Fluid Mechanics
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Lecture - 31
Brownian motion and electrophoresis

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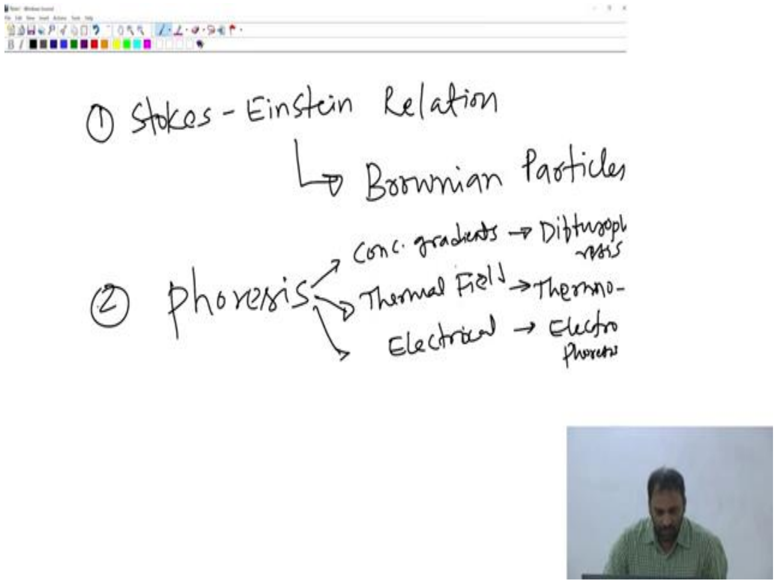

One is to look at, one is to look at something called as Stokes Einstein relation this is applicable to something called as Brownian particles ok. As, I was mentioning in the previous class this is one of the widely used relationship for a or relation for finding of particle size data ok.

If, you want if you have a particle dispersed in a fluid, if you want to measure it is diffusivity, or if you want to measure it is particle size ok. This is one of the widely used relation ok. We are going to talk something about Phoresis ok, which basically refers to if you have a particle and in a fluid, and if you set it to motion ok. Motion of a particle in a fluid what is called as phoresis.

And, you can set a particle into motion by using external field right. And, either you could use something called as a concentration gradients ok, or you could use thermal field or thermal gradient, or I can use some other force ok, it could be electrical forces you know or magnetic forces right. So, if you set the particle into motion by using you know by exploiting the concentration gradient, this is something called as a diffuso-phoresis ok. If, you use thermal fields something called thermo-phoresis ok. And, if you use electrical field it is what is called as a electrophoresis right ok.

So, we are going to look at some aspects of you know phoresis ok. This is what is going to be the plan for today. So, I am just going to start by showing you again a movie which I showed in the last class ok.

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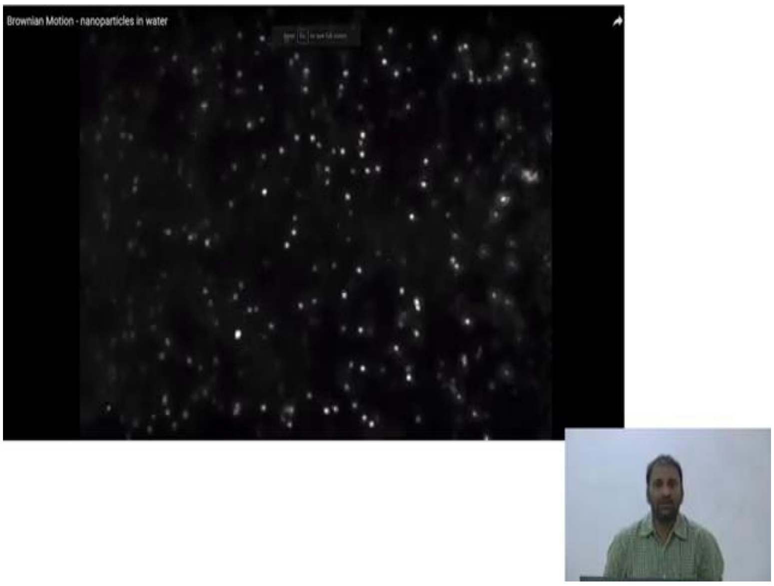

So, this is what has been done is that you know the white dots that you see, these are particles ok. These are something called as a fluorescent particles ok, when people use fluorescent particles the idea is that, if you use a regular optical microscope ok, which works by using the white light, you can see objects up to about a micrometer or larger ok.

Of course, you can also look at things that are smaller than micrometer, but you cannot resolve it ok, you cannot get a good image by using optical microscope. What people do is they use fluorescent particles ok, by which I can actually push the limit of microscopy I can also look at things that are much smaller than a micrometer size. You can even look at things that are 200 nanometers, 300 nanometers ok.

So, this is sub micrometer particle and these are fluorescent particles and white dots as I said these are spherical particles dispersed in the fluid, nothing is being done. All that has done is you are just putting the particles in the fluid and you are just watching you know with a microscope ok. And, what do you see is that particles are moving right, this is without the influence of any external force they are just moving by themselves ok.

And, if you can see there is no particular direction in which the particles move right they are just moving chaotically and that is because ok. So, you have molecules of the fluid around each of these particles and there is a bombardment of the fluid molecules with the particle ok. And, depending upon the bombardment it will just move in some random direction ok, it could be in x y z any direction ok.

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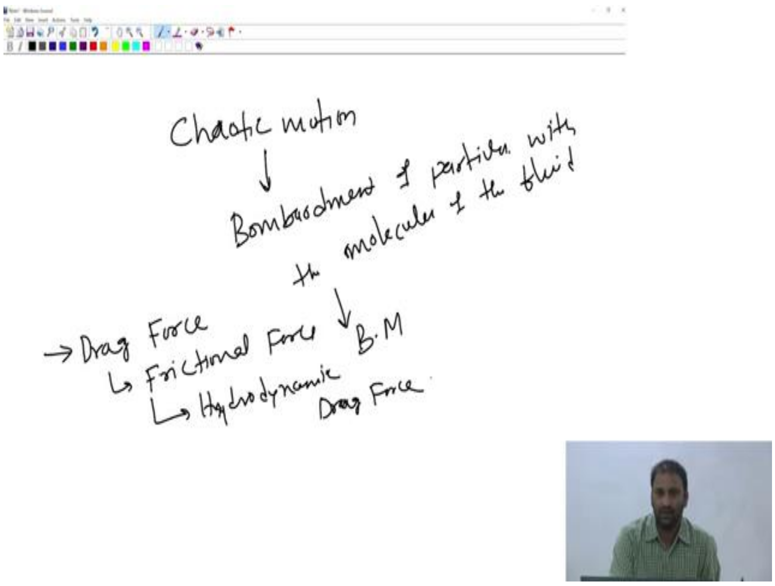

Now, such a chaotic motion is something called as Brownian motion right ok. Such a chaotic motion ok, such a motion which is because of bombardment of particles with the molecules of the fluid is what is called as a Brownian motion ok. So, the particles really do not move in any particular direction ok, this is a random motion ok, which is purely existing, because there are molecules and atoms that constitute the fluid in which these particles are dispersed ok. Now, from yesterday’s lecture, we know that whenever we have a relative motion between the particle and the fluid ok. There is going to be something called as a drag force right ok.

We also said it is also called as frictional force ok, you can also call it as hydro dynamic drag force right. Now, so, you can think about of course, we already know what this hydrodynamic force is right yesterday we already wrote up an expression for it right, but the other way of thinking about this you know drag force is going to be you can actually bring in the concept of friction factor ok.

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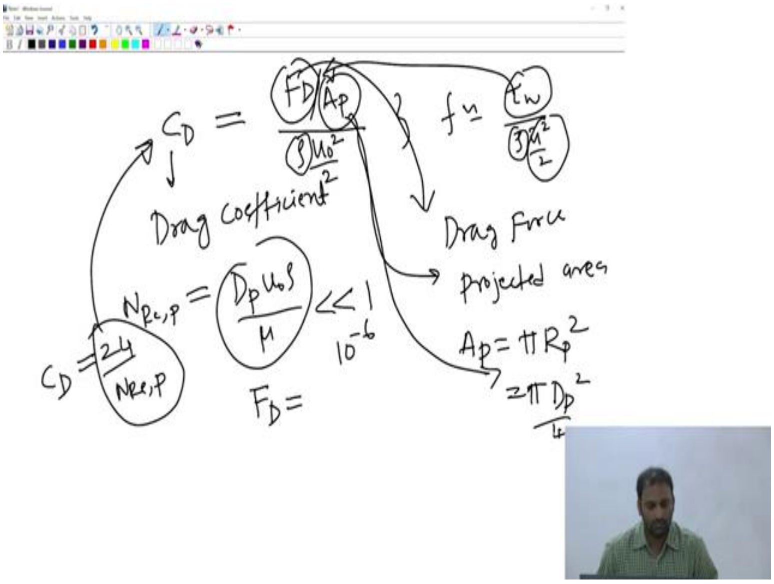

So, in this case C D is something called as what was that?

Oh it is. So, know oh my god is that ok. C D is something called as a drag coefficient and it is defined something like this ok. Drag force divided by some area over density time some velocity head. Do you recognized this formula, some similarity that you may have seen in the previous lectures. So, if you look at this carefully, this is of the form your friction factor, you know was something like wall shear stress divided by you know some velocity square right, that is some something like that right that is what it was density ok, multiplied by the velocity head and there was a wall shear stress ok.

$$C_D = \frac{\left(\frac{F_D}{A_P}\right)}{\left(\frac{\rho u_0^2}{2}\right)}$$

$$A_P\ (Projected\ area) = \pi R_P^2$$

Now, your shear stress is actually force per unit area right. So, F in this is what is called as a drag force and your A P is something called a projected area ok. And, this projected area what is what is being done as if you have a spherical particle ok. If, it is that is fixed in space and if there is a liquid moving over it ok. Now, what you do is you look in the direction perpendicular to the flow ok. What is that area that you see ok.

If, you have a spherical particle, if I look perpendicular to the flow what I would see is a a circle right. So, your A p is going to be area of the circle that you see, that is your projected area ok.

And, of course, rho is the density of the fluid and u 0 is the velocity with which the your particle is moving in the fluid ok. Now, lot of people have done, so now, again we did this calculation yesterday if you take the Reynolds number for the particle, we said you know it is going to be a diameter of the particle times some average velocity, times rho the density of the fluid divided by mu right. And, it turns out that because of the particle dimension that we are working with this is going to be much much less than one right, yesterday we calculated this is going to be of the order of 10 power minus 6 ok.

$$N_{Re,P} = \frac{D_P u_0 \rho}{\mu} \ll 1$$

Now, whenever you are working under conditions where the Reynolds numbers are much much less than 1, we said that comes into some kind of a low Reynolds number of flows or the laminar flows right. And, people have done a lot of experiments and they have found that this C D for the Reynolds number much much less than one goes as 24 divided by the Reynolds number ok.

$$C_D = \frac{24}{N_{Re,P}}$$

Now, what I can do is, I can take this relationship and substitute for C D in this equation, I know what is the average velocity ok. I know what is rho and as I said your A p is the projected area which is you know pi R p square. If, you substitute that can you just let me know what your FD is can you just do this simple math? So, you substituted for C D as 24 by the Reynolds number and an Reynolds numbers is given by this ok.

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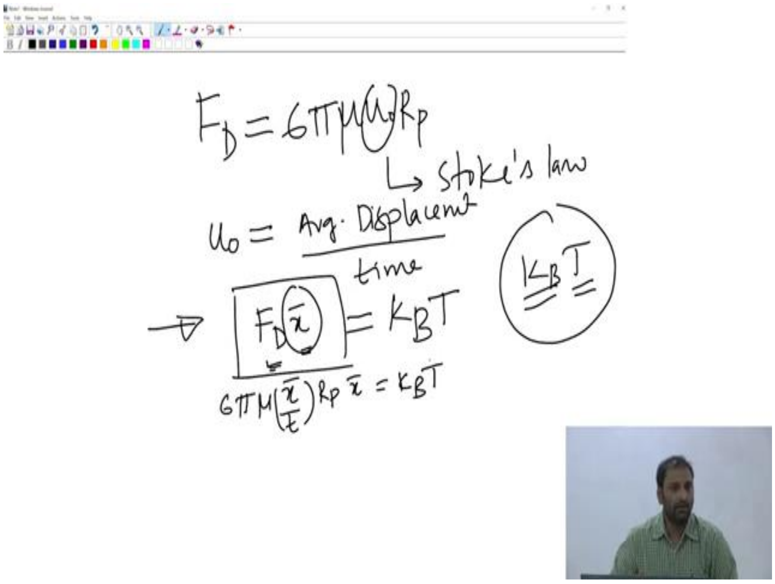

And so, your A p is pi R p square or if you want to you know is pi D p square by 4 right ok, if you do that can you guys let me know what FD is right.

$$F_D = 6\pi\mu u_0 R_P$$

So, you basically recover back the Stokes law right that is what we are done right, now if this is your velocity with which the particle is moving ok. If, I know what is the average displacement over time is what you your average velocity right. Now, I have a movie in which the particles are moving ok. I can track you know the particles in every frame of the video; I can get their location ok.

And, therefore, I have a way of calculating, what is the average displacement of the particle ok, per unit time is going to give me what is the velocity with which the particles are moving right. Now, if you if I want to calculate what is so, now, that I know that there is a particle that is moving there is a drag force. So, I want to calculate, what is the energy that is required to move the particle? Ok.

So, how do I calculate that, I want to calculate what is the energy that is required to move the particle right. So, the work that has to be done for moving the particle or the energy that is required to move the particle is essentially your FD times x bar right. Your force multiplied by distance and we know that you know it is moving it has more than average distance x bar.

Now, so, this energy that is required to move the particle, where does it come from it comes from the thermal energy right your K B T. So, we said that you know the reason why the particle are moving is because the solvent molecules are hitting the particle ok. And, why do solvent molecules are hitting the particle, because your fluid is at a is at a finite temperature ok, whenever you have a finite temperature.

So, you are going to have every molecule is going to be associated with the energy which is given by Boltzmann constant times your temperature ok. Therefore, your the energy that is required to move the particle, which is FD times x bar actually comes from the thermal energy ok. Now, what I can do is I can substitute for FD is 6 pi mu u naught is x bar divided by t times R p times x bar is equal to K B T right.

$$F_D\bar{x} = k_B T$$

$$6\pi\mu\left(\frac{\bar{x}}{t}\right)R_P\bar{x} = k_B T$$

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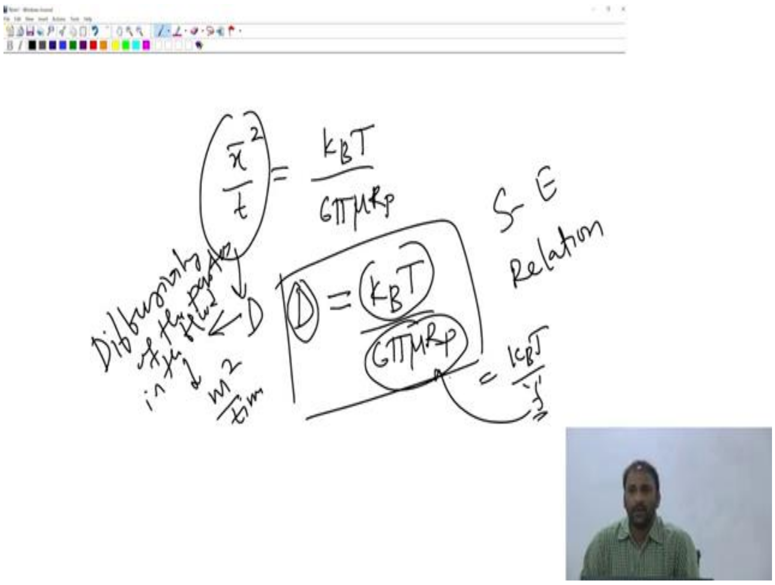

I can rearrange this and I can write it as x bar square by time is equal to K B T divided by 6 pi mu R p right. Yeah. And, this is D which is the diffusivity of the particles in the fluid ok. And, it should have dimensions of meter square per time right meter square per second ok. Therefore, your diffusivity of the particle is equal to K B T divided by 6 pi mu times R p, this is what is called as a the Stokes Einstein relation ok.

$$D = \frac{\bar{x}^2}{t} = \frac{k_B T}{6\pi\mu R_P}$$

This is a simple arguments of you know getting this equation, but there are other ways of doing this ok.

So, all that we did was we said that you know there is a particle is in motion and because of it there is going to be a drag force ok. And, we said that this is basically Stokes drag because of the fact that it knows numbers comes out to be much much less than 1 ok. And, the energy associated with moving the particle is your drag force times the average displacement ok. And, that has to come from the thermal energy just by equating that, you will get in the relationship between the diffusivity of the particles in the fluid, and the thermal energy. And, this is some kind of a friction factor ok. People also write this as K B T divided by f friction factor which is basically 6 by mu R p yeah correct.

Yes, why is it not the case? So, all that we are seeing is you know I mean ok. So, this is going to be I would say this is kind of more of an ideal idealized case right ok. And, it turns out that you know of course, if you take particles which could be rough for example, if the particle is kind of set into rotation, because of you know this bombardment.

In such cases you would have to worry about you know accounting those you know cases, but if you take like say rigid spheres, smooth spheres of course, there are some kind of assumptions you know where you can use this, but this is typically applied for rigid particles ok. And, the particles has to be have to be in colloidal size range of course, because they have to exhibit Brownian motion. And, of course, this is for a smoother surface and things like that ok.

Of course, you know in real systems you know, but it turns out you know this kind of this equation. Typically is valid for you know a lot of colloid that people use and you know every days you know experiments or life so, yeah ok. So, now that we know that there is a relationship that exists between your diffusivity and you know K B T and in the friction factor, what someone called John Perin ok.

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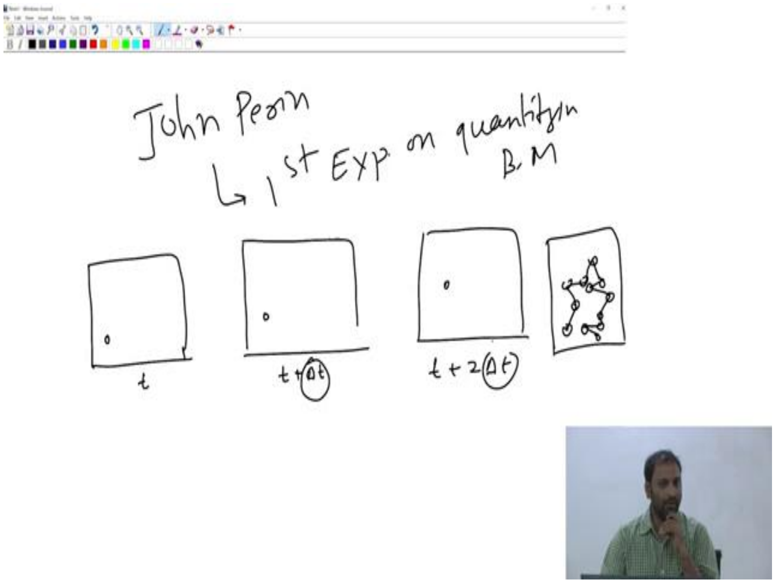

Did was he basically did the very first experiments ok. On quantifying Brownian motion ok, this happened around 1920s ok. And all he did was he basically had this video of the particles moving in a fluid and he tracked the particles. So, what I what he did is this is a the you know the frame of the movie that I have got, I have one particle here. And, what I do is add some if this is time t ok. I take at some time other time interval say t plus delta t, I look at where the particle is ok. Now, I look at another frame say t plus 2 times delta t, I look at where the particle is ok.

So, so, in the end what he did was he basically came up with a picture of the location of particle as a function of time right. So, you know it was basically exhibiting some chaotic motion. So, all that he had was he had some information about the time frame ok, that is you know the distance you know he had information about what is the delta t between the 2 frame that he was considering. And, of course, he had tracked the particles; that means, he had access to the particle position as a function of time ok. So, once he did that. So, he calculated what is called as a mean square displacement ok.

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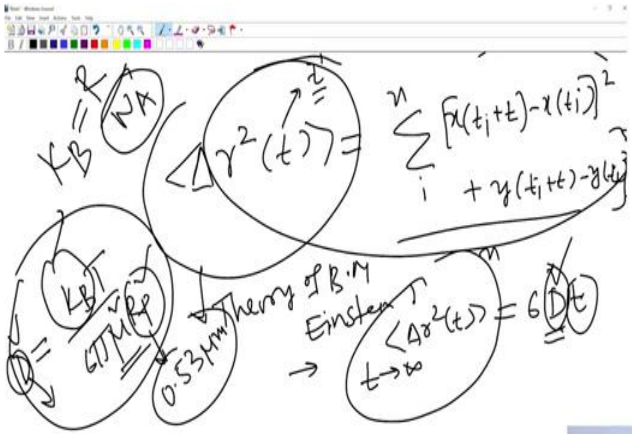

And, that mean square displacement is given by something like this ok. All, you have to do is if you have basically tracked you know the particle for a time t ok, if you have observed it for enough time. So, what he what he did is your x at time t i plus t minus x at time t i whole square plus y at t i plus t minus y at t i whole square right, divided by n is the mean square displacement ok. All that you do is you basically know the positions right ok. And, if I have like say I have taken 10 frames right, I know the distance it travels in every frame ok. So, that is your mean square displacement.

$$< \Delta r^2(t) >= \frac{(\sum_{i=1}^{n}[x(t_i + t) - x(t_i)]^2 + [y(t_i + t) - y(t_i)]^2)}{n}$$

Now, that the mean square displacement could be measured by experiment what he did is he made use of the theory of of Brownian motion that Einstein had developed ok, which basically said that, if you observe a particle for a for long enough time that is for t going to infinity ok. Your mean square displacement ok, go says 6 times D t, where t is your observation time and D is the diffusivity of the particles ok.

$$As\ t \rightarrow \infty; < \Delta r^2(t) \geq 6Dt$$

Now, because he was able to measure this ok, Perin was able to measure it he can actually calculate what is diffusivity ok. Now, your Stokes Einstein relationship is K B T divided by 6 pi mu R p ok. Now, he was careful enough to pick particles of exactly same size ok, because he had a access to an electron microscope, he basically took particles which are about 0.53 micrometer in radius, he was able to work with well characterized particles.

So, he knew R p ok. And, because he could do Brownian motion experiments, he was able to calculate D, that is known now ok. And, of course, he used water as a fluid in which the particles were put ok. He knew the viscosity from this what he did is he calculated K B ok, the Boltzmann constant ok. And, we know that Boltzmann constant is basically your universal gas constant divided by the Avogadro number ok. That is why that is how he was basically able to calculate what is the Avogadro number and the number that he got from his experiments, as I said yesterday was very close to 6.023 into 10 power 23 ok. So, this is yeah go ahead.

Which one?

Student: The mean square.

The mean square displacement.

Student: Yeah.

So, if you look at the video right. So, you had particles all the particles were kind of exhibiting some motion right. Now, what I can do is I can actually go and pick one particle. I can look at that particle as a function of time ok. Now, in each frame I locate the same particle ok. Now, so, therefore, what I can do is for every frame, I can associate a location right, which is basically your x comma y ok, because you are looking at in 2 dimension ok.

Now, once I have access to the position of the particle ok. And, if I know what is the time frame that I am basically considering from my the video right. I can choose that hey I have a like say video for say 5 minutes, I am going to look at every 5 seconds you know what is the location. So, if I have information I can basically back calculate what is it the mean square displacement yeah ok.

So, you know so, as I said right this is a useful equations which you should remember, you know and it is kind of used in a lot of commercial instrument that people buy for measuring particle sizes. The basic equation that basically goes into the calculation of the sizes is this particular equation ok. They will have some way of measuring diffusivity ok. It could be done either you know if you use a microscope. There will be some algorithm by which I can actually calculate the mean square displacement from which I can calculate D ok. Plug in that D here ok, I can calculate you know R p, which is the size of a particle right or there are other ways of getting D ok.

And, there are some instruments where what people do is they measure, if I have a particle in a fluid you shine a laser light ok. Because, the particle is moving ok, you detect what is called as a scattered intensity ok. And, because of the chaotic motion of the particle the laser intensity also fluctuates and from that fluctuation there is another way of back calculating your D ok.

So, no matter what the instrument is ok, whether you get d from the fluctuations of the scattered intensity or by using some kind of particle tracking. In the end the size of the particle is basically determined by using stroke size in Einstein relationship ok. So, we will move on to the next topic, which is for phoresis ok.

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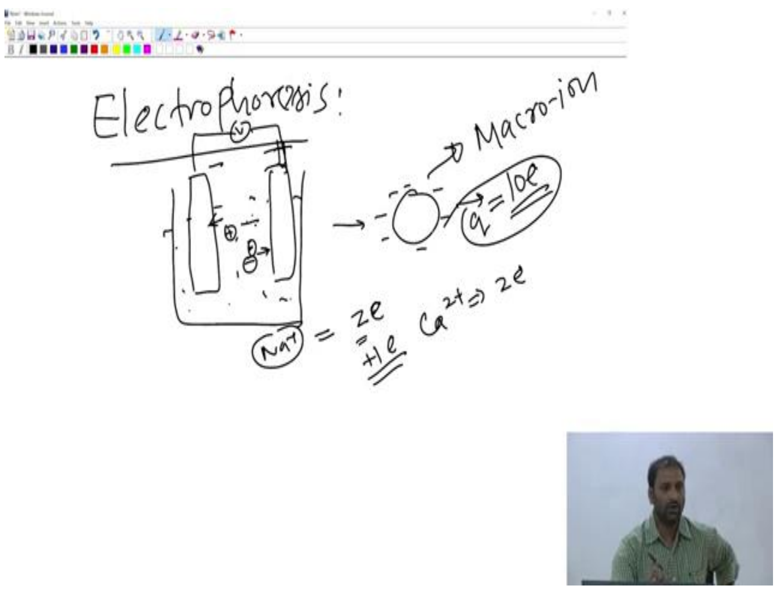

In specific we are going to talk about something called as electrophoresis ok. Now, for electrophoresis so, what you do is. So, all of you know if you have like say, I have a cell say, if I have a cathode for example, and an anode right. Now, if you have ions in solution ok. If, you have like say positively charged ions or negatively charged ions in solution like this is say this is going to be your a fluid right.

Now, we know that you know the moment you apply some kind of a voltage difference right a potential difference, we know that you know ions are going to move right. Now of course, you know the positive charged ions are going to move towards the cathode right. It is going to be moving this way and negatively charge is going to be if this is your negative and positive right. So, negative ions is going to be moving in this direction right.

Now, so, we know that the charged ions do move when you apply an electric field right. Now, similarly you can also consider a charged particle ok; say that you know I have a particle that has charged ok. I can consider this is a macro-ion ok. So, now, if I take Na plus Na plus right so, the charge on that is your valency times e right, where e is the fundamental elementary charge right. So, in this case for Na plus Ze is equal to plus one times e right that is your the charge on Na plus ok.

Now, if I have Ca 2 plus is going to be 2 times e right. Similarly, if I have a Macro-ion say that you know there are some 10 charges on the particle surface ok. Therefore, you know I can say that you know there is there are 10 charges multiplied by e is going to be the charge on the particle this that say q. Now, in electrophoresis what is actually exploited is the fact that you know if you have similar 2 ions, the particles have to be charged for it to move in a potential you know that you apply right.

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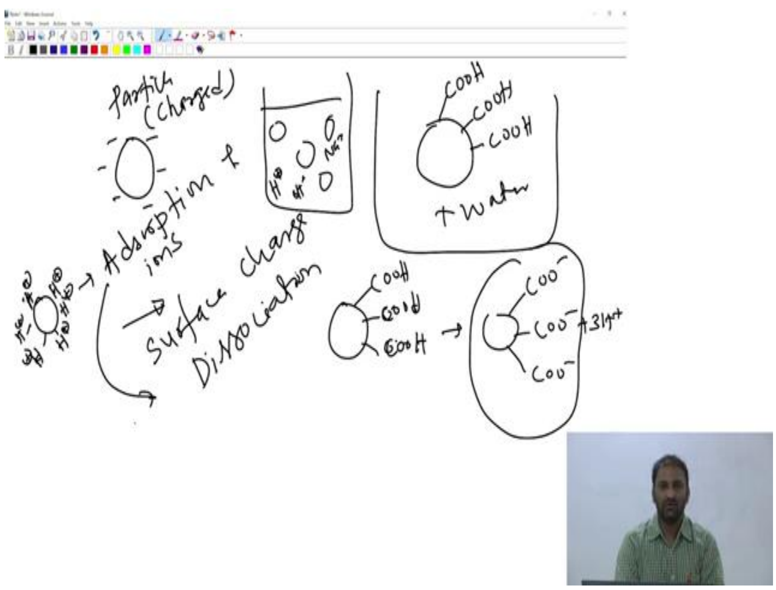

Now, let us think about, how does the particular acquire charge? So, I have a particle ok. And, that is charged any thoughts as to how the particles can be charged yeah have something to say.

If, you have surfaces you know the particles would get charged right, I mean that you would have you know learnt in your you know 10 plus 2 or something like that, but that would happen you know that is because of friction right. Now, if you have particles in solution ok. Now, we are talking about particles that are dispersed in a fluid ok. Now, would have I would like to have them to be charged, there are different mechanisms by the by which the particles can be charged ok. One is that if I have a particle ok.

Now, the chemistry is so, advanced that I can actually graft the particle surface ok. I can actually put some charges on the particle surface ok. I can maybe make the surface, functionalized with some charges. Now, whenever I have particle like that, the moment I put it in water, what will happen is this particle with you know this surface groups, it gives 0 COO minus ok. This mechanism of charging a particle is by, what is called as a surface charge dissociation ok.

You can buy particles like this ok. If, you want particle with any functional groups, you can get them in the market ok. So, if I say hey I want a particle with the COOH groups on the surface you can buy it ok.

So, therefore, one of the ways by which the particles can acquire charge is that, you know, you have a particle and there are some surface functionalization. This surface functionalization is done by putting some chemical molecules right, molecules on the surface. The moment you put such particles in water there is going to be some dissociation and that is going to leave a particle charge ok, this is one mechanism. There are other mechanisms, where if you have particles in a solution, if there are some ions in solution ok.

It could be H plus or OH minus or you know or Na plus or so, whatever ok, then what could happen is your ions can go and get adsorbed on the particle surface ok, there could be a physical adsorption of ions on the particle surface ok. So, this is this mechanism is something called as adsorption of ions right. It could be absorption of ions, it could be adsorption of any charged molecules, it could be adsorption of charge surfactants, it could be adsorption of charged polymers ok.

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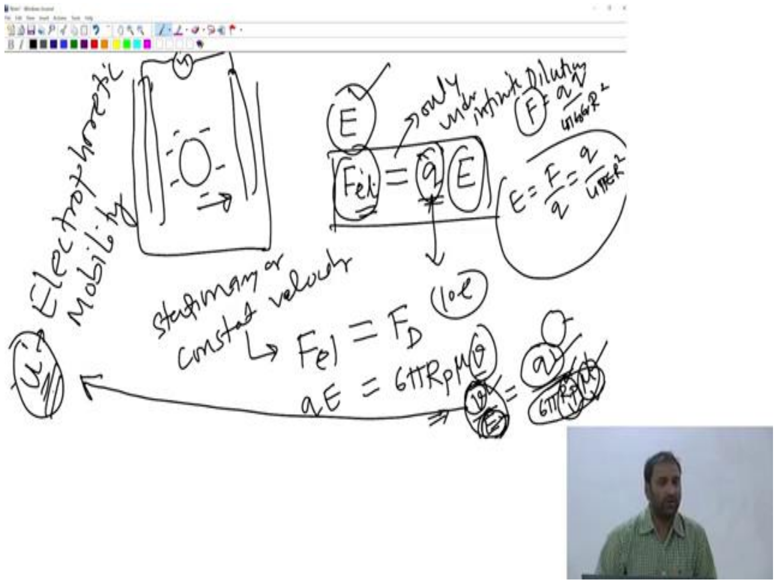

So, now that we have a charged particle ok. And, say that you know I am going to apply a potential difference right. He is going to move right just similar to the ions that we talked about. Now, if you apply an electric field E ok, if you are applying electric field E the force the electrical force or you know if the force with which the particles move in the applied field is given by the charge ‘q’ times E ok. So, you have done this at some point right. If, you have you know coulombs law right, your force is q 1 q 2 by 4 pi R square right.

Now, if you want that is the force of attraction or repulsion between you know of course, there is 4 pi epsilon 0 epsilon R right sorry yeah ok, that is your right. Now, electric field is basically yours force per unit charge right is q if you say q 1, q 2 instead of that if you have q squared all right. So, let us say I am going to do that ok, you have 2 charges right. So, q divided by 4 pi epsilon 0 epsilon R times R square, you know that is your electric field right. That is the definition of so, that is how the force and the field are related right all of you know this right yes, no.

So, basically the way you know the electric field is defined is it is basically force per unit charge ok. So therefore, if I am saying that I know I am applying an electric field E ok. The force with which the particle start moving, either towards a positively charged electrode or a negatively charged electrode is given by F eq, which is q times E and as I said q is the charge that the particle carries ok. And, we have been saying that you know I am going to consider that this is a Macro-ion.

So, if I say that you know I have a particle surface with let us say 10 charges, 10 dissociable groups ok, your q is going to be 10 times e ok. But for in general if you can call it as q, which is the charge that the particle has right. Now so, of course, you know if you did not apply the electric field the particle was moving, because of the Brownian motion right. Now, that now that you applied a field is going to first it is going to accelerate right; it is going to start moving faster towards one of the electrode ok. And, how fast it moves it depends on the strength of the applied field right.

Of course, you know it cannot accelerate infinitely right, because it is also going to feel the drag, because of the presence of liquid is going to be slow down right, as it moves ok. And, ultimately it is going to start moving with some stationary or a constant velocity and that constant velocity is basically determined by the balance between F e l and your drag force right, because you know whenever you have a particle moving in the fluid there is a drag force.

Now, the drag force basically opposes the motion ok, ultimately there is going to be an equilibrium and after that initial acceleration the particle slows down and it is going to start moving with a constant velocity ok. Now, this F e l is q times e ok, and F D is your 6 pi R p times you know mu times some velocity v right. That is the velocity with which the particles would move right, after that initial acceleration.

Therefore, I can actually get what is v by E, which is the velocity which with the particle is moving divided by the applied electric field that basically goes as q divided by 6 pi R p into mu right ok.

$$F_{el} = F_D$$

$$qE = 6\pi R_P \mu v$$

$$\frac{v}{E} = \frac{q}{6\pi R_P \mu}$$

This velocity, velocity per unit field is something called as a is denoted by a quantity ‘u’, which is called as electrophoretic mobility ok. So, the velocity which with the particle is moving per dived by the field that you apply ok, that velocity is what is called as electrophoretic mobility.

And, if you have a way of calculating what is the electrophoretic mobility ok, you can if you know the parameters of the particle and the fluid that you are using, I can actually calculate what is q that is the charge on the particle ok. Therefore, what people do is they p people exploit this concept called electrophoresis; that means, the fact that I can put up I can set a charge particle into motion by applying electric field, I can exploit that to basically measure the charge of the particle ok.

And, again the experiments are going to be very similar ok. What they do is they will construct a rectangular cell ok, that has 2 electrodes an anode and a cathode you put up a dilute dispersion of particles. The reason why dilute dispersion of particle is important is because it turns out, that this expression that we wrote up right. If, F e l is equal to q times E it is actually valid only under infinite dilution; that means, the number of ions that you should have in solution or the number of charged particle that you have in solution should be very very few.

Because, if that is not the case what is going to happen is if there are a lot of particles you know next to each other ok, the motion of one is going to be influenced by the other as well right. So, you would have to avoid that ok. So, this kind of formalism is valid only if you are working with a very you dilute cases ok, where the concentration of ions in your solution is very very less, or if you want to talk about colloidal particles that your the particles number of particles in your dispersion is going to be very very few ok.

So, and the and the experiment that is done is as I said we take a rectangular cell you put in 2 electrodes ok, you put in this dilute dispersion. I can put this below a microscope I apply a known electric field ok; that means, I know what I am applying and basically I know what is the either I am applying ok. Now, I am recording a video of how the particle is moving, because I can track particles I can actually get what is the velocity with which the particle is moving right. All, I have to do is take different frames I locate their position and from that I can get that what is the velocity with which the particle is moving.

So, therefore, I have some way of calculating at the electrophoretic mobility ok. Once, I do that ok. If, I know what is the if I have some other independent way of measuring the particle size either by you know some using an electron microscope or you know some other means I know R p. If, I know what is the fluid, that I am using ok, I can basically calculate what is the electrophoretic mobility. Again, this is again one of the very common technique that everybody uses for measuring the charge on the particle.