Colloids and Surfaces
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Lecture - 24
Depletion Interactions

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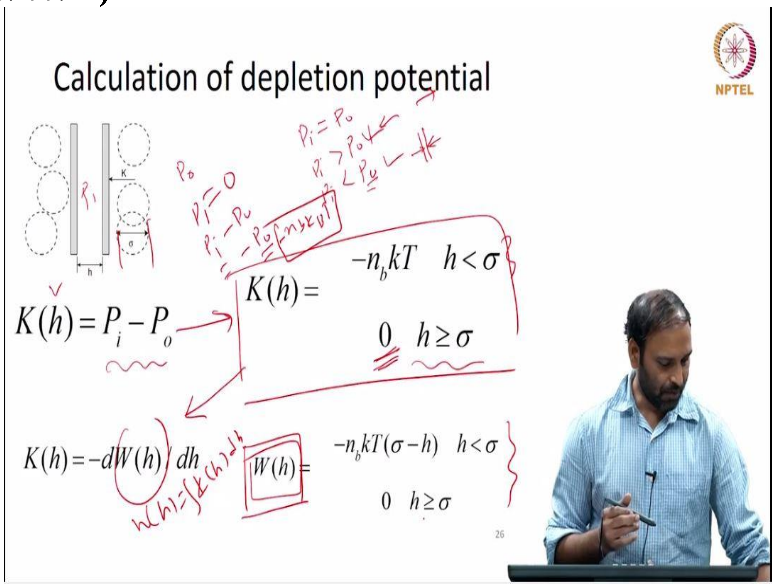

We will continue with deriving an expression for depletion interaction. So, what we had done in the last class was this we took a very simple case of 2 plates which are embedded in a polymer solution and we found out what is the depletion interaction between the 2 plates. This is one of the simplest geometry and it will you know help you to calculate this calculation is fairly simple. So, what we said is that, if you have 2 plates which are separated by distance h then the force that acts between the 2 plates P's.

We wrote it up as Pi - Po where Pi is the osmotic pressure force in the region between the plates and Po is the osmotic pressure force in the region outside the plate. And I mentioned that depending upon you know whether P i = Po or P i is greater than Po or you know Pi is less than Po the plates will be pulled towards each other in this case in this case the plates will be in that not in this case. If this is a case then the plates would be pulled towards each other because osmotic pressure in the interior is less than the osmotic pressure outside.

The you know the plates would attract and if you have a case where Pi is greater than Po then the plates to be pushed apart and Pi = Po is the plates will continue to exist in whatever configuration they are in. And now, because we have you know, when we are talking about depletion interaction, we have been saying that, when the distance of separation is larger than you know the size of the you know the particles in this case or the polymers in this case.

The depletion you know force are 0 that means, in this case, Pi = Po when the distance between the plates is much much larger than you know sigma, this Pi = 0 Pi = Po therefore, the depletion interaction becomes 0. But for any distance which is h less than sigma your Pi becomes 0, therefore, Pi - Po = - Po itself. And where P o is the osmotic pressure force which is governed by the constant which is determined by the concentration of the polymer that you added to the sample.

And that becomes n b times $k_B T$. That is what we have. That is by the definition of osmotic pressure force. So, we know how we got this, starting from this, then, to obtain the interaction potential W of h, that is what is interested, that is what we are interested in and W of h is the interaction force per unit area in this case. And you can just simply integrate, you know, W of h is going to be integral of K of h into dh. And that is how you obtain this expression. So, it was a fairly straightforward derivation.

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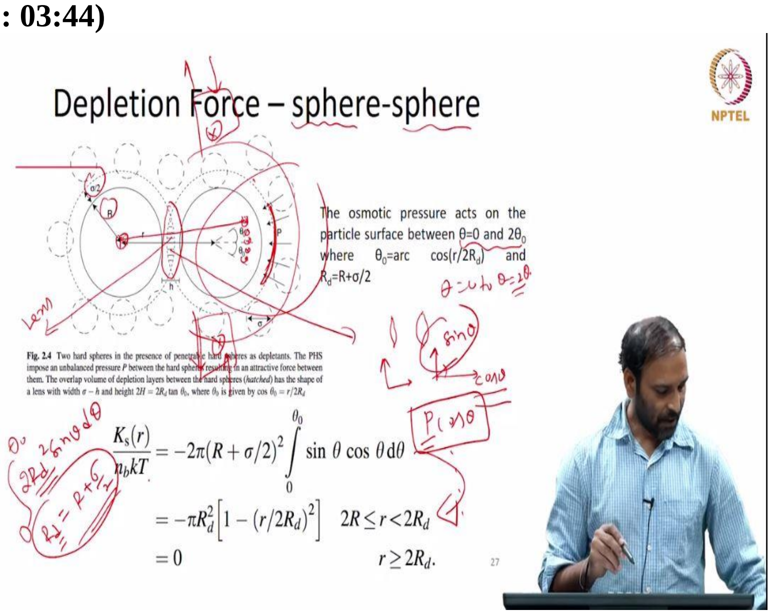

However, if you go to you know, other geometries like you know, if you want to calculate what is the depletion interaction between spherical particles, then the derivation becomes a little bit more involved. And in this case, so, now, if you look at this spherical configuration, so, you have, this is the, the, overlap volume, or the, it is the this is the the lens that is formed, this is the lens that is formed when there is a overlap of the depletion layers.

Now, in the previous case, we talked about whether the pressure is 0 here and you know, what is the pressure there? But in this case, it turns out that, you know, the osmotic pressure force does not act all across the surface. That means, if I take one surface here, and one point here and one point here the concentration of the polymers in this region is going to be same? That means there is not going to be any osmotic pressure either attraction or repulsion because of the imbalance of the osmotic pressure, it would not act so it only acts in certain cone.

And so, typically, it acts in a cone, which is, you know, theta = 0 to theta = 2 times theta 0, where the magnitude of this theta 0 depends on the overlap itself. Is there a higher overlap or lower overlap. That means, it will essentially depend on this lens volume. Whether the volume of the lens is something like this, or something like that? Depending upon the extent of overlap, your theta is going to change. Now, to calculate depletion force, what you should do is, I am going to take a point there, I am going to take so I am going to take multiple points.

In that in the cone region and I would like to calculate I am going to join them then go to calculate what is the pairwise interaction. It turns out that if I do like that, and if I you know, it turns out there are no I will have 2 components one is the horizontal component and the vertical component I would have to add them up. Now, it turns out that the vertical component will cancel each other, what I mean by that is, if this is the, line of force that connects the 2, you know, points.

So, therefore, I am going to have a horizontal component which is going to be the cos theta component and vertical component that going to be sin theta component, because of the symmetry of the problem, the sin theta component is going to cancel each other. The only contribution that will is going to come is going to be because of the cos theta component, if P is the osmotic pressure, then P cos theta will give you the component of the force.

That is acting you know, across you know the 2 point that we are considered and the summation of that is what is going to give you the total osmotic pressure force. So, it is a little bit involved you know, like the previous case, it is not as simple you know method to do it people have worked it out if you want to read a little bit more than you can go back and look it up it turns out that you know, the surface or which you know, this the surface that is you know, this particular surface or which the depletion forces are acting.

You know is given by something like 2 times Rd square sin theta into d theta and with this Rd is given by Rd is = R + sigma / 2 there is a effective volume of the particle where R is the radius of the particle that we consider sigma / 2 is the half the size of the polymer molecules. That will be the effective size and it goes as to Rd square sin theta into theta if you want to get the overall force I would have to I can integrate this over all angle going from 0 to theta, theta 0. So, from that you can actually get what is the expression for the force that is acting between the 2 spherical particles.

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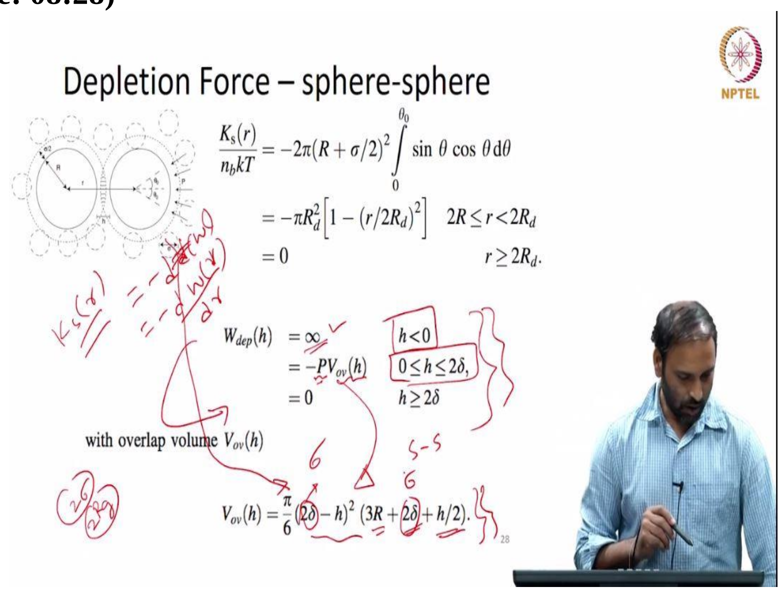

And then once you know the force, you can actually get the depletion potential again if again you know in this case, it is represented K of r if you know this, that is going to be again minus d of W or you know, W of t is going to be minus or d of W of d or in this case r divided by dr. So, I can integrate that and then so, essentially you will have a expression similar to what we have seen. So, for any you know distance less than 0 you know you go to have the repulsion that is come because of the overlap of the electron cloud that is this.

And you are going to have an osmotic pressure times the overlap volume, when the distance is in this particular range, and this overlap volume we can actually get it as you know, if you do the derivation all that. So, you will get the overlap volume, which is something like the grade depends on the extent of overlap, it depends on this is the separation distance. So, h is essentially the separation distance, but it is the surface to surface separation distance.

And R is the size of the particle 2 times delta is the size of the polymer molecule that has been considered. So, you will see that in a lot of cases, people kind of they use sigma or Rg you know R you know, so, in sigma / 2 times sigma is the size in some cases you will take the size to be 2 times Rg and stuff like that, but you just have to look it up you know what exactly each of these terms mean in this case 2 times delta is same as sigma that is the if you look at this nomenclature, sigma is same time the same as 2 times delta again this is going to be sigma itself, that is the expression.

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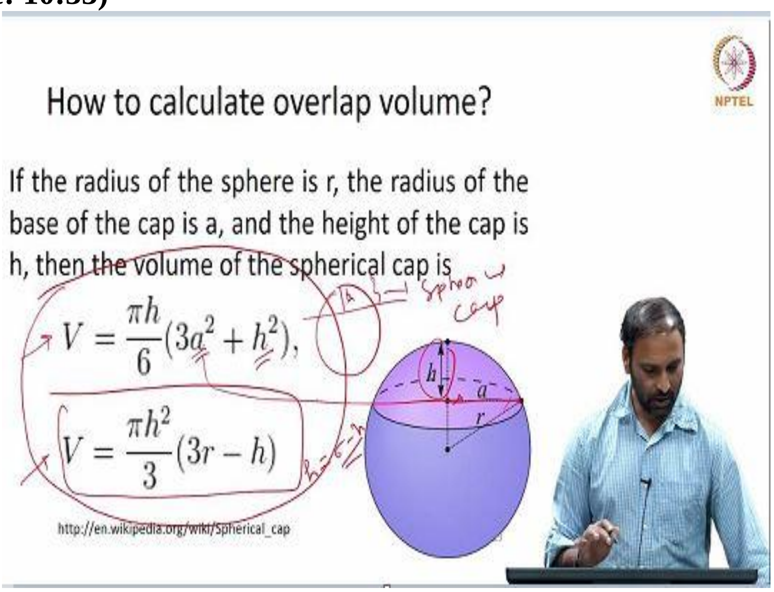

Now, again, so, the other way to think about this calculate the overlap volume is going to be you know, there are expressions available for what is the so, if I have a spherical cap, if I have a sphere, if I cut this up I am going to be get what is called as a spherical cap. Now, there are expressions that are available for calculating what is the volume of the spherical cap it depends on you know, this height h that is this height h, it depends on what is the you know the when you cut the sphere you get a circle, you know.

So, you have part of the so, you will have again a circular surface that is the area of that circle and h is the separation distance. Now, if you look up the depletion volume, what you actually have is 2 spherical caps that are put together. So, there are expression that are available for calculating how does this you know the volume of the spherical cap change you know with the height or the radius of the particle.

And it turns out that of course, in this case this h you know is going to be the height of the lens that you get is typically is going to be sigma - h that is the height of the lens that is this particular. So, this the half of this distance is going to be sigma - h. And similarly, there are expressions you can actually calculate what is going to be the so, essentially, if I know the extent of overlap, I can actually use an approach like this.

Where there are expressions available for what is the volume of the lens that is formed between the 2 spherical particles as the particles overlap. And you can also use an approach like this also to calculate what is the depletion volume? So, the important point is in any calculation that involves you know depletion interactions, only thing that you have to worry about is how do we get the overlap volume. So, as long as you have a method of obtaining that and as I said it is much simpler to get an expression for overlap if you look at simple geometries.

However for sphere-sphere case and for other cases, it becomes a little bit more complicated. And as long as you have a approach of getting it that is what will help you to calculate what is the depletion volume.

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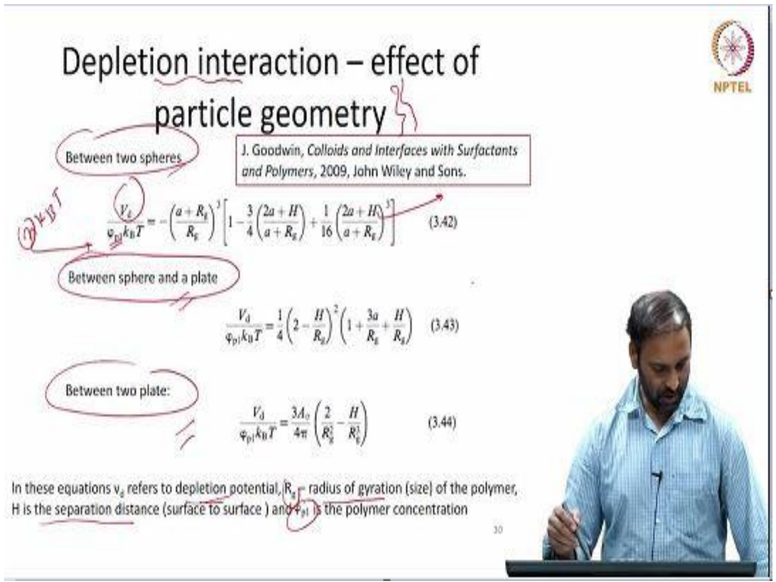

These are there are some again literature reports where you depletion interaction does depend on the particle geometry. So, there are 3 expressions that are given 2 spherical particles spherical particle and a plate and 2 plates. So, in this case, h is the, separation distance h is the separation distance on a surface or surface separation distance and Vd is the depletion volume, Vd is the depletion volume Rg is the radius of gyration of the part the you know the polymer that is added.

And there is a term called phi p l p l stands for polymer phi is the volume fraction of the particle of polymer that is poured. So, we used to have a n times k_BT where n is the number of number per unit volume? So, you know, of course, I can also express n also in terms of the volume fraction of the polymer, so, that is phi p. And, of course, a is the, characteristic dimension of the particle that we are considering. So, this is an expression for a sphere-sphere, the sphere plate and this is for 2 plates.

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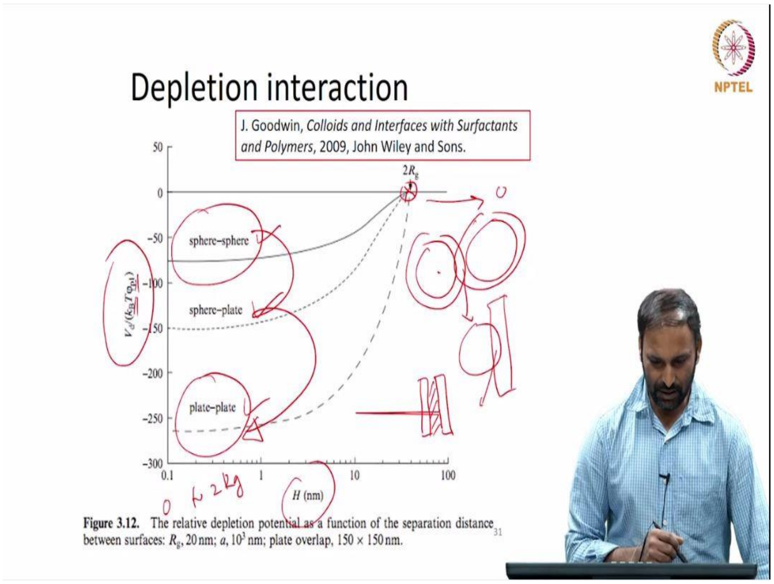

So, an interesting observation if you plot these 3 quantities, it turns out that you know the in this case V d is the depletion potential. So, the depletion potential that is scaled with the volume of the polymer multiplied by k_BT it shows a trend which is like this. Now we are mentioned that for any distance greater than 2 times Rg your depletion interactions are not present that means is essentially 0, but if you look at the distance between 0 to 2 times Rg the trend looks something like this this is for sphere-sphere case sphere-plate and plate- plate.

So, any thoughts as to why this why the variation is in this way. So, simple explanation is more overlap volume that means, if I look at a 2 plates like this if remember the entire area between the 2 plates was contributing to the overlap volume. However, if I look at 2 sphere case there is only a small area that is between the 2 particles was contributing to the overlap volume and of course, if I take the 2 case of sphere and a plate, again the overlap polymer is going to be something in between.

So, in this case everything else has been kept constant the concentration of the polymer is kept constant the particle you know and the temperature is the same. So, if you just plot the scaled depletion potential as a function of separation distance, it turns out that the strongest attraction would be felt for the plate, plate combination and the least you know for a given separation distance the least you know attraction would be felt for the sphere-sphere.

You know plate this is solely because of the effect that comes from the fact that the depletion volumes for the 3 cases are different and it increases in this order least for the spheres. The next highest is going to be sphere-plate and the highest you know the overlap volume is going to be further the plate-plate combination. So that is about depletion interaction.