Lifshitz approach

Dr Manigandan S.

Department Chemical Engineering

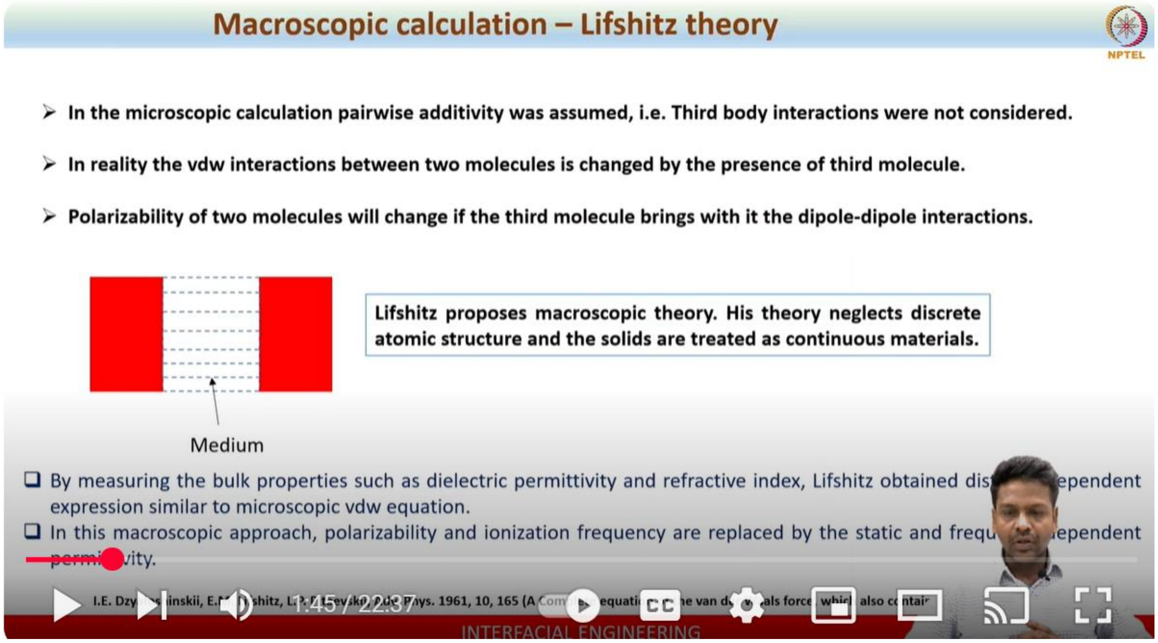
Indian Institute of Technology, Ropar

Lecture-31

Lifshitz approach; surface energy approach, retarded and non-retarded Hamaker constant

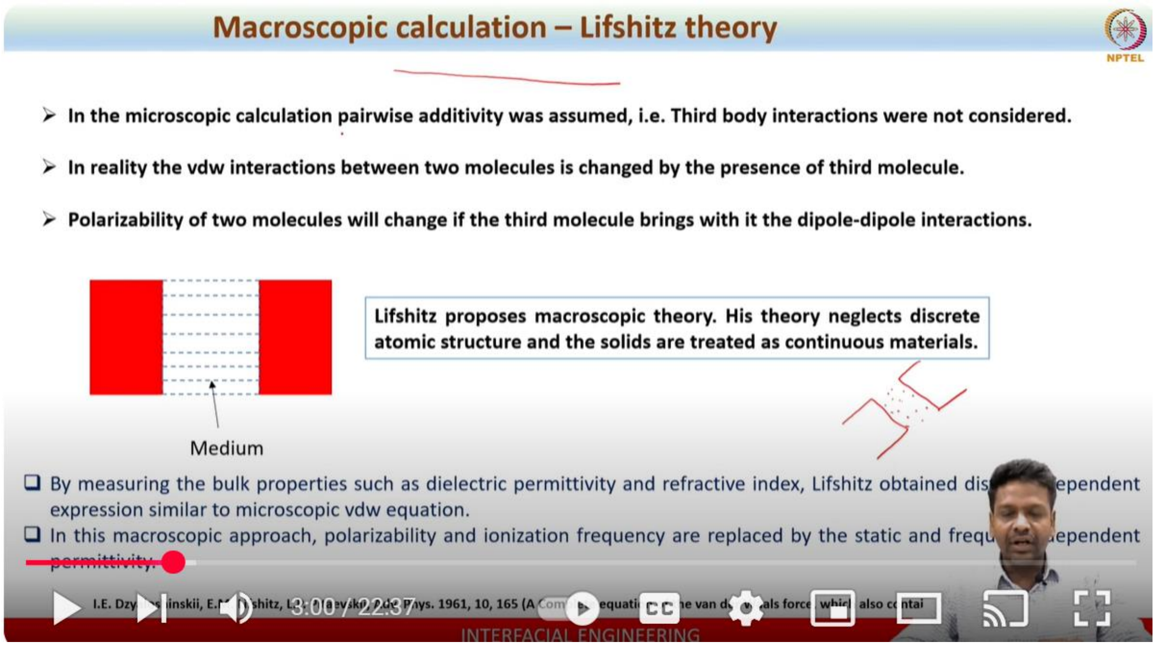
Welcome back. So in today's video lecture, we will look at the Lifshitz approach for calculating the Hamaker constant between any macroscopic bodies by measuring some bulk properties. So this will be a macroscopic approach. So, in previous lecture, we dealt with the pairwise interaction based on the Van der Waals force between, you know, macroscopic body. One of the assumption that we made was there was no, you know, third body interaction, right? There was no third body interaction. So which means that the two macroscopic objects were kept in the vacuum, right? So there is no molecule between two macroscopic object. So based on which we did the pairwise interaction calculation and we obtained the Van der Waals equation. But what if there is a medium? Let's say if two objects are kept in the medium, which can be liquid or gas. So we are going to look at the Lifshitz approach to calculate Hamaker constant in this case. Let's begin.

(Time: 1:45 min)



So as we just now described, we are going to look at the Lifshitz theory, which is nothing but a macroscopic approach. This is because, let's say, in the previous lecture, we discussed the pairwise interaction, which is additive. Okay, based on the assumption that there is no molecule in between. So we only consider the pairwise interaction between the molecules or the objects between the macroscopic objects, right? But the problem here is we actually have ignored the third body interaction. Let's say in between, let's say if we incorporate these two macroscopic objects into the liquid medium or gas medium, so there will be molecules in between. What if the molecules carry dipoles within it? There can be, it can be, I mean, dipoles, permanent dipoles or induced dipole within it, then there can be, it can actually interfere with the Van der Waals interaction, right?

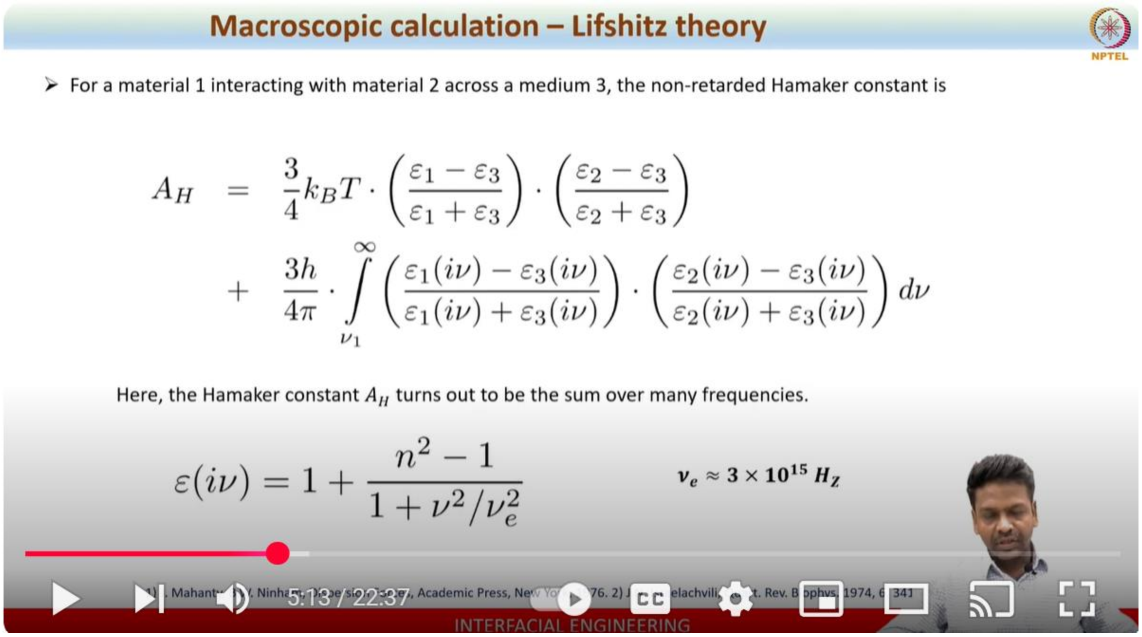
(Time: 3:00 min)



So the pairwise additivity, this property is no longer valid in such situation. So we have to look at the approach, different approach to calculate the Hamaker constant in such case. So if we incorporate this third-body interaction, and try to obtain the solution based on the microscopy theory, which will be a little bit more cumbersome and complicated. One has to use the molecular simulation to compute the total energy of the molecules present. So the other approach which can be used by measuring the bulk properties, such as dielectric permittivity and the refractive index. So when we say bulk property which means that the theory assumes the continuum approach.

So the molecular theory is no longer valid in this case. So all you can do is just measure the bulk property such as dielectric permittivity and refractive index based on which you can actually calculate the Hamaker constant. So that is the idea proposed by Lifshitz in his theory. Okay, so that is exactly what they're going to look at.So when I say macroscopic theory, you can actually ignore some of the, you know, the parameter that is polarizability and ionization frequency, which are very much required when you want to carry out the calculation using macroscopic approach, okay? But in this macroscopic approach, these two parameters you know, you don't need to really worry about these two parameters, right? Because you don't need to really measure and worry about these two, you know, parameters because we are not considering the molecular approach, right? We are only looking at the macroscopic approach in which the theory assumes the continuum approach, right? Yeah. It is based on the continuum approach.

(Time: 5:13 min)



So here we will look at the, so let's say we have, material one, material two, they are interacting through the material, I mean, through the medium, which is numbered as three. In such situation, the non-retarded Hamaker constant, so remember, when I say non-retarded Hamaker constant, this implies that it includes the third body interaction as well. So the regular molecular theory, the approach based on the regular molecular theory is called retarded Hamaker constant because that actually ignores the third body interaction. Whereas non-retarded Hamaker constant, meaning it is a macroscopic approach proposed by Lifshitz in which the third body interactions are considered, very much considered. So this is what the Hamaker constant. So this equation has got two part. One is the real part of the permittivity and another one is based on the imaginary permittivity based on the imaginary frequency which also involve the integration and all that. So one has to evaluate this equation, solve this equation to get the Hamaker constant.

$$A_H = \frac{3}{4}k_BT \cdot \left(\frac{\varepsilon_1-\varepsilon_3}{\varepsilon_1+\varepsilon_3}\right)\cdot\left(\frac{\varepsilon_2-\varepsilon_3}{\varepsilon_2+\varepsilon_3}\right) + \frac{3h}{4\pi}\int_{\nu_1}^{\infty}\left(\frac{\varepsilon_1(i\nu)-\varepsilon_3(i\nu)}{\varepsilon_1(i\nu)+\varepsilon_3(i\nu)}\right)\cdot\left(\frac{\varepsilon_2(i\nu)-\varepsilon_3(i\nu)}{\varepsilon_2(i\nu)+\varepsilon_3(i\nu)}\right)d\nu$$

The permittivity, you know, at different imaginary frequency can be defined like this way in a compact form.

$$\varepsilon(i\nu) = 1 + \frac{n^2-1}{1+\nu^2/\nu_e^2}$$

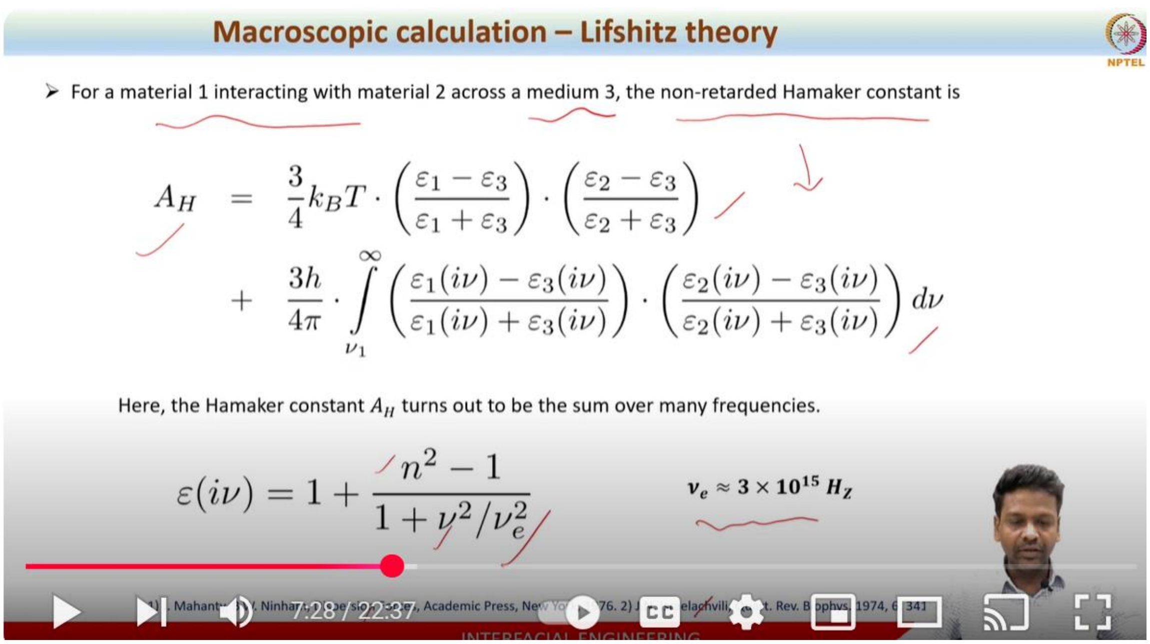
So which is function of refractive index. So n - Refractive index

ν - Absorption frequency

ν_e - mean frequency , $\nu_e \approx 3 \times 10^{15}$ Hz

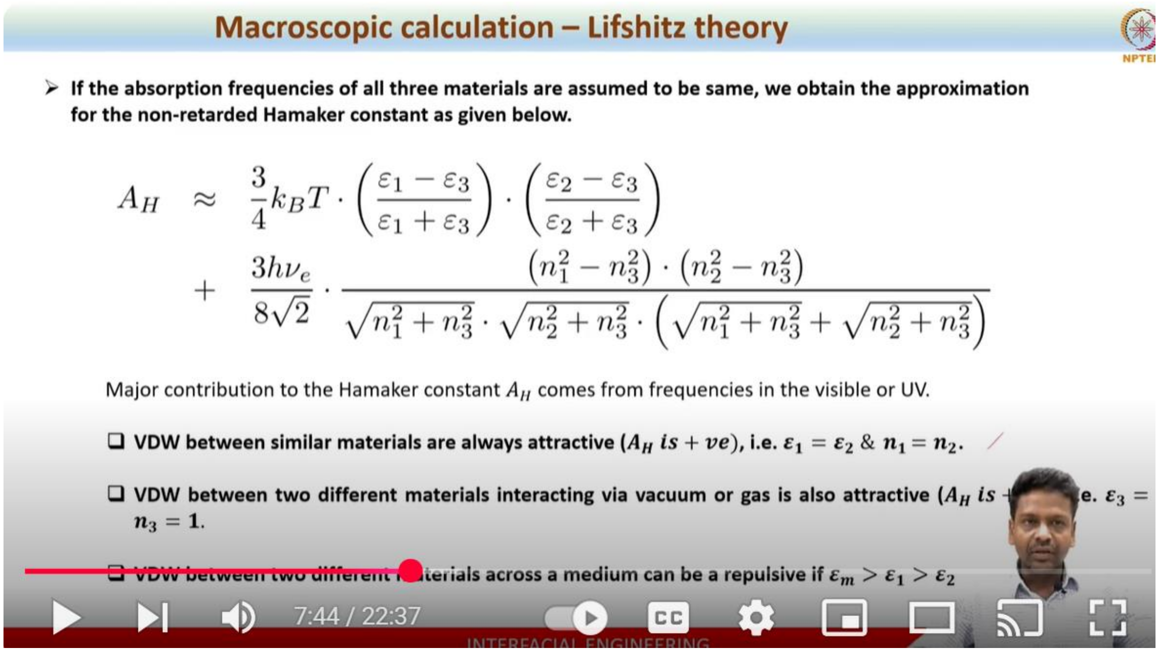
Right? So this is constant. This can vary from material to material, right? Right. All right. So if you want to know further in details, you can actually refer to these books, right? So, you can understand, if you want to understand the origin of this equation, or if you want to get more insight into this, you know, Lifshitz theory, you can actually refer to this book, right?

(Time: 7:28 min)



Now, if you assume that the material that we deal with, let's say all three materials are assumed to be same, the absorption frequency that is new is same for all three material,

(Time: 7:44 min)



then you can actually reduce the level of complexities of the equation that we just now described. So this equation has got no imaginary frequency term, right?

$$A_H \approx \frac{3}{4}k_BT \cdot \left(\frac{\varepsilon_1-\varepsilon_3}{\varepsilon_1+\varepsilon_3}\right) \cdot \left(\frac{\varepsilon_2-\varepsilon_3}{\varepsilon_2+\varepsilon_3}\right) + \frac{3h\nu_e}{8\sqrt{2}} \cdot \frac{(n_1^2-n_3^2)(n_2^2-n_3^2)}{\sqrt{n_1^2+n_3^2}\cdot\sqrt{n_2^2+n_3^2}\cdot\left(\sqrt{n_1^2+n_3^2}+\sqrt{n_2^2+n_3^2}\right)}$$

So which means it's a simple equation, arithmetic equation. You don't even have the integral in this equation. So it is easy to compute the Hamaker constant by using this approximation. That is, when you say that absorption frequencies of all three materials are going to be same, then you can very well use this equation. This is quite compact equation. So, this Hamaker constant is always positive, except for a few cases. If Hamaker constant is positive, the Van der Waals equation that we get will be negative always negative right but in some situation so Van der Waals I mean in some situation let's say when the permittivity of medium is, uh, you know, slightly, uh, you know, larger than the permittivity of the materials.

Right. Okay. In such situation, uh, you can expect the Van der Waals, uh, force between the material can be, uh, you know, repulsive and, uh, the Hamaker constant in such situation can be negative. Right. So for, in a special case, uh, one can encounter, uh, this scenario.

- VDW between similar materials is always attractive (A_H is $+\nu_e$), i.e.,

$$\varepsilon_1 = \varepsilon_2 \quad \text{and} \quad n_1 = n_2$$

- VDW between two different materials interacting via vacuum or gas is also attractive (A_H is $+$), i.e.,

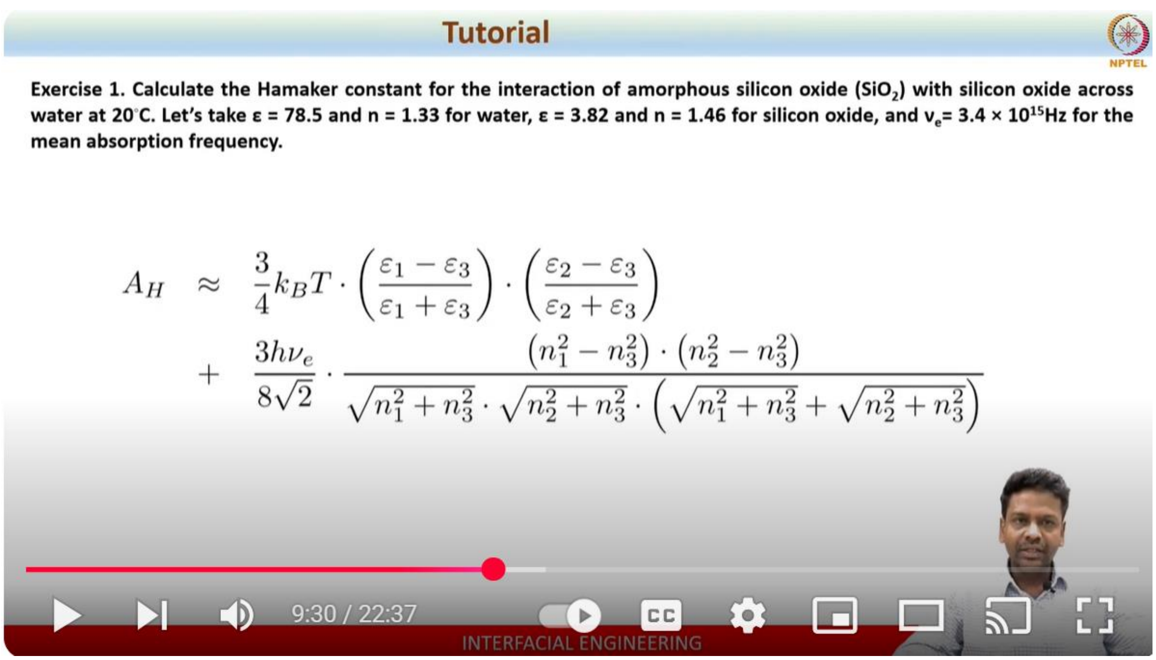
$$\varepsilon_3 = 1 \quad \text{and} \quad n_3 = 1$$

- VDW between two different materials across a medium can be repulsive if:

$$\varepsilon_m > \varepsilon_1 > \varepsilon_2$$

Right. Right.

(Time: 9:30 min)



So just a small exercise for you. You can actually calculate what is known as the Hamaker constant. For the amorphous silicon oxide, so silica, you can actually use Right. So in this case, all you need to do is you need to calculate Hamaker constant. Right. For the interaction between SiO_2. Right. SiO_2 molecules kept in the medium called water. Right.

So here the

- ε for water that is ε_3= 78.5
- n_3= 1.33 whereas the
- n_1= ε_2 ,so ε_1= ε_2= 3.82

So one can calculate what is the so the mean frequency is also been given is also given in this problem. So one has to evaluate what is the Hamaker constant. So I leave this exercise to you. You can calculate what is the Hamaker constant and comment whether the A, Hamaker constant, whether it is negative or positive, if it is positive, is it a repulsive force or attractive force? So you need to comment on that. Okay,

So in the previous case, we know that there was some shortcoming, right? So let's say the original equation which Lifshitz proposed is itself quite complicated because you need to know you need to know what is the dielectric permittivity, real part and imaginary part, and then you need to also integrate it, right? So computationally, this is a little bit more cumbersome, okay? But one can use the approximation, that is based on the assumption that the absorption frequencies of all three materials are same, almost same, In such case, you have the compact equation, which is actually, you know, which doesn't have the, in that you don't need to actually calculate the real part and imaginary part. Okay and you don't have integration it is a simple arithmetic equation so one can easily calculate by knowing or by measuring what is known as the dielectric permittivity and refractive index for all these three materials ,Now another exercise for you is you need to find out what technique one can use to determine the dielectric permittivity and refractive index okay because this is going to be the bulk property so when it is a bulk property one can use by one can measure by using the technique right there are some techniques that measure these properties, right? So, you need to understand, find out, you know, which technique can you use to determine the dielectric permittivity and the refractive index, okay? Right. Okay,

The next approach that we will see is based on the surface energy approach and Hamaker constant. There is going to be a relationship between surface energy and Hamaker constant, right? So that is exactly what we are going to look at. In the previous approach, Lifshitz theory approach, so we know there is approximation, right? So if you use that approximation, but then sometime you may not get the precise solution, right? Because the approximation sometime may go wrong, right? Because you don't expect that in every situation you will have the absorption frequency of all three materials will be same. right so in such case can we use some other method alternative you know method to calculate the Hamaker constant and the van der Waals equation right so van der Waals force I mean energy right total energy based on the van der Waals force, right of attraction right so that for that one has to use this simple surface energy approach, okay? So here, all you need to know is, so what we are considering here is, let's say you have the atoms which are held together in a square lattice, right? So, you know that when even though atoms are very closely, you know, packed together, there will be what is known as the separation distance, right? That is D_o. That is the minimum separation distance beyond which atom cannot, you know, approach closer than that because there will be a bond repulsion, right? you know, there is something called Pauli's exclusion principle, which doesn't allow the atoms to, you know, explode or access all the space, right? So there will be a boundary beyond which atom cannot penetrate further. So that is nothing but D_o, which is the minimum separation distance, right?

$$\Phi_{\text{VDW}} = -\frac{A_H}{24\pi D_0^2}$$

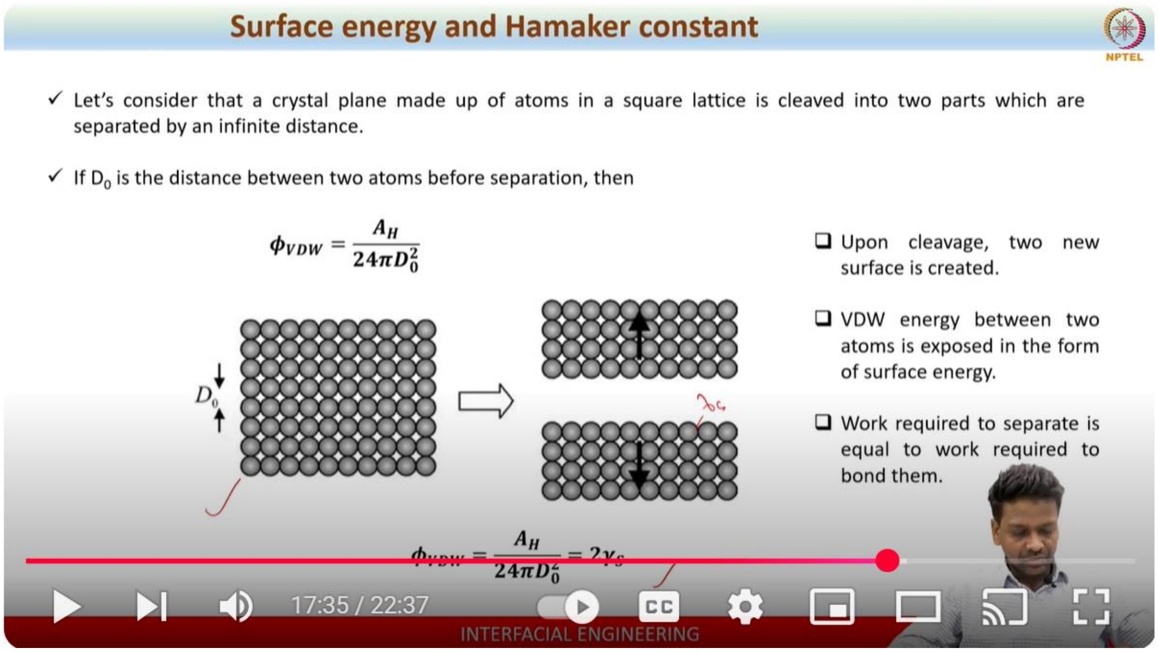
So if you know that, you know that when atoms are held together in a square lattice, at a distance called D_o,So can you calculate what will be the Van der Waals force between the molecules? So to do so, let's say if you know that the energy required to break them apart, let's say if you want to cleave this atom, the crystal structure into two half, then you can basically what you will know what is the energy required to break them apart. If you know the energy required to break them apart, then you have the answer. That is, the energy required to combine them. So energy required to break them apart is same as energy required to combine them. So you know that when you calculate what is energy required to break them apart, so that much energy was actually used, right, between the atoms.

that much energy was, you know, imposed, right, when they were held together, right, when they were held together. in a crystal lattice right and that energy is nothing but van der Waals energy right so you can actually calculate based on this by equating the van der Waals energy, total energy to the the surface energy here, because when you break them apart into two, you create two new surfaces, right? So two new surfaces. So you will have, so there will be two, you know, two new surfaces are created, right? For each surface, you will have one, you can assign a surface energy, right? In that way, you will have two surface energy, right? So that means $2\gamma_s$.

$$\Phi_{\text{VDW}} = \frac{A_H}{24\pi D_0^2} = 2\gamma_S$$

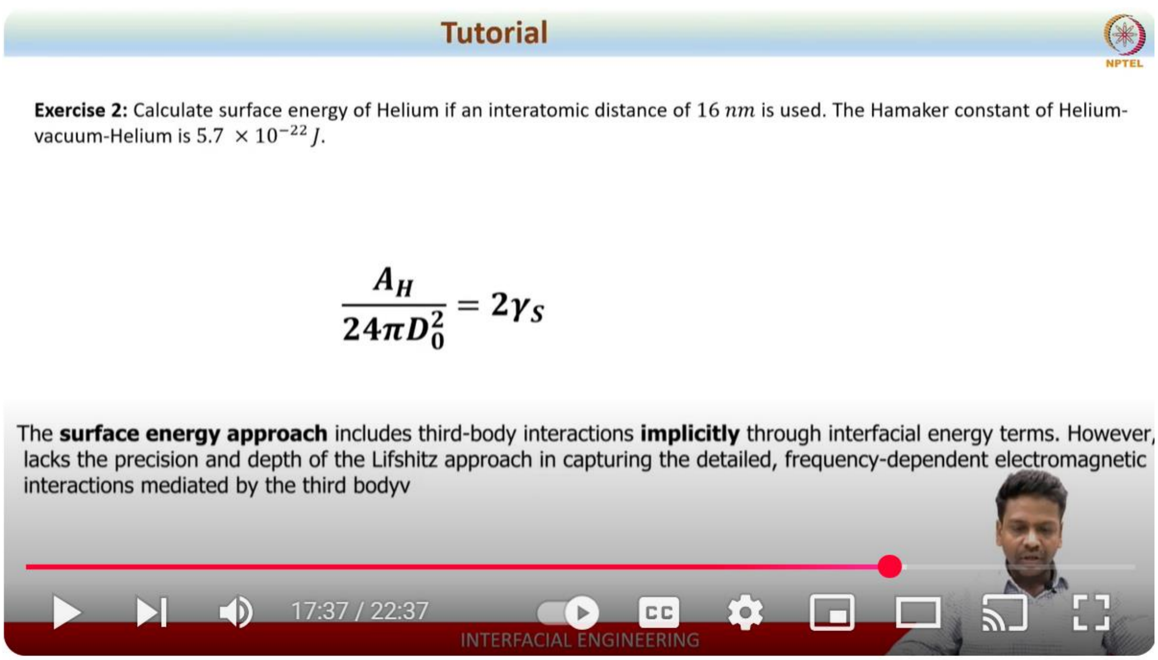
What is the separation distance, minimum separation distance? or Hamaker constant or surface energy itself, right?

(Time: 17:35 min)



So we are going to do this exercise.

(Time: 17:37 min)



So in this equation,

$$\frac{A_H}{24\pi D_0^2} = 2\gamma_S$$

So what is given is the, you know, the Hamaker constant, right, of helium, vacuum helium. So here there is no third body interaction. So no third body interaction. Interactions, because our approach is based on by, you know, separating them into two, right? Yeah.And in this way, you know

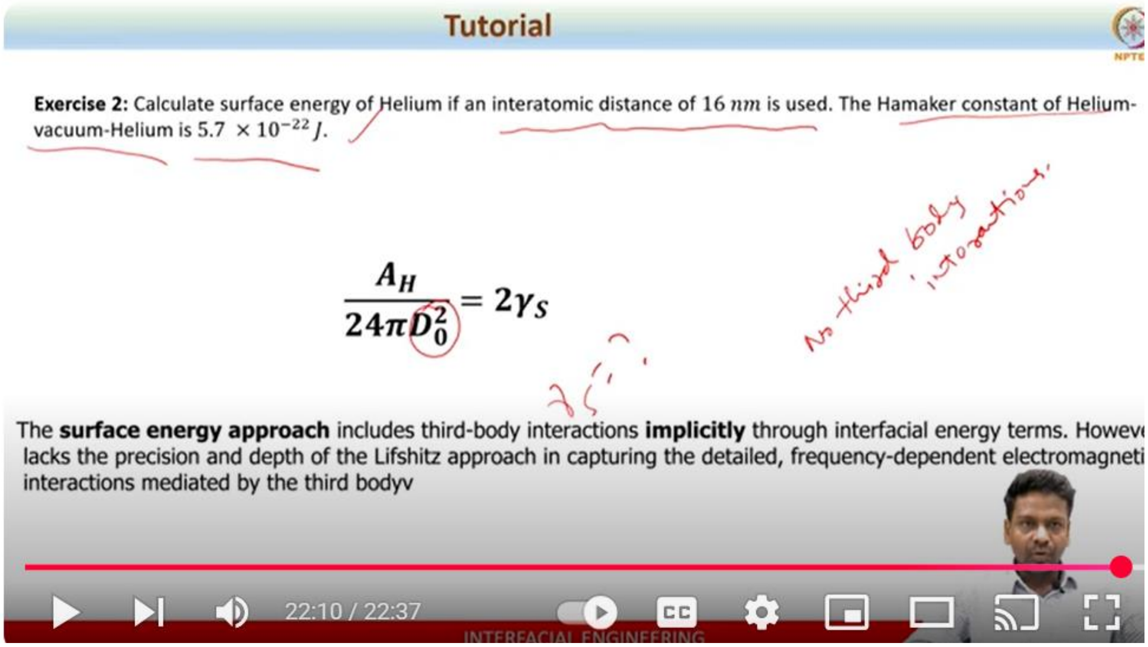
- Hamaker constant = 5.7* 10 $^{-22}$ joule
- D_0 = 16 nanometer

So what exactly is asked in this question is surface energy. So you need to calculate what is the surface energy.So idea is you calculate the surface energy and then compare the surface energy with the literature value. You know what is the surface energy of helium. So you can compare this value with the literature and comment on. If the value is very close, you just have to say yes, this equation. you are able to calculate the surface energy based on this equation also. Okay, so that is all about the surface energy approach.

So we have seen so far Lifshitz approach. Lifshitz approach is the macroscopic approach, right? So here in this approach, you use the measurement, you measure the bulk property such as, you know, dielectric permittivity and refractive index, right? Using some technique, okay? So, when I say bulk property, which means that the theory assumes continuum approach. Okay. Right. So, we are not going to bother about the molecular theory. Right. Because this approach incorporates the third body interaction as well. Now, that is first thing that, first thing we saw was the Lifshitz approach. And then we looked at, so there is some complication because one has to measure the real part and imaginary part and there is also integration and all those things, right? So then what we did is we approximated by assuming that the absorption frequencies of all three materials are almost same. In such scenario, you will get rid of those complexities, right? So you will be simply having the refractive index for all the materials and permittivities of all the materials that you will be having. So that is the approximation, right? So by simply measuring the refractive index and permittivity, you can calculate the Hamaker constant.

Next, what we saw was the surface energy approach. The surface energy approach was like, again, it doesn't include the third body interaction, but it is somewhat easier than the Lifshitz approach. Okay, because you don't need to really calculate or determine, you know, any dielectric permittivity, refractive index and things like that. So all you need to know is the surface energy of the material that you talk about. Okay. And if it is between two molecules, same molecules, it is quite easier. Okay. So for that case, you can use this approach. Okay. So if you know what the surface energy of a given material is and you are calculating the Van der Waals force between two similar materials, right, considering a vacuum. then can you can use this approach right so this is again measuring the surface energy so you can actually if you know the surface energy you can actually calculate the Hamaker constant but one has to know what is the minimum separation distance that is D_0 okay so based on that you can actually calculate the unknown okay

(Time: 22:10 min)



I think you got enough insight into what is retarded Hamaker constant, non-retarded Hamaker constant, based on the Lifshitz theory.And we'll stop here. We will continue from the next lecture. Thank you.