Colloids and Surfaces
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Lecture-19
Effect of Medium on Vanderwaal's Interactions-II

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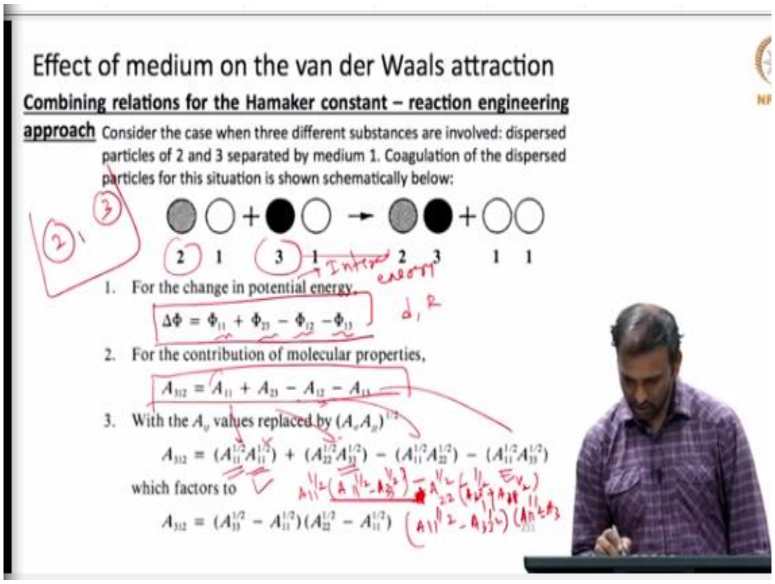

Effect of medium on the van der Waals attraction

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2. For the contribution of molecular properties,

$$A_{312} = A_{11} + A_{23} - A_{12} - A_{13}$$

3. With the A_{ij} values replaced by $(A_{ii}A_{jj})^{1/2}$

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

which factors to

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

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

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

Now let us look at a case where I have 2 dissimilar particles exactly similar approach ok, instead of similar particle that you had you have 2 dissimilar particles. That means I have a container where you have a particle 2 and particle 3 which are interacting via a medium 1. Then exactly similar fashion I can write what is the change in the potential energy or the change in the interaction energy, ok.

But again if I assume that you know each term depends in a exactly similar way on the distance of separation and the dimension of the particles. Then I could write A_{312} as A_{11} + A_{23} - A_{12} - A_{13}, right. And this A_{11} ok, I can write it as A_{11} power half multiplied by A_{11} power half, right it is just a right. Now A_{23}, I can write it as A_{22} power half you know A_{33} power half this is actually from again the geometric mixing rule ok.

Similarly I can write A_{12} as A_{11} power half multiplied by A_{22} power half and this is A_{11} power half multiplied by A_{33} power half ok, I can rearrange a few things. So, if I look this up, right, so, what is common here I can take this term ok and this term. So, therefore I can write it as A_{11} power half to the power A_{11} half – A_{33} half right, that is if I take these 2 terms, right, A_{11} power half is common, right, I have taken that.

So, what is left here is A_{11} power half - A_{33} power half, now here what I can do is plus I can do A I can take minus, I can take let us do this way, what is common here is A_{22} I take + A_{22} power half right this plus here right. So, A_{33} power half - A_{22} power half right, is it ok, with these 2 terms ok. Now, what I can do is what is that, no this is A_{11} sorry, this is A_{33}, this is A_{11} right ok.

And you know I can rearrange this, so if I were taken minus here, ok, then what I would have had is + A_{11} power half - A_{33} power half right. So, therefore A_{11} power half - A_{33} power half multiplied by A_{11} power half - A this is you know this no ok, let me do it again, let us do it again, ok.

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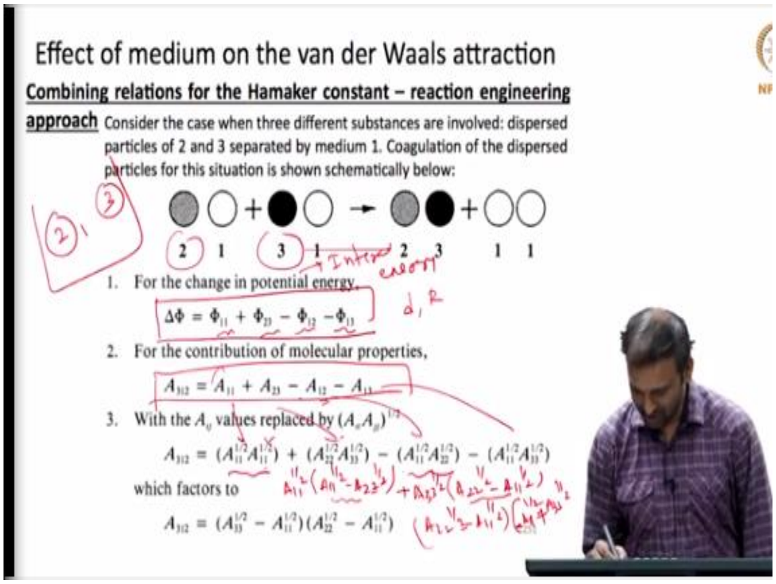

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$(A_{22}^{1/2} - A_{11}^{1/2})(A_{11}^{1/2} + A_{33}^{1/2})$

So, if you look at these 2 terms A_{11} power half, right that is common. So, what I can do is I can write A_{11} half I can take it out, right. And I have A_{11} half - A_{22} half is that ok, that is with these 2 terms, yes, ok, plus I have A_{33} half I have taken this is common. Now I have A_{22} half - A_{11} half that is ok. Now what I do is because you know, I have one is positive other one is negative here, right.

So, what I can do is I can take like say A_{22} half - A_{11} half common, ok, I am going to take this as common, therefore this becomes minus I have - A_{33} half, sorry that becomes plus right, that is correct, that becomes plus, ok. And I have minus, so - A_{11}, then it is correct, it is - A_{11} half, right, see, it does not match with no it matches. So, it matches, I will tell you it matches, right.

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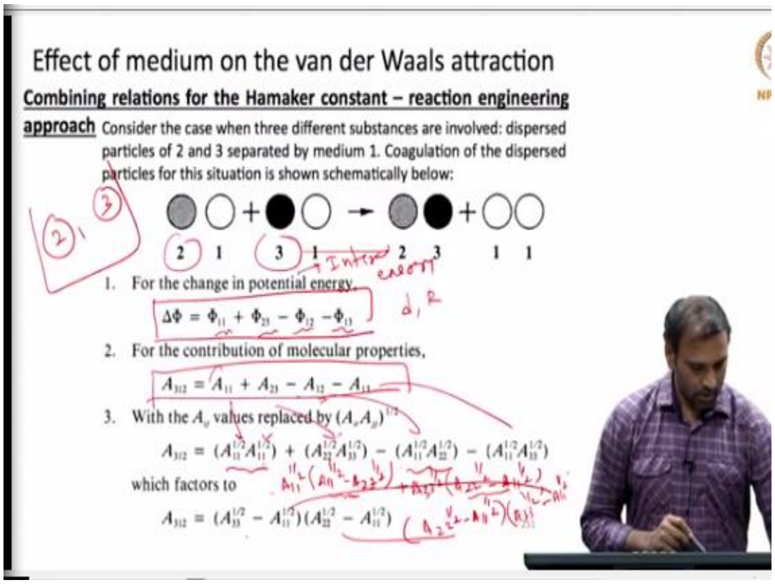

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which factors to

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

So, what I do, so, I take A_{22} half - A_{11} half as common right, multiplied by because I have taken this is ok, therefore this becomes negative right, - A_{11} half ok, negative. And I have + A_{33} half right, that is A_{33} half - A_{11} half that is this term, right this term ok and this is this term, is that ok.

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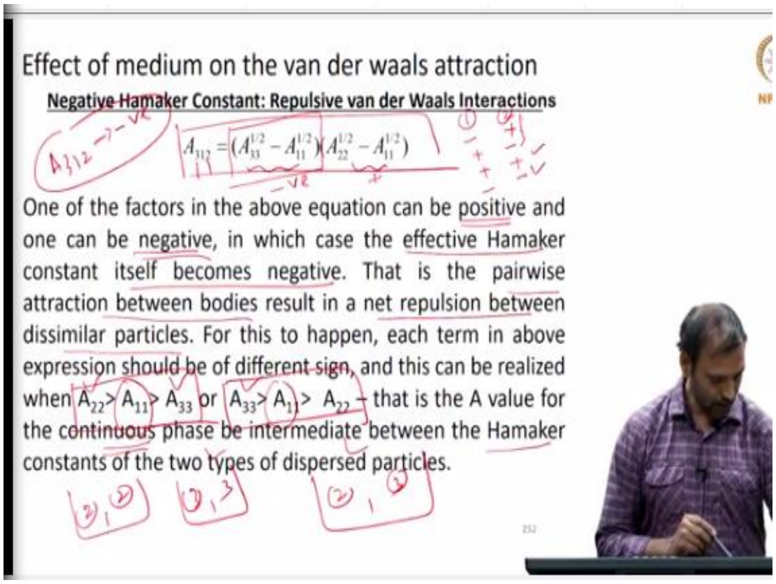

Effect of medium on the van der waals attraction

Negative Hamaker Constant: Repulsive van der Waals Interactions

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

One of the factors in the above equation can be positive and one can be negative, in which case the effective Hamaker constant itself becomes negative. That is the pairwise attraction between bodies result in a net repulsion between dissimilar particles. For this to happen, each term in above expression should be of different sign, and this can be realized when $A_{22} > A_{11} > A_{33}$ or $A_{33} > A_{11} > A_{22}$ – that is the A value for the continuous phase be intermediate between the Hamaker constants of the two types of dispersed particles.

Now.

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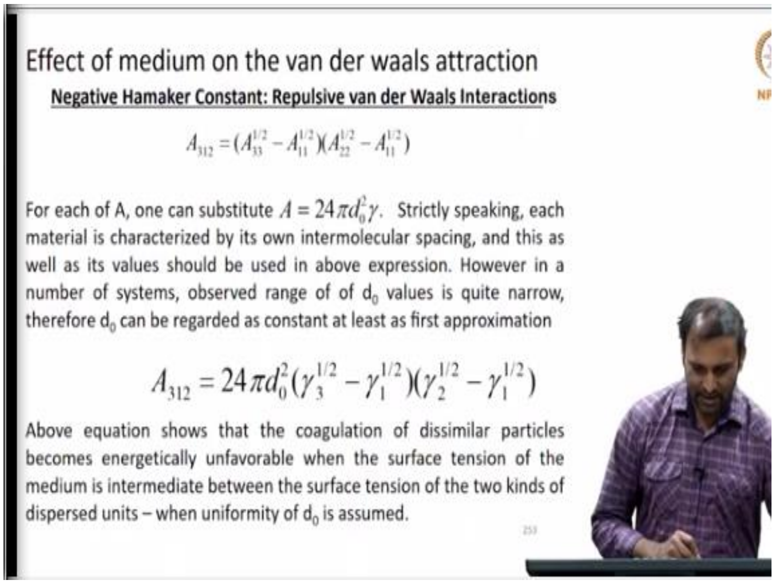

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Negative Hamaker Constant: Repulsive van der Waals Interactions

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

For each of A, one can substitute $A = 24\pi d_0^2 \gamma$. Strictly speaking, each material is characterized by its own intermolecular spacing, and this as well as its values should be used in above expression. However in a number of systems, observed range of of d_0 values is quite narrow, therefore d_0 can be regarded as constant at least as first approximation

$$A_{312} = 24\pi d_0^2 (\gamma_3^{1/2} - \gamma_1^{1/2})(\gamma_2^{1/2} - \gamma_1^{1/2})$$

Above equation shows that the coagulation of dissimilar particles becomes energetically unfavorable when the surface tension of the medium is intermediate between the surface tension of the two kinds of dispersed units – when uniformity of d_0 is assumed.

So, there are again very nice implications of this expression ok. So, therefore Hamaker constant in the case where you have 2 dissimilar particles that is 3 and 2 interacting via you know 1 ok. So, you can write them you know in terms of the Hamaker constant for individual species when they are you know interacting in vacuum, ok. So, one of the see if you look at this expression, you could have a case where either the first term could be negative and the second term is positive.

Or you could have a case, so I could have a case where the first term is negative and the second term is positive. And the first term is positive second term is negative right and both could be positive, both could be negative, the first and second term ok. Now if you have this and this case overall Hamaker constant is going to be positive ok, in which case you can have a attractive interaction between the 2 particles 3 and 2 interacting via medium 1.

But however if you have case 1 and 2, you have A_{312} will become negative. That means instead of Van der Waals attraction, you have what is called as a repulsive interaction that kick in because of Vanderwaal’s forces, ok. So, one other factor in the above equation can be positive and one can be negative right, in which case the effect Hamaker constant itself becomes negative, ok. That is the pair wise attraction between the bodies it actually results in a net repulsive forces if you have dissimilar particles ok.

We mentioned that if we have same particles that is you know 2 and 2 interacting via 1 or 3 and 3 interacting via 1, we said that the net Vanderwaal's forces are always attractive is what we mentioned. But however, if you have a case where I have 2 dissimilar particles interacting via medium 1, ok, turns out that you can have a net repulsive force between the particles ok. And this will happen when each term in this particular expression ok would be of different sign right.

As I said one could be positive other one could be negative ok or the vice versa ok and that would actually happen when this particular condition is met. A_{22} must be greater than A_{11} greater than A_{33} or A_{33} should be greater than A_{11} should be greater than A_{22}. That means if the value of A for the continuous phase ok is intermediate to the Hamaker constant for the 2 particles that you are considered.

If that is the case, that is when this particular condition is met ok. So, if the Hamaker constant for the solvent molecules or the continuous phase or the liquid in which the particles are dispersed. If that is in between the Hamaker constant for the 2 particles are dispersed. In such a case you could have A_{312} will be negative, that means you will have a net repulsion between the particles ok.

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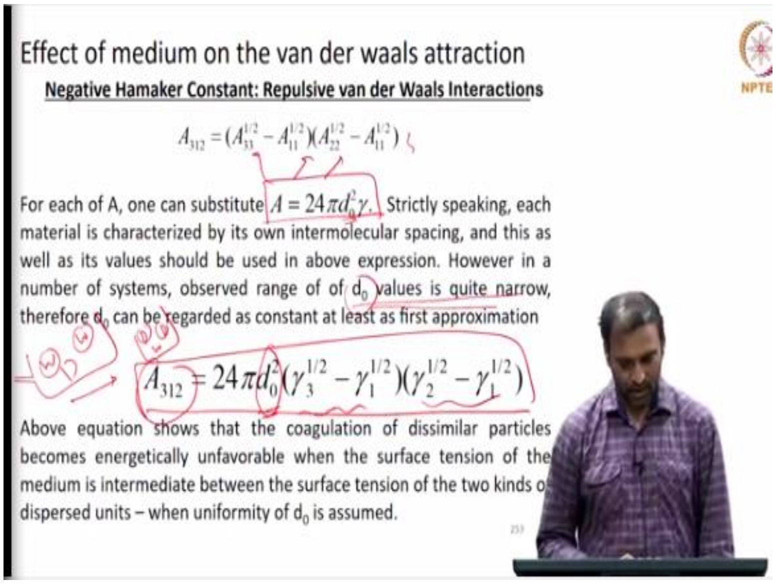

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For each of A, one can substitute $\boxed{A = 24\pi d_0^2 \gamma.}$ Strictly speaking, each material is characterized by its own intermolecular spacing, and this as well as its values should be used in above expression. However in a number of systems, observed range of of d_0 values is quite narrow, therefore d_0 can be regarded as constant at least as first approximation

$$\boxed{A_{312} = 24\pi d_0^2 (\gamma_3^{1/2} - \gamma_1^{1/2})(\gamma_2^{1/2} - \gamma_1^{1/2})}$$

Above equation shows that the coagulation of dissimilar particles becomes energetically unfavorable when the surface tension of the medium is intermediate between the surface tension of the two kinds o dispersed units – when uniformity of d_0 is assumed.

So, you can also think about you know extending this particular concept, further in which because we have kind of developed we have discussed macroscopic theories that people have developed in which you can relate you know Hamaker constant to you know the equilibrium separation distance between the molecules and gamma ok. So, you could actually I can substitute for A ok A for each of these Hamaker constants.

And of course if you assume that on an average if d_0, that is the equilibrium separation distance between the molecules is very similar ok. For both the particles and the dispersed phase and the continuous phase, if I take this d_0 out, I can actually express A_{312} as 24 pi d_0 square multiplied by gamma 3 half - gamma 1 half multiplied by gamma 2 half - gamma 1 half ok.

So, you can also you know work out like this, I mean this I think would be a nice approach if you are looking at something like say emulsion for example. See if you look at like say water droplets in you know Deccan for example ok. An oil or if you are looking at you know droplets in water ok you know. In such a case when you are working with liquid in liquid dispersion ok. You can assume that you know your d_0 ok it is very similar in magnitude, if that is a case you know I can actually take d_0 out.

And then I can express gamma 312 in terms of the surface tension values itself ok. That again is of course an approximation ok, we are assuming that you know d_0 values you know they are typically in an narrow range, if you look at d_0 values for different liquids.

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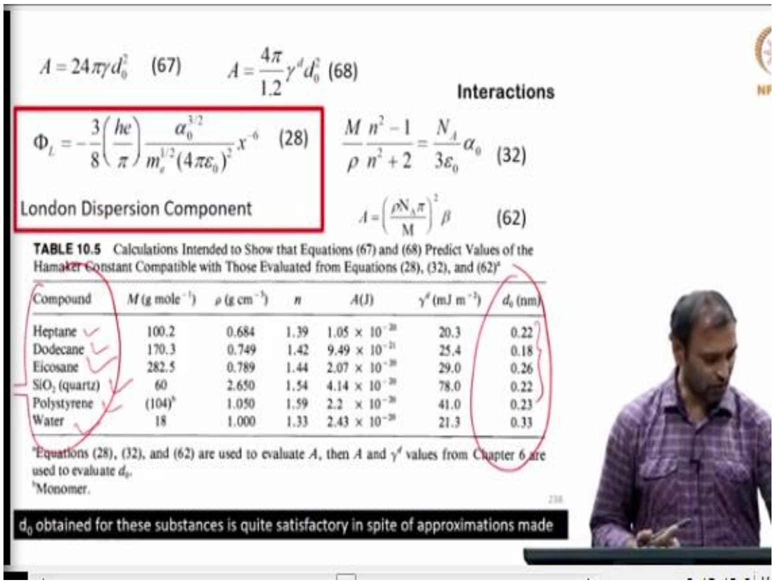

$A = 24\pi\gamma d_0^2$ (67) $A = \frac{4\pi}{1.2}\gamma^d d_0^2$ (68)

Interactions

$$\Phi_L = -\frac{3}{8}\left(\frac{he}{\pi}\right)\frac{\alpha_0^{3/2}}{m_e^{1/2}(4\pi\varepsilon_0)^2}x^{-6} \quad (28)$$

London Dispersion Component

$$\frac{M}{\rho}\frac{n^2-1}{n^2+2} = \frac{N_A}{3\varepsilon_0}\alpha_0 \quad (32)$$

$$A = \left(\frac{\rho N_A \pi}{M}\right)^2 \beta \quad (62)$$

TABLE 10.5 Calculations Intended to Show that Equations (67) and (68) Predict Values of the Hamaker Constant Compatible with Those Evaluated from Equations (28), (32), and (62)[a]

Compound	M (g mole^{-1})	ρ (g cm^{-3})	n	A(J)	γ^d (mJ m^{-2})	d_0 (nm)
Heptane	100.2	0.684	1.39	1.05×10^{-20}	20.3	0.22
Dodecane	170.3	0.749	1.42	9.49×10^{-21}	25.4	0.18
Eicosane	282.5	0.789	1.44	2.07×10^{-20}	29.0	0.26
SiO_2 (quartz)	60	2.650	1.54	4.14×10^{-20}	78.0	0.22
Polystyrene	(104)[b]	1.050	1.59	2.2×10^{-20}	41.0	0.23
Water	18	1.000	1.33	2.43×10^{-20}	21.3	0.33

[a] Equations (28), (32), and (62) are used to evaluate A, then A and γ^d values from Chapter 6 are used to evaluate d_0.
[b] Monomer.

d_0 obtained for these substances is quite satisfactory in spite of approximations made

You will see that I can there was a table here, so let me just go back to the table. Let us look at this table, right, this is d_0 ok these are compounds, ok. There is heptane, dodecane, Eicosane, SIO_2, polystyrene, water, ok. You look at in the numbers there you know except for water, right 0.22, 0.18, 0.26, 0.22, ok all nanometers say it is a fairly narrow range, right.

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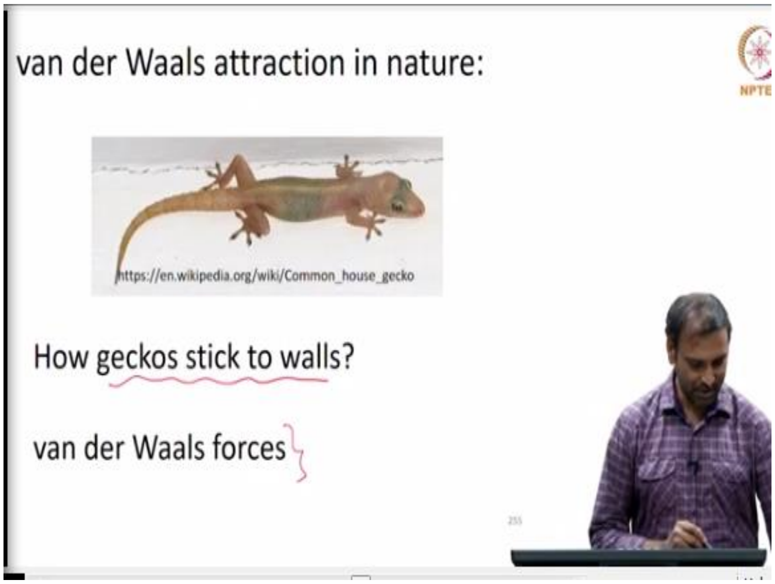

van der Waals attraction in nature:

https://en.wikipedia.org/wiki/Common_house_gecko

How geckos stick to walls?

van der Waals forces

So if you have cases like that, you know I could indeed you know go and look at approaches like this, you know where you know I can express Hamaker constant in terms of the surface tension itself. Because you know value of d itself would be in a fairly narrow range, ok. I just want to end with talking a little bit about Van der Walls attraction in nature, ok. Any examples that you have come across where you think that you know there exist cases where you can you know think about Van der Waals forces or Van der Waals attraction in nature.

Very famous example that everybody gives, its geckos right ok. So, there is a lot of you know there have been a lot of recent experiments you know where people talk about how do these geckos stick to the walls, ok. And it turns out that it is because of Van der Waals forces, ok, there are some really nice experiments that people have done, ok.

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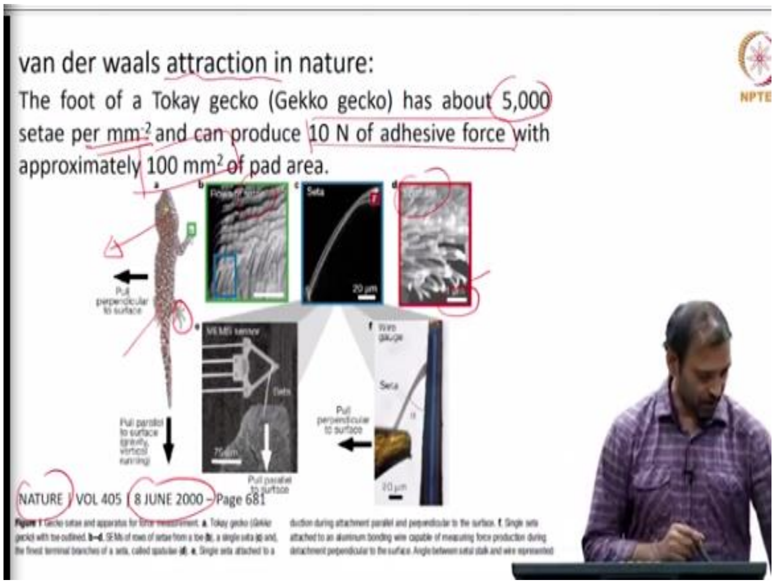

van der waals attraction in nature:

The foot of a Tokay gecko (Gekko gecko) has about 5,000 setae per mm^{-2} and can produce 10 N of adhesive force with approximately 100 mm^2 of pad area.

NATURE | VOL 405 | 8 JUNE 2000 – Page 681

This is some this is a result from a paper that appeared in NATURE 2000. So, what they do is, they say that you know this is the magnitude of adhesive force that they can produce, 10 Newton’s that is really large, ok. And everything is kind of what they do is, this is a macroscopic you know picture of a gecko, right. And then you can look at the mesoscopic structure you know when you look at you know it is palm for example.

Then if you zoom in, and if you look at it you know with a microscope, right, it turns out that they have what is called as setae, ok. And each of this actually has a large number of tiny you know tiny flat structures, ok. And that is the length scale here, that is 1 micron ok. And you can look right there are so many number that if you calculate the Vander Waals force of adhesion between each of these you know fibre like things.

And the wall and if you add them up you know because there are so many number, ok, so the number is something like that, ok. There are about 5000 per nanometer square sorry per millimeter square, right 5000 per millimeter square, ok. And if assume that you know typical if you look at a big gecko you know you could have you know hundreds of millimeters square you know area, ok.

And if you sum up the van der Waals interaction because of each of them, ok with the wall, it turns out that you know you really get a very huge number, ok. So, this is one example where you can think about of course there are other examples as well. So, I would like you guys to go back and read up a little bit about you know these aspects looking at van der Waals you know attraction in things that you see in nature, ok. So, that would be the end of module 2.

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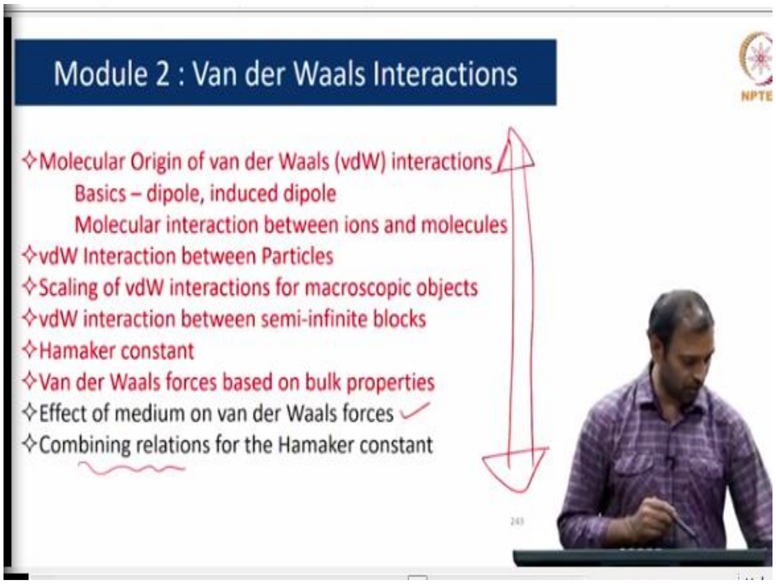

Module 2 : Van der Waals Interactions

- ✧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

So, we have kind of looked at various aspects, so what I will do is we will try and think about some tutorial you know in the next class.

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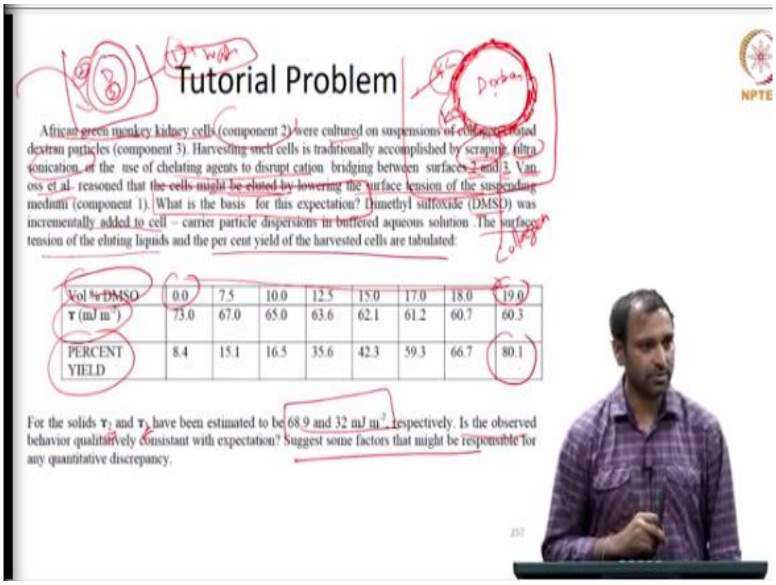

Tutorial Problem

African green monkey kidney cells (component 2) were cultured on suspensions of collagen coated dextran particles (component 3). Harvesting such cells is traditionally accomplished by scraping, ultra sonication or the use of chelating agents to disrupt cation bridging between surfaces 2 and 3. Van oss et al. reasoned that the cells might be eluted by lowering the surface tension of the suspending medium (component 1). What is the basis for this expectation? Dimethyl sulfoxide (DMSO) was incrementally added to cell – carrier particle dispersions in buffered aqueous solution .The surface tension of the eluting liquids and the per cent yield of the harvested cells are tabulated:

Vol % DMSO	0.0	7.5	10.0	12.5	15.0	17.0	18.0	19.0
γ (mJ m^{-2})	73.0	67.0	65.0	63.6	62.1	61.2	60.7	60.3
PERCENT YIELD	8.4	15.1	16.5	35.6	42.3	59.3	66.7	80.1

For the solids γ_2 and γ_3 have been estimated to be 68.9 and 32 mJ m^{-2}, respectively. Is the observed behavior qualitatively consistant with expectation? Suggest some factors that might be responsible for any quantitative discrepancy.

So I have one problem, we can just quickly run through it. African green monkey kidney cells, ok, you can think about that as component 2 ok were cultured ok, on a suspension of collagen coated dextran particles. So, what you should think is you have a dextran particle ok and that is coated collagen ok. And because you know collagen is biocompatible because collagen is biocompatible you know you can kind of you know you can grow cells on it, right.

You can think about something like, ok, this could be I will say kidney cells, ok. So, harvesting such cells is traditionally accomplished by scraping or ultra sonication or the use of chelating agents to disrupt cation bonding between surfaces 2 and 3, ok. So, that means if you have a dextran particle which is coated with collagen and if you know culture such cells on the surface. It turns out that you know if you want to take the cells off now, after you are cultured them, ok, I should somehow get them off from the surface, right.

And people have practiced different kinds of things scraping that is a using physical force or using sonication or you could add some agents, ok, which essentially some kind of chelating agents which so if there is a kind of bonding between the cells and the dextran, ok. I add in the reagent and it helps you in you know disrupting that bond and you know you can actually take kidney cells off from the surface ok.

Now, there is a study ok, in which the reason that cells might be eluted, that means cells can be taken off from the surface by lowering the surface tension of the suspending medium 1 ok. Whenever you do these things, you do it in a medium right. That means I should imagine that I have a container with medium 1, ok, and I have dextran which is coated with collagen that is your component 3 ok.

And on that you have kidney cells, which is competent 2 ok. Now, ok because people have reasoned out that cells might be eluted or easily removed from the surface of you know these particles of type 3 or the component you know 3 particles by lowering the surface tension of the suspending medium that is of component 1, ok. So, the question is, what is the basis for this explanation, why do you think that they are saying that I can reduce the surface tension of the medium and then elude the cells.

So, DMSO was incrementally added to cell carrier particle suspension ok. I have a fluid in which I have you know the components 2 which is attached onto particle 3 they are in a fluid medium 1, ok, the fluid medium 1 is water. And to that they systematically add DMSO ok, so this is an aqueous buffer solution is what they have, that is 1 is a aqueous buffer solution and to that they are adding DMSO ok. And the surface tension of the eluting liquid ok, the surface tension of the fluid that elutes the particle ok and the percentage yield of the harvested cells is given here.

So, this is the volume percentage of DMSO that is added. So, which is of course, increasing 0 corresponds to case when you have only the buffer solution in water and that is the surface tension. And this is the percentage yield, that means the amount of cells that have been you know extracted or eluted, ok. And it turns out that you know if you add about 19% you know by volume of DMSO, your yield goes up to 80.1 % ok.

So for the solid because you know 2 and 3 are solids, right. Your 2 is a dextran coated with collagen, that is a solid particle, ok, that is number 3, right, the solid particle. And 2 is the kidney cells, ok, so they have estimated the surface tension values are just given, ok. Now the fact that with increasing the DMSO concentration, the yield goes up is this observation, ok, is observation qualitatively consistent with the expectation, is that what he expect ok.

Suggest some factors that might be reasonable for any quantitative discrepancy, ok, that is a problem, ok. Take a look at this problem, think about you know what could be happening so maybe we will try and discuss that in the next class, yeah.