Colloids and Surfaces
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Lecture-09
Application of Brownian Force: Measurement of Diffusivity and Size

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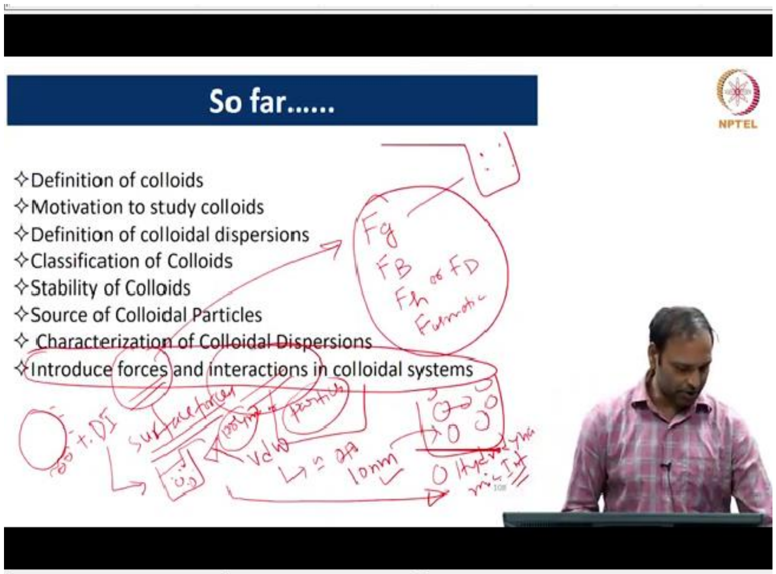

Okay, so we will begin right. So, in the last class we introduced forces and interactions in colloidal system.

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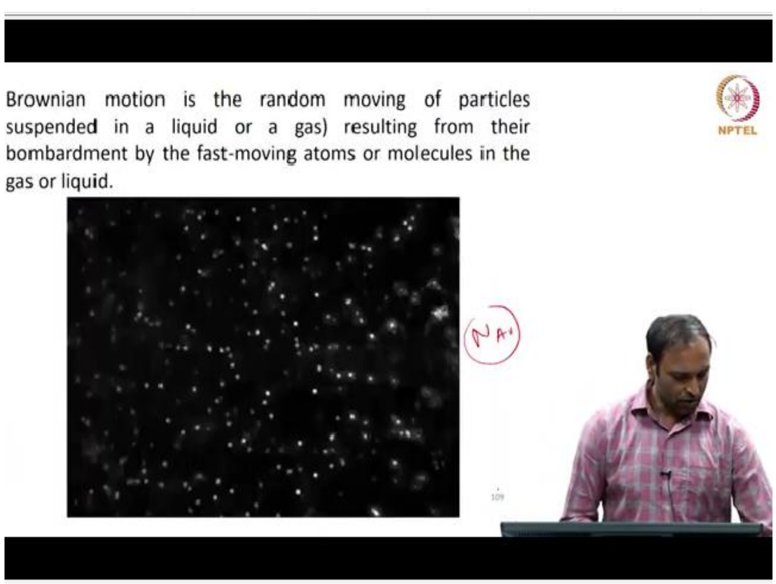

And the way we did that was by looking at Brownian motion, right. This video did not play the other day. So, I just want to play this. So, that is these are fluorescently labeled particles, which appear bright, you know, they more like look spherical, right. They are spherical particles, which are being continuously bombarded by the solid molecules and if you look carefully they are not really moving in any particular direction, right.

They are just about there in some location and they are jiggling around, right. And that is what is called as a Brownian motion. And what we did was we use this as an example. And then I told a little bit about how carefully these experiments were designed right to estimate, you know, the Avogadro's number right. And then, in doing so, we just said that, you know, there should be absence of certain forces on the system.

And there should be some absence of interaction between the particles and the particles on the wall right in which the experiments are done. So, therefore, that is how we kind of, you know, introduce you to the concept of interaction of force on the particles and then interaction between the colloidal systems in terms of force, we talked about the force of gravity right Brownian force okay, we talked about hydrodynamic force okay.

It is also called as you know drag force as well in this case, plus we also mentioned something about osmotic pressure force okay. Okay and having an idea about what is the typical you know magnitude of each of these forces on the particles or the magnetic forces in a colloidal system would help you to design in a good experiment okay. And similarly we said that you know whenever you have many more particles, okay.

If the particles are very, very far apart, then you do not have to worry about interactions, but you know typically when you work with you know a dispersion which contains large number of particles, when the particles are sufficiently close, then we should talk about what are called as a inter particle interactions okay, that is not on the individual particles, but if you have particles in the immediate vicinity okay then you talk about the interaction between the colloidal particles.

When I say vicinity, again it is relative right depending upon the kind of forces that you are dealing with okay. For example, if you talk about van der Waals forces, which will you know, expand further typically, you know, this van der Waals force of interactions is operative and the distance between the particles is about you know 10 nanometer or less okay. That means, if you have any distance which is larger than this, you do not have to worry about van der Waals force of interaction, okay.

So, we talked about van der Waals force of interaction, we talked about surface forces right and surface forces we said that the surface forces can come about if you have particles that could have charge and the particle you know, which could have some adsorbed ions, absorbed polyelectrolytes, surfactants, nanoparticles right. So, it could be anything on the surface of the particle and that could lead to some interactive forces.

Then we also mentioned about something called as a depletion interactions, okay. And we mentioned that such interactions would only come into picture whenever you have a colloidal particles you know in a fluid and to that, you add a polymer or any particles such that the size of the polymer or the particle that you added is much, much smaller than the particles, you know, which make up the dispersion okay.

So, again we will discuss this at length plus we also mentioned the final type of interaction what are called as hydrodynamic interactions okay and we said that such interactions would only come into picture whenever there is flow, right, that is where we had stopped okay.

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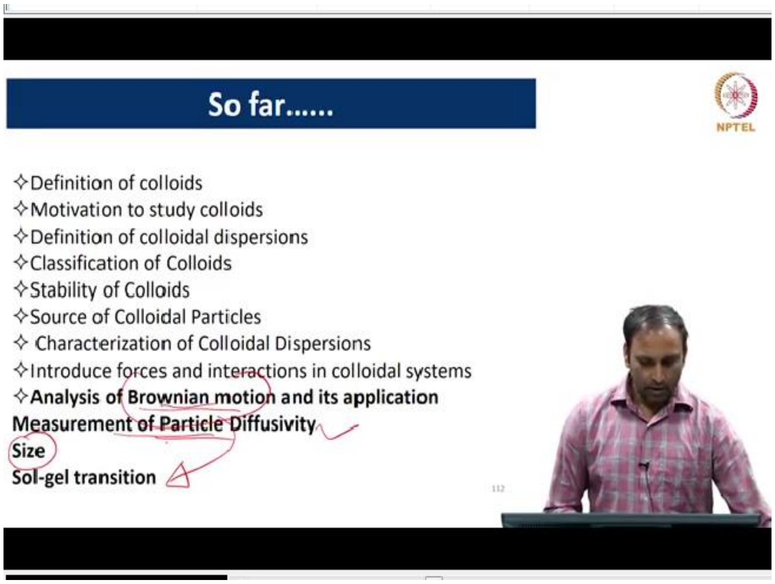

So what we are going to do today is to look at, you know, the analysis of, you know, the Brownian motion a little bit more than what you have done so far okay. And then we look at its application okay. That is what we are going to do today okay, more specifically, I am going to look at these 3 things. Use of Brownian motion for measurement of what is called as a particle diffusivity okay and extend that to measuring the size of the particle.

And then I will also hopefully give you some, you know, hint as to how can one use this Brownian motion for looking at what is called as a Sol gel transition, okay, that is what we will try and do in this lecture okay.

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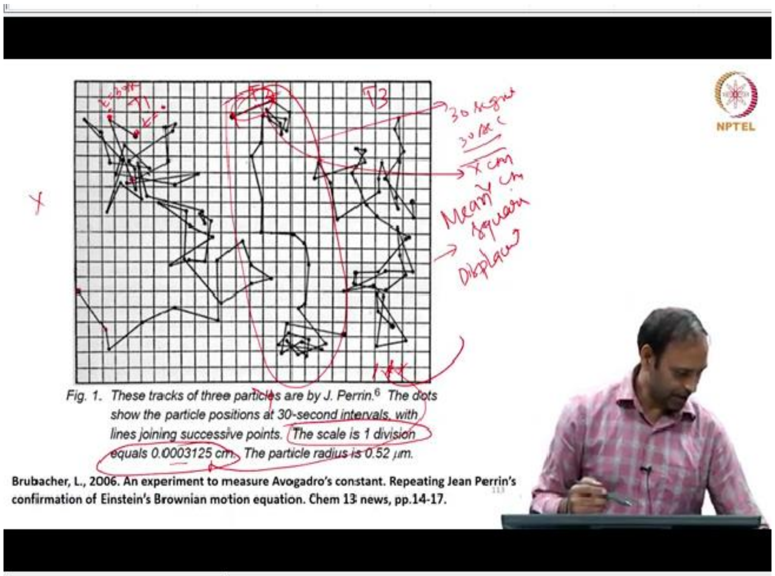

So, this is again, I have already showed this right, 3 tracks of this is track 1 you know track 2, track 3 of 3 particles that are exhibiting Brownian motion. And so you have these dots right. These dots correspond to particle position, okay at some time okay. So, in this case, I could say that this could be particle position at time T is equal to 0, okay. Next whatever dot that you see here it is at time T is equal 30 seconds okay.

And the next one again, you know from here it has come somewhere here, right. That is your, you know, so basically the way it is done is you take a video of a particle exhibiting Brownian motion, okay and I locate the particle position, right. This is a 2D space, right x and y okay, I can find the coordinates of the particle. I get that and that is what I plotted here okay, and I take another frame 30 seconds apart.

I look at what is a particular position in that image and I put that here okay, I go on doing that, you know, until I have done sufficient averaging. In this case, what do you see is you know is for example, if you look at this, I think there are about 30 segments, what do you mean by segment is the distance between, you know, particles in 2 consecutive frames, that is a segment okay. So, there are 30 segments and each segment is 30 seconds apart, okay.

I mean, if you look at right if I look at the distance between the 2 particles, it has traveled so much distance in 30 seconds, okay. Now, so if I have a figure like this, okay, from this, let us say that I want to calculate what is called as a mean square displacement okay. I can do that by an image like this okay. So, what information that I know is I should know that what is the scale of one division right.

Because this is a graph okay and this one division that is the distance going from maybe like say this to this right that distance okay that is 0.0003125 centimeter I know that distance okay, if you want to do it manually what I can do is I can print it on a you know sheet of paper and I can take a scale okay and I can find out what is the distance between this and this right in you know if you are going to use a scale which are centimeters.

I am going to say it has some say x centimeter okay. And I can I can similarly I can get what is the, this distance in terms of centimeter that is a y centimeter okay, if we know the scale and what are the actual distance I can actually get what is the actual distance that the particle you know as moved for every 30 seconds, right I can do that, right.

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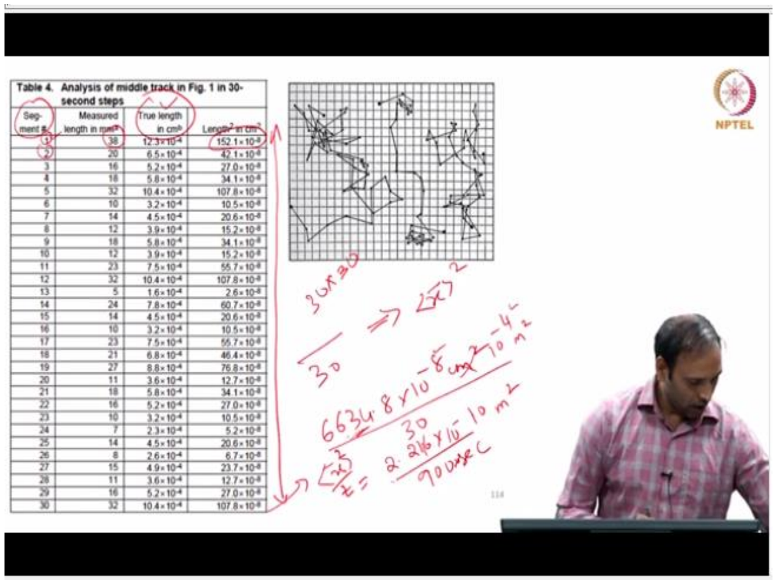

Table 4. Analysis of middle track in Fig. 1 in 30-second steps

Segment #	Measured length in mm	True length in cm	Length² in cm²
1	38	12.3×10⁻⁴	152.1×10⁻⁸
2	20	6.5×10⁻⁴	42.1×10⁻⁸
3	16	5.2×10⁻⁴	27.0×10⁻⁸
4	18	5.8×10⁻⁴	34.1×10⁻⁸
5	32	10.4×10⁻⁴	107.8×10⁻⁸
6	10	3.2×10⁻⁴	10.5×10⁻⁸
7	14	4.5×10⁻⁴	20.6×10⁻⁸
8	12	3.9×10⁻⁴	15.2×10⁻⁸
9	18	5.8×10⁻⁴	34.1×10⁻⁸
10	12	3.9×10⁻⁴	15.2×10⁻⁸
11	23	7.5×10⁻⁴	55.7×10⁻⁸
12	32	10.4×10⁻⁴	107.8×10⁻⁸
13	5	1.6×10⁻⁴	2.6×10⁻⁸
14	24	7.8×10⁻⁴	60.7×10⁻⁸
15	14	4.5×10⁻⁴	20.6×10⁻⁸
16	10	3.2×10⁻⁴	10.5×10⁻⁸
17	23	7.5×10⁻⁴	55.7×10⁻⁸
18	21	6.8×10⁻⁴	46.4×10⁻⁸
19	27	8.8×10⁻⁴	76.8×10⁻⁸
20	11	3.6×10⁻⁴	12.7×10⁻⁸
21	18	5.8×10⁻⁴	34.1×10⁻⁸
22	16	5.2×10⁻⁴	27.0×10⁻⁸
23	10	3.2×10⁻⁴	10.5×10⁻⁸
24	7	2.3×10⁻⁴	5.2×10⁻⁸
25	14	4.5×10⁻⁴	20.6×10⁻⁸
26	8	2.6×10⁻⁴	6.7×10⁻⁸
27	15	4.9×10⁻⁴	23.7×10⁻⁸
28	11	3.6×10⁻⁴	12.7×10⁻⁸
29	16	5.2×10⁻⁴	27.0×10⁻⁸
30	32	10.4×10⁻⁴	107.8×10⁻⁸

So, that data is basically plotted here okay. So, this is a segment number, okay, starting from 1 all the way up to 30 here, okay and in the first segment the distance that is measured, okay, in millimeter is about 38 okay and the last one is 32 okay, let us go back and look at these right The first one was here, right. That is your first and the last one is your right okay, that the distance look comparable, right.

You know one is 32 38, other one is 32. Looks like that they start from here. That is your first segment okay, and then go on tracing it and come all the way there right. So, that is the distance that you know the particle has moved okay in every 30 second time interval okay. Now of course you know you can use a scale and all of that you know your scaling factor all that and you can get what is the actual distance that the particle travels in a given 30 second interval.

Now, I have the actual length the particle has traveled, I can take the square of that okay, the square of the distance the particle has moved, okay, okay in the first segment, second segment I can do all of that for all the segments, okay. And then so this is basically your now if I add them up all and if I divide the number that you get by 30 that is what will give you what is the mean square displacement okay.

Typically it is given by you x bar square okay, that is your mean square displacement, okay. So, it turns out that if I add all these numbers up, okay. Now here, what you get is something like this it is 6634.8 into 10 power - 8 centimeter square, okay. And if I want to convert that into meter square, so that is going to be 10 power - 4, right meter square right. And that divided by 30 okay, we will give you a number which is something like 2.2116 into 10 power - 10 okay.

Because you have 8 here that becomes 12 right and you have a you know, this is 1000 right. So, it becomes something like -10 meter square okay, that is the x bar square, right, that now you have, so I said that every segment is you know it is at a 30 second time interval right. And therefore, I can actually calculate what is the total time right, the total time is going to be, I have 30 segments, okay right multiplied by 30, right, that is going to be your okay 900 okay. Therefore, divided by 900 second okay, that is going to be my x bar square divided by t okay.

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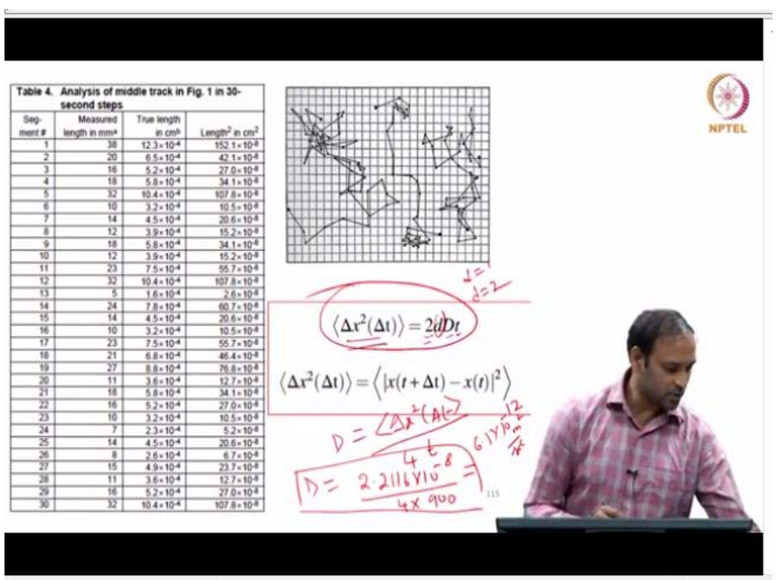

Now we kind of introduced this equation that was derived by Einstein, right. So, where the mean square displacement, okay is equal to 2 times d times capital D times t, where d corresponds to the dimension, right. So, if you are doing experiments in 1 dimension d is going to be 1. If you are doing experiments in 2 dimension, d is going to be 2, right. Therefore, if I put all these numbers, okay, turns out so that because this is a trajectory in 2 dimensions, okay. Therefore, whatever x bar that I have calculated, right.

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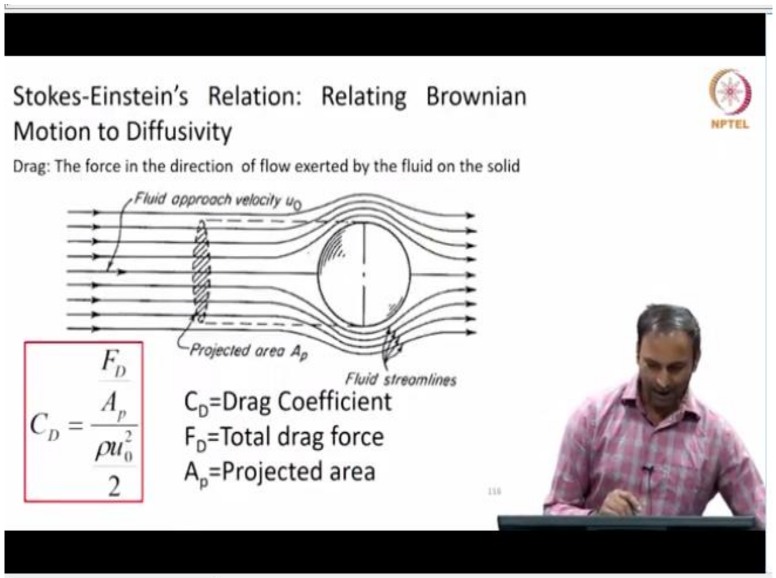

This is for 2 dimension, okay. If I want to get what is diffusivity, what I need is delta x square of t, that is average divided by 4 times t right, because I am doing experiments in 2 dimensions,

$$D = \frac{< \Delta x^2 (\Delta t) >}{4t}$$

Therefore, your D is going to be whatever the number that you got here, that is 2.2116 into 10 power - 8 divided by 4 into 900 right, can you get this number for me if you have a calculator. Let's do that. It is 2.2116 divided by 4.

And then divided by 900 okay, that comes out to be something like 6.1 into 10 power - 12. Yeah, that is going to be in meter square per second. So, from these experiments, what you can do is you can actually get what is the diffusivity of the particles right. So, you can ask a question as to what is the why do we need diffusivity right, it turns out that I can use these diffusivity measurements for calculating what is that.

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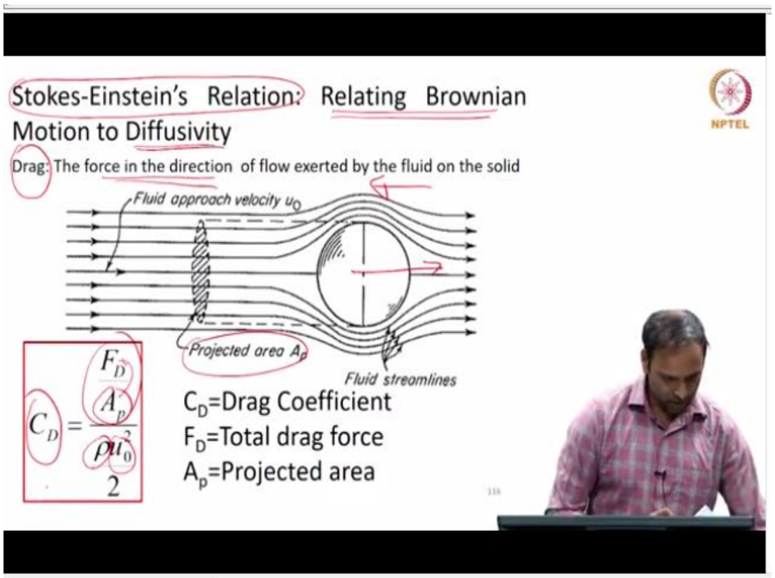

So, in these experiments, so, wherein did experiments with particles whose size was known okay, 0.52 micrometre was the size of the particle right. Now, if you do not know the size, I can actually use these mean square displacement calculations okay, from which I can get diffusivity to estimate what is the size of the particle okay. The way it is done is by using what is called as Stokes-Einstein relation okay.

So, again you know what we are trying to do is we want to relate the Brownian motion that the particles exhibit to the diffusivity of the particles okay. Now, whenever you have a particle moving in a fluid we say that you know there is going to be a drag force right, that is the force that is exerted in the direction of flow right. So, the drag force is exerted in the direction opposite to the flow of fluid right okay.

So, if the particle is moving like this, okay and this movement is going to be hindered by the, the fluid, right and it is going to experience a force in the direction opposite to its movement, right. So, again you would have learned this concept of drag coefficient in fluid particle mechanics or in your mechanical operation course, where this the drag coefficient goes as what is called F_D by Ap. This Ap is what is called a projected area that the fluid of the particle right.

$$C_D = \frac{\frac{F_D}{A_p}}{\frac{\rho u_0^2}{2}}$$

If I have ahh like say if you have a stationary column of liquid and you know if the particle is falling like this, if I see from the top, what I see is this circle, right, that is your projected area, right. And of course, if it was to fall like this, okay, then I am going to see you if it is going to be cylinder, I am going to see a rectangle, right. So, that is your projected area. So, that is Ap is the projected area and F_D is the drag force and u_0 is the velocity with which the particles moving okay. And rho is a density of the fluid okay. Now okay.

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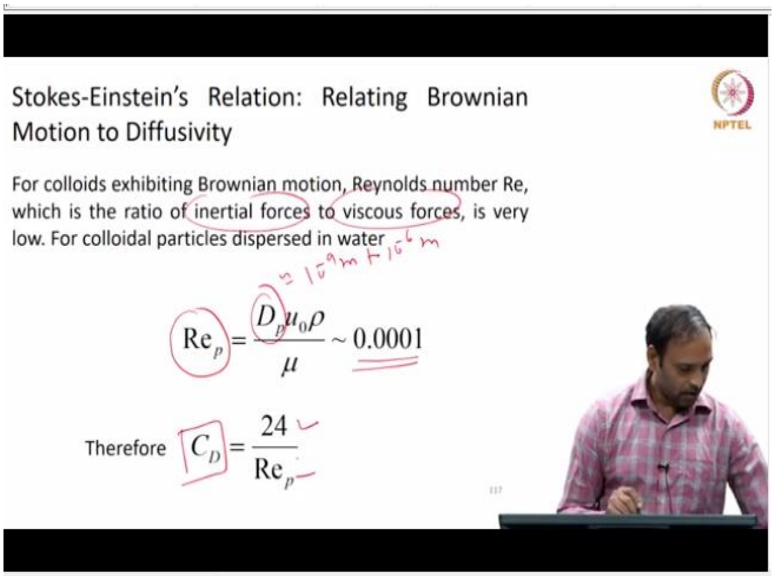

So, because we are working with colloidal particles, okay it turns out that because of the fact of the particles that we dealing with are very, very small right of the order of 10 power - 9 meter to 10 per - 6 meter, it turns out that the Reynolds number that you calculate for any problem that involves colloidal particles is going to be very, very small okay. That means, you know Reynolds number which is the ratio of inertial forces to viscous forces is going to be always small okay. In such cases, your C_D go says 24 divided by Reynolds number okay.

$$C_D = \frac{24}{Re_p}$$

$$C_D = \frac{24}{Re_p} = \frac{24\,\mu}{D_p u_0 \rho}$$

$$C_D = \frac{24\,\mu}{D_p u_0 \rho} = \frac{4F_D}{\pi D_p^2}\frac{2}{\rho u_0^2}$$

$$F_D = \frac{24\,\mu\pi D_p^2(\rho u_0^2)}{8D_p u_0 \rho} = 3\pi\mu u_0 D_p$$

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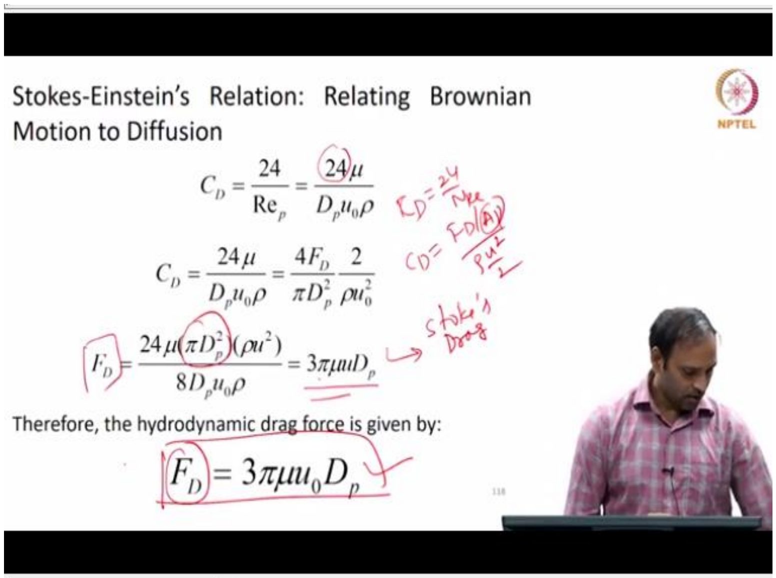

Now, I can substitute for Reynolds number that is going to be mu divided by Dp, u_0 into rho okay. And if I do some simplification, because I know that you know, if C_D is 24 divided by Reynolds number I know that now, because your C_D is again F_D divided by Ap divided by rho u square by 2, right and Ap the projection area is going to be the area of the circle right okay, that is going to be pi Dp squared.

If a substitute for all of that you get F_D as 3 times pi mu u into Dp, this is again the well known Stoke's drag right okay essentially, you end up with the expression for drag for a spherical particle moving in a fluid right. Again you can do this you know by again starting with this stokes equation, you know, start with the general equation I can do appropriate modifications and I can also obtain a similar expression.

But it is one of the simpler ways of doing it. So, all that we have done is we got an expression for the drag for that is experienced by the particle right.

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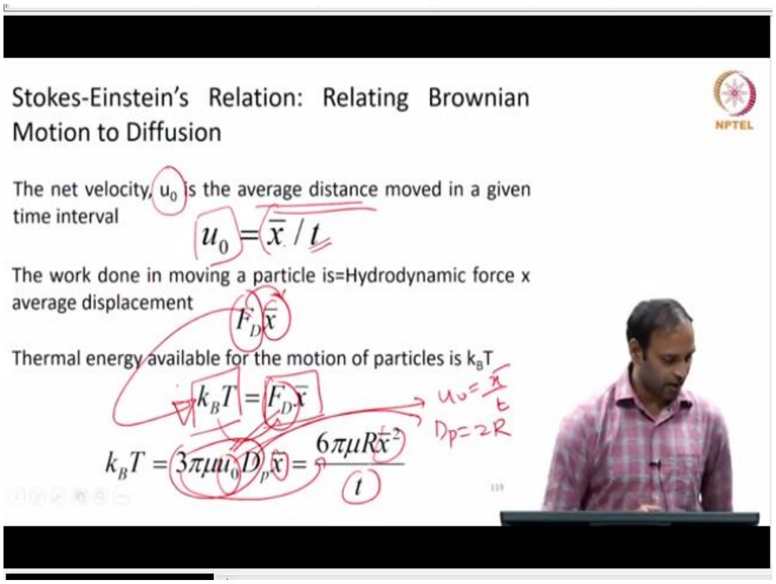

Now because the particles are constantly moving in the fluid the net velocity u_0 okay with which the particles are moving is the average distance the particle moves, okay, in a given time interval, right, that u_0 is x bar divided by t, but now whenever a particle is moving, okay it has to get some energy right okay or okay, so the work that is done okay by the moving particle is F_D multiplied by x bar.

$$u_0 = \frac{\bar{x}}{t}$$

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

$$k_B T = 3\pi\mu u_0 D_p \bar{x} = \frac{6\pi\mu R \bar{x}^2}{t}$$

That is force times the distance okay, the average distance that it travels okay that is your the work that has to be done you know in moving the particle right. Now that energy where does it come, it comes from the, the thermal energy right therefore, the equating the thermal energy to the work that is required you know for moving the particle okay what I can do is I can equate them okay and because I know what is F_D.

I can substitute for F_D from the Stokes drag right. And this I mentioned that your you have u here right u_0 okay is x bar divided by 2 okay and you have an x bar here. Therefore, it becomes x bar square divided by t okay. And because you have Dp here, okay and Dp is 2 times R right.

Therefore, this becomes 6 here therefore, K_BT is equal to 6 pi mu R x bar square divided by t okay.

$$k_B T = 3\pi\mu u_0 D_p \bar{x} = \frac{6\pi\mu R\bar{x}^2}{t}$$

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

$$D = \frac{k_B T}{6\pi\mu R}$$

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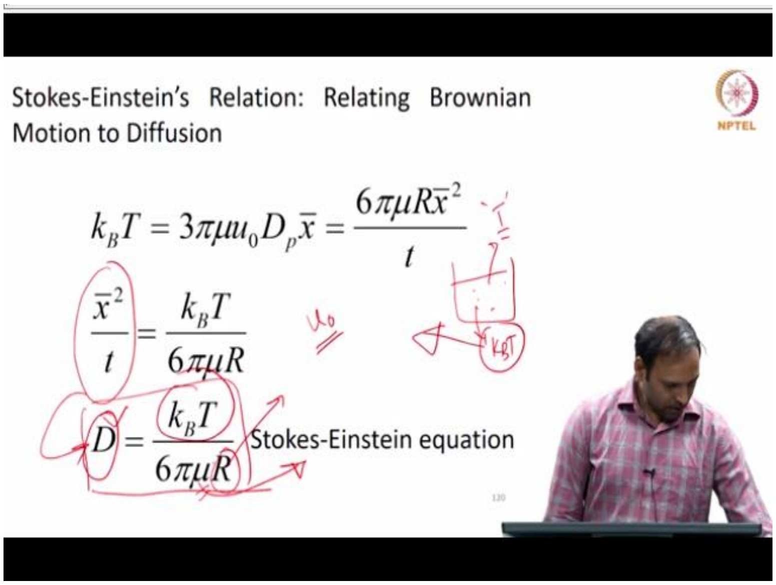

The cause for Brownian motion is the constant bombardment of the fluid molecules with the particle. Yeah, that is because see, if you take any container right say that you know I have water right and say that this water is maintained at a temperature T, okay. Now, so, the energy that every molecule of water in this container will have is K_BT yeah, every molecule will have this energy correct.

Now, that is what is being used for the mobility of the particle. No, we are saying that the molecules of water will have this energy and this energy is being used for moving the particle which will have constant velocity yeah the particular will have a u know some average velocity.

See, if you go back here, right okay, let me put it this way. I mean, if you look at the length that we have got, right.

Let's look at these numbers, right. The length of the every segment is what is calculated right, look at the length here, so you have 152.1 10 power - 8 centimeter squared, but you have numbers which are as low as 2.6 10 power - 18 okay, I mean if you want to calculate okay velocity for every segment it will vary in a certain range right. But if you know, watch them for sufficiently long time if you calculate the velocity it will have I mean you know, if you go back when we did this force calculation right on different okay.

We said that you know, micrometre particle will typically you know move with 1 micrometre per second velocity okay, numbers like that are kind of obtained from experiments like this, okay. Yeah so on an average particles in a fluid, which is maintained at a particular temperature will move with the velocity which is typically again depends on the size of the party right if you have 10 power - 9 meter size particle, nanometer size particle.

Of course, it is going to move with a much larger velocity in a compared to 10 power some particle which is a 10 power - 6 meter size right. Yeah. Now this x bar square by t that is what is the diffusivity you know of the particle okay. Therefore, even you have an expression which relates the diffusivity of the particle to the thermal energy and the viscosity of the fluid in which the particles are dispersed or the particles are moving right.

R is a size of a particle therefore, if I have done an experiment where I have studied the Brownian motion, if I am able to calculate, what is the diffusivity, if I know what is the viscosity of the fluid u know a particle dispersed, I can actually use this expression measured what is the size of the particle okay. Therefore, in essence, I could use some technique like microscopy, wherein I have measured Brownian motion.

And I can back calculate what is the size of the particle if you do not know what is the size okay. So, you can think about this as a one nice application of Brownian motion where people exploit you know, this particular phenomena and then estimate the size of the particle right. Any questions. No okay.

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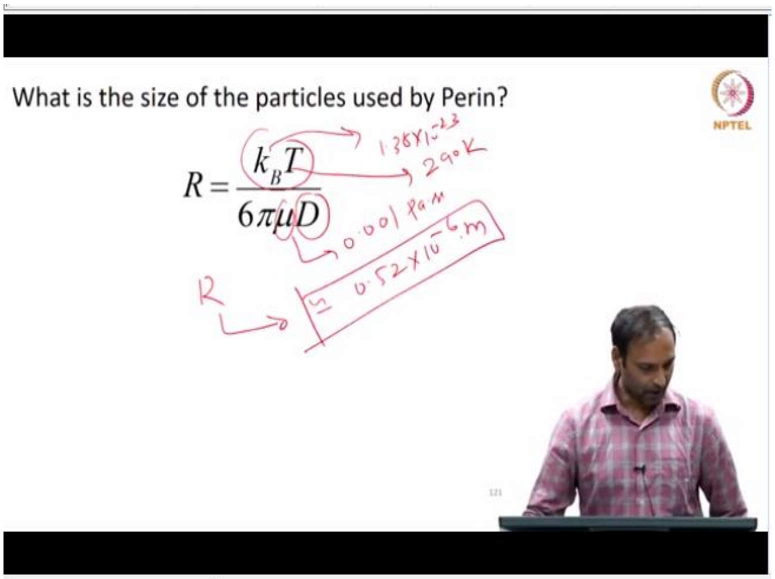

So, we will okay, now you can go back and you know, take a look at so because we are measured diffusivity, right from, you know, the earlier track that we looked up, right. And if you take the water, say 0.001, you know, Pascal second, right, that is your that is viscosity and you know, putting appropriate values for k_BT 1.38 into 10 power - 23 and temperature I think what is taken in this reference is 290 Kelvin.

If you put in all of that you can back calculate R and the value that you should get should be very close to 0.52 10 power of - 6 meter okay. You can try and do that and see know how it works out okay.