Colloids and Surfaces
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Lecture-13
Calculation of Vanderwaal's Forces Between Semi-Infinite Blocks and Hamaker Constant-I

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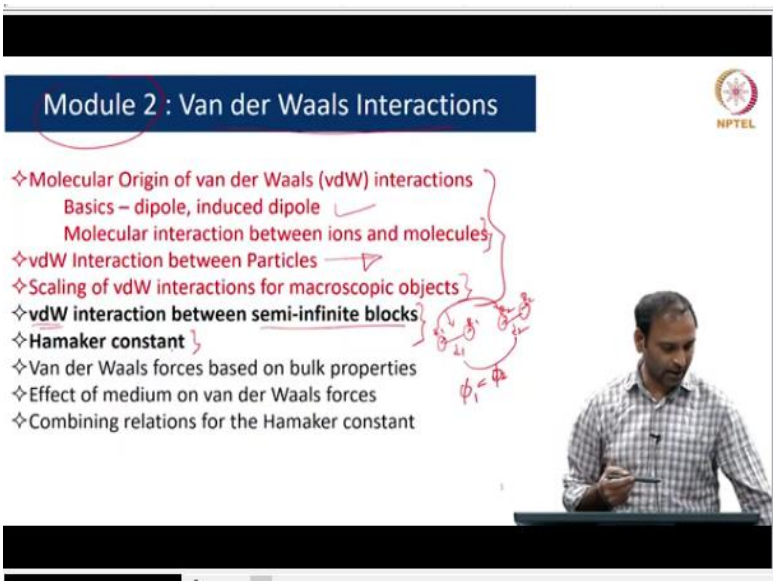

So, we are at module 2, we are looking at van der Waals interactions and what we have done so far is these 4 you know pieces we have introduced van der Waals interactions you talked about the molecular origin of van der Waals interactions. Then we briefly discussed about van der Waals interaction between ions and molecules. Then how does one think about van der Waals forces between the particles.

And then we discussed what is called as a scaling of van der Waals interaction for macroscopic objects in which we found that you know if you have 2 particles separated by a particular distance d 1 and other set of particles separate by distance d 2, if the radius of these particles is R 1 identical particles and in this case if is R 2 okay, as long as the sizes and the distances scale in a similar fashion.

We said that the van der Waals force of interaction in the case 1 will be exactly same as van der Waals interaction in the case 2 okay. That is what we are done and today what we will do is we will try and talk about these 2 aspects, one is will try and derive an expression for van der Waals interaction between semi infinite blocks and then will introduce a constant which

is what is called as Hamaker constant which is useful if you really want to quantitatively calculate the van der Waals force of interaction.

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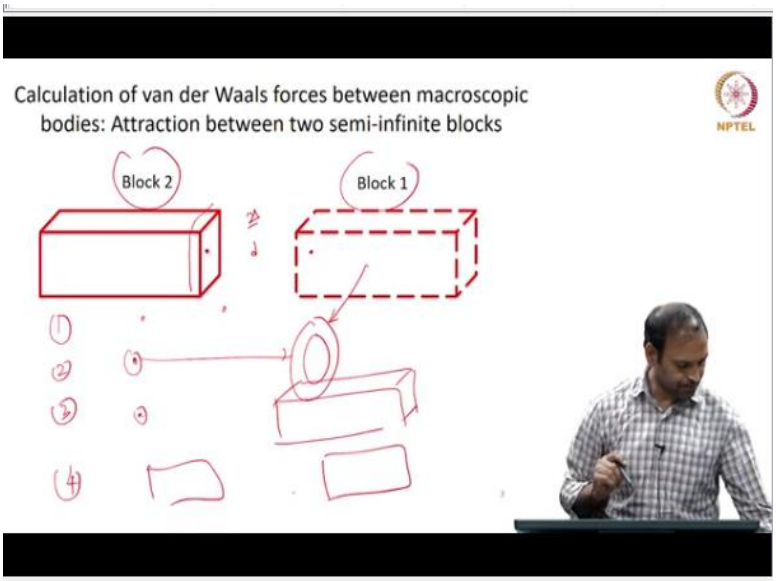

So, what we are going to do is a simple you know derivation in which you have block 1 okay and block 2, they are separated by distance d, in this case d is the surface to surface separation distance, we would like to calculate what is the van der Waals force of interaction between the 2 blocks okay and the reason why they are called semi-infinite is because. So, if you look at you know if I just write a coordinate system okay.

So, the length in this direction is finite okay and the length in this 2 directions are infinite okay, what I mean by this length is the only thing that you have to worry about is these dimensions are much, much larger compared to the separation distance okay, that is all it actually means okay. So, how do we go about doing this okay and the procedure followed is very simple.

So, first what you do is all of us know that you know if I take like say a molecule present in block 2 and a molecule present in block 1 and if they are separated by a distance d or you know or x whatever right, the separation distance I know how to write an expression for the van der Waals force of attraction between the 2 atoms okay one present in each of the blocks right. Then what we will do is we will consider a disk like element.

Disk like element could be something like this okay. So, this is a thin disk okay of some dimension okay and then we will calculate what is the interaction between an atom and a disk

like element that we have considered in block 2 okay. Then that is a step 2 okay, step 3 would be what I will do is I will integrate the van der Waals interaction between this and you know the disk like element that we have considered over the entire volume to get an expression for the van der Waals force of interaction between an atom and the entire block okay.

That is your step 3 okay, then fourth step what we are going to do is we are going to assume that I am going to consider a thin section and then have this molecule embedded in that thin section and then again do another integration essentially to get the van der Waals force of interaction between this block and this block okay, that is the procedure okay, start with interaction between 2 atoms present in each block.

Then interaction between the atom in one block or a molecule in one block and a disk like element, third step is to get an interaction between you know this molecule and the entire block then the block, block interaction okay, that is the typical procedure right.

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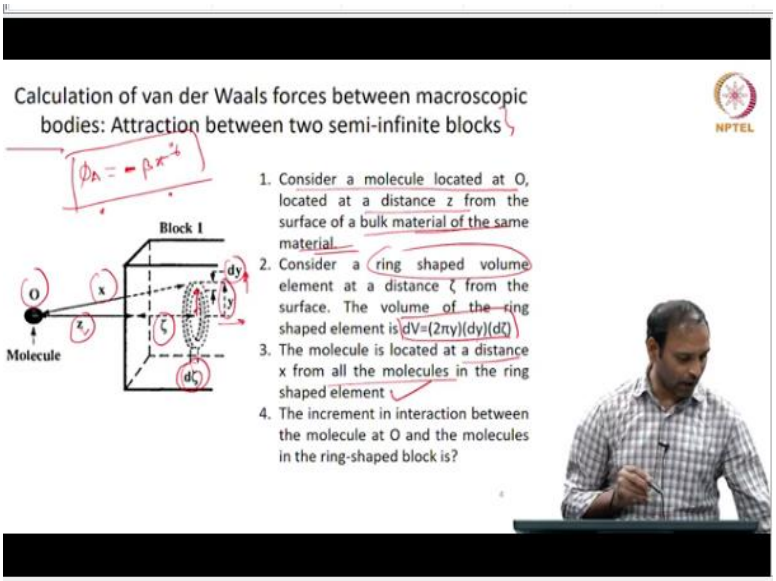

So, for that what we will do is we will do some simple. So, the interaction between the atoms we already know right. So, we know that phi a or phi van der Waals interaction would be something like some - beta times x bar - 6 right. We already know what is the van der Waals if I were to take one molecule here and maybe another molecule there okay, the van der Waals interaction between the 2 is given by this right.

That is going to be minus because of the attraction right. Now what we do is we have a molecule here and I have a disk like element okay and that disk like element is so the this

distance y okay is the from the center okay what is the this distance okay, that is your y okay and the thickness of I know the disk is dy okay, this the distance between the surface of the block and the molecule is z.

And I am assuming that this particular element is at a distance zeta from the surface okay. So, this particular disk like element is located somewhere inside the block right. That is what we have written right. So, consider a molecule located at O okay at a distance z from the surface that is this distance okay and of course the assumption here is that block 1 and block 2 are made up of the same material right.

That goes without saying that when we talk about when we are trying to derive an expression for the van der Waals force of attraction between the 2 blocks we are assuming that the block 1 and block 2 are made up of the same material okay. Of course you can you know work out and you can think about derive an expression for 2 blocks if the materials they are made up of dissimilar material.

But for this particular class we will assume that they are made up of the same material okay, then we are going to take a ring shaped volume element okay as I said it is at a distance zeta from the surface. Now and of course there are 2 thickness right okay, one is the thickness you know along this zeta other one is a thickness along this y direction right. And the 2 thicknesses are d zeta and dy okay.

So, therefore we know that the volume of this you know ring shaped element that we have considered is dV is equal to 2 pi y dy into dz right, that is the volume of the ring shaped element that has been considered is that okay right. Now if you look at any molecule okay, if you look at any molecule that is on this disk I can say that every molecule on this disk okay. Because we are we are taking a disk which is of very small dz and dy I can assume that every molecule is at a separation distance x right.

So, I can say that, so therefore the this particular molecule is located at a distance x okay from all the molecules in the ring shaped element right, I can make the statement right, then what you can do is I can actually write up an expression. So, instead of considering 2 single molecule the fact that I have considered a molecule you know in one block. And a ring shaped element I can write an expression for what is the increment in the van der Waals force

of attraction between this molecule and all the molecules that you have in the ring shaped element right.

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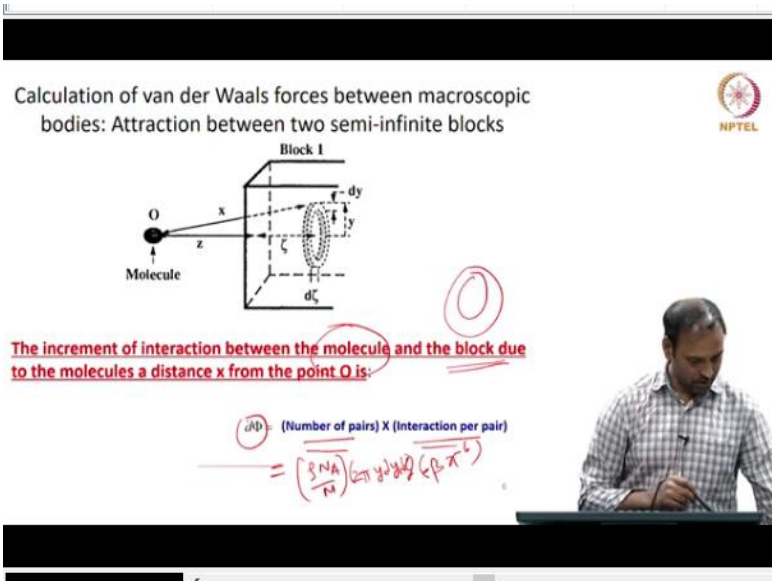

We can do that. So, that I can write it as d phi is equal to what do we write the increment in the van der Waals force of attraction okay, when I have considered a molecule in one block under ring shaped element in the other block instead of 2 molecules present in each of the blocks that for d phi is going to be number of pairs of interaction multiplied by interaction per molecule right okay.

That is what we are done right, that is number of pairs multiplied by the interaction per pair is what is going to give you what is the increment in the van der Waals force of attraction right. So, then how do we calculate the number of pairs. So, we had defined rho N_A by M right, what does that give you, that is the number of atoms or number of molecules per unit volume right, that is what it will give you.

Okay multiply it by the volume okay, that is 2 pi y dy into d zeta okay, that is the volume of the ring shaped element that we have considered multiplied by the interaction per pair is going to be - beta times x power - 6 right, that is the increment in the interaction between the molecule and the block okay and in this case molecule and the ring shaped element that we have considered right okay.

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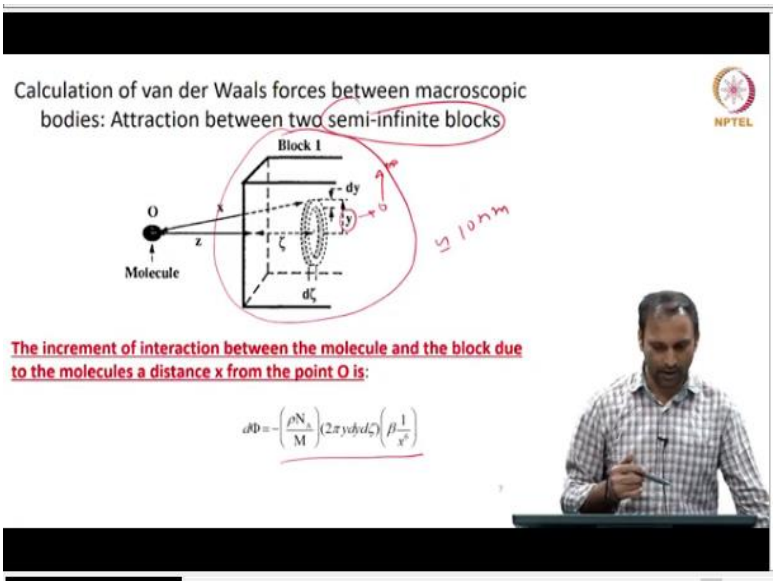

That is what this is right, yeah, yeah, this is attraction towards the block, what is that yeah I mean depending upon so, the question is there is the attraction towards each other, yeah both the block too I mean. So, one okay so what you can also imagine. So, this is the attraction between the blocks right. I mean are you saying that you know if I have block 1 is it that the block 1 drags the particles towards block 2 is that what you are trying to ask or which angle no, no see.

The simple concept that we are trying to do is I mean I think there is a reason why people considered this ring-shaped element because you know your x is going to be identical right, that is the reason why they have considered okay. So, now so when you say so what you are trying to say is that you know is it that, so your question is it that this block is going to be moved in some other direction is that what you are trying to ask, no correct. Why 2 forces, suppose there is a ring then equal in opposite direction there will be 2 particles right okay, correct.

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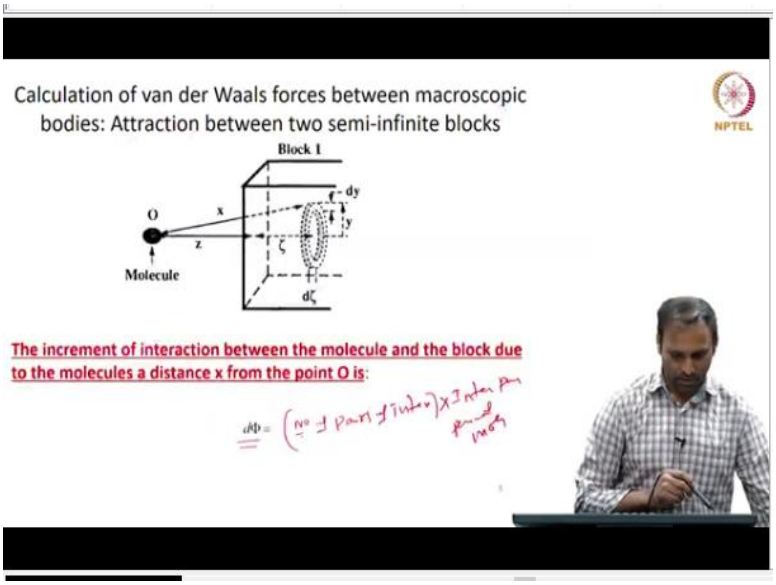

Now in this case what we are trying to do is I **i** have a molecule one here and there is another molecule one there, what is the force of attraction between the 2 okay. Next there is one here and another molecule of course there right because there are several molecules in the ring okay. So, we are talking about the force of attraction between the molecule one present here and a molecule there, that is about it okay.

And then we just adding it right, that is what we discussed you know when we talked about the van der Waals you know interaction between macroscopic particles, all that we are trying to say is that look it is the interaction between every atom or a molecule present in one with the every molecule or an atom present in the other one okay. So it is the mutual interaction between you know the molecules in each of the particles.

And then the pairwise addition okay, in that connection it is an attraction towards each other okay, that is what I would say at this point yeah right. So, we know how we wrote this up right. Now what I want to do is I want to calculate the van der Waals force of interaction between this molecule and all the molecules in this block okay. So, what do we do for that.

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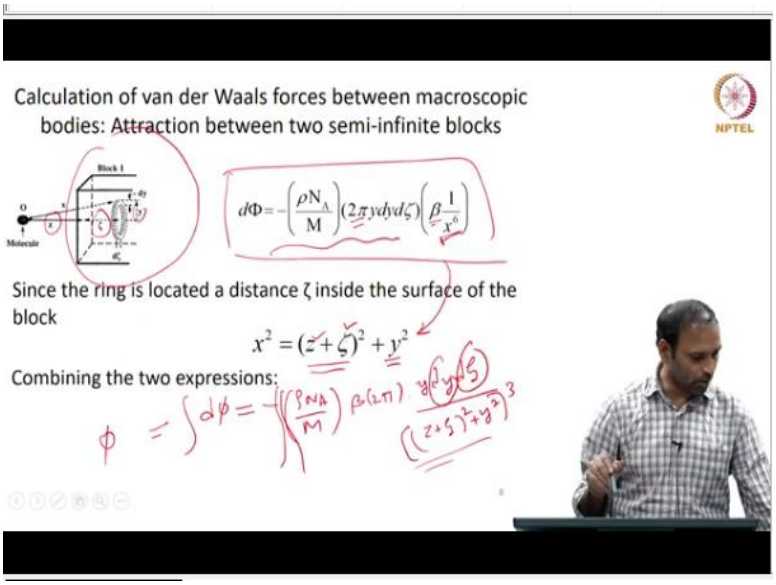

Okay so, we know that so this x right, this x is the separation distance okay and we know that and x as I said for every atom or a molecule present on the disk because we are considering a very small disk, this x is going to be same and I can relate x to the other distance that we have right, you have z here, zeta and y. Therefore your x square is going to be z + zeta whole square + y square okay.

Therefore combining these 2 what I can do is I can write d phi is equal to - rho N A divided by M okay and I am going to take this constant beta and you have 2 pi okay, you have y dy d zeta divided by instead of x power 6 I am going to write as z + zeta whole square + y square to the power of 3 right. We have done that, now I have to integrate this expression to get what is the total van der Waals force of attraction between this molecule and all the molecules in block 1, okay.

So, that is going to be a double integral right, because you know you have dy and d zeta here. So, I would have to do a double integral and because the variation in the y and zeta are not dependent what I can do is I can do integration one by one.

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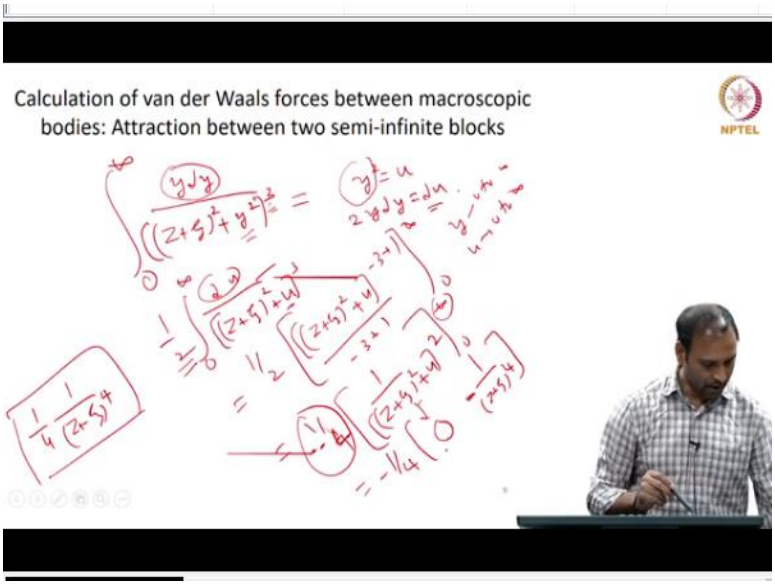

So, what I can do is I can consider the first term that is y dy okay divided by z + zeta whole square + y squared to the power of 3 okay, I can do the integral okay from you know the distance I mean y can go from 0 to infinity right. So, if I do that I can substitute for if you say y square is equal to u 2 y dy is going to be du. Therefore this becomes 1 over 2 du divided by z + zeta whole square + u to the power of 3 right okay.

And that is between 0 to infinity, therefore this becomes 1 over 2 if I integrate this, this is going to be z + zeta whole square + u into - 3 + 1 divided by - 3 + 1 okay 0 to infinity that is equal to 1 over 2 there is a - 2 here that I will become - 4 1 over 4 and at infinity you know you have 1 over z + zeta whole square + u square right and 0 to infinity. Therefore this becomes 1 over 4 into 1 over z + zeta.

At infinity this becomes 0 right okay 0 - 1 divided by z + zeta to the power of 4, therefore you know if I do the first integral what I get is 1 over 4 1 divided by z + zeta to the power of 4 is what I get that okay yeah. So, you have yeah first is 0, first term is going to be 0, that is what is sorry okay first term is going to be 0. So, one more thing why are you integrating from 0.

Because I mean I have considered a ring shaped element okay and if I say that you know the coordinate system I am going to start with the center of the disk you know the coordinates are 0 0 okay it can be infinite in the other direction, we are trying to calculate for the whole block yeah, yeah. So, y is the see if you go back here right, see that is your y right. So, I can have a very small disk okay.

So, essentially you can your y could vary from 0 when you are at the center and you it can go all the way up to infinity yeah, should be the yeah I mean so all that we are trying to say that these distances we are thinking about is of course if you see we are talking about when you say semi-infinite blocks okay. So, all that we are trying to say is that look I see we have been saying that van der Waals force of interactions typically.

If you work with any case where the van der Waals force of interaction we said that you know + or - 10 nanometer you know up to over 10 nanometer is when you should bother about the van der Waals force of interaction right. That means any distance more than that it does not matter okay. But for the sake ease of derivation what you are doing is you are assuming that okay it is a semi-infinite block.

That means the dimension that your of the block that you are considering are much, much larger than the separation distance that you are trying to deal with okay. That is the only significance here okay. So, similarly I can do the yeah, you have a question, we can go back, yeah, yeah, yeah, one more slide, okay yeah. So, is this okay everybody gets this point right, that essentially is the number of pairs multiplied by you know the interaction per pair, that is okay right.

And then all that we are doing here is your separation distance is related to your you know z zeta and y through this relationship okay. And then therefore and I said if you want to the interaction between this molecule and the entire block okay I would have to do a double integral right and because the variation in y and zeta are independent I can do integration one by one okay. So, we considered one of the you know the y dy divided by z + zeta whole square + y square to the power of 3 right and you can substitute for you know y square is equal to u 2 y dy is equal to du right.

And therefore I can instead of y dy I can substitute dy divided by 2 should be done here okay, divided by z + zeta whole square + instead of y square I am substituting u okay and if I integrate this I get z + zeta whole square + u to the power of - 3 + 1 divided by - 3 + 1 okay. Therefore I have a 1 over 2 and 2 - 1 over 4 factor here okay and therefore I have 1 divided by z + zeta whole square + u whole square.

And when you have y is infinite this becomes 0 - 1 divided by. So, in this case you know when you say y goes from you know 0 to infinity u also goes from 0 to infinity right okay, therefore when u is infinity this becomes 0 - 1 over z + zeta to the power of 4 okay. So, that is we essentially end up with this okay.

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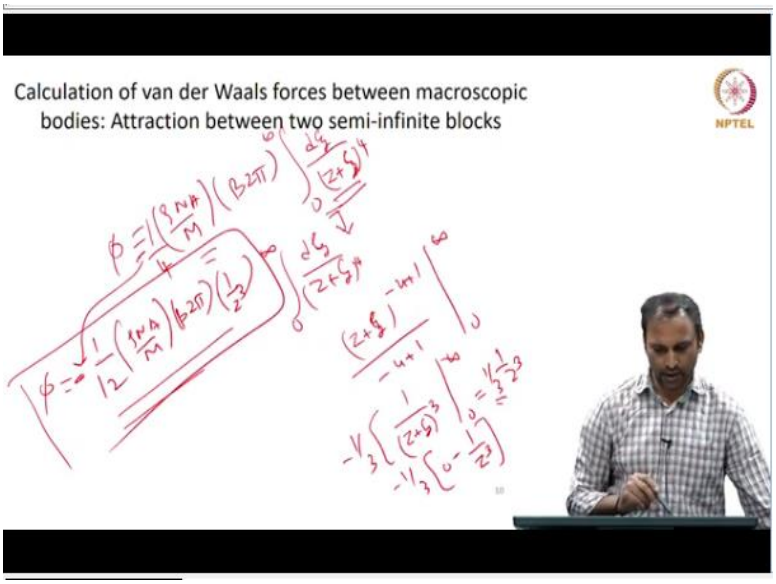

Similarly I can do the next one now. So, therefore now I have done this. So, therefore your phi is going to be okay I will just write those things back rho N A by M into beta 2 pi okay. Now integral from 0 to infinity d zeta divided by z + zeta whole to power 4 right okay, because see we had we were doing a double integral okay. So, this I am retaining this okay and the result of you know integrating this okay would be right.

And of course I have 1 over 4 right, yeah, yeah, yeah. This is also negative here sorry, yeah okay let us do this derivation. So, 1 over if you do in a similar way so integral of d divided by z + to the power of 4 okay 0 to infinity if you do that so therefore this becomes again z + zeta - 4 + 1 divided by - 4 + 1 going from 0 to infinity, is it okay yeah.

Therefore this becomes 1 over z + zeta whole cube 0 to infinity and I have - 1 over 3 here okay. Therefore your phi is going to be again. So, this - 1 over 3 into, this becomes 0 - 1 divided by z cube, is it okay. So, therefore your phi becomes there is 1 over 4 minus, minus will become plus right, this is going to be 1 over 3 into z cube. Therefore if I substitute this back here. So, I have 1 over 12. 4 3 is a 12 okay rho N A divided by M into beta 2 pi into 1 over z cube with a minus yes, because the minus sign is carries okay.

So, that is the, so this is now what we have done is this is the interaction between the molecule one that was here and all the molecules of block 1 okay.

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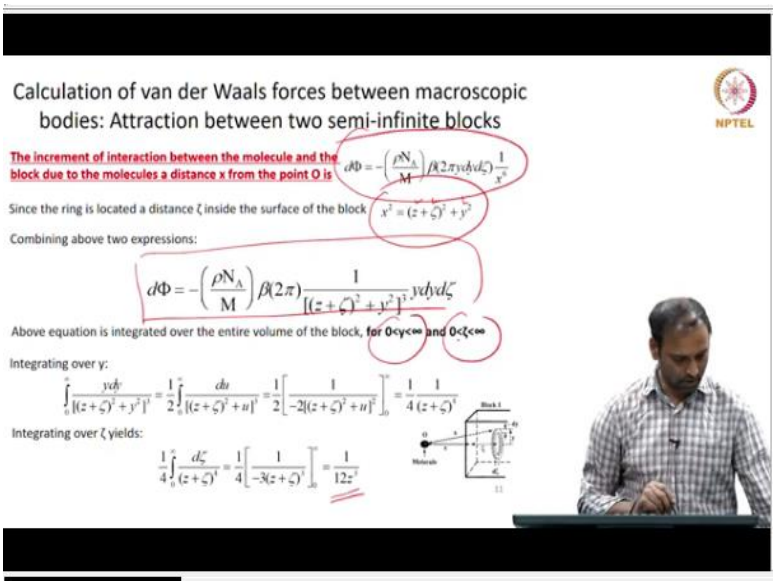

Okay that is what is actually done here okay. So, we had this as an incremental in the interaction so we wrote x square in terms of you know the other distances okay, the combining the 2 expressions we wrote this and then in doing a double integral okay for varying y from 0 to infinity and zeta from 0 to infinity we essentially end up with you know an expression like this right.

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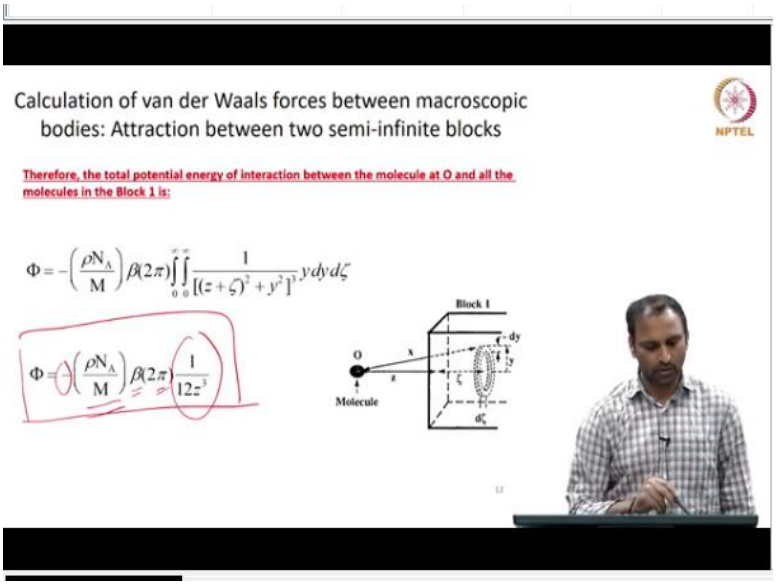

That is in the end that is what we have okay, that is again attractive there is a negative sign here okay and that is the number per unit volume okay and beta is the coefficient and we have 2 pi and 1 over z cube.