Colloids and Surfaces
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Lecture-18
Effect of Medium on Vanderwaal's Interactions-I

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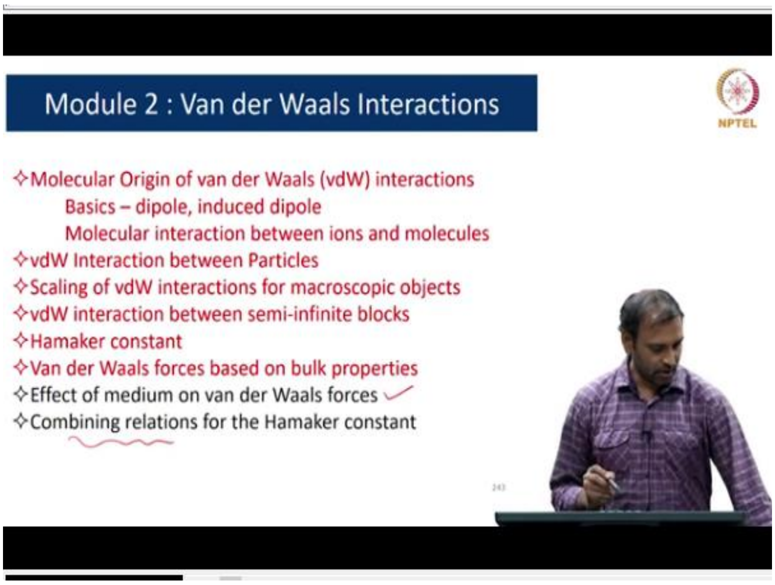

Module 2 : Van der Waals Interactions

- Molecular Origin of van der Waals (vdW) interactions
  - Basics – dipole, induced dipole
  - Molecular interaction between ions and molecules
- vdW Interaction between Particles
- Scaling of vdW interactions for macroscopic objects
- vdW interaction between semi-infinite blocks
- Hamaker constant
- Van der Waals forces based on bulk properties
- Effect of medium on van der Waals forces
- Combining relations for the Hamaker constant

Okay, so we come to the last 2 topics in this module, one is looking at effect of medium on Vander Waals forces. And then the second one is to look at what are called as combining relations for Hamaker constant.

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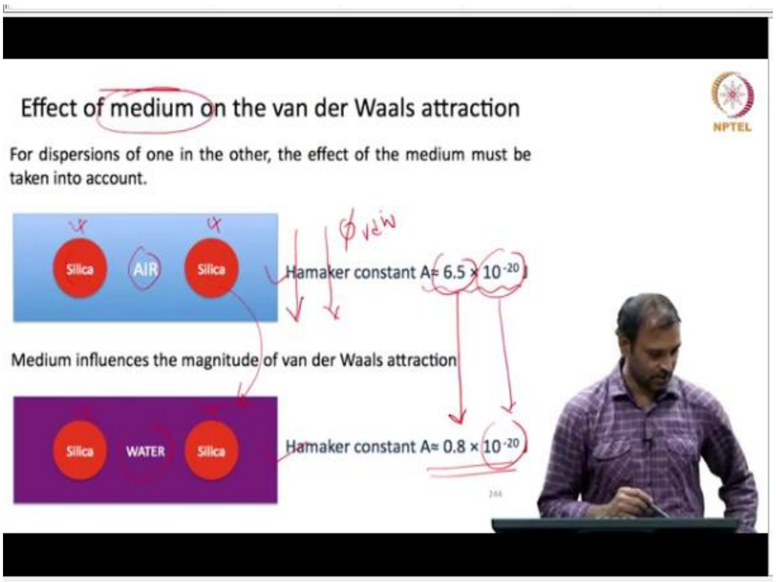

Effect of medium on the van der Waals attraction

For dispersions of one in the other, the effect of the medium must be taken into account.

Medium influences the magnitude of van der Waals attraction

Hamaker constant A≈ 6.5 × 10^{-20}

Hamaker constant A≈ 0.8 × 10^{-20}

So, this particular picture highlights the role of medium on the van der Waals force of attraction, what you are looking at is a case where you have silica particles, ok, in embeded in air, these are the 2 silica particles that and this one, and they are embedded in air and then they are interacting via you know the interactive medium in this case is through air. And the effective Hamaker constant that people have reported for this case is A is 6.5 10 power - 20 joules, okay.

Now, the same particles when they are put in a different medium, in this case, water, again the same particles interacting via water, it turns out that the Hamaker constant is 0.8 into 10 power - 20, ok. So, though the you know this is the same, but there is a significant reduction, right. Though the order is the same, ok, there is still a decrease in the value of Hamaker constant.

That means that if I were to think about calculating the van der Waals force of attraction between silica particles and air and compare it to silica particles in water, when the medium is changed from air to water, the effective Hamaker constant is lower that means the effective van der Waals interaction is going to be okay lower right, that is the gist okay. So, therefore, in general, what is understood is the presence of any medium other than vacuum, ok is always going to reduce the magnitude of Hamaker constant. That in turn would reduce the magnitude of van der Waals forces ok, that is the gist ok.

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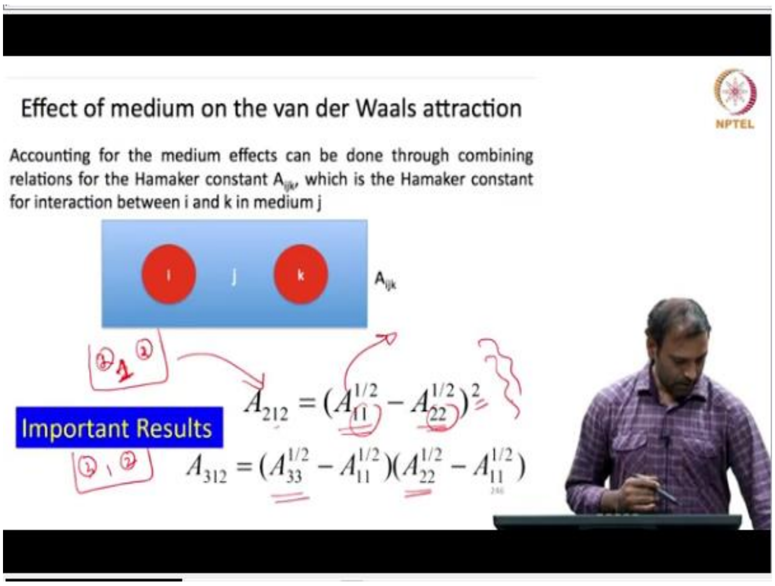

Effect of medium on the van der Waals attraction

Accounting for the medium effects can be done through combining relations for the Hamaker constant A_{ijk}, which is the Hamaker constant for interaction between i and k in medium j

Important Results

$$A_{212} = (A_{11}^{1/2} - A_{22}^{1/2})^2$$

$$A_{312} = (A_{33}^{1/2} - A_{11}^{1/2})(A_{22}^{1/2} - A_{11}^{1/2})$$

So, in order to consider the effect of medium on van der Waals forces, one of the approach that is followed is by using what is called as combining relations okay for obtaining a general you know, this is a general method that is available to obtain Hamaker constant between maybe similar or dissimilar particles embedded in the medium. So, in this case you have medium as j and there are 2 dissimilar particles you know i and k.

And the Hamaker constant for this particular case is designated as a_{ijk}, the first you know, subscript corresponds to you know the one index for that one particle second substrate corresponds to the next particle and what is in between is the as the medium, right, that is a general convention. So, in essence, what we are going to do is to these are the important details that we are going to discuss okay.

So, what you have is a case where you have 2 similar particles particle 1 and again particle 1 interacting via medium 2 okay and it turns out that you know for such a case Hamaker constant that is a sorry this is 2 ok sorry that ok, the particle is described as 2 and 1 is a medium in such a case I can write A_{212} as the Hamaker constant between the species involved, that is A_{22}, that is a particle A_{11} does for the particle.

And these are Hamaker constants when the medium is vacuum okay. So, therefore, A_{212} goes as A_{11} power half - A_{22} power half okay to the power of 2, okay. And you could have a case where I have 2 distinct particles that is particle 3 and particle 2, which are interacting via medium 1, okay, for such a case, A_{312} goes as A_{33} power half - A_{11} power half, multiplied by A_{22} power half - A_{11} power half, okay.

So, we are going to look at you know how do we get such relations okay. And then we will try to talk a little bit about what are the implications of these results, ok, that is what we are going to do.

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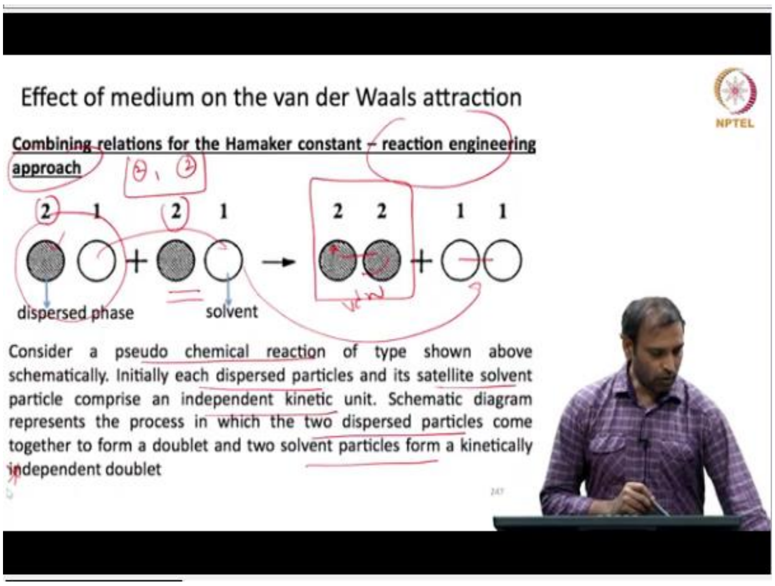

Effect of medium on the van der Waals attraction

Combining relations for the Hamaker constant – reaction engineering approach

Consider a pseudo chemical reaction of type shown above schematically. Initially each dispersed particles and its satellite solvent particle comprise an independent kinetic unit. Schematic diagram represents the process in which the two dispersed particles come together to form a doublet and two solvent particles form a kinetically independent doublet

So, one of the approach that has been available in the literature is to use what is call as a reaction engineering approach. What you have is a schematic, okay that is particle 2, okay and so you should think about this case, okay. There is a particle 2 interacting via a medium 1, okay. Now, if you have a case like this and if you say that look you know I can imagine that for every dispersed particle there is going to be some solvent molecules surrounding it right.

There is going to be for every particle that you have the dispersion there is going to be some solid molecule surrounding it okay. That means you know you have a dispersed phase and the solvent phase, I am thinking about a reaction okay, where I have dispersed phase and solvent phase which coexist together okay, that kind of you know combines okay with a another particle and dispersed phase giving rise to an aggregate right.

So, you can think about this is a doublet okay, which is formed because of van der Waals forces okay. And similarly you know this solvent molecules again they combined to give a again a doublet of solvent molecules, okay. And so, you can also think about you know in the before this aggregation happens, because of van der Waal forces, both the disperse phase and the solvent phase, they are free to move wherever they want.

They are kinetically independent. However, when this aggregation occurs, when it forms a doublet they become kinetically dependent on each other okay, wherever this would go the other one would also follow right. In that sense, there is the kinetic dependence you know independent is lost okay, they become kinetically independent okay. So, what is being shown here is a pseudo chemical reaction okay initially you have a dispersed phase and a satellite solvent particle okay.

Because as I said that you know in solution you will always have particles coexisting with solvent okay. And they are kinetically independent to begin with okay. However, because of the action of van der Waals forces, okay. So, what you do is in this particular process, you get a doublet of 2 dispersed particles come together to form a doublet and the solvent molecules again come together to form a doublet. And they become kinetically independent right critically sorry with that kinetically dependent right, okay.

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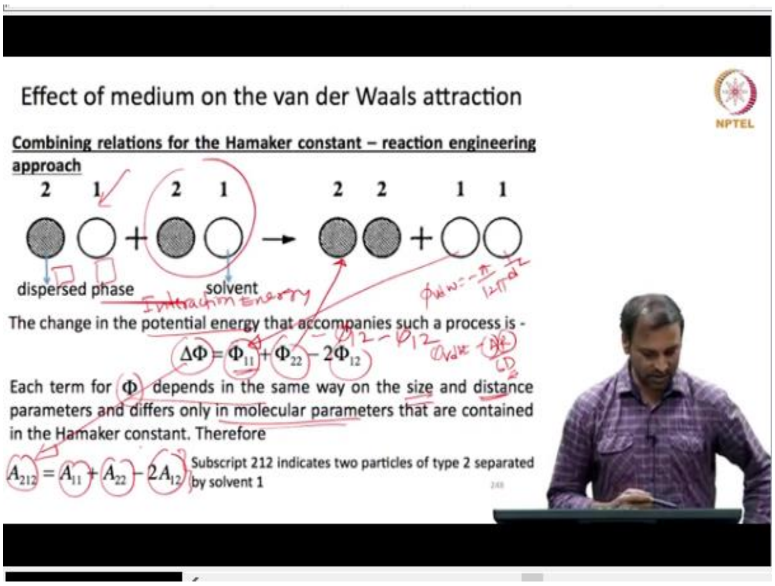

Effect of medium on the van der Waals attraction

Combining relations for the Hamaker constant – reaction engineering approach

The change in the potential energy that accompanies such a process is -

$$\Delta\Phi = \Phi_{11} + \Phi_{22} - 2\Phi_{12}$$

Each term for Φ depends in the same way on the size and distance parameters and differs only in molecular parameters that are contained in the Hamaker constant. Therefore

$$A_{212} = A_{11} + A_{22} - 2A_{12}$$

Subscript 212 indicates two particles of type 2 separated by solvent 1

So, now, if you want to think about you know you can think about writing an expression for what is the change in the potential energy okay or change in the interaction energy okay, that accompanies such a process okay. If delta phi is the change in the interaction energy I could write going to the reaction engineering concept okay. That is the energy associated with the formation of a doublet of solid molecules.

And the energy associated with the formation of a doublet of the dispersed particles 0k - energy associated with the phi 1 2, right you know and then another - phi 1 2, right. Therefore, delta phi becomes phi 11 + phi 22 - 2 times phi 12 okay. So, this is a general picture, I could have imagined that you know I could have you know what is shown here is a looks like a spherical particle right.

But you know I could write a similar thing for a cube like particle or any geometry right. But what would be interesting to note is that, if you look at each of the terms, ok, the moment I fixed the geometry of the dispersed particles and the solid molecules, phi dependence, okay, the each term on the right hand side, the phi depends in the same way on the size and the distance parameters.

What I mean by that is if I were to imagine these to be spherical particles, we know that phi van der Waals okay phi van der Waals is going to be - A times R divided by 6 D, right, where D is the separation distance, A is the Hamaker constant, R is a radius of particle right or if I were to think about block you know semi-infinite blocks van der Waal force of attraction goes as - A divided by 12 pi 1 over d square right.

So, that means all these phi 11 phi 22 and phi you know 12, they depend in a similar way on the distance of separation as well as the size of the particles okay. Now, if that is the case then what we can do is I can actually cancel out the distance dependence okay. And in essence I can you know reduce this particular expression to A_{212} is equal to A_{11} + A_{22} - 2 A_{12} okay.

I can do that, because I am assuming that or because it comes from the fact that each term here the phi depends the same way on the size and the distance parameters okay. And it differs only in the molecular parameters and because it differs only in the molecular parameters, the only parameter that will be different for each of these terms is the Hamaker constant right, that is the concept okay.

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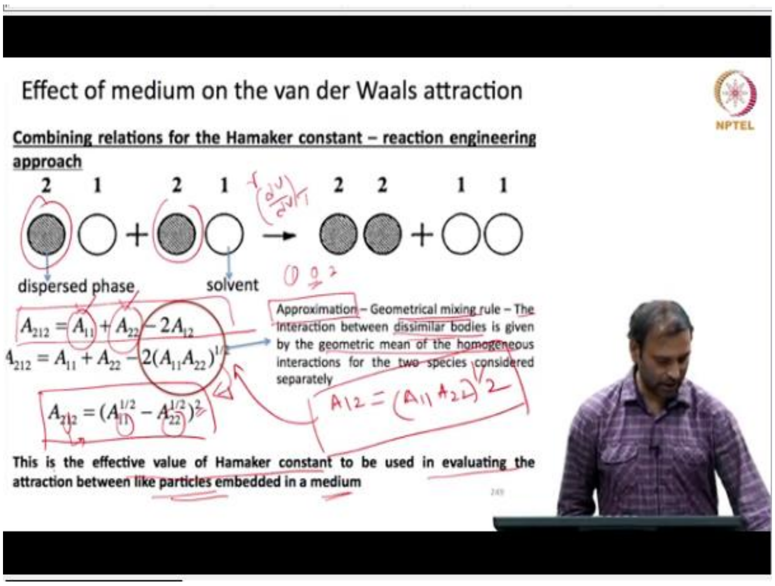
Effect of medium on the van der Waals attraction

Combining relations for the Hamaker constant – reaction engineering approach

$$A_{212} = A_{11} + A_{22} - 2A_{12}$$

$$A_{212} = A_{11} + A_{22} - 2(A_{11}A_{22})^{1/2}$$

$$A_{212} = (A_{11}^{1/2} - A_{22}^{1/2})^2$$

Approximation – Geometrical mixing rule – The interaction between dissimilar bodies is given by the geometric mean of the homogeneous interactions for the two species considered separately

$$A_{12} = (A_{11}A_{22})^{1/2}$$

This is the effective value of Hamaker constant to be used in evaluating the attraction between like particles embedded in a medium

So, now I am able to write A_{212} as A_{11} + A_{22} - 2 times A_{12} okay. So, I know from the tables that are available, I know what is A_{11} and A_{22}. And of course, I can use the some of the theories that we discussed in the last lecture, I know I can relate A_{11} to you know the dielectric constants, right, we talked about it, I can relate A_{11} to like say the surface tensions, right.

If I know how the interior energy changes with volume you know at a constant temperature, okay. So, I can you know there are theories available where I am either like, they are already tabulated, or I have a way of calculating this Hamaker constants for when the species interact in vacuum, okay. But however, I do know A_{12}, okay. So, A_{12} is the Hamaker constant for interaction between 1 and 2, okay interacting via vacuum, okay.

I do not have that information, okay. So, what people do is again, they make some approximation. So, one of the approximation that is typically done is to use what is called as a geometric mixing rule, okay. So, in which, what is stated is that the interaction between 2 dissimilar bodies, okay, is given by the geometric mean of the homogeneous interactions were the 2 species considered separately, okay.

That means you are A_{12}, you can actually write it as A_{11}, A_{22} power half, okay. That is a geometric mean, okay, that is via geometric mixing rule, okay. So, if I use our approximation, okay for 2 A_{121} I can substitute it as - 2 A_{11} A_{22} power half okay. And which I can further reduce it to A_{11} power half - A_{22} power half to the power 2 right. So, that means, so, this is a effective value of the Hamaker constant to be used in evaluating the attraction between like particles okay.

That is similar particles that are embedded in a medium, okay. So, therefore, by this approach, if I know, what is the Hamaker constant of interaction for the solvent molecules and the particles when they are interacting via vacuum I can use that information to assess what is the interaction between them when they are embedded in a fluid okay, that is 1 okay. So, that is what you know one of the combining relation is all about.

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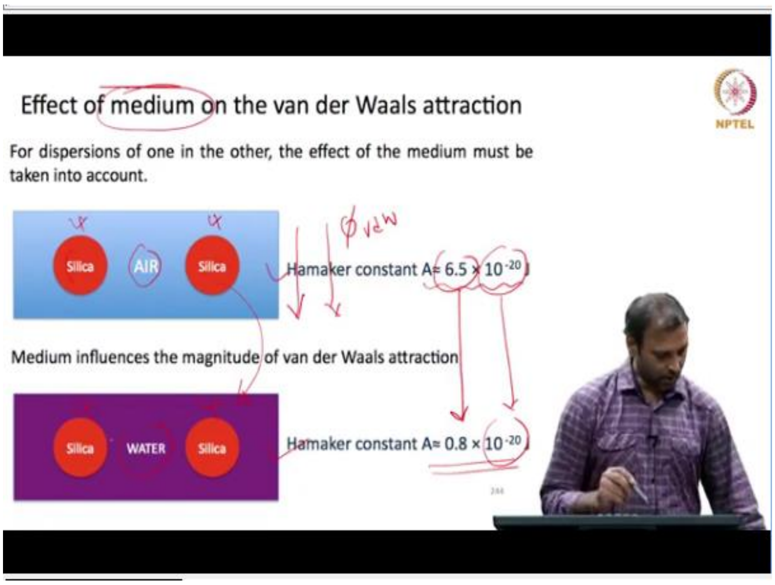

Effect of medium on the van der Waals attraction

For dispersions of one in the other, the effect of the medium must be taken into account.

Hamaker constant A≈ 6.5 × 10^{-20} J

Medium influences the magnitude of van der Waals attraction

Hamaker constant A≈ 0.8 × 10^{-20} J

Now, okay. So, there are some really nice consequence of this particular result okay, that is when you have 2 particles that is 2 okay, interacting while fluid 1, okay, your A_{212} is A_{11} power half - A_{22} power half right. So, what you can learn from this particular expression is that the effective Hamaker constant there is A_{212} is always positive, okay, because it is A_{11} power half - A_{22} you know whole square, therefore, okay,

This is always going to be positive regardless of the magnitude of A_{11} and A_{22}, okay. That means if you take identical particles, okay, which was the case right. We took 2 identical particles. They are identical in terms of surface chemistry okay. If you take such a case then they exert a net attractive force on each other due to van der Waal forces in a medium okay and that is also true for also in vacuum as well okay.

The other important you know result that comes out of this particular formula, we already discussed it. So, embedding a particle you know a medium generally diminishes the van der

Waals force of attraction right. Because you have a difference term here right, if you know A_{11} was some x and if A_{22} was some y okay because you have a difference term okay, your A_{212} is going to be smaller right**.**

Therefore, A_{212} is going to be smaller if you compare the particles being in vacuum okay right. So, if this is A_{101} if you want to call it you know make it more clear, 0 for vacuum – A_{202} okay. Again okay for vacuum right okay, this is van der Waals. This is interaction between the same particles in vacuum okay that is the interaction of the solid molecules therefore, okay.

So, the magnitude of A_{212} is always going to be smaller than A_{202}, there is A_{22} yeah, ok or A_{22} okay. Therefore, embedding particles in a medium generally diminishes the van der Waals force of attraction between them. Again you can take some examples if you take A_{11} is equal to so much and A_{22} is equal to so much, then you know A_{22} you know turns out to be A bar 10 power - 21 joules almost 2 orders of magnitude less than the individual particle.

So, okay. See, these relations that we are trying to write up right okay or let me go back to the table that we had put up okay.

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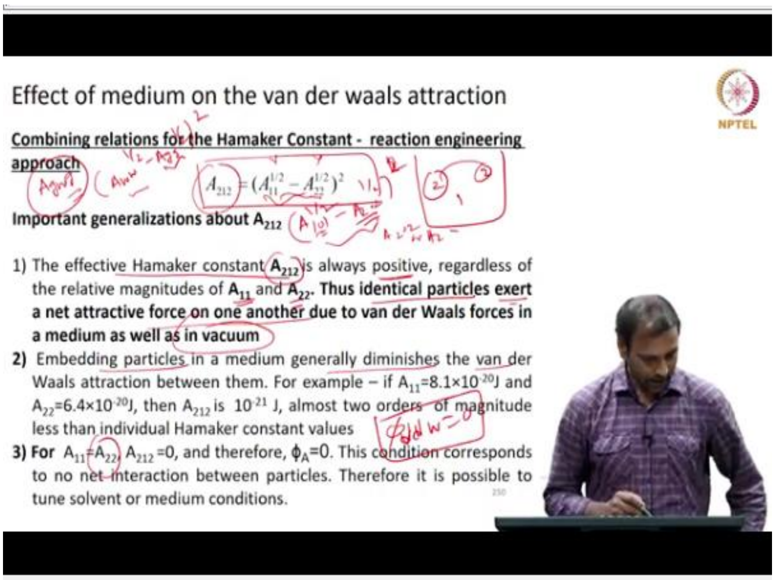

Effect of medium on the van der waals attraction

Combining relations for the Hamaker Constant - reaction engineering approach

$$A_{212} = (A_{11}^{1/2} - A_{22}^{1/2})^2$$

Important generalizations about A_{212}

1) The effective Hamaker constant A_{212} is always positive, regardless of the relative magnitudes of A_{11} and A_{22}. **Thus identical particles exert a net attractive force on one another due to van der Waals forces in a medium as well as in vacuum**
2) Embedding particles in a medium generally diminishes the van der Waals attraction between them. For example – if $A_{11}=8.1\times10^{-20}$J and $A_{22}=6.4\times10^{-20}$J, then A_{212} is 10^{-21} J, almost two orders of magnitude less than individual Hamaker constant values
3) For $A_{11}=A_{22}$, $A_{212}=0$, and therefore, $\phi_A=0$. This condition corresponds to no net interaction between particles. Therefore it is possible to tune solvent or medium conditions.

So, we have this table right, what you have is a list of different materials and different Hamaker constant right. Whenever you see a value like this okay, A 10 power whatever, you know this number right. If nothing is given, you should assume that these are Hamaker constant of interaction between a acetone molecule and another acetone molecule which are interacting via vacuum, okay, that is what is okay. That is your basis okay.

And the theories that we talked about right, you know like for example yeah. So, yeah. So, now, but however, you could or for example, this one right a gold particle that is A gold, gold is what you have okay 45.3 into 10 power - 20 joules okay. Now, if you want to work with like say gold particles, you know Ag, Ag and if you want you know if the medium now is not vacuum, okay, this is the value you know when the medium is vacuum.

And if they are in water now, how would you calculate what is the effect to Hamaker constant right, that is what we are after okay. It turns out that for this particular example okay, this particular example okay, your A gold, gold interacting via water okay is going to be equal to A water, water half - A gold, gold half whole square okay. So, A gold, gold you can get from the table that is there.

A water, water also you can get the from the table that was there okay, I can actually essentially get what is the Hamaker constant for interaction of gold particles you know via water medium okay. So, the first implication is that you know the effect Hamaker constant especially when you are dealing with identical particles, okay is always positive, okay. And embedding the particles in a medium generally diminishes the van der Waals force of attraction between them.

The next one is you could of course, have a case where A_{112} is equal to A_{22}, you know I could design an experiment you know where I could choose a solvent such that A_{11} is equal to A_{22} okay. Therefore, you could have a case where the van der Waals force of attraction indeed could be 0. That means this condition essentially corresponds to no net interaction between the particles okay.

Therefore, it is possible to tune the solvent or the medium okay and I can essentially get rid of van der Waals force of attraction okay. And one of the important consequences of that could be now that I choose a solvent such that you know the van der Waals force of attraction is not there. Now, if I choose such a solvent that is if A_{11} is a Hamaker constant for that particular solvent.

Now, I know that I can relate A_{11} to 24 pi d_0 square gamma right. If I choose a solvent I can actually add that because I know the surface if I know the surface tension of those fluids, I can easily calculate A_{11} okay in turn I can get A_{22} okay, you could actually use this approach for. So, what I do is I take a particle put them in different fluids and identify a fluid where A_{11} is equal to A_{22}.

If I achieve that condition and because for the solvent molecules, there are easier ways of getting the surface tension which in turn will let me calculate A_{11}. If I know A_{11} the fact that A_{11} is equal to A_{22}, I can exploit that to actually calculate you know the Hamaker constant itself for the particles of interest yeah. So, what do you do I mean, yeah, so, yeah, you should know that condition. For example, yeah, this is a kind of what is it, we can make it that way.

I mean, this is an approach that one could use, that is what I am trying to say okay, this is an approach that one could essentially use to calculate. For example, if you have a particle fluid combination, and if you know that look, there is no other type of interactions. For example, like say you know electrical double layer interactions and steric interactions or other kinds of interactions if you know that the only interaction that are you know present are van der Waals, okay.

Now, if you have such a dispersion and if you see that they are very highly stable, okay, then that could be a case where you know your phi van der Waals you know be 0, right. Now if you have conditioned like that. So, it could you know give you a way of actually calculating what is A_{22} okay by that approach is what I was trying to mention. Yeah.