Colloids and Surfaces
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Lecture - 25
Steric Interactions / Osmotic Repulsion

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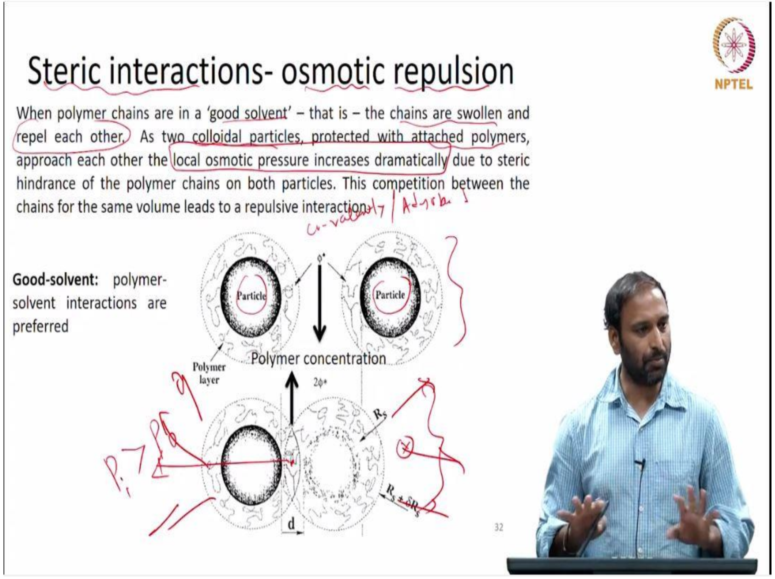

Steric interactions- osmotic repulsion

When polymer chains are in a 'good solvent' – that is – the chains are swollen and repel each other. As two colloidal particles, protected with attached polymers, approach each other the local osmotic pressure increases dramatically due to steric hindrance of the polymer chains on both particles. This competition between the chains for the same volume leads to a repulsive interaction.

Good-solvent: polymer-solvent interactions are preferred

So, when we talked about steric interactions that is if you have cases where you have you have particles and on the surface of the particle you have you know some long chain molecules that are either covalently bonded to the surface or they could be adsorbed onto the surface. So, if you have cases like that, then I had mentioned that there will exist what is called a steric repulsion, you can think about steric repulsion also as something as an osmotic repulsion.

So, we will see we know what it actually means. So, when the polymer chains are in good solvent. That means the polymer molecules are happy being in a solvent, then you can say that, when you say that the chains are swollen, that means they are in a, you know, expanded configuration. And in a sense, that the reason that they know they are in an extended configuration that means they do not like to be in contact with you know, the polymer chains, they are happy being in contact with the solvent molecule.

That means you know, this, the chains essentially repel each other. So, now, so, if you have a case where so, this is a case, where the particles are sufficiently far apart, now, this is a case where the particles have come sufficiently close to each other, then what will happen is that, as the 2 particles which are with these polymer chains, which are attached covalently are adsorbed, when they approach each other, you can think about it as a there is a local increase in the osmotic pressure force, what you can think about is if I look at the region here.

Now, there are many more polymer molecules you know, in the volume in the region between the 2 particles, than you have the polymer molecules elsewhere, it is exactly the reverse of depletion interaction. In depletion, we said that, when they overlap, when you have polymers that are not adsorbed.

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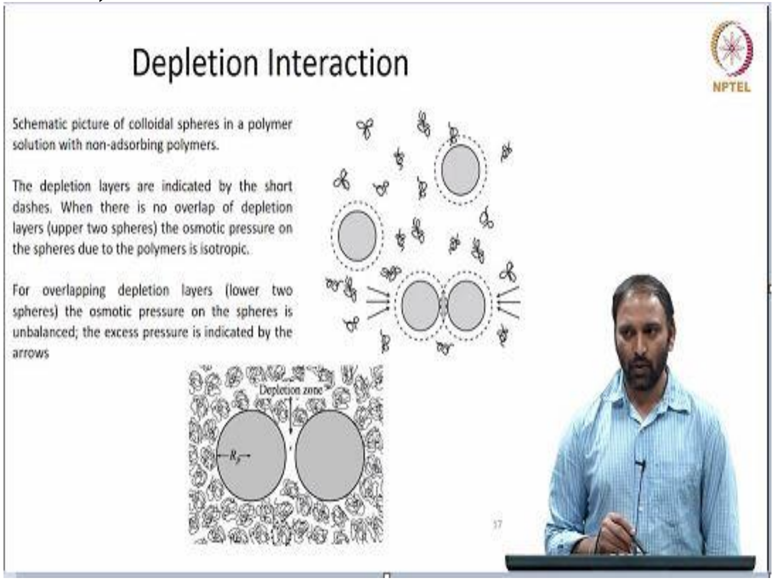

Depletion Interaction

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

When they when you have a non adsorbing polymer, I said that, when the particles come to sufficient the particles come sufficiently close, you get a region where the polymers are depleted that means, there are no polymers there. However, in the case of steric repulsion, what happens is something that is contrary, on an average, there is an increase in the concentration of polymers in the gap between the particles.

Therefore, I can say that effective osmotic pressure force in the region between the particles, there is inner is going to be larger than the osmotic pressure force that is outside in the region that is outside. So because of which, now there is going to be a force it is going to be the opposite direction. To what we saw for the depletion attraction case that means the particles are going to be pushed away.

So, therefore, when they approaches to the local osmotic pressure increases dramatically, due to you know, the fact that you know, there is a competition you know, between the polymer chains to occupy that volume and this competition, what leads to repulsive interaction.

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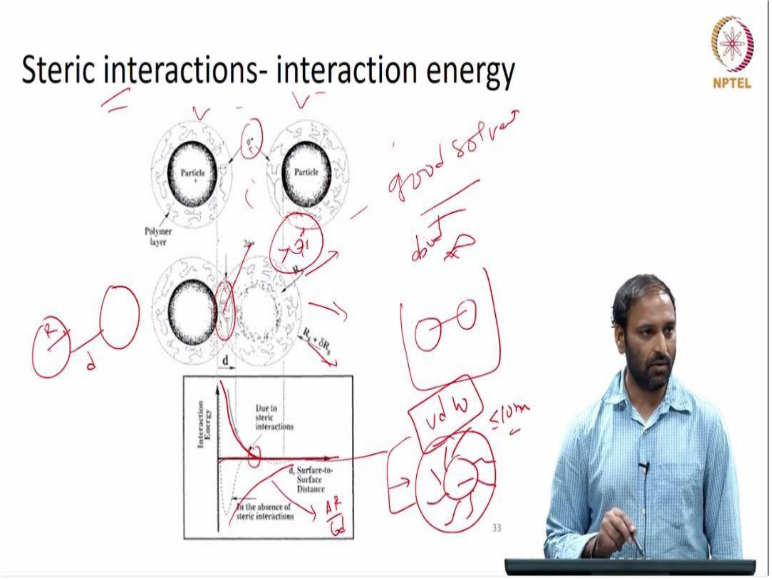

Steric interactions- interaction energy

And this is essentially a plot of interaction energy as a function of separation distance. So now, there is a dotted line, that dotted line corresponds to the interaction where correspond to the case when you have absence of steric repulsion, there could be van der Waals or other kind of attractive forces in the system, that is this particular curve, there is a dotted dashed line. And however, this continuous line that you see is, you know, where you have steric interaction, present the system.

And it essentially is going to again, depending upon the separation distance and depending upon the concentration of polymer molecules, you know, in the gap between the particles is going to increase. So that is a typical thought that you will see. When I say polymer repel each other, you should think about it more like they are more happy being in contact with solvent molecules than with the polymer molecule, maybe you can think about along these lines. So, that means I have a particle, which is in a pool of solvent.

It would rather prefer because, you know, we are talking about a good solvent, the polymer would prefer to be in contact with solvent given a chance. If you talk about bad solvent, the polymer does not want to be in contact to the solvent, therefore, the polymer you know interactions are preferred. So that is the analogy. So, the steric interaction the only thing it does is see there are some you know, like say if you look at say that I have a system of particles.

And you know, we know that we are always going to have this van der Waals attraction between the particles. Now, how do I get rid of such interactions? One of the ways we thought about is if I take these particles, if I put them in a medium where the Hamaker constant of the medium and the particles of the same then you know I can get rid of van der Waals interactions. Now, the other way of you know, somehow negating the effect of van der Waals interaction.

Is to look at a case where I somehow ensure that the particles would never approach the separation distance know where the van der Waal forces become important. So, one of the ways of doing that would be by introducing some change on the particle surface. So, that know that now, the separation distance between the 2 particles is never going to be less than 10 nanometer something like that. So, that you know, you do not have van der Waals attraction dominating in the system.

One of the ways of thinking about you know, the steric interactions could be in terms of osmotic repulsion. So, that the fact that you know, locally you know, so, for example, so, this phi star that is seen here is the you can think about this as a grafting density . In a phi star you know, it refers to the concentration of polymer molecules that is attached onto the surface, we think we are grafting density.

Now, what will happen is when they are sufficiently close, you know, the in the region between the polymers a particles your know your the overall concentration is definitely going to be greater than phi star. So, when that happens, there is a the osmotic pressure imbalance again in this case only thing is it is opposite to the direction that we saw for the depletion attraction case, that is the crux.

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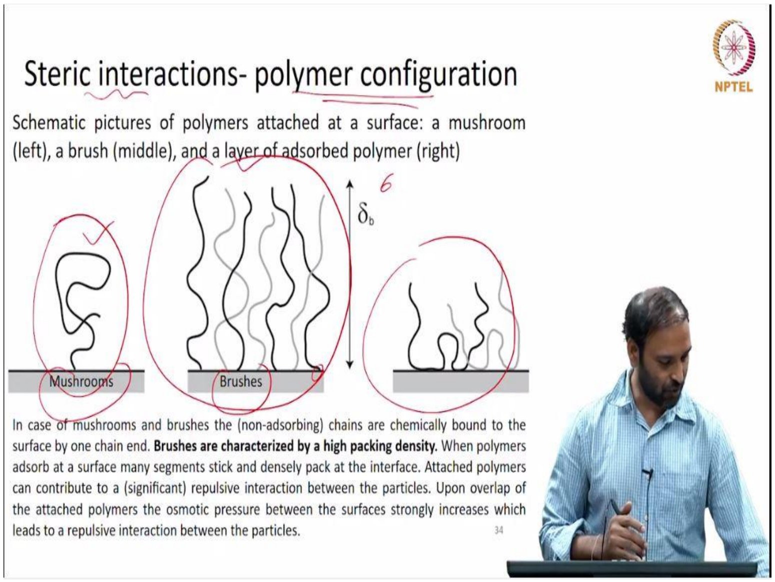

Steric interactions- polymer configuration

Schematic pictures of polymers attached at a surface: a mushroom (left), a brush (middle), and a layer of adsorbed polymer (right)

In case of mushrooms and brushes the (non-adsorbing) chains are chemically bound to the surface by one chain end. **Brushes are characterized by a high packing density.** When polymers adsorb at a surface many segments stick and densely pack at the interface. Attached polymers can contribute to a (significant) repulsive interaction between the particles. Upon overlap of the attached polymers the osmotic pressure between the surfaces strongly increases which leads to a repulsive interaction between the particles.

Now, it turns out that the steric repulsion depends again on the polymer configuration you know, whether you know the polymer that is adsorbed or grafted onto the surface is it you know, does it take a shape like this or does it shape it you know, take a shape like this, this one because a brush like configuration, this something becomes a mushroom like configuration, these configurations are seen.

When the polymer chains or polymer molecules are covalently bound to the surface such configuration is when you have polymer molecules that are adsorbed onto the particle surface. So, depending upon it will depend on the configuration of the polymer it will depend on the grafting density itself, what is the number of chains per unit area that is, attached to the surface. So it depends on a lot of factors. Calculating, you know, steric interactions is a little bit more complicated than the depletion because of all these effects?

Because, you know, you would have to have an idea about the configuration of polymer chains, you should have a definite understanding of, or measurement of the grafting density, all of that. So I do not have any more stuff on steric repulsion, again, the book that I mentioned does have sufficient bit of you know chapters on steric interactions if you want to read more, you can go back and read up a little bit.

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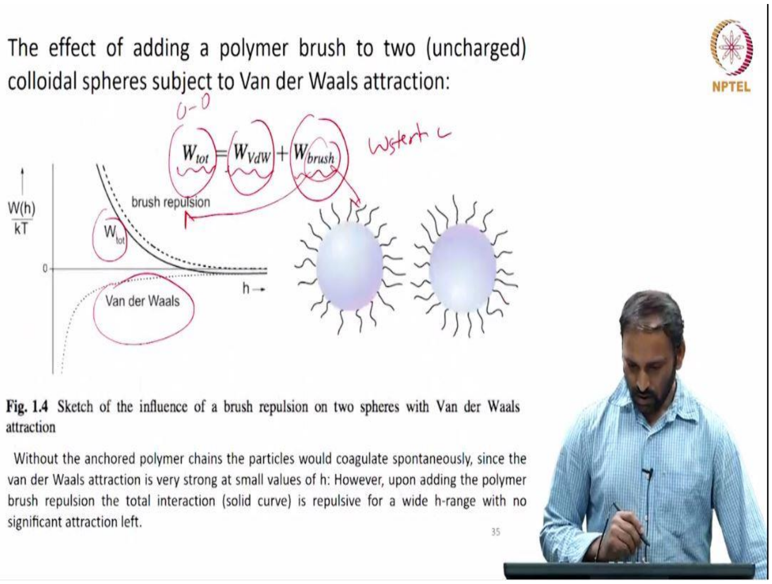

The effect of adding a polymer brush to two (uncharged) colloidal spheres subject to Van der Waals attraction:

$$W_{tot} = W_{VdW} + W_{brush}$$

Fig. 1.4 Sketch of the influence of a brush repulsion on two spheres with Van der Waals attraction

Without the anchored polymer chains the particles would coagulate spontaneously, since the van der Waals attraction is very strong at small values of h: However, upon adding the polymer brush repulsion the total interaction (solid curve) is repulsive for a wide h-range with no significant attraction left.

So, this is again general it like in any colloidal system, the total interaction potential will always be a summation of van der Waals + W brush in this case w brush essentially corresponds to W steric if you want to call it as. And the steric repulsion or W brush is going to be repulsive, that is this and the van der Waals is going to be attractive. So, the whole idea of putting W brush is that you know or the steric repulsion is the overall interaction would still be repulsive.

That is your W total depending upon you know the contributions of polymer molecules depending upon the grafting density everything. So, this curve could be shifted up or down depending upon what problem you are trying to look at. So, this is essentially to tell you that the total interaction in a case where you have steric repulsion is a summation of van der Waals interaction plus the interaction that comes because of the adsorbed polymers.

This is actually this is so, this W total is the particle, particle interaction. See, when we plotted this, let me do it this way, this plot, let us see that you know, so, we are worried about just 2 particles. And say that I want to calculate what is the van der Waals force of interaction between the 2. So, we know that you know, it goes something like this. And if given that the particle sizes R, and the separation distance is d, we know that you know, this basically goes as something like a times R divided by 6d, something like that. So we know how to do that.

Now, what you have is, I have 2 particles, on which I have these grafted chains. Now we are again, I am still talking about the particle, particle interaction. Now, in this case, in the case of particle, particle interaction with these grafted chains, so it turns out that depends. So if they are in a configuration like this, of course, the interaction is going to be 0? I do not have any steric effects at all? Now, of course, that will happen for large separation distance? Now, when there is not overlapping.

So there is going to be again the lens that is formed. And the moment that lens you know, or the overlap occurs, then phi star is going to be larger, so that is typically is happening here. That is where you know, you are see start seeing some repulsion that happens here. And then of course, depending upon the overlap, now you are going to have an increase in this case again, it is the interaction between the particles, with the grafted molecules on the surface. So, if we go back here I mean. Similarly, if you look at expressions like this.

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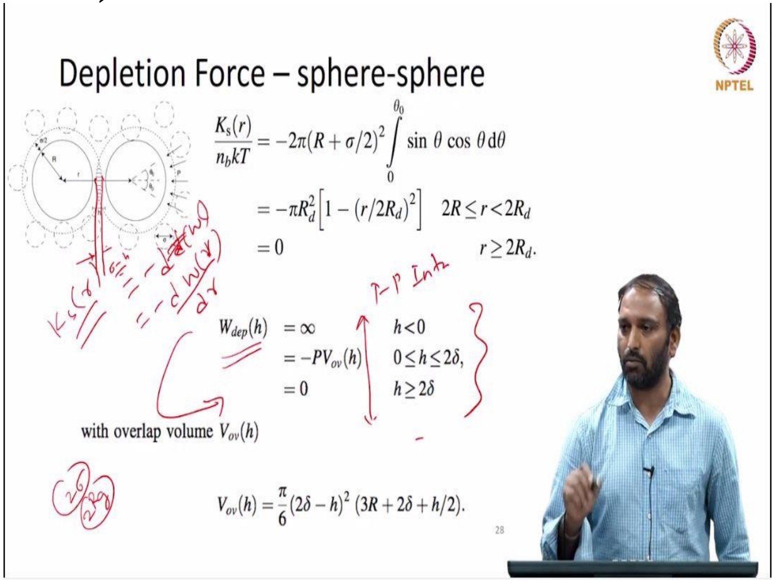

Depletion Force – sphere-sphere

$$\frac{K_s(r)}{n_b kT} = -2\pi(R+\sigma/2)^2 \int_0^{\theta_0} \sin\theta \cos\theta \, d\theta$$

$$= -\pi R_d^2\left[1-(r/2R_d)^2\right] \quad 2R \le r < 2R_d$$

$$= 0 \quad r \ge 2R_d.$$

$$W_{dep}(h) = \infty \quad h<0$$

$$= -PV_{ov}(h) \quad 0 \le h \le 2\delta,$$

$$= 0 \quad h \ge 2\delta$$

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

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

This again is the particle, particle interaction is nothing to do with you know, the polymers on the you know, in this case of course, you have polymer molecules in the solution. But these expressions are again the, particle-particle interactions is what we are talking about.

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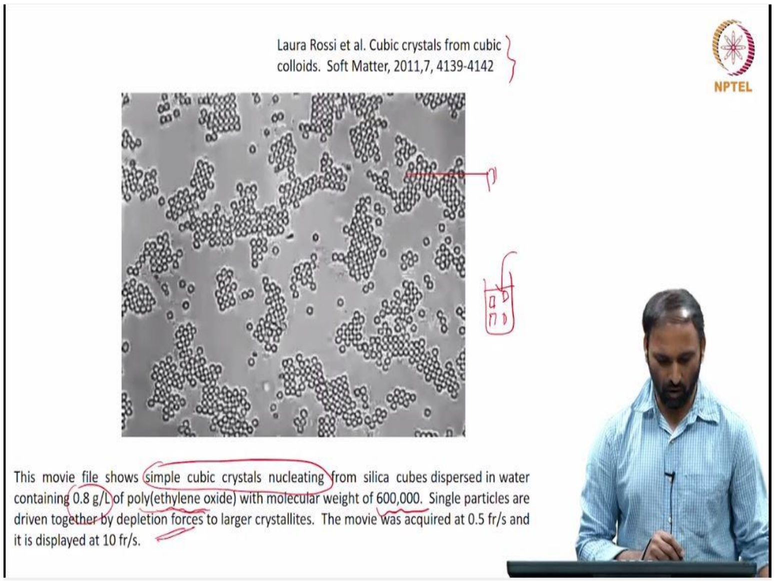

Laura Rossi et al. Cubic crystals from cubic colloids. Soft Matter, 2011,7, 4139-4142

This movie file shows simple cubic crystals nucleating from silica cubes dispersed in water containing 0.8 g/L of poly(ethylene oxide) with molecular weight of 600,000. Single particles are driven together by depletion forces to larger crystallites. The movie was acquired at 0.5 fr/s and it is displayed at 10 fr/s.

I have a this is a recent people some nice work, so, you can what they have is a, this is a movie it shows the formation of cubic crystals. And the way this is done is they have a dispersion of cubic particles. And to that, they add 0.8 grams per liter of PEO polyethylene oxide is a polymer of so much molecular weight. That is the movie (15:09) definitely there were few individual particles to begin with you know, as time goes, you see that you know more and more you know the particles come.

And this is a you know, video microscopy image which tells you that there is a, they talk about formation of a simple cubic crystal or if you look at, you know, like it is a cubic crystal. So, that is movie 1 in which case a polymer has been added. Everything is exactly the same, all that is being done is I have a container with particles. And then to that you add a polymer particles, this is cubic particles. So, again an example where the depletion forces come into picture to form large crystals.

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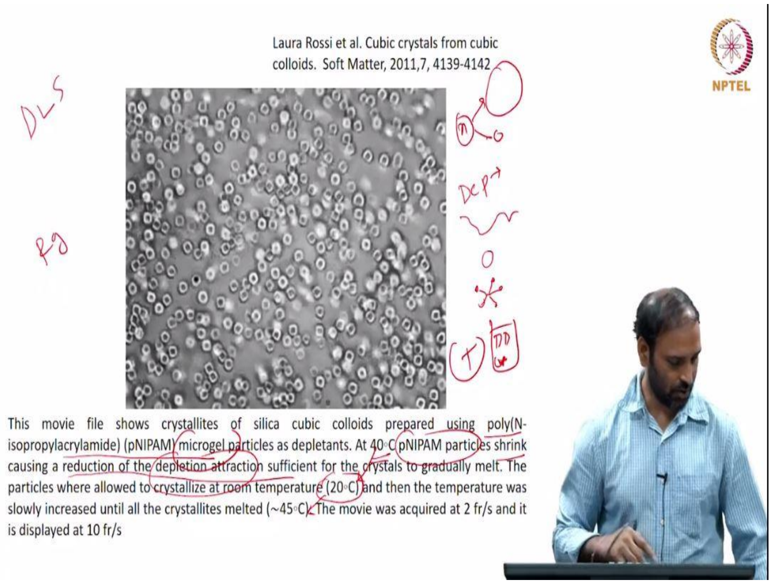

Laura Rossi et al. Cubic crystals from cubic colloids. Soft Matter, 2011,7, 4139-4142

This movie file shows crystallites of silica cubic colloids prepared using poly(N-isopropylacrylamide) (pNIPAM) microgel particles as depletants. At 40°C pNIPAM particles shrink causing a reduction of the depletion attraction sufficient for the crystals to gradually melt. The particles where allowed to crystallize at room temperature (20°C) and then the temperature was slowly increased until all the crystallites melted (~45°C). The movie was acquired at 2 fr/s and it is displayed at 10 fr/s

This is another experiment, where instead of I mentioned about I can induce depletion effects, by adding up a polymer by adding a small particle or by adding a Micelle solution. So, this is an example where to a dispersion of cubes, they have added a particle which is called a poly NIPAM micro gel I had introduced this at some point, when I talked about DLS measurements, dynamic light scattering measurements, had mentioned that there are particles which are which can shrink, or which can expand, depending upon temperature.

So, that is a microgel particles, and these particles at 40 degrees centigrade, pNIPAM particles shrink, causing a reduction in their depletion interaction. So in this case, we know that the strength of depletion interaction depends on the, size of the polymer molecules you know, Rg, we will be talking about. So if I am using pNIPAM as a depleted, or pNIPAM is something that is causing depletion interaction, depending upon the size of the pNIPAM particle, pNIPAM particle, I can tune the effective attraction between the particles.

So and then what they do is they do an experiment where they heat the sample to from they start with 20 degrees centigrade. So they start with 40, they cooled it to 20. And again, they heated back to 45, this is a state to where, this is the crystals are already formed. I guess the temperature scale is not given, but you can imagine that they are heating up. So let us see what happens. So, you should imagine that you know, the crystals were already there.

Now, you know, you can see that now the crystals melt away, they all become, you know, individual particles. Then you can recreate them let us come back here. So, this is basically what is being done is I can work with a system of cube like particles, and this pNIPAM this pNIPAM. So, I can just subject that to heating and cooling cycles, I can tune the depletion interaction depending upon their size.

I am keeping the, number of pNIPAM particles same, because you know, I am not playing with that I kept this concentration of pNIPAM particles, but just by making it either larger or smaller, I am able to control the strength of depletion attraction that leads to either the formation of a large aggregate or a crystal or I can melt the crystal away, just by tuning the dimension.

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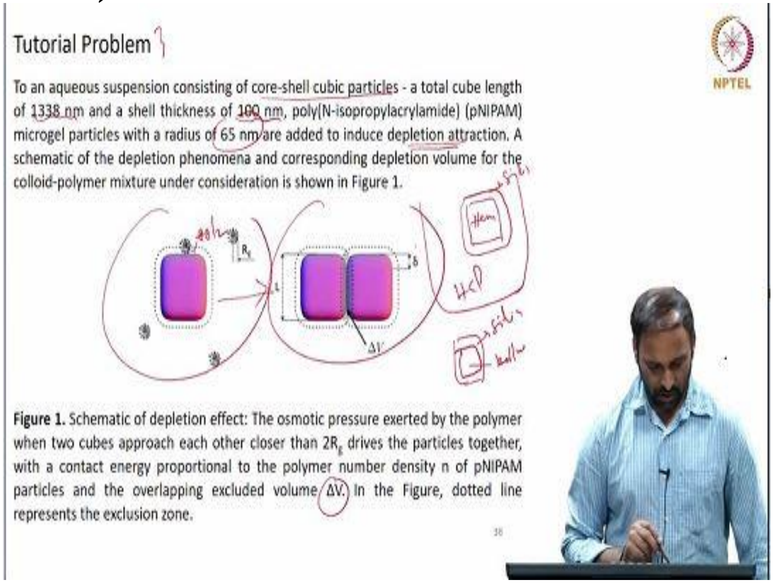

Tutorial Problem

To an aqueous suspension consisting of core-shell cubic particles - a total cube length of 1338 nm and a shell thickness of 100 nm, poly(N-isopropylacrylamide) (pNIPAM) microgel particles with a radius of 65 nm are added to induce depletion attraction. A schematic of the depletion phenomena and corresponding depletion volume for the colloid-polymer mixture under consideration is shown in Figure 1.

Figure 1. Schematic of depletion effect: The osmotic pressure exerted by the polymer when two cubes approach each other closer than $2R_g$ drives the particles together, with a contact energy proportional to the polymer number density n of pNIPAM particles and the overlapping excluded volume ΔV. In the Figure, dotted line represents the exclusion zone.

So I have just found a problem based on this it is a tutorial problem to an aqueous suspension consisting of these are actually core-shell cubic particles, what they do is they form a particle which is made of hematite, and then they coat it with a layer of silica and then, if you put these particles in HCL solution, what happened is you can remove the inner core. You get a core-shell particle, this is hollow that silica, so it is a core-shell cubic particle the length of the cube is given the shell thickness is also given.

And pNIPAM micro gel particles of 65 nanometer are added to induce depletion attraction given a schematic diagram. So that is you know the cubic particle you can think about a depletion layer, the size of this depletion layer is going to be Rg / 2. And this is when you know then when they are sufficiently close there is going to be a depletion volume. Now, so that is a schematic the depletion volume is delta V.

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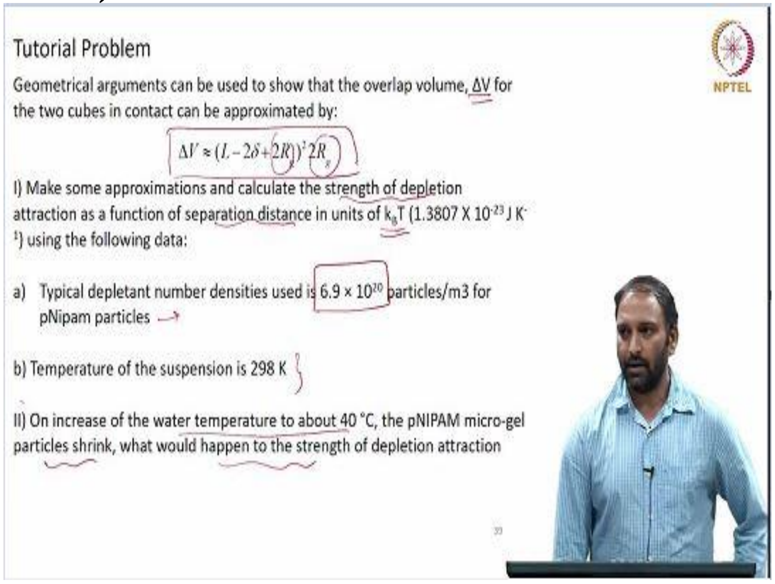

Tutorial Problem

Geometrical arguments can be used to show that the overlap volume, ΔV for the two cubes in contact can be approximated by:

$$\boxed{\Delta V \approx (L - 2\delta + 2R_g)^2 2R_g}$$

I) Make some approximations and calculate the strength of depletion attraction as a function of separation distance in units of k_BT (1.3807×10^{-23} J K^{-1}) using the following data:

a) Typical depletant number densities used is $\boxed{6.9 \times 10^{20}}$ particles/m3 for pNipam particles →

b) Temperature of the suspension is 298 K

II) On increase of the water temperature to about 40 °C, the pNIPAM micro-gel particles shrink, what would happen to the strength of depletion attraction

Now, the geometrical arguments can be used to show that the depletion volume delta V for the, 2 cubes in contact can be given by this make some approximations and calculate the strength of depletion attraction as a function of separation distance in units of k_BT. So, the following data has been given the typical depleted number density is this that is 6.9 10 power 20 particles per meter cube that’s the.

And temperature of the suspension is also given to you on that is so you are supposed to calculate what is the strength of depletion attraction given these 2 conditions? The other question that has been that you can ask is on increase of the water temperature to 40 degrees centigrade, the pNIPAM micro gel particles shrink. So then what will happen is your Rg is going to change. Then you are supposed to think about what would happen to the strength of depletion attraction, so that is what will be asked to you.

So think of, I will just post this problem. Take a look at it. Read up a little bit. We can discuss the solution in the next class. Which is essentially based on the work that is there in this paper so, thanks.