Colloids and Surfaces
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Lecture - 23
Colloid Polymer Mixtures: Depletion Stabilizations

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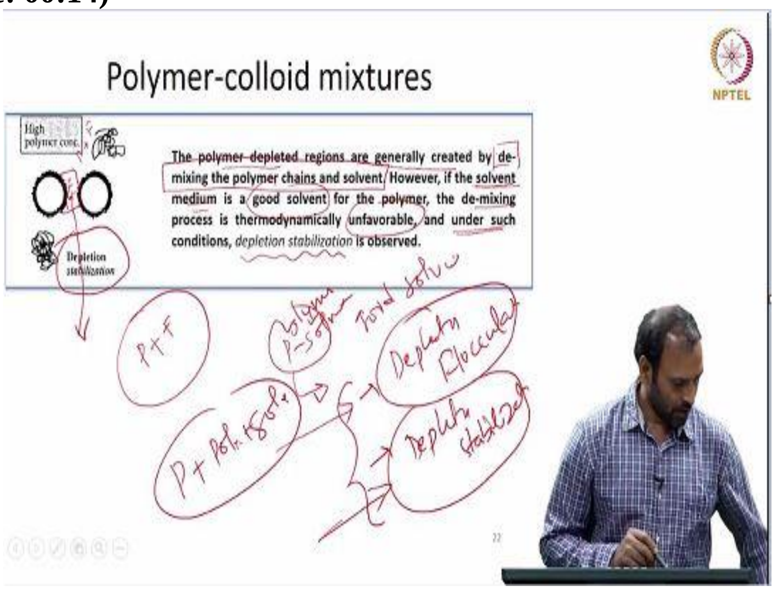

Other concept which is what is called the depletion stabilization. Now, when I say that so, we mentioned that for the depletion attraction to occur the polymers have to more of the gap. Now the polymer depleted regions they are generally created by de-mixing of the polymer chains and the solvent could you understand this statement so, when I said that the polymer will go to the gap i can think about that as a de-mixing initially the solvent and the polymer everything was in a mixed state there was a homogeneous solution.

Now, the fact that in the previous case you know the particle so, the polymer left the gap you have a region of pure fluid and a region of polymer plus fluid you can think about this as a de-mixing process. So, therefore, the polymer depleted regions are generally created by de-mixing of polymer chains and the solvent. However, if the solvent medium is such that it is a good solvent for the polymer that means, if there is a favorable interaction between the solvent and the polymer.

This de-mixing process becomes unfavorable that means, it is be very hard or it will be very difficult to or it will be practically impossible to move this particle out of the gap. That means, so, the region between the particles will continue to have polymer so, because the de-mixing is what should happen only then the particles can come sufficiently close. But however, if somehow this de-mixing is prevented then what will happen is you will always have the region between the 2 particles will always be having particles polymer plus the fluid.

And such a case is referred to as what is called depletion stabilization. So, depletion stabilization is a case where the formation of depletion zone is not favored so, that is, you have some question? No, so, I think a look as it is mentioned, you are, it really depends on the polymer solvent combination that you are using, whether depletion stabilization will occur or not, it will depend on the polymer solvent combination. Because, I said that you know, if you have a case where the polymer molecules are happy to be in a solvent that is a good solvent case. Now, if you have a good solvent too.

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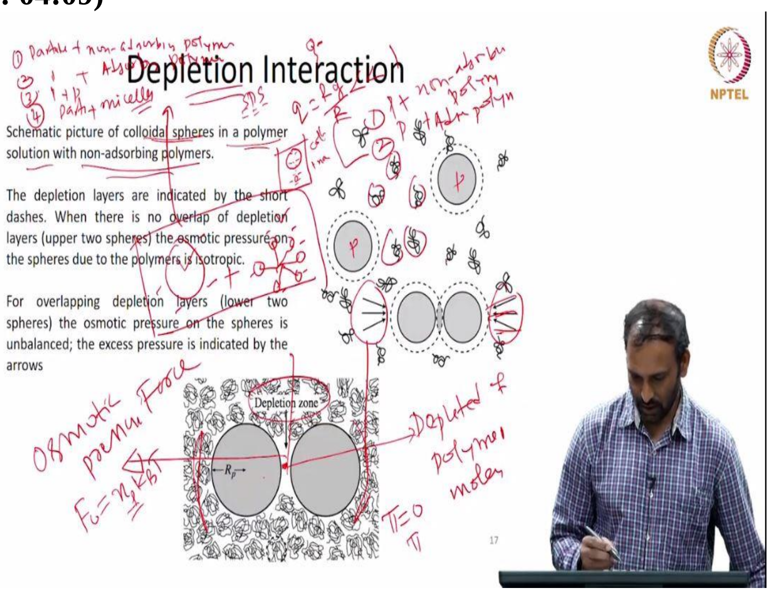

So, one way of thinking about you know, this, like, let us go back to this carton. So, if you look at this depletion zone formation.

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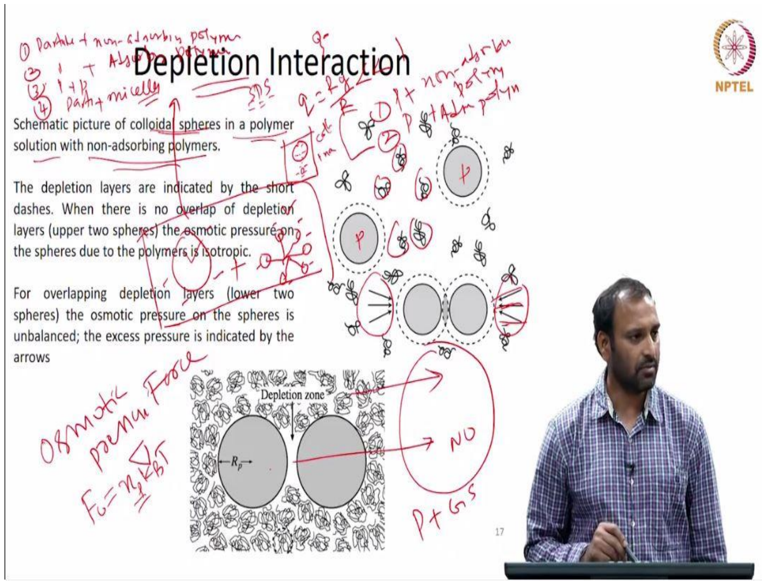

So you can other way of saying which it look, I have I am able to create regions of no polymer and regions with polymer. So now, there are cases where such you know, things are not favored. So, one of the case in which this does not happen is a polymer good solvent combination so that is. What is the reason for this depletion stabilization? I think this does not depend on the particle concentration it depends solely on the particle solvent, polymer know solvent combination that you use. So, let me put another thing. I want to make this clear.

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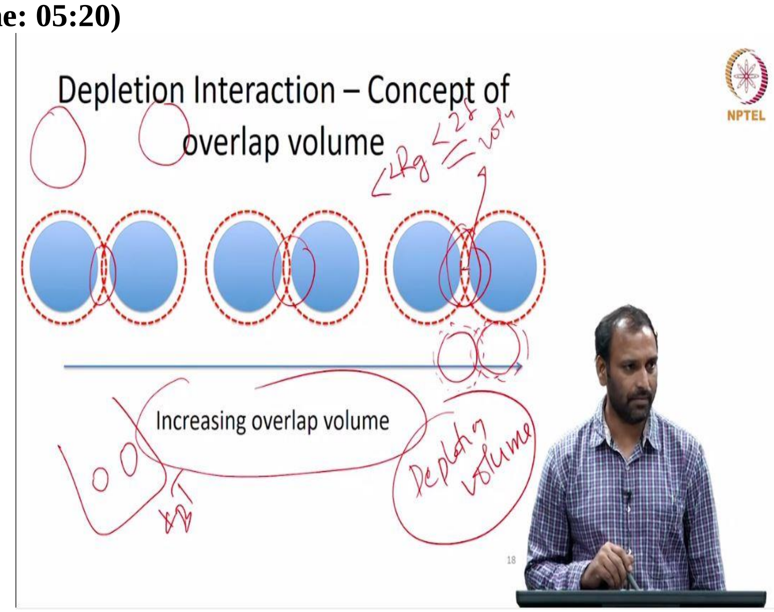

When I say that, when you? Let this carton? So I am, when I was explaining I said that. You know, there is a depletion volume, you know and it you know it kind of the depletions volume increases is what I mentioned? So, what brings the particle together? Or what you know, so of course, these depletion interactions will kick in only when the particles sufficiently close. Now, what brings them together to such distances? Again, Brownian motion, you are not, externally doing anything

You have particles in a fluid, they are jiggling around. And they because they are free to move, because they have thermal energy, they are free to move. And if it so happens, that because of this no chaotic motion that they are exhibiting, if the distance between the particles, you know, could reduce depends, it depends on the particle concentration, it depends on the diffusivity of the particles, all of that.

Now, if you if there is a case where the separation distance becomes smaller than this, you know, 2 times Rg or 2 times delta, is when all these depletion effects will kick in. Any question with so, we looked at? Depletion flocculation. And we also looked at depletion stabilization so far. Any questions with these 2 concepts? So in one case, so again, this is another case you know, again, to read, you know, this read what I have said.

So, this is a case where the addition of polymer leads to destabilization is again a case where the additional polymer does lead to stabilization. Again, it depends on the polymer plus particle plus solvent combination that we are trying to use.

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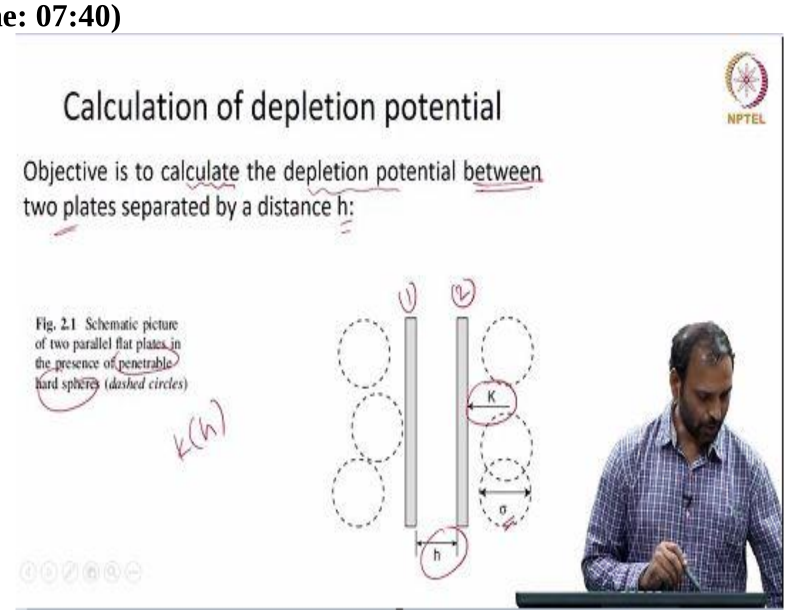

We can think about get back to the simple way of deriving an expression for depletion potential we will take a very simple case. And this particular geometry is chosen because again, it is very easy to do calculation. So, the objective is to calculate the depletion potential between 2 plates, which was separated by distance h. And that is plate 1 that is plate 2. And you have, so, these dotted lines that you see you can imagine them to be you know, polymer molecules.

So, they you know, it says, penetrable hard spheres, but you can think of them to be you know, polymer molecules, the size of these molecules is sigma. And h is the separation distance and so, this K is the force between the 2 particles.

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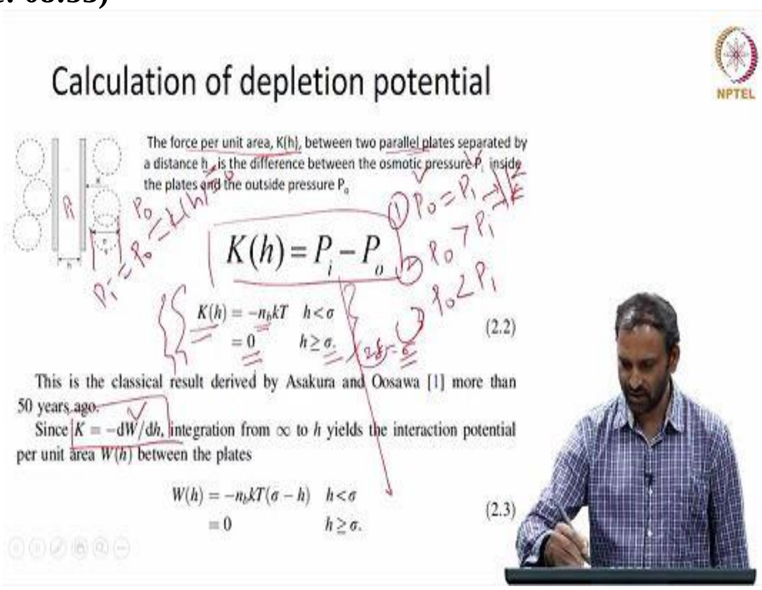

And K is actually the force per unit area between the 2 parallel plates which are separated by distance h. That is the difference between the osmotic pressure inside and the osmotic pressure outside, this is when the, plates is sufficiently far apart when the plates are sufficiently far apart, this Pi would be equal to Po, and essentially your K of h is going to be 0 that means there is no force that is either pushing the, you know them towards each other.

So, if the so, let us look at 3 cases, case 1, where P0 = Pi in this case, you know, there is essentially no force between the 2 because, you know, on an average the number of molecules polymer on either side is the same therefore, you are in the osmotic pressure outside and osmotic pressure are the same and the case 2 could be where Po is greater than Pi that means osmotic pressure outside is larger than Pi in such a case the plates are going to be you know pulled they could be pushed towards each other.

And the third case could be where you know your Po is less than Pi in such a case the polymer concentration higher is in the center is going to be higher than the exterior region that is when the particle pushed apart these are the only 3 situations that can happen. Now, if you have case like this, if you go back to what we wrote up earlier, the depletion potential as a function of h is going to be is 0 if h is greater than or equal to sigma?

That is what we wrote up earlier when this distance of separation between the plates is greater than sigma could be reduced 2 times delta there? So just a change of symbols 2 times in this case 2 times delta is same as sigma. So any distance greater than the diameter of the particles or diameter of the polymers or diameter of these dotted objects? Is distance greater than that your K of h going to be 0 And for any, distance less than sigma is going to be minus n b into k_BT That is what we would like to prove?

Now, that is the expression for the force. So, essentially, the force and the potential are related in this particular way. And so, if you look up this so, what is written here essentially comes from this expression right.

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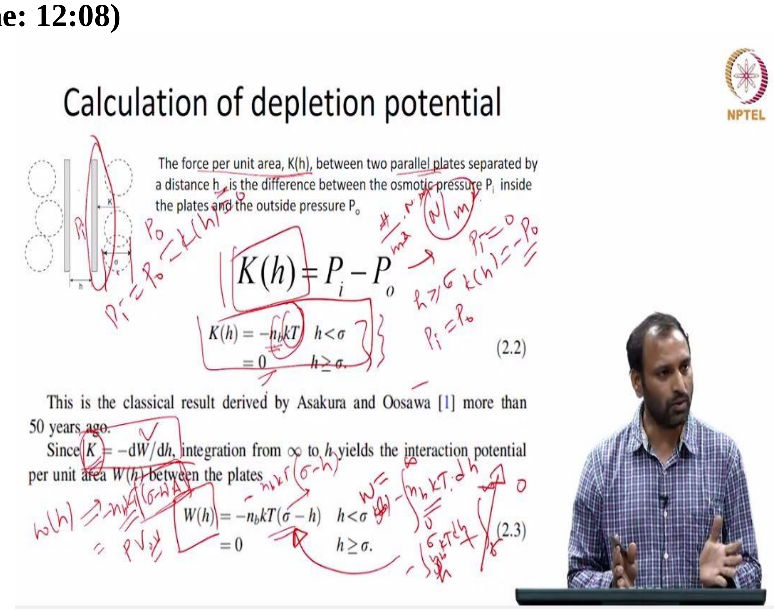

You guys do not if you guys let me just do it again. What is written here actually comes from this expression. Because for any distance h greater than or equal to sigma, for any distance greater than or equal to sigma, your Pi is = Po Therefore, your h is going to be 0 For any distance, which is between h and sigma. Essentially, Pi is going to be 0. Therefore, K of h is going to be minus Po. And minus Po, Po is the osmotic pressure, which essentially is nb times $k_B T$, that is how the osmotic pressure was defined, because it is force per unit area.

Therefore, it is I have only written up n b into $k_B T$ this is this will also have units of force per unit area. So, this will have n b will have number per volume, meter cube $k_B T$ will have units of energy that is newton meter is cancelled, so, it is so therefore, it is consistent. So we know how to write this up. Now and when you want to look at h, when you want to get W all had to do is I know what is you know the dependence of k with h you know, I will just integrate that I would get an expression for interaction potential.

That, so therefore, I need to take this minus n b kT. And that is going to be K of h. So therefore, if you want it is integral from 0 to infinity times dh, if you want W, W is going to be integral of n b times $k_B T$ into dh going from in this case your you should go from 0 infinity. I can split this integral from 0 to sigma. Or any distance of separation h to sigma h could be 0 as well plus going from sigma to infinity the contribution sigma to 0 infinity is going to be 0 because we know that any distance greater than sigma you know the interaction is not there.

So, therefore, this going to be 0. So, when you know work this out minus n b $k_B T$ dh you will get essentially this. So, you had n b kT minus is going to be sigma - h that is what you simple integral. Now, if you look at this term, I have W of h, I said this is the energy per unit area interaction energy per unit area. If I take h to the other side, I can write this as minus n b kT into sigma - h multiplied by A this area multiplied by the separation distance is essentially the depletion volume.

Therefore, the W of h becomes this is P, there is an osmotic pressure force multiplied by overlap volume sigma - h multiplied by A is the overlap volume that will that essentially is the area of the plate multiplied by the distance between the plates that essentially is the volume and depending upon h by overlap volume is going to be change. So, essentially we recover an expression like this.

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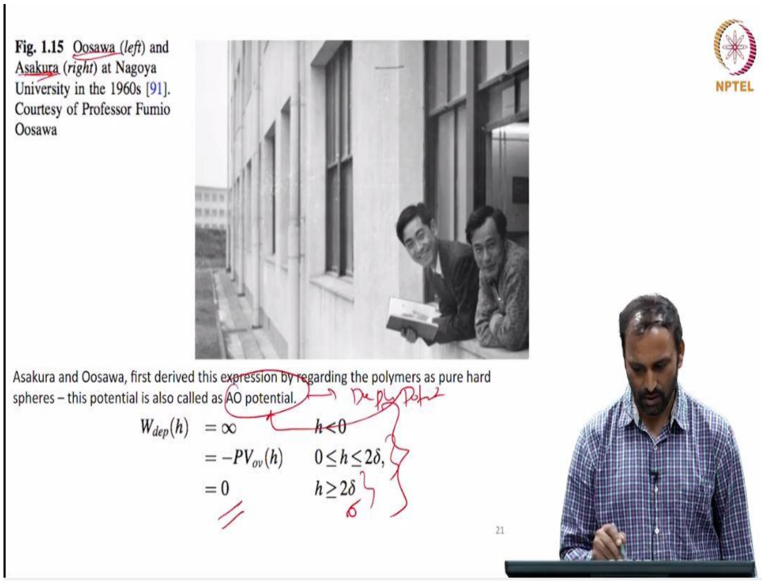

For any distance greater than, you know, 2 delta or sigma you have W depletion is 0. And for any distance between 0 and you know 2 times delta, you have depletion interaction going yes. The osmotic pressure force multiplied by osmotic pressure multiplied by the overlap volume, that is. So this is a simple derivation to think about how you know, the expression for depletion interaction is calculated, so maybe we will stop here.

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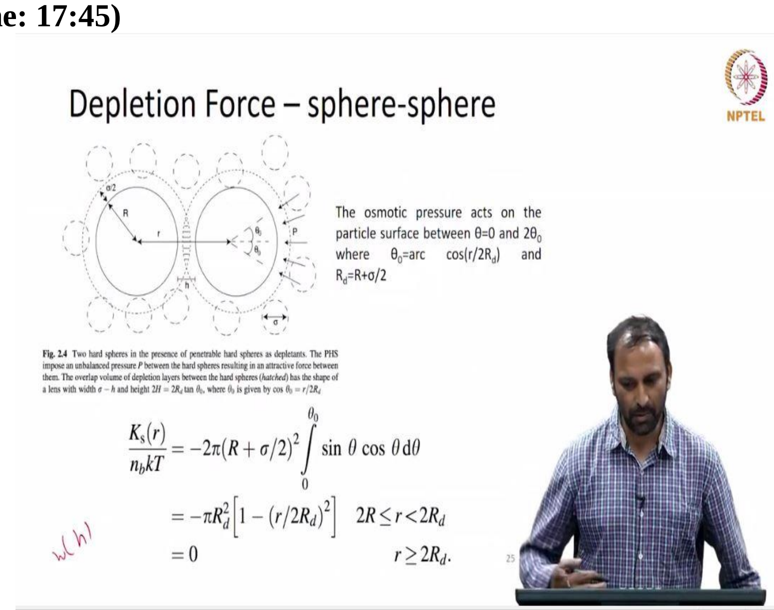

We will talk a little bit about how do people do when you have 2 spherical particles and in a medium, how do people think about obtaining an expression for depletion forces is what we will do in the next class.