Colloids and Surfaces
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Lecture-08
Application of Brownian Force: Introduction to Interaction Between Colloidal Particles

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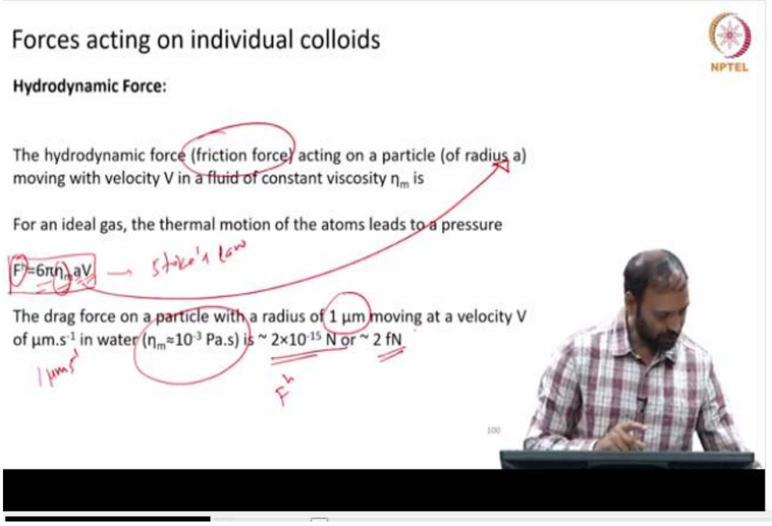

Forces acting on individual colloids

Hydrodynamic Force:

The hydrodynamic force (friction force) acting on a particle (of radius a) moving with velocity V in a fluid of constant viscosity η_m is

For an ideal gas, the thermal motion of the atoms leads to a pressure

$F^h = 6\pi\eta_m aV$ → stoke's law

The drag force on a particle with a radius of 1 µm moving at a velocity V of µm.s^{-1} in water ($\eta_m \approx 10^{-3}$ Pa.s) is ~ 2×10^{-15} N or ~ 2 fN

Okay, so you know hydrodynamic all of you know this expression already. So, this is the famous Stokes law right okay, the hydrodynamic force acting on a you know a particle it is 6 pi eta m is the viscosity of the medium in which the particle is dispersed a is the okay it is the size of the particle okay and V is the velocity which is the particles are moving okay**.** People also call it as a friction force right and a is the radius of the particle okay.

And typical numbers if you do experiments it turns out that you know the if you measure the velocity which is the particle moving if you have a 1 micrometer radius particle okay and typically you know the velocity of the particle would be of the order of again 1 micrometer per second. And if they are in water okay it turns out that this F^h the hydrodynamic force is of the order of 2 into ten power - 15 newtons okay which is 2 femto newtons right that is a number okay.

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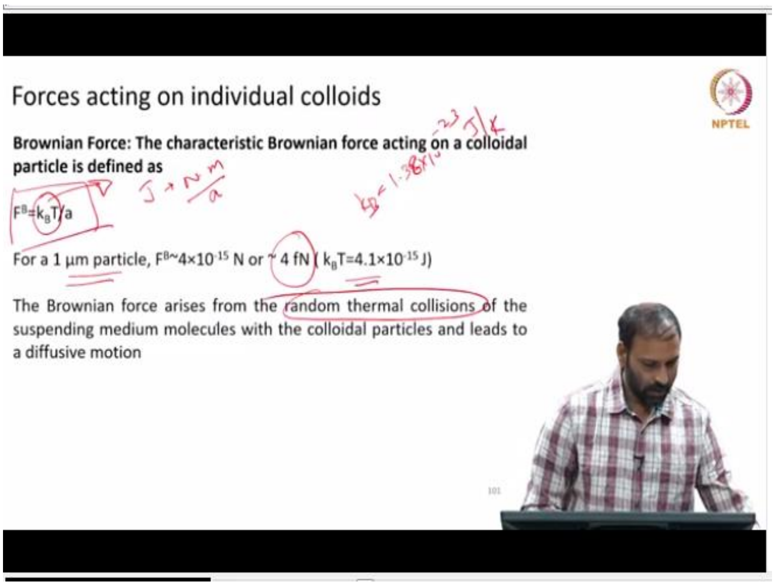

Forces acting on individual colloids

Brownian Force: The characteristic Brownian force acting on a colloidal particle is defined as

$F^B = k_B T/a$

For a 1 μm particle, $F^B \sim 4\times10^{-15}$ N or ~ 4 fN ($k_BT = 4.1\times10^{-15}$ J)

The Brownian force arises from the random thermal collisions of the suspending medium molecules with the colloidal particles and leads to a diffusive motion

The second force is the Brownian force, it is so basically this $k_B T$ right that is the thermal energy I mentioned right, thermal energy as units of joules right okay joules that is newton meter if I want to convert that to force I should have some length scale I am going to use the size of the particle itself is a length scale. Therefore the Brownian force is given by $k_B T$ divided by a okay.

And again if you take 1 micrometer particle it turns out that this Brownian force is of the order of 4 femto newton okay here. So, for that all you have to do is k_B a is you know 1.3 into ten power - 23 joules per Kelvin right and then multiply that with the temperature and then you can get these numbers okay and as we already said this Brownian force arises because of the random you know collisions of the molecules with these particles right.

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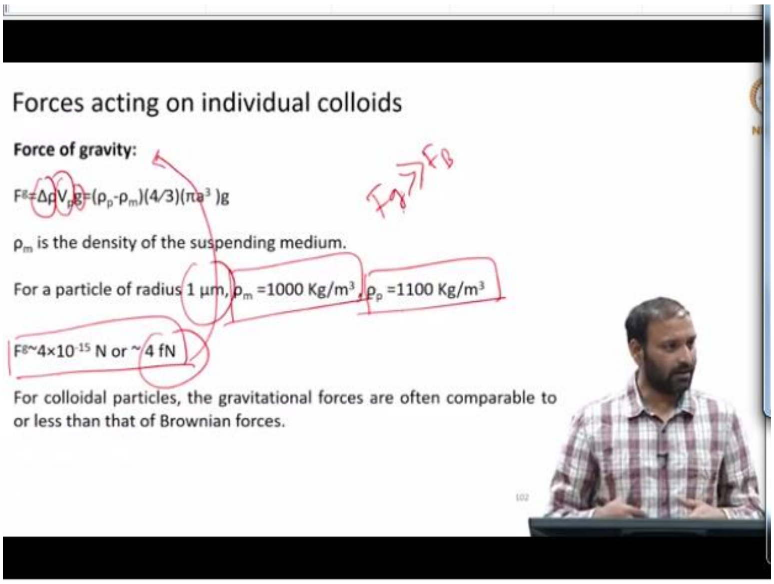

Forces acting on individual colloids

Force of gravity:

$F^g = \Delta\rho V_p g = (\rho_p - \rho_m)(4/3)(\pi a^3)g$

ρ_m is the density of the suspending medium.

For a particle of radius 1 μm, ρ_m =1000 Kg/m^3, ρ_p =1100 Kg/m^3

$F^g \sim 4\times10^{-15}$ N or ~ 4 fN

For colloidal particles, the gravitational forces are often comparable to or less than that of Brownian forces.

The force of gravity that is the density difference multiplied by the volume of the particle multiplied by g right and again if you put in typical numbers like you know the density is 1100 for the particles density of you know the fluid is about 1000 if you take 1 micrometer particles it turns out that your Fg is of the order of again 4 femto newton. What is interesting to note is that you know if you look at this 4 femto newton that is what you got for gravitational force is very much comparable to the 4 femto newton that you got for the Brownian forces okay.

Therefore if you take particles of colloidal length scale okay of 1 micrometer size you know the gravity and Brownian force are very much comparable okay. Therefore now if you make the particle bigger okay then your gravity will dominate okay. Therefore you will see that your F gravity start becoming greater than F Brownian, if it is too large it is much, much larger.

Therefore gravity is going to overweigh okay. So, the Brownian force would like to keep the particle suspended in the fluid but the gravity would like to make it sink right. So, that is so you have to think a little bit about these numbers.

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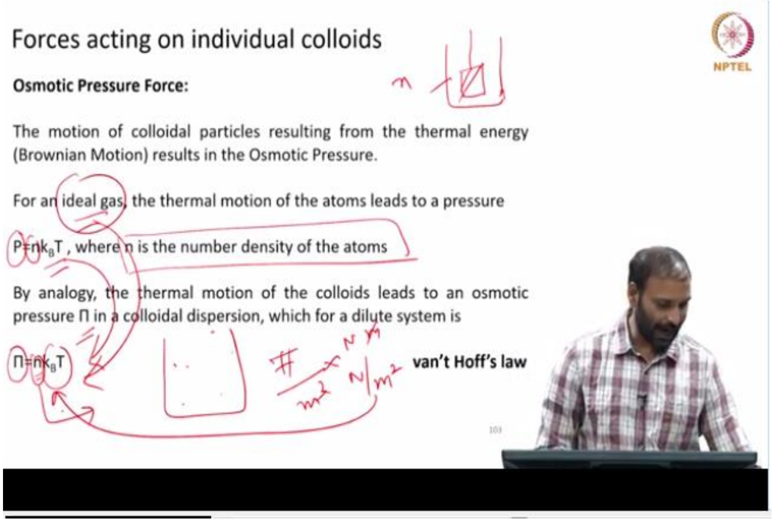

Forces acting on individual colloids

Osmotic Pressure Force:

The motion of colloidal particles resulting from the thermal energy (Brownian Motion) results in the Osmotic Pressure.

For an ideal gas, the thermal motion of the atoms leads to a pressure

$P = nk_BT$, where n is the number density of the atoms

By analogy, the thermal motion of the colloids leads to an osmotic pressure Π in a colloidal dispersion, which for a dilute system is

$\Pi = nk_BT$ **van't Hoff's law**

The last force I am going to talk about is something called as the osmotic pressure force which is defined as pi which is equal to n times k_BT where n is the number density of atoms okay . So, basically this comes from what is called as a ideal gas law kind of a concept where the pressure okay, that is exerted. So, what you do is you take a container okay. And say that I have I put a some kind of you know plate for example okay.

Now you can ask a question as to what is the pressure that is generated because of an ideal gas law okay and say that the number density of atoms in the container is n okay. So, the pressure that this plate would feel okay, it will go as n times k_BT okay. Now people have translated the same thing to particulate systems okay. So, there again the reason why this ideal gas law and this particular system kind of analogy is because again you are working with a very dilute dispersion okay, very few particles in the fluid okay.

You can bring in analogy from the ideal gas or gas like state to colloidal dispersions okay and in such a case you know your pi the osmotic pressure force okay goes as again n, where n in this case is the number density of the particles in the system okay which is number of particles divided by the volume of the dispersion okay right. So, again the units match right because n is number density which is number per volume number per meter cube and your k_BT has units of joules.

That is newton meter okay 1 meter, 1 meter you can cancel that becomes n newton per meter square which is pressure right okay. So, therefore it is a good idea to know a little bit about the magnitude of all these individual forces that are acting on the system.

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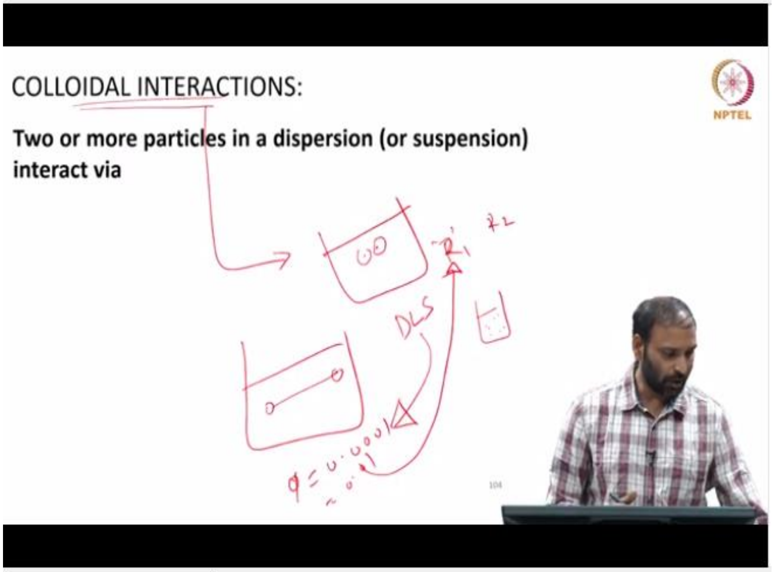

COLLOIDAL INTERACTIONS:

Two or more particles in a dispersion (or suspension) interact via

When you look at term you know dilute dispersions or you know when you are looking at particulate systems. The second point brings down to what is called as the colloidal interactions okay. So, again this becomes important when you are working with colloids or a dispersion where the particles are sufficiently close, that means if I take you know the dispersion with like say phi is equal to 0.0001 okay or something of that order right or even 0.01 for example okay.

The distance with the particle is so large that there is I can practically say that there is no interaction between the particles okay. Therefore whenever you are using like say dynamic light scattering setup for measuring particle sizes okay. One other thing that one people ensure is that you are working with a very dilute dispersion okay. So, if you get a size by using a dilute dispersion.

And if you get size by a concentrated dispersion okay or at least a reasonably concentrated system you will see that the size that you get okay R1 and R2, they are very different because in the second case the size that you get is also could also be because there is a interaction between the colloids as well okay. Therefore these the interactions become important when you are working with the sufficient dispersion of sufficient concentration.

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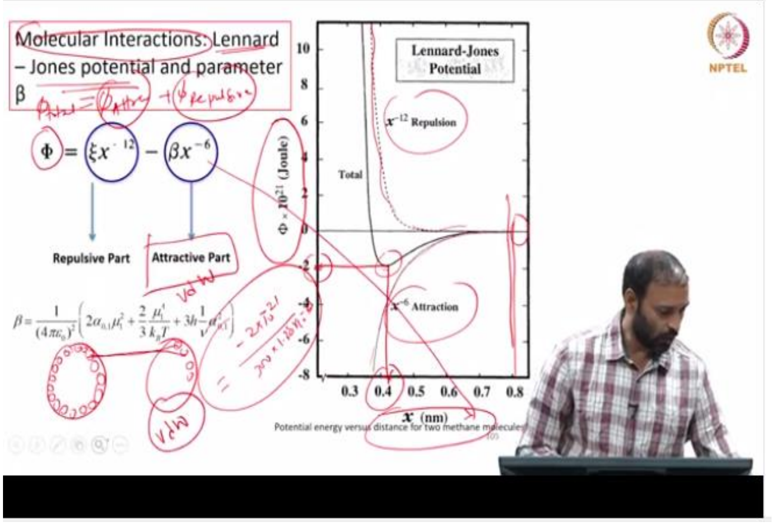

Molecular Interactions: Lennard – Jones potential and parameter β

$\phi_{total} = \phi_{attrac} + \phi_{Repulsive}$

$$\Phi = \xi x^{-12} - \beta x^{-6}$$

Repulsive Part

Attractive Part

VdW

$$\beta = \frac{1}{(4\pi\varepsilon_0)^2}\left(2\alpha_{0,1}\mu_1^2 + \frac{2}{3}\frac{\mu_1^4}{k_B T} + 3h\frac{1}{\nu}\alpha_{0,1}^2\right)$$

VdW

$= \frac{-2\times10^{-21}}{300\times1.38\times10^{-23}}$

Potential energy versus distance for two methane molecules

And before I tell you a little bit about the colloidal interactions I just want to introduce you to the concept of interaction itself okay. How many of you have heard of Lennard-Jones potential okay 1 no 2 okay. So, 2 people have heard okay this is I mean Lennard-Jones potential is people use it for mimicking what is called a molecular interactions okay. If you look it up that is a total potential okay.

And there are 2 terms here right Xi x power - 12 - beta x power - 6, typically whenever you talk about interactions in any system in general phi total that is a total interaction will typically be a summation of phi attractive plus phi repulsive, as in general of course you should have cases where there could be only attraction, only repulsion okay, but typically it could be a combination of the 2 okay.

Now so what you are seeing here is a plot of phi, that is the total interaction as a function of separation distance okay. So, all these interaction potentials that people talk about they tell you that if you have an idea about the interaction potential you can say something about whether at any given distance the particles are attracting each other, repelling each other or is the combination of both are important okay. That is what it will tell you okay.

Now if you look at this plot, if you look at this region right, your both the repulsive term goes to 0, attractive term goes to 0, the total also goes to 0 right. Therefore if these molecules in this case any molecule that obeys Lennard-Jones potential, what is plotted here is a case of 2 methane molecules okay, what I can for sure say is that if the distance between the 2 methane molecules is more than 0.8 nanometers.

There is no interaction between them right, I can say that for sure right. Now if I bring them closer right at some point you know they are going to start repelling that is given by this curve and of course they are going to start attracting as well as given by these and because you have repulsion and attraction which have opposing tendencies when you are going to add them up you are going to have a minima right.

This minima tells you something about okay what is the stable okay at equilibrium if I were to have you know a container which is filled with methane molecules okay. So, they are going to have a separation distance typically of the order of you know maybe 0.4 to 5 nanometer and the energy corresponding to that equilibrium configuration is something like about - 2 into 10 power 21 okay, - 21 because you know you have 10 power 21 here.

So, therefore this value is going to be - 2 to 10 power - 21, if I divide that by k_BT okay, that is like say 300 times 1.38 into 10 power - 23 right. If you do that you know you can kind of get an idea as to you know what is the total interaction energy in terms of k_BT okay. Now this is for a molecular system right. Now you can kind of use a similar concept to look at interaction between colloidal particles as well okay.

The only difference is that again we will talk a little bit about this later, if I have colloidal particles, this is the particle 1 and particle 2 okay. Now we know that these particles are also made up of atoms and molecules right. If these are the atoms that constitute the particles right, maybe something like this. So, what do I mean by interaction between the colloidal particles is that if I look at this attractive term okay.

This comes from what is called the van der Waals interactions okay, this is in the case of methane molecules, if I want to kind of adapt this concept to van der Waals interaction between 2 particles what I have to do is I should take one atom find out the van der Waals interaction of that with another atom present with other particle, again the same atom go to the next one, I do what is called as a pairwise addition okay.

I find out what is the total number of molecules or atoms in one particle, I find out what are the total number of atoms of you know molecules in the other particle and then I start doing pairwise addition of the interaction between the individual molecules okay and total pairwise interaction is what will be the total van der Waals interaction between the colloidal particles okay.

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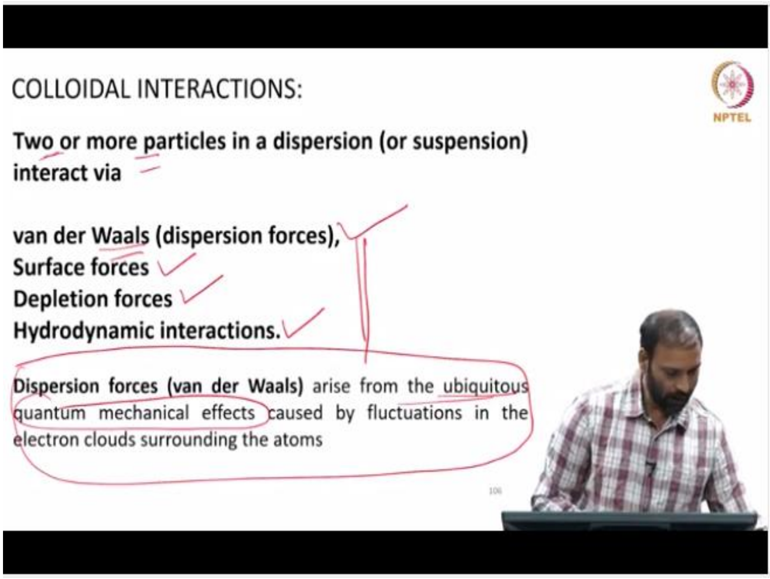

COLLOIDAL INTERACTIONS:

Two or more particles in a dispersion (or suspension) interact via

van der Waals (dispersion forces),
Surface forces
Depletion forces
Hydrodynamic interactions.

Dispersion forces (van der Waals) arise from the ubiquitous quantum mechanical effects caused by fluctuations in the electron clouds surrounding the atoms

Now so in colloidal system 2 are more particles in the dispersion can interact via several forces okay, one is the van der Waals interactions, there are also what are called as surface forces, depletion forces and hydrodynamic interactions okay. Now we will have a whole chapter dedicated to van der Waals forces in maybe starting next week. So, the van der Waals forces they arise because of what is called the quantum mechanical effects okay.

Because we know that you know atoms and molecules have electron cloud around them right, a fluctuation of atoms you know electrons in these clouds gives rise to some you know attractive interactions okay. That is what is you know the van der Waals forces.

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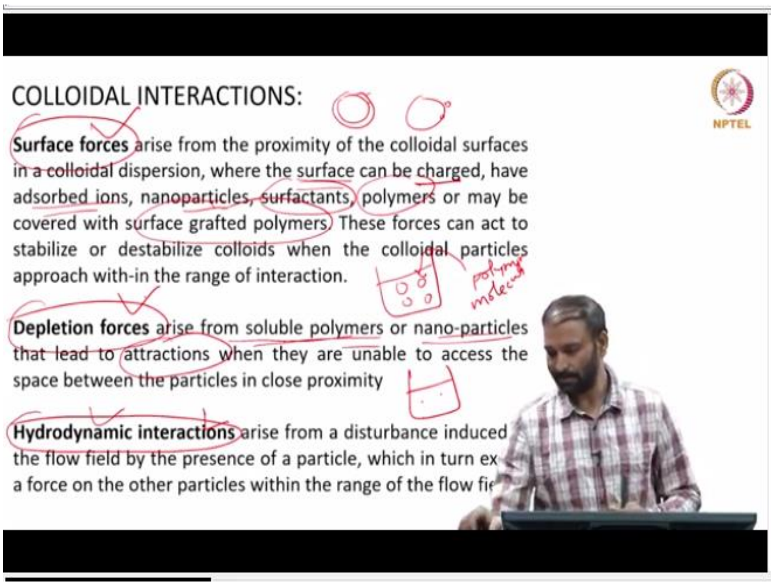

COLLOIDAL INTERACTIONS:

Surface forces arise from the proximity of the colloidal surfaces in a colloidal dispersion, where the surface can be charged, have adsorbed ions, nanoparticles, surfactants, polymers or may be covered with surface grafted polymers. These forces can act to stabilize or destabilize colloids when the colloidal particles approach with-in the range of interaction.

Depletion forces arise from soluble polymers or nano-particles that lead to attractions when they are unable to access the space between the particles in close proximity

Hydrodynamic interactions arise from a disturbance induced the flow field by the presence of a particle, which in turn ex a force on the other particles within the range of the flow fie

Now the surface forces I mean as the name itself says right, these interactions become important if you have particles you know and surfaces are ubiquitous of the particle right. The moment I have a particle I have a surface of the particle right. Now whenever you have 2 particles whose surface come into close proximity okay, when I say close proximity I will again go back to this diagram okay.

Close proximity is again relative okay, it depends on what you are trying to deal with for the case of you know the methane molecules here, close proximity is any distance that is less than 0.8 nanometer okay, anything beyond that it is not close proximity right okay. So, typically what will happen is whenever you have a colloidal particle you may have the surface of the particle that is charged okay.

You could have adsorbed ions okay, the particles can even have nanoparticles on the surface okay, the particles could have surfactant molecules on the surface or polymers you know the grafted polymers you know are absorbed polymers right and now whenever you have such things on the surface and if the particles come to close proximity that is when you are going to have the surface forces or surface interactions okay.

Depletion forces are typically come into picture whenever you have a system which has colloidal particles and you add polymer molecules to them okay. So, that is they arise from soluble polymers or nanoparticles and typically when you had such things there are some attractive interactions that come about okay. Again we will have a chapter dedicated to you know depletion forces in you know in a few weeks.

And the last kind of interaction what is called a hydrodynamic interaction that come whenever you have a dispersion and they are kind of disturbed by some kind of flow field okay, that means I could have 2 particles in a fluid you know and if I apply some kind of a shear they could come together, they could be a attractive interaction that is purely because of the flow that you have induced okay.

And such kind of you know interactions are what are called as hydrodynamic interactions okay. These kinds of interactions only are important whenever you have such dispersions under flow okay, under stagnant conditions they are not important okay, under stagnant conditions what are important are the van der Waals forces, the surface forces and the depletion forces okay.

Maybe we will stop here think through a little bit of these things and so, I think with this we kind of finished the intro part of the colloidal course okay, we will try and look at some you know advanced topics from next week onwards.