}^{LW} = NZ\sqrt{v_{11}^{LW} v_{22}^{LW}}$$

$$= 2\sqrt{\Big(\underset{\gamma_1^{LW}}{\tfrac{1}{2} NZ v_{11}^{LW}}\Big)\Big(\underset{\gamma_2^{LW}}{\tfrac{1}{2} NZ v_{22}^{LW}}\Big)}$$

$$\Delta G_{12}^{LW} = -2\sqrt{\gamma_1^{LW}\cdot\gamma_2^{LW}}$$

$\Delta G = G_f - G_i$ | Only the VdW interaction

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

Let us assume that V12 comprises only of the Van der Waals interactions and as a consequence the delta G12 we get is actually delta G12 due to the l w component of Van der Waals sources. Now at this point I will invoke some sort of a mixing rule that is, prevalent it is quite prevalent that for Van der Waals interaction. It is conveniently assumed is an under route of V11 w into l w V22 so, it is sort of a geometric mean.

That also you can see here. So, that is sort of a geometric mean and once you incorporate this into the equation that we already have or the expression of this particular expression for delta G12. So, I will just write down once more what we have is, delta G12 is minus NZV12 and since we are only considering the van der walls interaction therefore, we can further write it has - delta G12l w is minus NZV 12l w and then, once you incorporate this expression into this particular term NZV12 l w which you can further modify as a it is just a beta of algebraic manipulation that we are doing, just multiply the numerator and denominator by 2 is 2. Now if you take inside the under root it becomes 1 4th. So, it is half into half this n z you also take inside the under root. So, it becomes n z square. So, use one of this NZ here one of the NZ here anyway you have these 2.

And what you get, you suddenly see that you are getting an expression. These expressions are already known to you, this corresponds to gamma 2, but it is the l w component of gamma 2 and this is the l w component of gamma 1. Therefore, what you get is finally, is this now this is something very important and interesting, it is a pretty simple derivation, but is quite interesting in the sense that, now if we reconsider the expression of delta G which is delta GF minus Gi and we are considering only the van der walls interaction, then what we get is delta G12l w equal to GF l w and which turns out to be gamma 12 l w minus gamma 1 plus gamma 2 l w. So, by re arranging what we can get.

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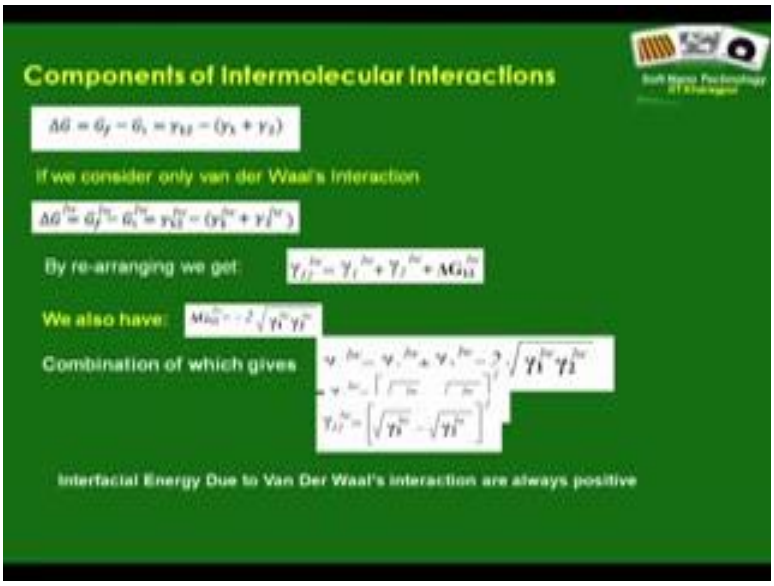

Components of Intermolecular Interactions

$\Delta G = G_f - G_i = \gamma_{12} - (\gamma_1 + \gamma_2)$

If we consider only van der Waal's Interaction

$\Delta G^{lw} = G_f^{lw} - G_i^{lw} = \gamma_{12}^{lw} - (\gamma_1^{lw} + \gamma_2^{lw})$

By re-arranging we get: $\gamma_{ij}^{lw} = \gamma_i^{lw} + \gamma_j^{lw} + \Delta G_{ij}^{lw}$

We also have: $\Delta G_{ij}^{lw} = -2\sqrt{\gamma_i^{lw}\gamma_j^{lw}}$

Combination of which gives $\gamma_{ij}^{lw} = \gamma_i^{lw} + \gamma_j^{lw} - 2\sqrt{\gamma_i^{lw}\gamma_j^{lw}}$

[illegible]

$\gamma_{ij}^{lw} = \left[\sqrt{\gamma_i^{lw}} - \sqrt{\gamma_j^{lw}}\right]^2$

Interfacial Energy Due to Van Der Waal's interaction are always positive

We also plug in let us say from here the expression that we have already got about this gamma 1l w is we combined this with the expression of G12 l w which we already have, we get, I will just write it again for all your understanding.

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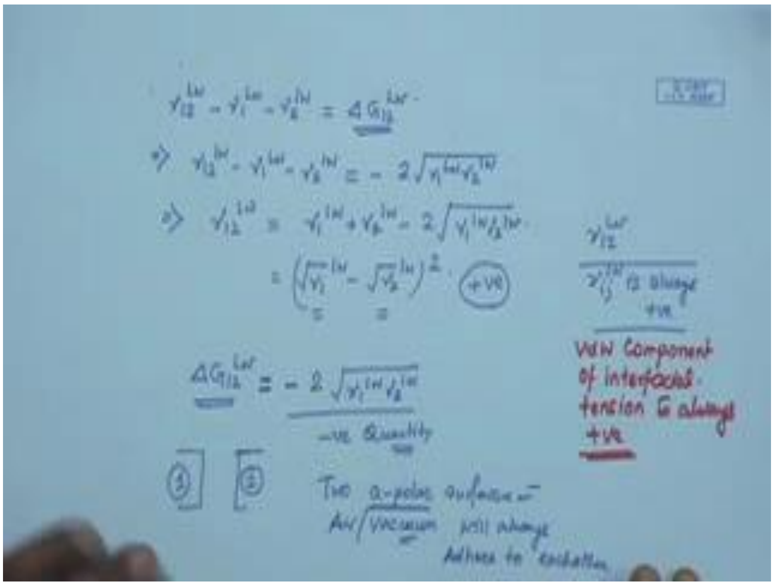

$\gamma_{12}^{LW} - \gamma_1^{LW} - \gamma_2^{LW} = \underline{\Delta G_{12}^{LW}}$

$\Rightarrow \gamma_{12}^{LW} - \gamma_1^{LW} - \gamma_2^{LW} = -2\sqrt{\gamma_1^{LW}\gamma_2^{LW}}$

$\Rightarrow \gamma_{12}^{LW} = \gamma_1^{LW} + \gamma_2^{LW} - 2\sqrt{\gamma_1^{LW}\gamma_2^{LW}}$

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

γ_{12}^{LW}

γ_{ij}^{LW} is always +ve

VdW Component of Interfacial tension is always +ve

$\underline{\Delta G_{12}^{LW}} = -2\sqrt{\gamma_1^{LW}\gamma_2^{LW}}$

-ve Quantity

① ②

Two a-polar surfaces in Air/Vacuum will always Adhere to each other

All we do, we substitute the expression of G12 l w which we have already got here and once you do that, if you do a transposition what you get now gamma 12 l w is gamma this particular expression and this turns out to be; which is a neat expression on the list, but there is some additional consequence of that, what is this consequence gamma 1 and gamma 2 both are positive real numbers.

Therefore, whatever is the difference, whatever is the numerical magnitude there square is always positive. So, what it means is gamma 1 or we can generalize it has gamma IJ is always positive or in other words the Van der Waals component of inter facial tension is always positive what is the consequence of that; consequence of that is if you should recall again, we got in the previous side is; or one can also straight away say that the expression of delta G12 l w is this and this is always a negative number.

What does it means 2 polar surfaces in here or vacuum; why I said a polar because there is no polarity therefore, the entire interactions is due to Van der Waals interaction. Here our vacuum will always and here to each other why because delta G is 2 negative and we had argued that any system which leads to minimization of energy is favored right.

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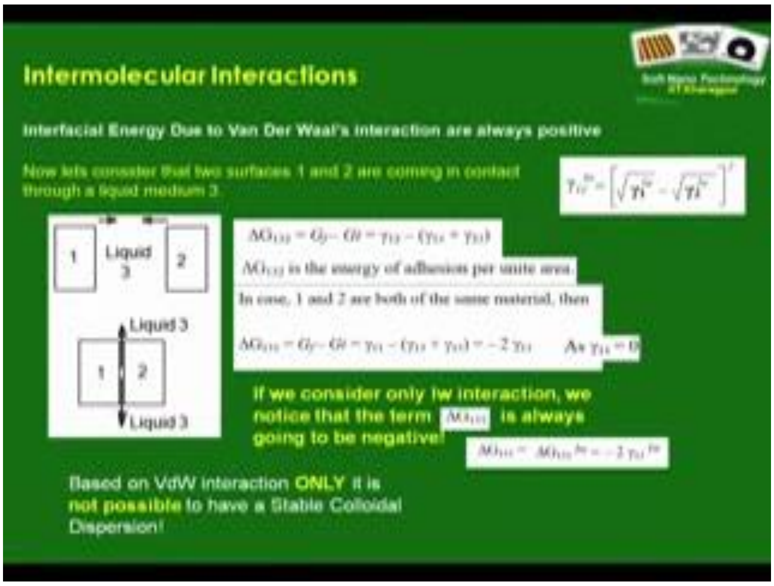

Intermolecular Interactions

Interfacial Energy Due to Van Der Waal's interaction are always positive

Now lets consider that two surfaces 1 and 2 are coming in contact through a liquid medium 3

$\gamma_{ij}^{lw} = \left[\sqrt{\gamma_i^{lw}} - \sqrt{\gamma_j^{lw}}\right]^2$

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

ΔG_{132} is the energy of adhesion per unite area.

In case, 1 and 2 are both of the same material, then

$\Delta G_{131} = G_f - G_i = \gamma_{11} - (\gamma_{13} + \gamma_{13}) = -2\gamma_{13}$ As $\gamma_{11} = 0$

If we consider only lw interaction, we notice that the term ΔG_{131} is always going to be negative!

$\Delta G_{131} = \Delta G_{131}^{lw} = -2\gamma_{13}^{lw}$

Based on VdW interaction ONLY it is not possible to have a Stable Colloidal Dispersion!

The situation; however, changes slightly if the objects are coming in contact let us say through a liquid medium.

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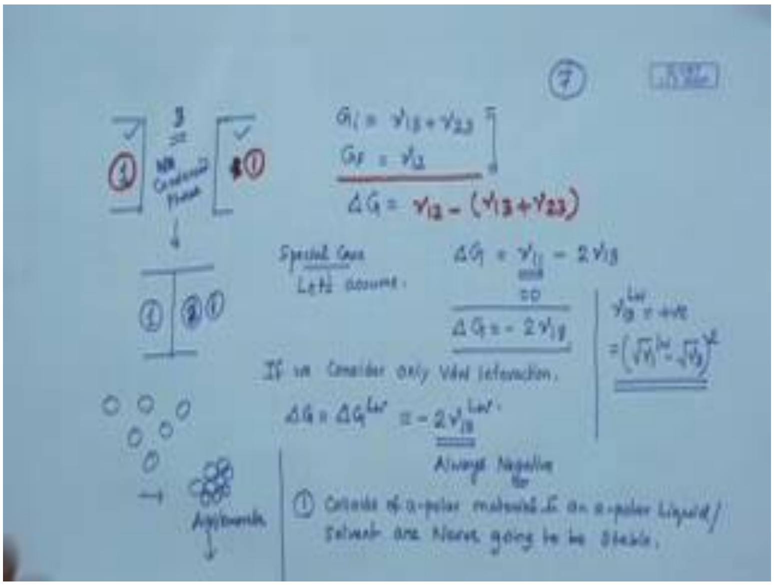

$G_i = \gamma_{13} + \gamma_{23}$

$G_f = \gamma_{12}$

$\Delta G = \gamma_{12} - (\gamma_{13} + \gamma_{23})$

Special Case

Let's assume.

$\Delta G = \underline{\gamma_{11}} - 2\gamma_{13}$

$= 0$

$\Delta G = -2\gamma_{13}$

$\gamma_{13}^{lw} = +ve$

$= \left(\sqrt{\gamma_1}^{lw} - \sqrt{\gamma_3}\right)^2$

If we consider only VdW interaction,

$\Delta G = \Delta G^{lw} = -2\gamma_{13}^{lw}$

Always Negative

① Colloids of a-polar materials in an a-polar Liquid/Solvent are Never going to be Stable.

We consider this the same 2 objects 1and 2. However, instead of here now they are initially this dispersed in a liquid medium 3. So, what is the Gi? Gi instead of gamma 1 plus gamma 2 is actually gamma 13 plus gamma 23 because this is a condense phase as well.

And these to now come in to contact. So, the GF is gamma 12 and one can write that delta G. Please note carefully that these expressions or this particular expression is generic, it does not consider Van der Waals interaction only right. Now let us consider a very special work is, let us assume that these 2 blocks are of the same material and which is a very practical situation because you might have a colloidal dispersion. So, where all the particles are of the same material; So, the question now changes instead of 2 different objects coming in contact through a liquid medium, 2 surfaces of the same material are trying to come in contact in a liquid medium. So, what is going to be the expression of delta G, delta Gis going to be gamma 11 So, that is what you get here, minus this is gamma 13, this is gamma 13.this is 2 gamma13.

Important to note gamma 11 is essentially and inter phase between 2 blocks of one and which is 0. So, this is 0. So, what you get is delta G is minus 2. gamma 1 3, now if you consider only Van der Waals interaction, or in other words delta G entirely constitutes of delta g l w, then what we get is gamma 1 3 l w what have we already learnt we have learnt that gamma 1 3 l w is always positive because it is expression is going to be gamma one l w minus gamma 3 l w whole square.

What does it mean that, this entity since this is always positive this is going to be always negative this one can physically explain in two ways, we have considered only Van der Waals interaction. So, one can argue a polar collides in a polar liquid medium will never be stable; why because they are additional of collides with each other is going to be favored and what eventually will happen. So, if you make an initial dispersion the particles because of the thermo dynamics of the system will join up. they will accommodate.

And eventually it will settle out. So, from a practical stand point, collards of a polar material, in a polar liquid or a solvent are never going to be stable. This also implies that, even in order to explain very common phenomena like a stable colloidal dispersion1. In fact, needs to consider the polar interactions or in other words you must have as we will see in the subsequent discussion that in order to have colloidal stability it is mandatory to have some bit of polar interaction.

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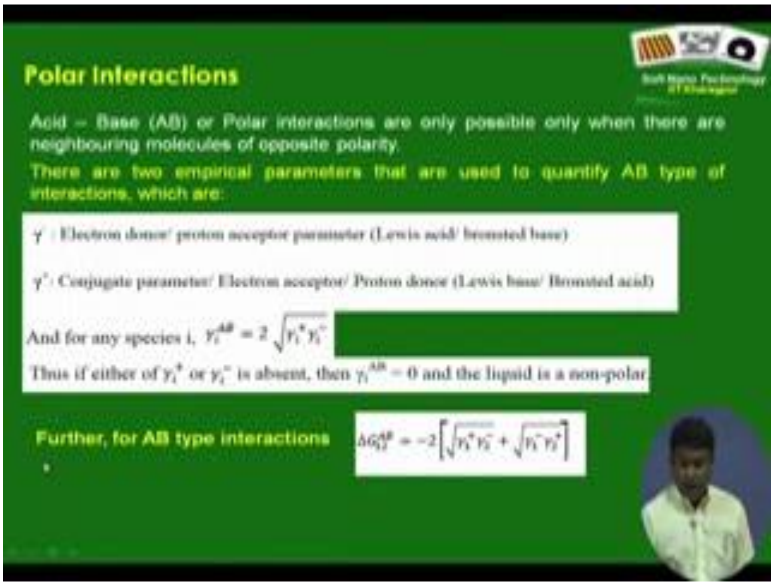

Polar Interactions

Acid – Base (AB) or Polar interactions are only possible only when there are neighbouring molecules of opposite polarity.

There are two empirical parameters that are used to quantify AB type of interactions, which are:

γ^- : Electron donor/ proton acceptor parameter (Lewis acid/ bronsted base)

γ^+ : Conjugate parameter/ Electron acceptor/ Proton donor (Lewis base/ Bronsted acid)

And for any species i, $\gamma_i^{AB} = 2\sqrt{\gamma_i^+ \gamma_i^-}$

Thus if either of γ_i^+ or γ_i^- is absent, then $\gamma_i^{AB} = 0$ and the liquid is a non-polar

Further, for AB type interactions $\Delta G_{ij}^{AB} = -2\left[\sqrt{\gamma_i^+ \gamma_j^-} + \sqrt{\gamma_i^- \gamma_j^+}\right]$

Therefore, we now need to consider in addition to Van der Waals interaction we have to know consider the polar interactions. So, let us see what the components of these polar interactions we have are.

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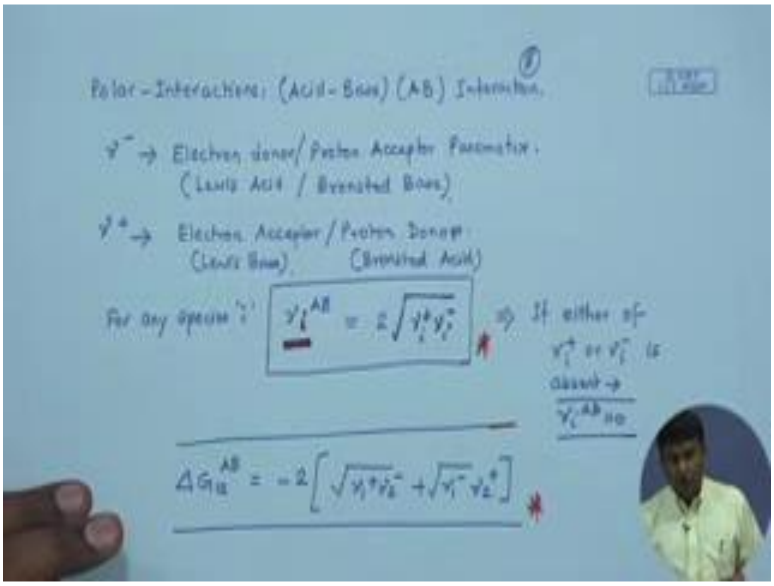

Polar - Interactions: (Acid - Base) (AB) Interaction.

$\gamma^- \rightarrow$ Electron donor/ Proton Acceptor Parameter.
(Lewis Acid / Bronsted Base)

$\gamma^+ \rightarrow$ Electron Acceptor / Proton Donor
(Lewis Base) (Bronsted Acid)

For any species 'i' $\boxed{\gamma_i^{AB} = 2\sqrt{\gamma_i^+ \gamma_i^-}}$ * $\Rightarrow$ If either of γ_i^+ or γ_i^- is absent $\rightarrow$ $\gamma_i^{AB} = 0$

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

Polar interaction for their commonly known as the acid base interaction interactions and it is obvious that polar interactions are possible only when neighboring molecules have a opposite polarity and therefore, it is not as generic as let us say Van der Waals interaction. So, you have to have when there are neighboring molecules of opposite polarity.

You must have polarity within your molecules and only then polar interactions are emphasized or possible. Typically to mathematically handle there are 2 empirical parameters that are used to quantify AB type interaction which are gamma plus and gamma minus this gamma minus essentially corresponds to the electron donor or proton acceptor parameter, if you can recall your high school knowledge about acids. So, this is. In fact, is represents a Lewis acid or a boasted base. Similarly, gamma plus is the conjugate parameter or it is exactly the opposite parameter; it is the electron acceptor proton donor. So, it is going to be the bronzed acid and Lewis base and for any species I gamma I AB the polar component of surface tension, is this. I repeat please do not confuse this with the mixing rule that has been used for Van der Waals interaction, I will show it to you side by side.

So that you do not confuse what we learnt there is this particular relation, that is the interaction between 2 dissimilar molecules due to the Van der Waals interaction we used the mixing rule which looks very similar, but please do not confuse this is what we have used. So, Van der Waals interaction this is. In fact, the interfacial interaction and that was a geometric means of the individual Van der Waals interactions, while we are considering the polar components, in order to describe the polar component of the surface tension of a particular material we sort of use a very similar looking mixing rule I would say comprising the gamma plus and gamma minus component, that is electron donor electron accept or the conjugate 2 conjugate parameters of polar interactions.

If this relation also tells either of gamma plus or gamma minus is absent, then gamma I is zero. This is very interesting and to the subsequent discussion, we will see how this manifest in different settings. May be before I stop this particular lecture, one more expression that is useful for polar interaction and this is sort of assumed is delta G AB is minus 2 gamma 1 plus gamma 2 minus plus gamma 1 minus gamma 2 plus.

These are the 2 important relations that you need to consider for the polar interactions. And based on these 2 concepts we will now discuss in the next lecture about the colloidal stability and other issues of how 2 surfaces which are coming in contact behave. In case there are polarities either in the liquid medium or within the surface.

Thank you.