Colloids and Surfaces

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Lecture - 22
Colloid Polymer Mixture: Depletion Flocculation

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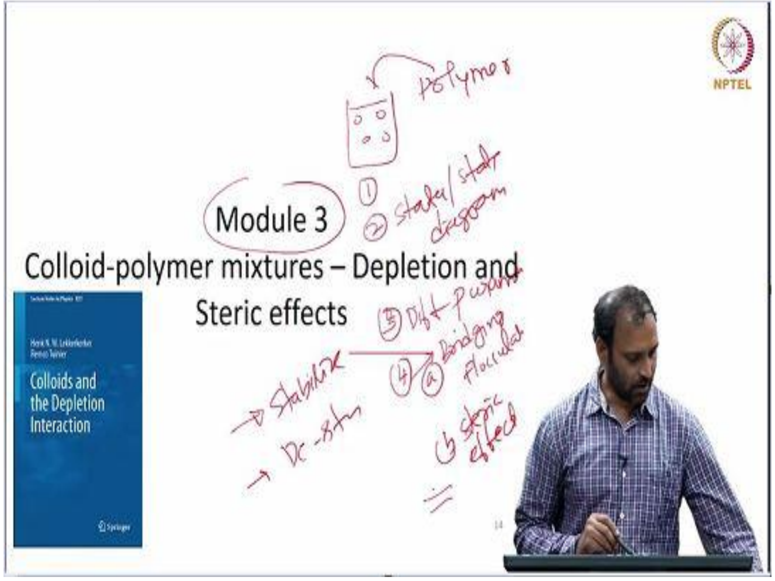

Module 3

Colloid-polymer mixtures – Depletion and Steric effects

Colloids and the Depletion Interaction

So, this is a module 3. What you looked at so far is if you have colloidal particles in a fluid if you add polymers to it we will looked at you know what are the consequences that means some applications where you know such a thing would happen plus we have discussed about different states or the state diagram of the different diagram of the different states that you know form when you mix colloidal dispersions and polymers and we have briefly talked about different parameters that would affect the behavior of colloidal polymer mixtures.

And then we went on to talk about some specific aspects such as bridging flocculation and what are called as steric effects. And we just said that in general addition of polymer can both stabilize as well as de-stabilize colloidal dispersion that is what we have done so far.

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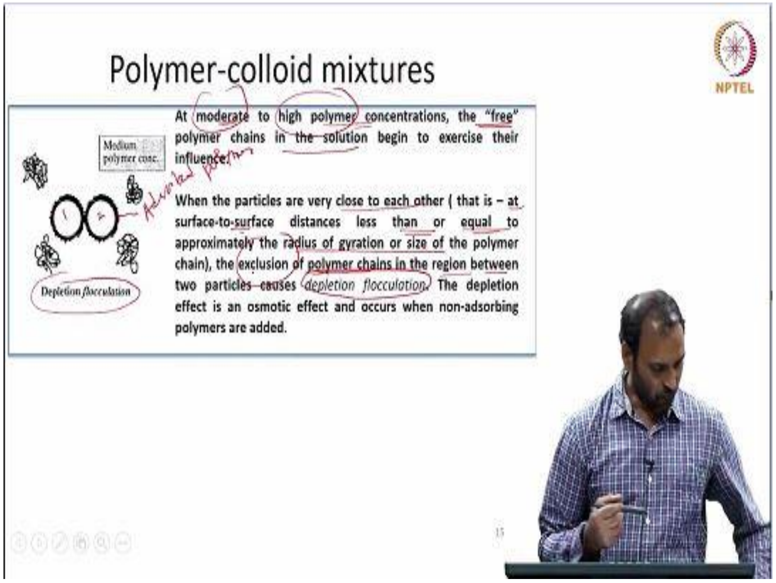

Polymer-colloid mixtures

At moderate to high polymer concentrations, the "free" polymer chains in the solution begin to exercise their influence.

When the particles are very close to each other (that is – at surface-to-surface distances less than or equal to approximately the radius of gyration or size of the polymer chain), the exclusion of polymer chains in the region between two particles causes *depletion flocculation*. The depletion effect is an osmotic effect and occurs when non-adsorbing polymers are added.

We will continue further with an important concept called depletion flocculation. Depletion flocculation can occur at moderate to high polymer concentration that means, I have a dispersion of particles and I have added polymers and if the concentration of the polymers is moderate to high again moderate and higher, very general terms, it depends on the type of particle polymer system that you are dealing with.

And I want to read what is written here and then explain later. The free polymer chains in the solution begin to so if you look at this particular cartoon, what is shown here is particle 1 and particle 2, and these dark region at you see this is the polymer that is adsorbed, that is the adsorbed polymer. When the particles are very close to each other, that is at surface to surface distance less than or equal to approximately the radius of gyration or the size of the particles size of the polymers. Then what happens is the polymer chains, are excluded from the region between the 2 particles, that results in something called as a depletion flocculation.

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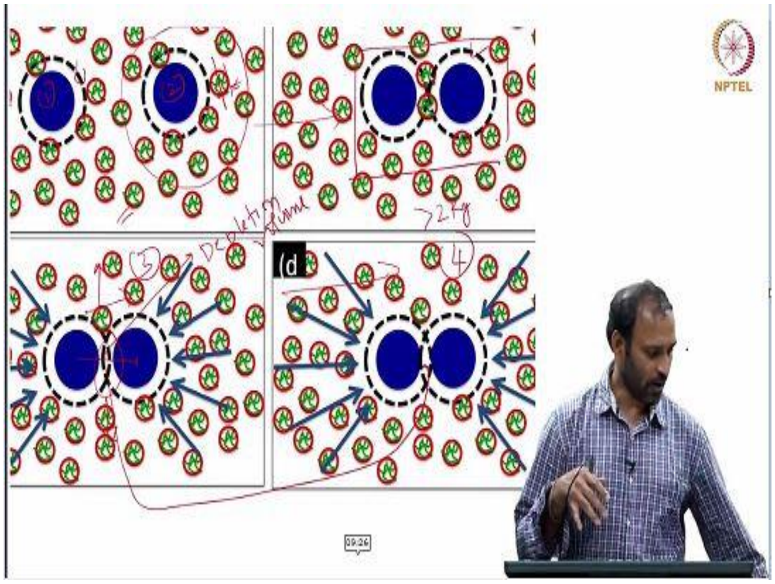

This is basically a cartoon, so, what is shown here is particle 1, and particle 2. And there is a dashed line. The dashed line, the size of that dashed line is, it is what is called the depletion layer. I will talk a little bit about it later. And the size of the dashed line is actually half the size of the polymer. Now, if you look at the picture of 1, that is this one. You see that on an average there is same number of polymer neighbors that particle 2 has and the similar number of neighbors will be there for particle 1 as well.

Now, the other images that are shown are what happens if the particles approach each other. Now, this is a case where you know, these dashed lines exactly touch. And I said that, you know, the typical size of this dashed line, which is also has a depletion layer is half the size of the polymer. So, in this configuration, the polymer molecules still have access to the, gap between the particles. Now, the next picture that is number 3 here, it shows a case where the distance between the 2 particles is smaller than the size of the polymer molecules.

What will happen then these polymers can no longer be in the gap between the particles they move out of the gap. And so, if you look at this region, this is what is called a depletion volume. And if you compare this and this the depletion volume in figure 4 is larger than the depletion volume in figure 3.

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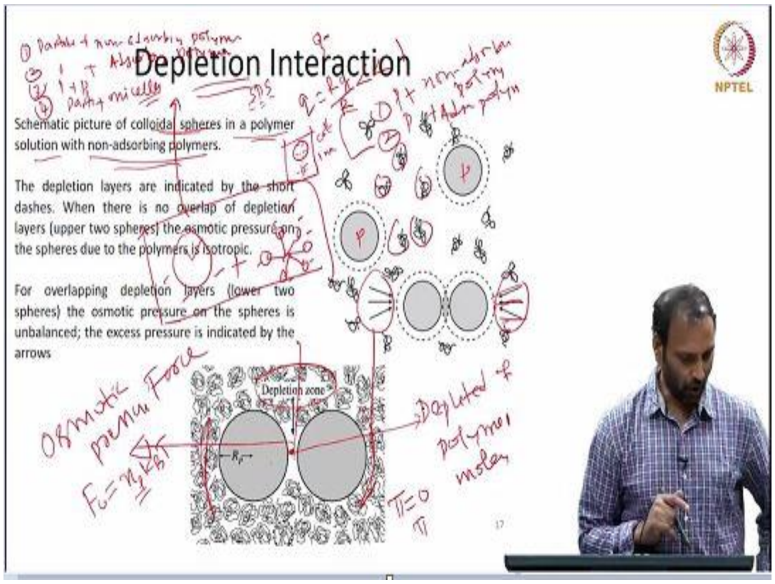

Depletion Interaction

Schematic picture of colloidal spheres in a polymer solution with non-adsorbing polymers.

The depletion layers are indicated by the short dashes. When there is no overlap of depletion layers (upper two spheres) the osmotic pressure on the spheres due to the polymers is isotropic.

For overlapping depletion layers (lower two spheres) the osmotic pressure on the spheres is unbalanced; the excess pressure is indicated by the arrows

Now, what happens when the polymers move out of the gap is basically explained in this particular picture. So, you get what is called a depletion zone and this depletion zone is a zone between the 2 particles which is depleted of polymer molecules. Now, we defined something called as a osmotic pressure force and if you remember osmotic pressure force F osmotic we define it as number density of the particles multiply by $k_B T$.

This number density is number per unit volume. This was defined for particles, but I can define the same thing also for the polymer molecules as well. Now, if I look at the osmotic pressure in the region between the 2 particles because there are no polymer molecules there, the osmotic pressure there is going to be 0. However, on the region outside the you know particles you have enough number of polymer molecules there is going to be therefore, there your osmotic pressure force is going to be finite.

But however, now, you have the imbalance in the osmotic pressure. The osmotic pressure here is lower the osmotic pressure is higher there. Because of this imbalance in the osmotic pressure, the particles are essentially pushed together. That leads to what is called as depletion flocculation. So, the origin of depletion flocculation is related to the formation of depletion zone and the creation of depletion zone leads to the osmotic pressure imbalance.

And this excess pressure, what are the arrows that you see here, these arrows essentially show you the, the way these excess pressure is going to act, that is what will bring the, particles together. Now, the schematic that you have shown, this is actually a schematic picture for colloidal spheres, these are the particles. And they are in a solution with non adsorbing polymer, in this case, the particles the polymer continues to remain in the solution, they are non adsorbing.

So, therefore, a mixture of particles plus non adsorbing polymer will exhibit depletion effects. That is number 1. Number 2, you could also have a case when you know what that is what is it depicted here, you could also have a case where initially the polymer continues to adsorb out of the particle surface and then when the polymer when the particle surface is saturated with the polymer, then the depletion can kick in.

Depletion can also be seen in cases where I have particle plus adsorbing polymers as well. Only difference between the 2 would be the in the case of particle plus absorbing polymer, you know, combination, the depletion effects will obviously occur at a much higher polymer concentration than what would happen for the particle plus non adsorbing polymer case. That is number 2 so, I just want to write down again.

So, the depletion effects can be absorbed in particles plus non adsorbing polymer case. Number 2 particle plus adsorbing polymer case. Can you think of other cases where the depletion can occur? So, if you go back and look at the way we talked about again one of the criteria for depletion to occur is that q which is defined as the size of the polymer divided by size of the particle should be less than 1.

That is the condition under which the depletion interactions would become important. Can you think of other systems where I can have a similar analog? So, you could have a case the third case is where I have a solution which contains large particles, say that they are negatively charged. Now, another combination of very small particles or a colloidal particle plus nanoparticle mixture, where the particles both the particles are similarly charged can also exhibit depletion interactions.

That is a third system. A particle, particle combination can also you know a similar phenomena about you know, the particles not having access to the region between the particles can also occur in the case where you have a combination of large sized particles and a small sized particle. And the fourth combination where this could happen is a system where I have particle plus micelles.

We know that typically micelles are the structures which are formed because of self assembly of surfactant molecules and typical size of micelles will be very, very small of course, it depends on the kind of suffering that you are dealing with. Imagine that you know, I have let say SDS, sodium dodecyl sulfate. Now, sodium dodecyl sulfate, the surfactant molecule is negatively charged.

Now, if I have a micelles that is form because of SDS, it looks something like this, the micelles would be negatively charged because the head group is negatively charged. And I have this in combination with large particles, which are also negative charged. When you have a combination like this, you can also people have done experiments and shown that the depletion effects can also occur in the case of particle surfactant combination in which both the particle and the surfactant structures or the micelles will be of similar charged. So, these are the 4 instances where you can think about depletion interactions.

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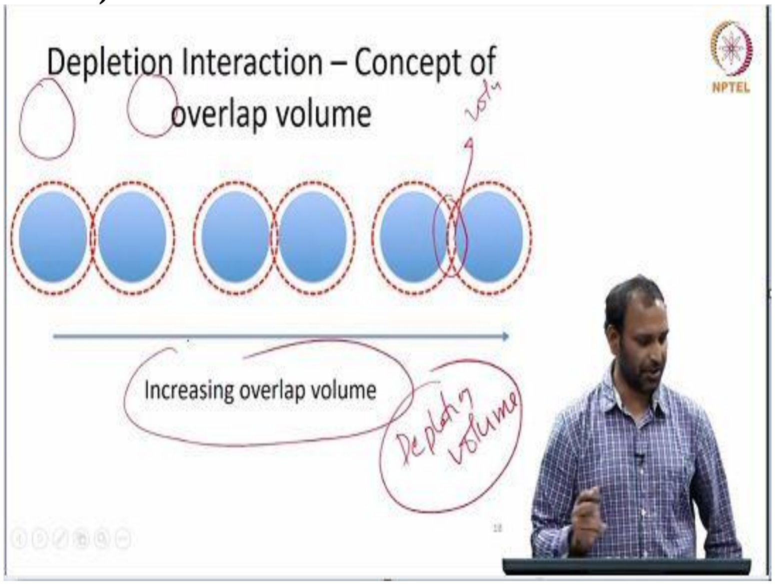

Depletion Interaction – Concept of overlap volume

Again, this is just a schematic which tells you about the depletion volume. If you have a case where the particles are really far apart your depletion volume is 0 as soon as the overlap of course, you are going to have this lens like region in the case of spherical particles and if as long as if you so this the volume of this lens, is what is called as a depletion volume and of course, that will depend on the the separation distance.

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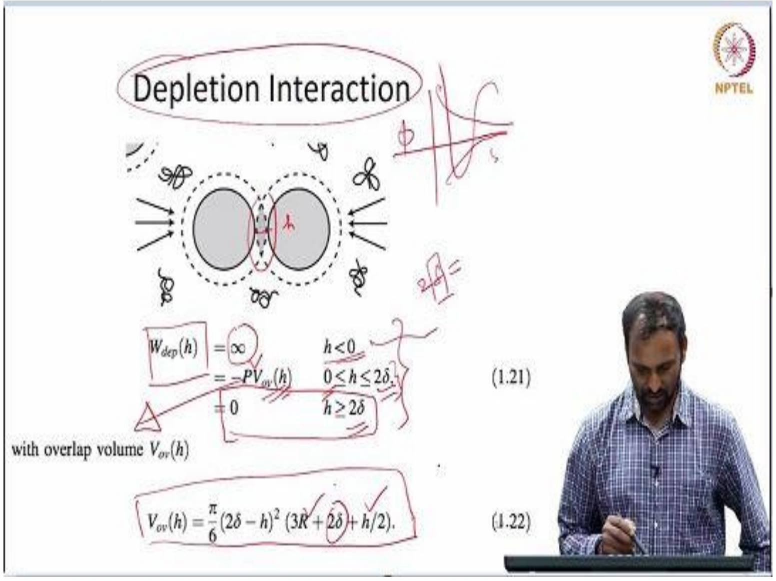

Depletion Interaction

$$W_{dep}(h) = \infty \quad h<0$$
$$= -PV_{ov}(h) \quad 0 \leq h \leq 2\delta, \quad (1.21)$$
$$= 0 \quad h \geq 2\delta$$

with overlap volume $V_{ov}(h)$

$$V_{ov}(h) = \frac{\pi}{6}(2\delta - h)^2\,(3R + 2\delta + h/2). \quad (1.22)$$

Now, so, this is a just like we wrote Lennard Jones potential I mean, we know how to write if your phi is a function of separation distance. So, we said you know, Lennard Jones is going to have one you know contribution because repulsion other contribution because of attraction, we wrote this overall potential and stuff like that. Similarly, people have kind of developed in the you know, if you have colloidal particles immersed in a pool of polymers, people talk about depletion interactions and the depletion interaction expression is given by this.

So, we will try and derive it a little later. So, what does this tell you. So, in this case 2 delta is the delta is the half so, let us go back. This case now, for any distance that is larger than 2 times Rg of the polymers, that means the gap between the 2 particles is in a big enough for the polymers to be there for any distance greater than 2 times Rg, the polymers will have access to the region between the particles that means the osmotic pressure imbalance is not set in. The osmotic pressure in both regions are the same.

For such a case, your interaction the W depletion, where h is a separation distance now is going to be 0, for any distance that is greater than 2 times the Rg of the polymer, or 2 times delta in this case the depletion forces are going to be not there that is 0. Now, for any distance of separation that is less than 0, your W depletion is going to be infinite. That is very similar to the repulsion between the electron clouds, of the particles.

I mean, there is so this is not a practical situation, I mean, you really will not have any situation where you know, you are, you know, is gonna be less than 0. How about this, this is the, separation distance going from 0 to 2 times delta 2 times delta essentially corresponds to when these 2 overlap that is 0. When, the particles are getting sufficiently close, right now I have something like this. I am going to draw another one is actually touching. That is the closest that they can go as h = 0.

That is h = 0 all the way going to 2 times delta, the depletion interaction is given by P times V overlap. V overlap is the overlap volume and P is the osmotic pressure. P is the the osmotic pressure which is determined by the, concentration of polymer that you have in the solution. And you know, people have worked out what this overlap volume would look like. Of course, it is a function of h. Overlap volume in the case this is a lens. If you look at this, it looks like a lens. There are ways by which I can calculate what is the volume of the lens.

As h changes that is the distance of separation changes, it turns out it is given by pi / 6 2 times delta - h whole square multiply by 3 times R + 2 delta + h / 2. R is the size of the particle ,2 delta is the size of the polymer that you have at initial separation distance.

$$V_{ov}(h) = \frac{\pi}{6}(2\delta - h)^2(3R + 2\delta + h/2)$$

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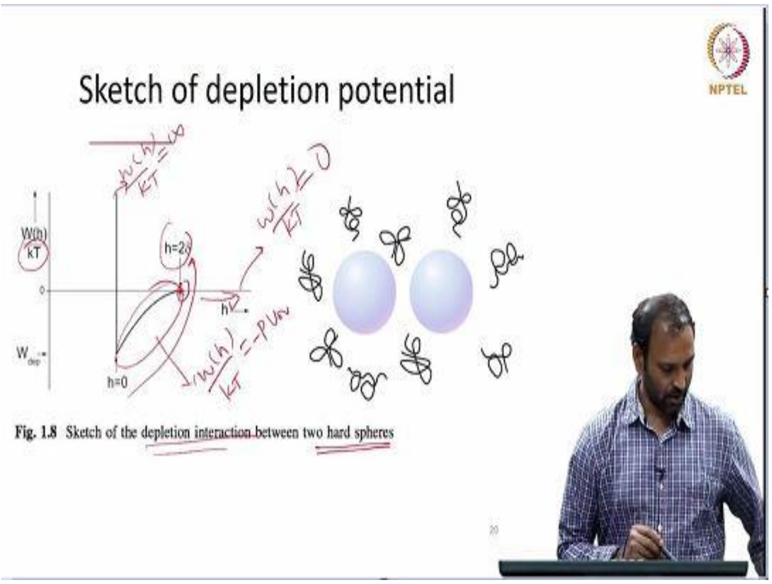

Sketch of depletion potential

Fig. 1.8 Sketch of the depletion interaction between two hard spheres

So if you plot this expression, it would look something like this. It will, it looks something like this. W of h, where h is the separation distance, it is scaled with k_BT, thermal energy. This is the point where h = 2 times delta any distance beyond that the interaction potential is 0. And it is attractive in the range from h = 0 to h = 2 delta and h = 0,we have a spike that corresponds to W of h, divided by k_BT being equal to infinity. That is your case here. And this is W of h divided by k_BT going to 0 and this region here is where W of h divided by k_BT causes minus P times V overlap. So that is I mean this is actually for depletion interaction between 2 hard spheres.

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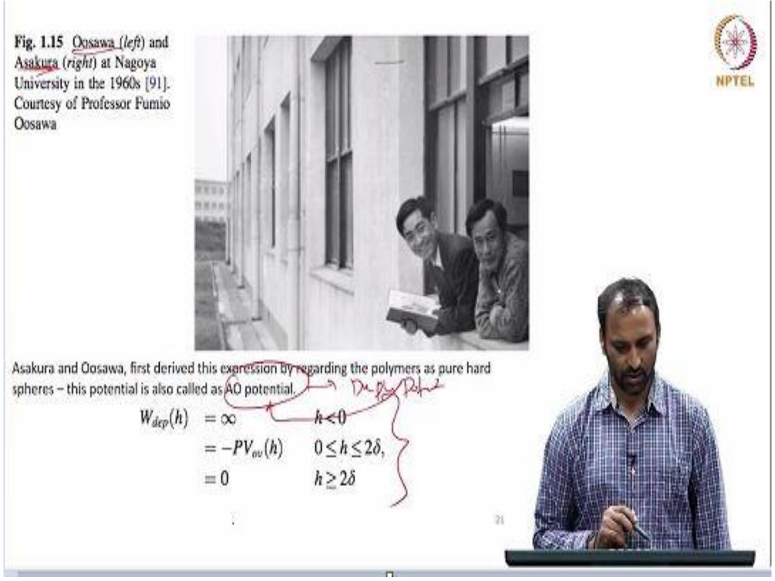

Fig. 1.15 Oosawa (*left*) and Asakura (*right*) at Nagoya University in the 1960s [91]. Courtesy of Professor Fumio Oosawa

Asakura and Oosawa, first derived this expression by regarding the polymers as pure hard spheres – this potential is also called as AO potential.

$$W_{dep}(h) \begin{array}{ll} = \infty & h<0 \\ = -PV_{ov}(h) & 0 \leq h \leq 2\delta, \\ = 0 & h \geq 2\delta \end{array}$$

So, this particular concept of the depletion interaction, was actually the expression that we see here. This was actually first proposed by 2 scientists Asakura and Oosawa. That is also called as AO potential the depletion potential. It is also called as AO potential that is because of the people who you know gave this concept of depletion interactions and things like that. That is about depletion you know, attraction or depletion interaction.