Colloids and Surfaces
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Lecture - 26
Tutorial Problem on Depletion Interactions

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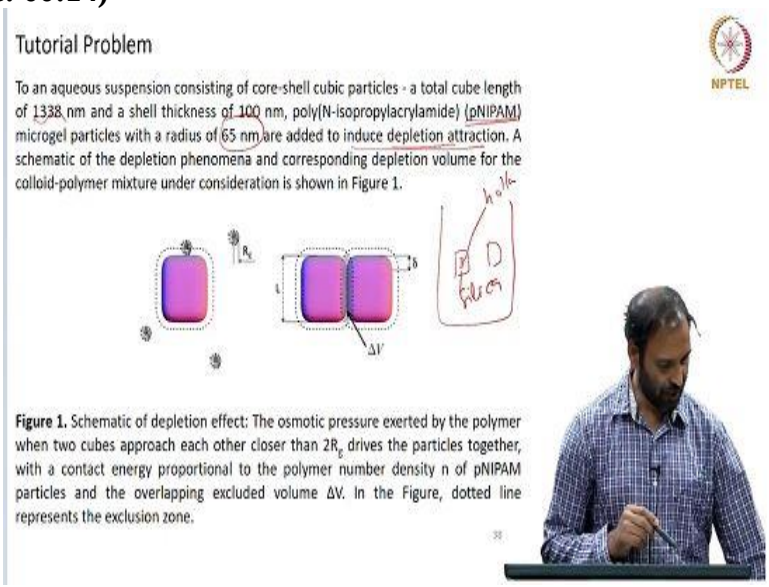

So, we were looking at this tutorial problem in the last you know lecture. So, this basically concerns a system where you have particles which are cuboids and the dimensions of the particles are given and it is mentioned that these are core-shell particles the core is made up of you know core is hollow and the shell is a silica cell. And what has been done is they have added pNIPAM particles of 65 nanometer radius. And you have been there added to induce depletion attraction.

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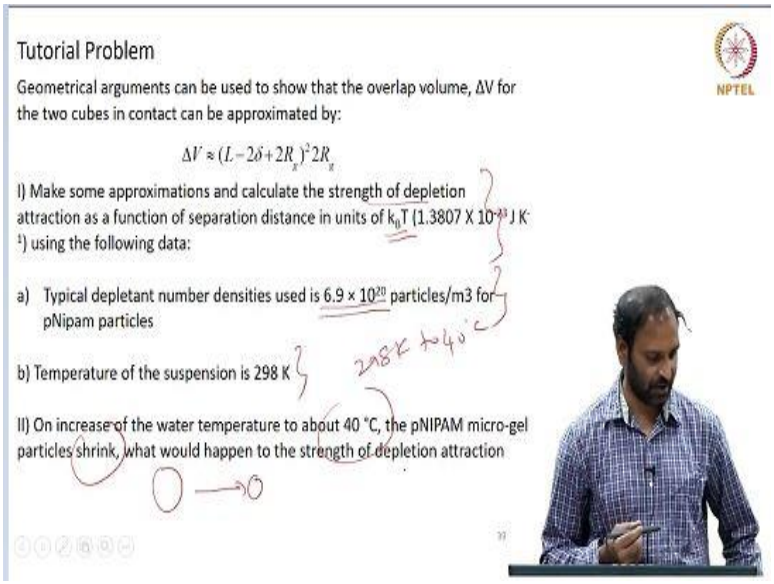

And you have been asked to calculate a few things. That is a make a approximation, you know, some approximations and calculate the strength of depletion attraction as a function of separation distance in units of k_BT and what has been given to you is also that the concentration of the depletants or the pNIPAM particles are 6.9 10 power 20 and the temperature is given to be 298 Kelvin. The second bit of question is on increase of the temperature of the dispersion from 298 Kelvin to 40 degree centigrade.

The pNIPAM micro-gel particles are known to shrink that means, if they are bigger in size, they will become smaller, and what would happen to the standard depletion interaction that is what is being given to you.

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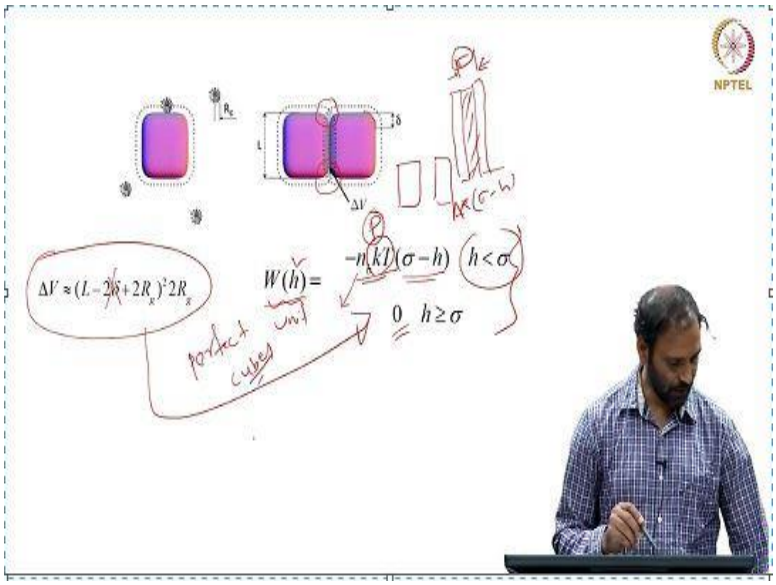

And what was also mentioned was the, the depletion volume was given something like this. So what we looked at is a case where if you look at what we are derived in the class, we had, you know, 2 plates. We had 2 plates. And, and we talked about what is the depletion volume, that is the region between the place the depletion volume. Now, if you look at this case, because of this roundedness, because these are cuboids.

You have a roundedness at these ends, edges, and because of which, in the depletion volume is going to be different. In this case, the depletion volume was something like the area of the plates multiplied by the separation distance. If sigma, is the, the size of the polymer that you are putting - h, which was the depression volume. Where h is the center of, which where h is the separation distance.

So now what we are going to do in this particular problem is we are going to assume that these are perfect cubes. Because we do not have we do not know what is delta. That delta is the roundedness we do not have a way of calculating this. So we do not know this. Therefore, what we will do is we will assume that the face of the cubes are flat, in which case I can actually go ahead and use the expression that we developed for the depletion interaction between 2 flat surfaces.

So, we had mentioned that in W of h, it depends on this is the osmotic pressure and that is a so, this is per unit area. If you remember, the way we did the calculation, this W of h is the interaction energy as a function of separation distance per unit area. So, therefore, I have the osmotic pressure I can calculate that because n_b is given to me the number concentration of depleted in the system is given and that is a thermal energy. Sigma - h which is going to be the separation distance. And of course, that is when h is less than sigma and for h greater than or equal to sigma your, the depletion interaction is going to be 0.

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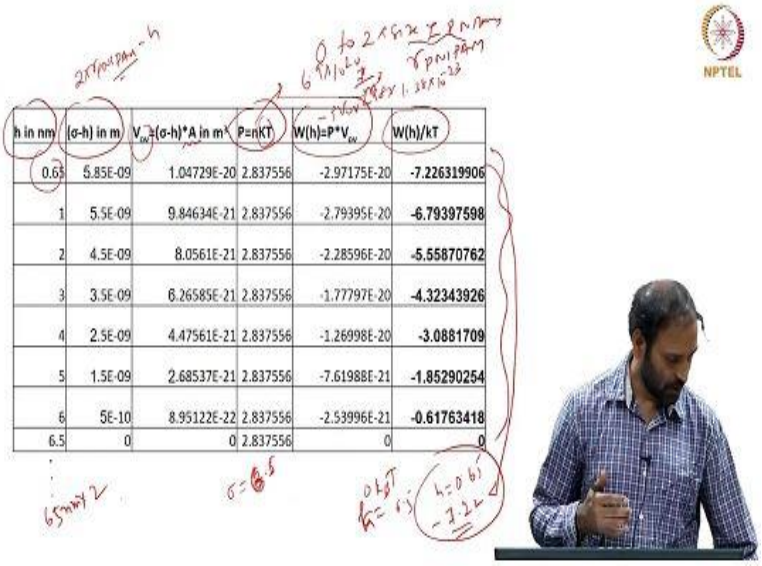

h in nm	(σ-h) in m	V_{ex}=(σ-h)*A in m³	P=nKT	W(h)=P*V_{ex}	W(h)/kT
0.65	5.85E-09	1.04729E-20	2.837556	-2.97175E-20	**-7.226319906**
1	5.5E-09	9.84634E-21	2.837556	-2.79395E-20	**-6.79397598**
2	4.5E-09	8.0561E-21	2.837556	-2.28596E-20	**-5.55870762**
3	3.5E-09	6.26585E-21	2.837556	-1.77797E-20	**-4.32343926**
4	2.5E-09	4.47561E-21	2.837556	-1.26998E-20	**-3.0881709**
5	1.5E-09	2.68537E-21	2.837556	-7.61988E-21	**-1.85290254**
6	5E-10	8.95122E-22	2.837556	-2.53996E-21	**-0.61763418**
6.5	0	0	2.837556	0	**0**

So there is a simple questions what I have done is I have taken of course, I should go on and then do it for 65 nanometers, that is the 2 times 69 nanometers, that is a distance or separation can be anywhere from 0 to 2 times the size of pNIPAM. When we say 2 times size 2 times the radius of pNIPAM particle. That is the range over which the interactions should be operated. So, therefore, I know what is h and I can calculate sigma - h that simply is 2 times the radius of the pNIPAM particles minus h that is a separation distance.

And that multiplied by A is going to give me what is the depletion volume. And the osmotic pressure force is given by P = nKT, n has been given. n is given as 6.9. 6.9 into 10 Power 20 number per meter cube has been given and k_BT is a thermal energy that is 298 times Kt which is 1.38 into 10 power - 23. So, I can calculate this of course, it has to be minus P V overlap because it is a attractive interaction. Now that I know W of h, I can scale everything with k_BT and you know, you get numbers which, which are like this.

So, this calculation actually what I have done is I have taken sigma to be 2.5 6.5 itself, that is the calculation I have done are taken sigma itself to be 6.5. So, I have taken some values of h going from 0.65 all the way up to 6.5 and this is the value of sigma - h you get that is overlap volume. So, therefore, you can see that the depletion interaction you know varies from about 0 k_BT or 0 kt when the separation distance is 6.5 that is sigma = 6.5 and when the separation distance becomes h is 6.5 when the separation distance becomes 0.65.

The thermal energy when you this becomes 7.22. So, this interaction energy is several times k_BT. Therefore, if they were to reach such a separation distance in order the particles will be attracted to each other and the energy corresponding to that attraction is given by 7.2 k_BT and this is much larger than the thermal energy therefore, we can say that, you know once they stuck, the Brownian motion would be the energy due to Brownian motion would be not sufficient to pull them apart.

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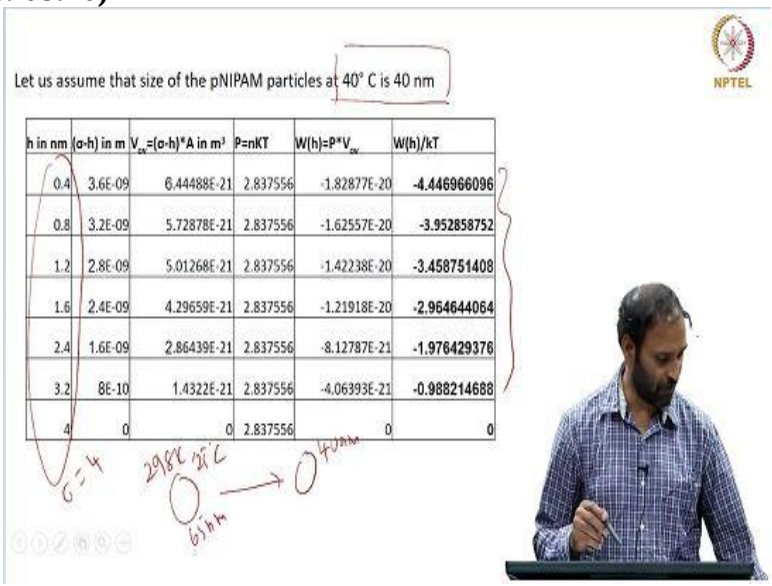

h in nm	(σ-h) in m	V_{ov}=(σ-h)*A in m³	P=nKT	W(h)=P*V_{ov}	W(h)/kT
0.4	3.6E-09	6.44488E-21	2.837556	-1.82877E-20	-4.446966096
0.8	3.2E-09	5.72878E-21	2.837556	-1.62557E-20	-3.952858752
1.2	2.8E-09	5.01268E-21	2.837556	-1.42238E-20	-3.458751408
1.6	2.4E-09	4.29659E-21	2.837556	-1.21918E-20	-2.964644064
2.4	1.6E-09	2.86439E-21	2.837556	-8.12787E-21	-1.976429376
3.2	8E-10	1.4322E-21	2.837556	-4.06393E-21	-0.988214688
4	0	0	2.837556	0	0

Now, I have done a similar calculation. So, I am going to assume that so, again the size information is not given 40 degrees centigrade, we know that they shrink. They become 298 Kelvin, or 25 degrees centigrade. So, the size is, you know, say 65 nanometer. So we know that it is going to shrink, I do not know what is the data for the size at 40 degree centigrade. So, I am going to assume that it is in a 40 nanometer.

If I assume that, I can do again a similar calculation. Again, what I have done is I have taken sigma to be 4 and I am showing the calculation here. So, therefore, a similarly what you can you know, what you can see is that the interaction energy. It varies from at least or the distance that I have taken, it varies from 0.98 to about 4.4 k_BT.

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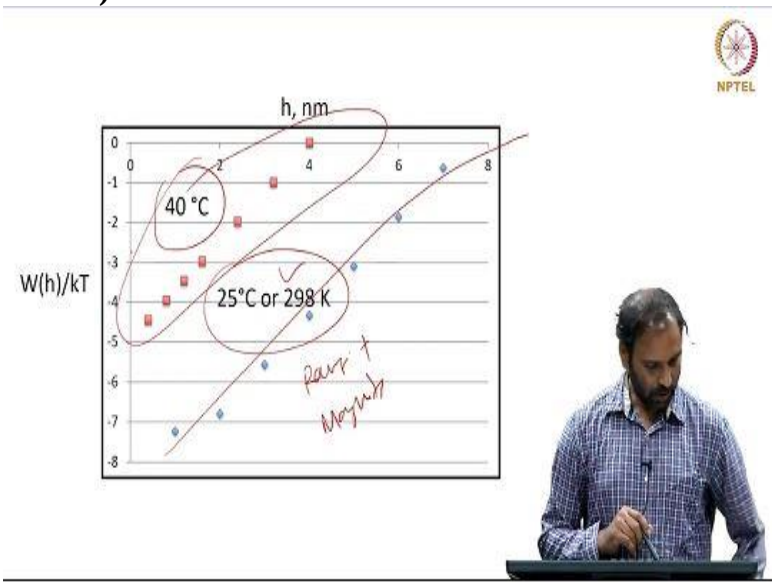

If I plot both the data, one for the 40 degrees centigrade and other one for 298 Kelvin, this is what is expected. So, I would expect that the, because of the fact that the size of the pNIPAM particles are larger or 298 Kelvin, you would expect that you know the range over which you know that these interactions are going to be effective is much larger. So, both the range plus the magnitude of the depletion interaction at 25 degrees centigrade are higher compared to both the, the range and the magnitude at 40 degrees centigrade.

Where the particle essentially shrink that is what these calculation would show you. So that is a simple problem in which you can think about. One good thing to note is that, you know the number that you are getting. So they seem reasonable. You know, typically when people talk about attractive strength, they talk about, you know, some numbers which are, you know, 10s of k_BT or, you know, several 10s of k_BT. If you get some values, which are like, you know, thousand k_BT or something, you know, they are not, they are unreasonable.

So, typically, when you do this calculation, you should look at, you know, what is the, the attractive strength as a function of you know you should always kill it with k_BT or kt, and you

just look at the numbers that will give you an idea as to whether these interactions are kind of more dominant over by the walls and are they compatible. So, you know, an idea like that would help you guys to understand, you know, the, the system that you are dealing with better. That is about the depletion interactions. And that brings to the end of colloidal polymer mixtures.