Colloids and Surfaces
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Lecture-07
Introduction to Forces Acting on an Individual Colloidal Particle

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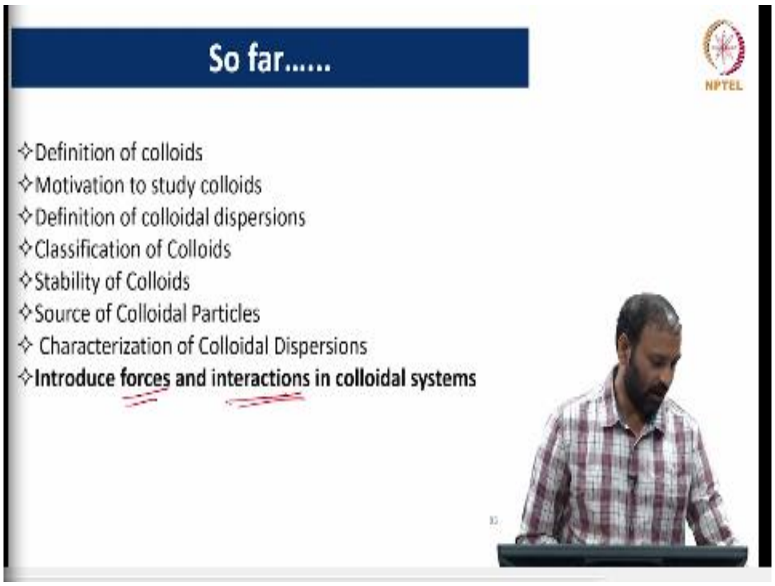

Yeah, so today what we will do is I would like to introduce you to forces and interactions in colloidal systems ok, that is goanna be you know the objective of today's class . So, I am going to do that through a little bit of history ok.

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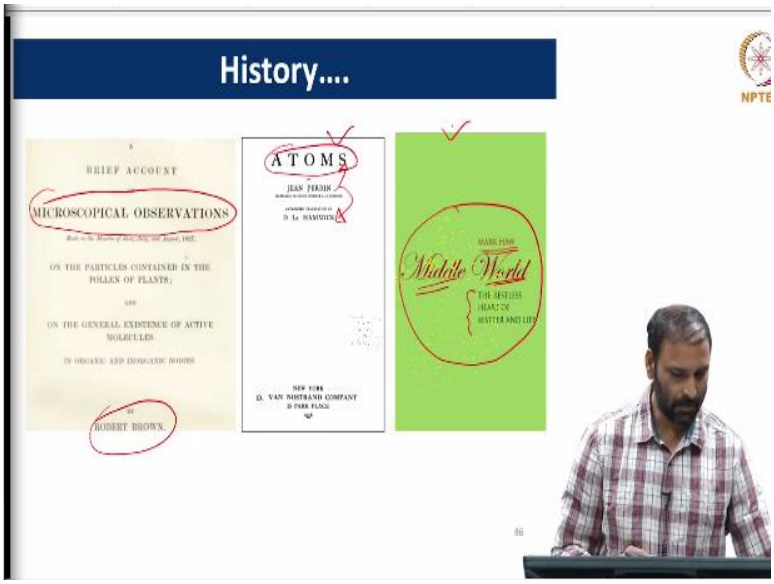

So, this is some really good books if you are interested you should read first one is of course something on microscopical observations, this is actually written by Robert brown ok. And the second one is actually a titled atoms which is actually written by John Perrin ok who was you know I am going to tell you little bit about him and you know what he has done. So, I mean the original book is in French, it is translated to English ok.

And this is a recent book it is written by a physicist called Mark Haw ok. And that is titled middle world and if you look at the alright it says the restless heart of matter and life ok, so that is the these are all very good books, I think you should deed up because you know you will get a account of some other developments in colloidal science ok. I have taken a lot of contents from you know this book and this book ok, so for today's lecture, ok.

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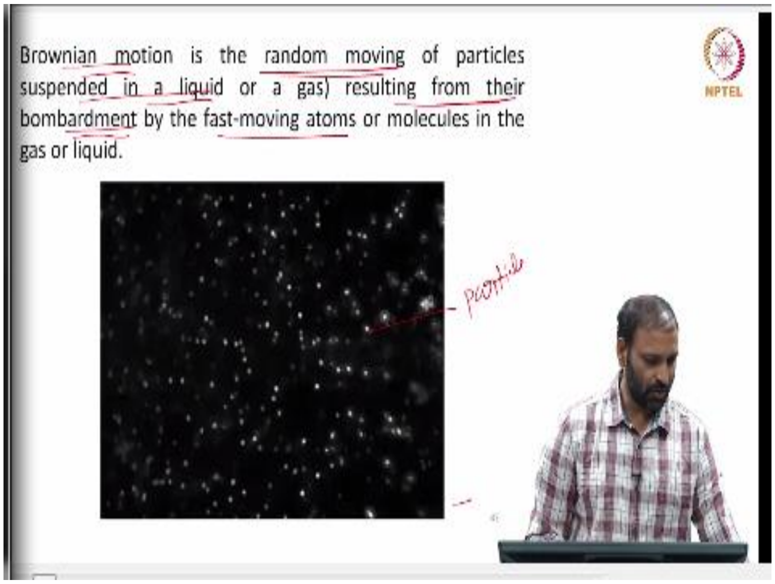

So, I am going to show you a movie to begin with. So, if you look up because I copied just the file ok. Anyway, so this there is a movie that is in the youtube ok what you do is you should go back and just type you know Brownian motion, you will have several movies that may come up. So, what I wanted to show you was that you know these you have this image ok and these dark regions in the bright regions and the bright regions are the particles ok, they are very tiny, there is no scale bar here.

But the size of these particles I guess is about less than a half of micron ok. And then if you see this movie, you will see you know they are moving around ok, they are jiggling around not in any particular direction is a chaotic motion, ok. And that motion comes about because you have these particles embedded in a fluid and these fluid molecules are constantly hitting you know or bombarding the particles ok, that is what ok, , so that is what is called a Brownian motion ok.

Brownian motion is the random movement of particles ok in a fluid ok, it could be liquid or a gas ok and that results from a bombardment or you know in a constant you know hitting ok of a atom or a molecule that is in the continuous medium, ok.

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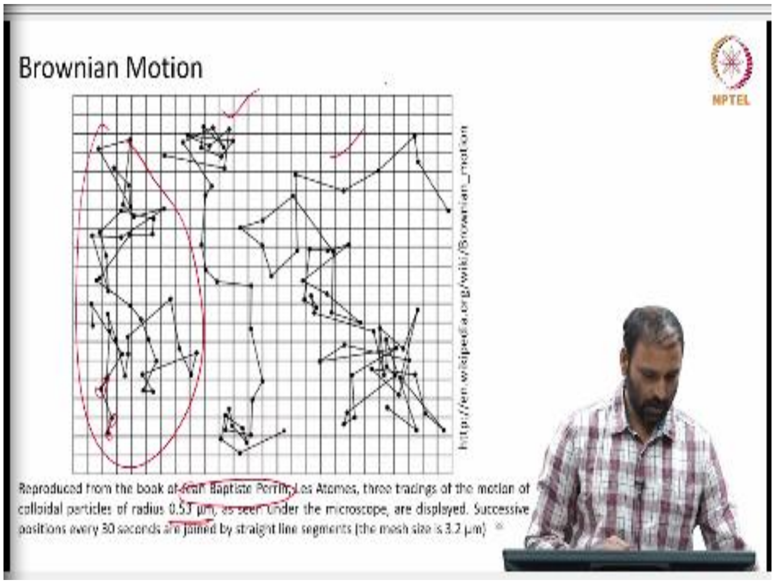

So, these are some typical trajectories of the particles that were recorded we back in the 1920s ok. And this is from the work of Perrin ok and what he did is, he used colloidal particles of 0.53 micrometer you know in radius. And he prepared a sample, he observed them under microscope and he was able to. So, every point that you see, that is every dot or the every point that you see that is the position of a particle at some time instant, ok.

And later time instant where it has moved, so he was able to track these particles and then he has trajectories of 1, 2, 3 particles, ok, that is what you see here.

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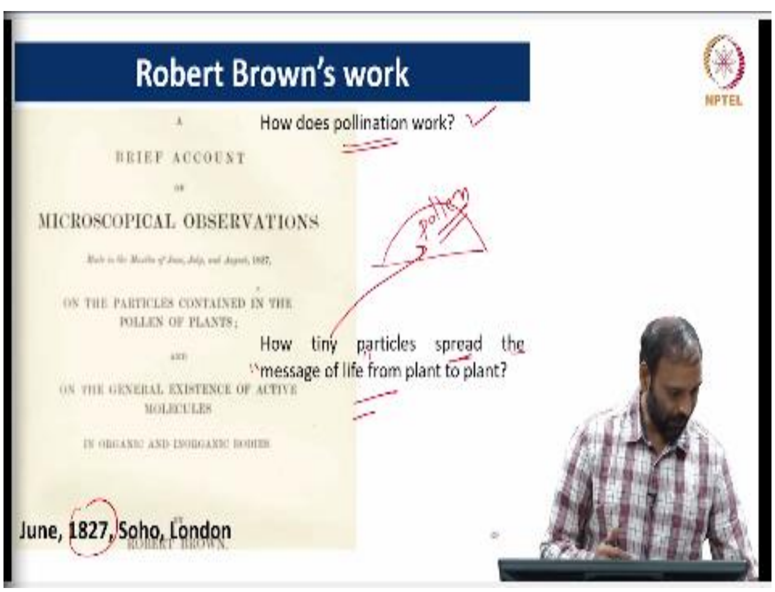

Now, of course this is a 1920s I said right, now way back in 1827 ok. So, Robert Brown what he was trying to do was, he took a droplet of water ok. And this droplet contained pollen particles ok pollen and he observed them under microscope. So, his intention was to answer questions like this ok. How does pollination occur ok or how do these tiny pollen particles they spread the message of life from plant to plant ok, that was a kind of question that he was trying to ask.

And he did a lot of experiments and you know ultimately he could not you know make a conclusion of you know what he was trying to do, ok.

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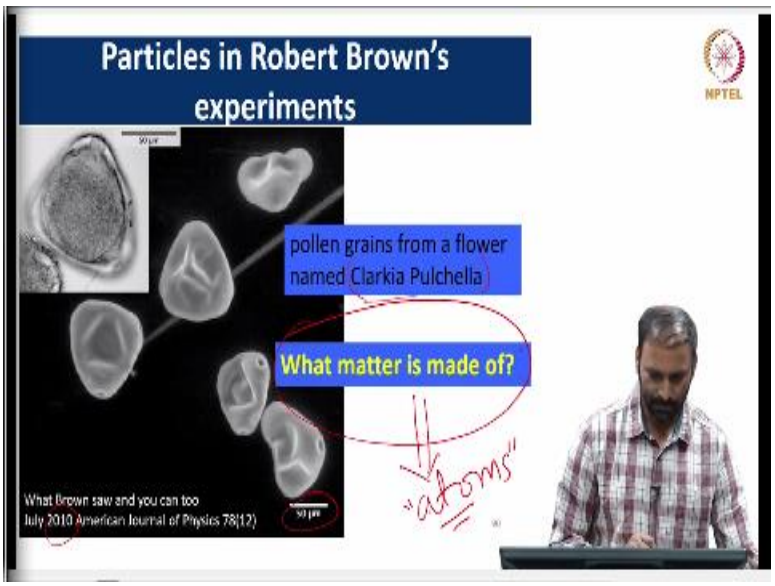

And these are actually the particle that we are used in you know Brown's experiment, this is a more recent you know stuff from 2010 ok. So, these are actually pollen grains from a flower called Clarika Pulchella ok. So, and you look at this scale bar you know 50 micron large enough . But they still he was seeing that you know they were constantly moving around ok.

And later on, it turns out that you know there is experiments of Robert Brown were essential to kind of answer this question what the matter is made of ok. That means, ok, we know that you know atoms are the building blocks of everything right. So, his experiments were instrumental in you know telling you that look atoms at the basic building blocks of everything that is around us right ok.

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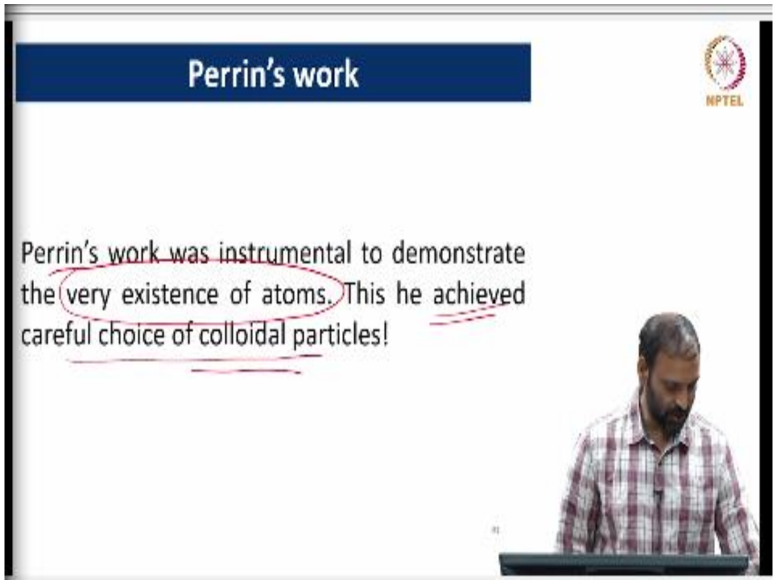

So, what Perrin did was, he did very controlled experiments ok, so unlike you know Pollen's ok, which as you saw, right. They were you know they come in different sizes, different shapes ok, so what Perrin was able to do is, he did very careful experiments and he was able to prove the very existence of atoms, I will tell you a little bit about how he did that. And this he achieved by a careful choice of particles ok, I think that is very important whenever you are trying to do any experiments.

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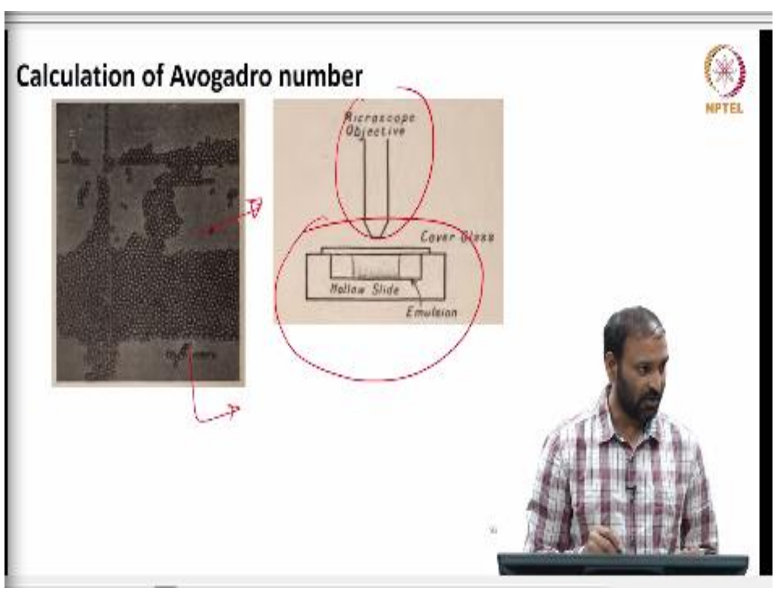

I have some again some pictures from his book, ok, these are the particle that he used ok. They look you know spherical, they look more or less of same size, ok and this is an experimental setup that he used, ok, that is a microscopy objective, ok. Typically whenever people want to do these Brownian motion experiments, what they do is they take 2 glass slides, ok and your dispersion of particles is embedded between these 2 slides ok and then you basically seal the entire container.

Because you know you do not want any influence of external conditions there could be some air all the types, you want to minimize all the disturbances as much as possible. And you put this onto a microscopy stage and then you look around, right. And then you basically record either the frames, images or the videos, right, that is how you typically do it.

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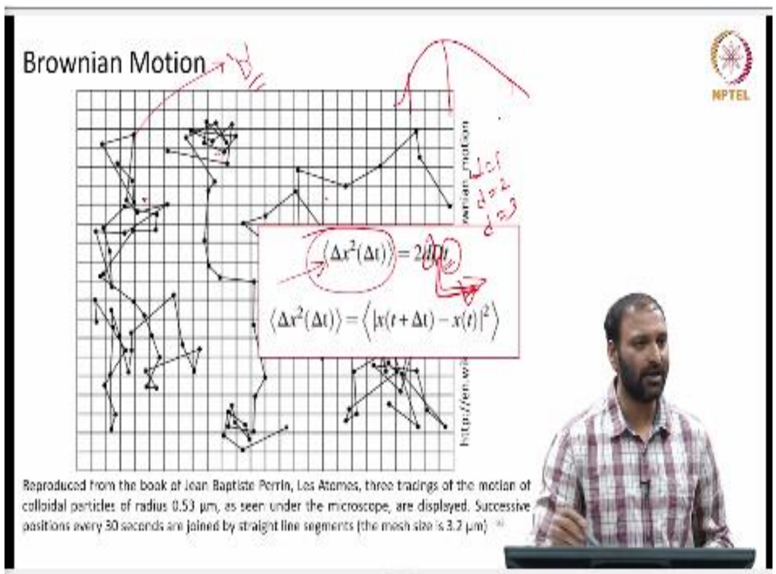

So, now so he did those experiments and because he knew the position of the particles you know at any given instant in time, he was able to calculate a quantity called mean square displacement ok. That is, what is the distance that the particles you know travel ok you know in a given time alright. And he knew this observation time ok he had done experiments over a time window, he knew that ok.

And he was actually able to calculate this D that is the diffusivity of the particles, this small d here corresponds to the dimension. So, D is going to be 1, if you are looking at 1 dimensional Brownian motion d is equal to 2. If you are looking at 2 dimensional system or D is equal to 3 ok. So, from his experiments he was able to calculate the mean square displacement ok and from that he could back calculate what is the diffusivity of the particles ok.

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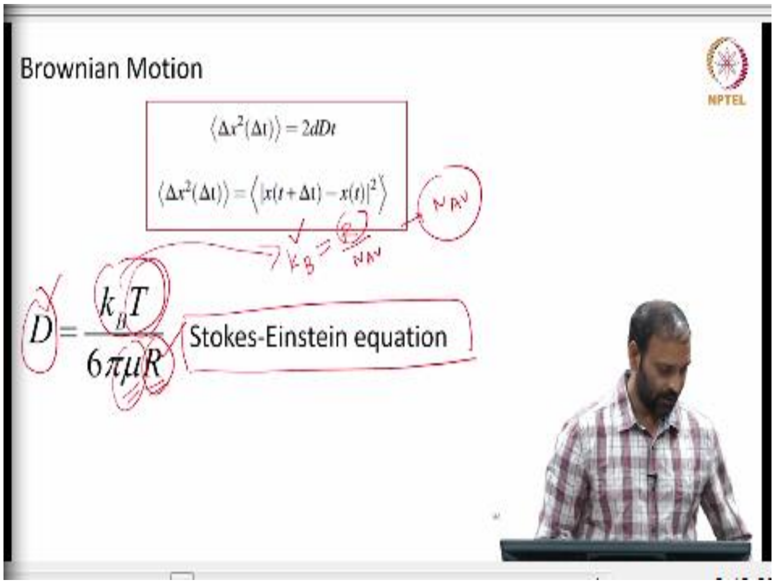

Now once you do that, so he used something called as Stokes Einstein equation ok which relates the diffusivity of the particles to this thermal energy ok, the radius of the particle and mu which is the viscosity of the fluid in which the particles are embedded. Because he knew what is R right I said that you know he had done he had microscopy observations of his particles themselves ok. Therefore, ok the value of R is known, and from these Brownian motion experiments he was able to calculate D ok.

And viscosity of the fluid he knew, ok, and the temperature at which the experiments were done, also he knew. From that what he did is, he calculate k B that is a Boltzmann constant, ok. And that is equal to R which is the, the universal gas constant divided by Avogadro number ok. Because he calculated from his experiments, this is known, he was able to calculate what is N_{AV} ok, that is what he did.

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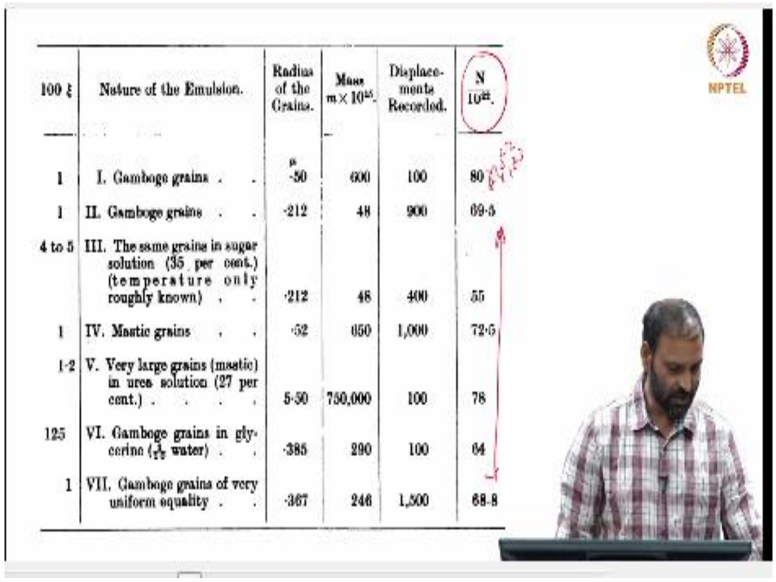

100 ξ	Nature of the Emulsion.	Radius of the Grains.	Mass $m \times 10^{15}$.	Displacements Recorded.	$\frac{N}{10^{22}}$.
1	I. Gamboge grains . .	μ ·50	600	100	80
1	II. Gamboge grains . .	·212	48	900	69·5
4 to 5	III. The same grains in sugar solution (35 per cent.) (temperature only roughly known) . .	·212	48	400	55
1	IV. Mastic grains . .	·52	650	1,000	72·5
1·2	V. Very large grains (mastic) in urea solution (27 per cent.)	5·50	750,000	100	78
125	VI. Gamboge grains in glycerine ($\frac{1}{10}$ water) . .	·385	290	100	64
1	VII. Gamboge grains of very uniform equality . .	·367	246	1,500	68·8

This is some data from his this is a tabulation of you know this N the Avogadro number that is obtained from such experiments ok, not bad, right. This is 80 in to 10 power 22 right with you know 8 into 10 power 23, ok fairly close to you know the Avogadro number ok, right, there are a series of numbers ok.

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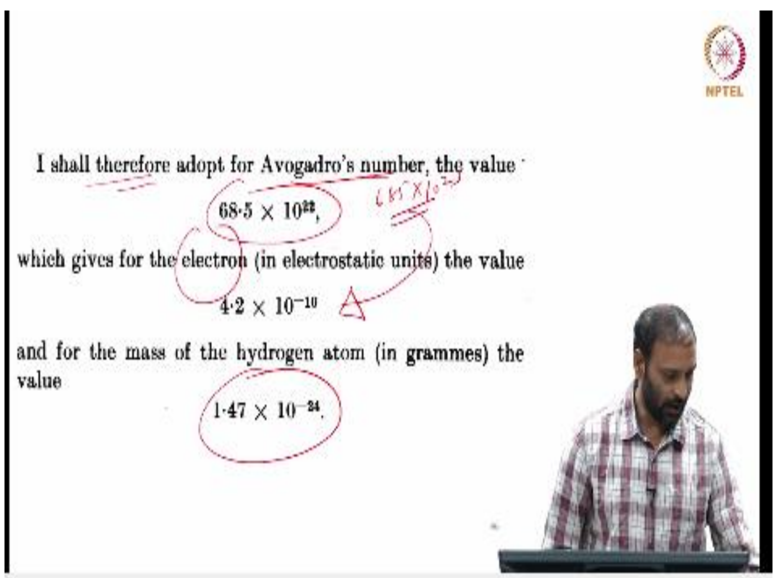

From this, I have taken this again from his book, so he made this statement, ok from these experiments. I shall therefore, get this Avogadro number to be 68 or 6.85 into 10 power 23, ok that is the value he assigns. And then he is also able to calculate what is a charge of the electron you know and the mass of the hydrogen atoms stuff like that, ok.

So, therefore Perrin's experiments were very much instrumental, ok in you know kind of coming up in the alternative way of measuring you know the Avogadro number, ok, which in turn he was able to kind of conclude that you know atoms do exist and the fact that you know this particles are undergoing Brownian motion is indeed because of the atoms of them or the molecules of the fluid in which the particles are dispersed, ok, that is ok. So, we will do you know exercise where will be able to calculate some numbers like this ok, in the next lecture or so, ok.

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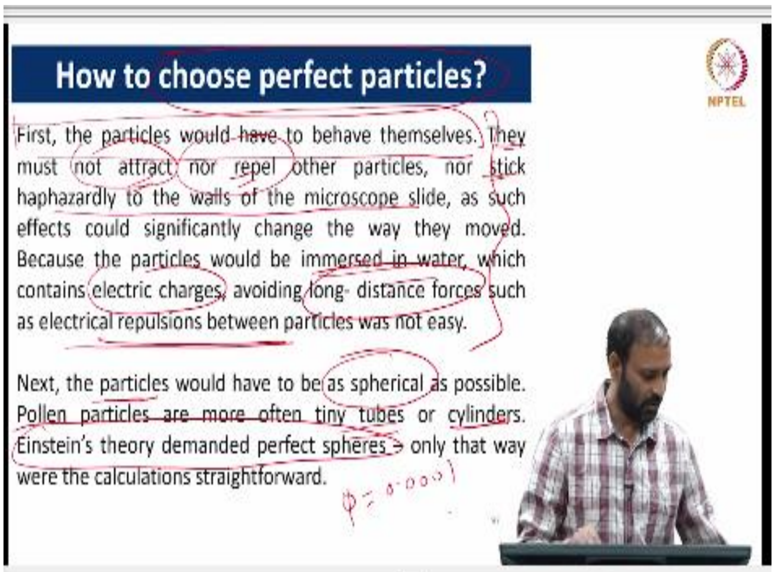

Now Brown's experiments 1827, right and then it took a very long time you know for perin to do these nice experiments you know and you know prove the existence of atoms, right. And the reason why he was able to do it and then the other people could not is because he was able to choose perfect particle for his experiments ok. Anytime you design an experiment what is really important is, you should ask a question as to what is the aim of my experiment ok.

And what is my objective ok and then depending upon what you want to study you should be able to choose a colloidal system of interest. So, there you know to for example, if I was interested to look at sedimentation for example, ok. Then if you do experiments with you know like say 10 nanometer particles, they would never settle, right or it will take a really long time to settle, right.

So, therefore, so it is good to ask a question is to look this is my object of my experiments ok. And then based on that you have to really designer a nice model colloidal system, ok to achieve that objective right. So, now, so how to choose perfect particles first, I mean this is a ok, the particles must have to behave themselves. That means they should neither attract nor repel with other particles in the system right.

Because say because you are trying to measure Brownian motion of particles, right, this is typically done with a very dilute fluid. That means, the concentration of your particles in the fluid is very, very low. Typically you know your phi could be as low as you know 0.0001 or something like that, ok. The reason for that is the particles have to be sufficiently far, that means there is no interaction between the particles ok.

That means the motion of the particle is not influenced by the other particle that you have in the system, right. So, therefore, so the particles in the system should neither attract nor repel with other particles, ok, nor stick to the walls of the microscope slides. Because you know you are doing these experiments under confined you know walls ok. And if the particles get stuck to the walls then in what will happen is again it is going to hinder the motion of the particles, right ok.

So, he basically says because the particles are immersed in water ok which may contain some charges right you know you could have some dissolved ions in the fluid ok. So, all that could influence the way the particles you know feel each other. So, therefore it is necessary to avoid what is called is a long distance forces, ok such as electrostatic repulsion. So, if you have charges in the system you know electrostatics could kick in.

So, therefore it is good to avoid all of that when you are trying to do an experiment of this short ok. This is very specific to the experiment that he had done, ok. Now the next thing is that the particles ok would have to be as spherical as possible ok, what it means is that. If you have a particle like this ok which is like say a rod like particle. Then people talk about you know what is called is a orientation dependent diffusion, ok, you could have translation, ok you could also have rotation, ok.

Therefore you know but that is because the Einstein theory right that was actually developed for perfect spherical particles, ok. But as you saw from the microscope image on the pollen grains that were used by Brown, they were aspherical right ok. Therefore the next requirement for his experiments was that the particles will have to be as spherical as possible. But the pollen particles are more often they are either tiny tubes or cylinders ok.

Therefore the calculation of diffusion coefficient for such things you know would not be straightforward, ok, this is a second you know kind of requirement you can say.

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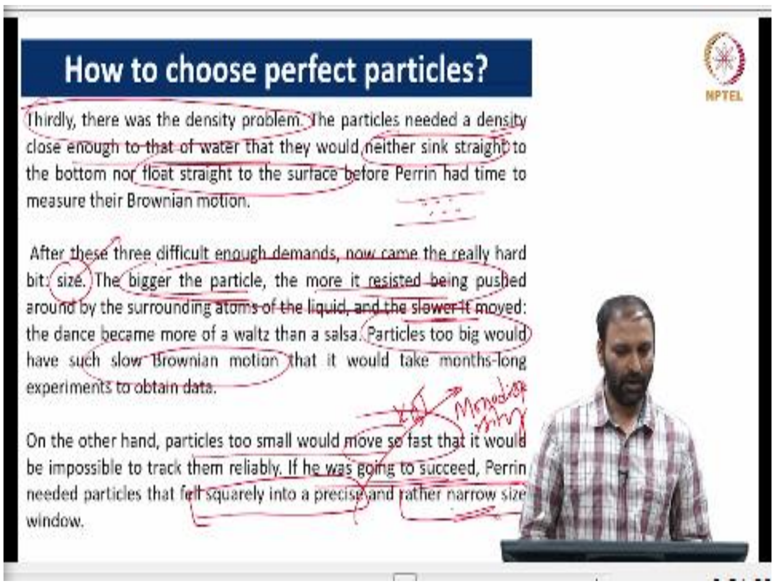

Now, thirdly there is a density problem, what I mean by that you know you have these particles in a you know to geometry like this right. Now the particles that you are going to use for such experiments should be such that the density should be close enough to that of water ok. That means they should neither sink to the bottom ok or they should not float to the surface, right.

Because you know you do experiments for a particular time window, at least in that time window, you should never have any influence of density of the particle or the gravitational forces on the particle. Therefore the particle that you have should always be suspended in the fluid, they should neither sink nor float. And the next requirement is that the particles have to be of appropriate size, ok, what I mean by that is.

That the bigger the particles the more it resisted being pushed by the surrounding fluid ok, the slower it moved, right. That means if I am doing experiments with the larger and larger particle as the particles becomes larger and larger, the inertia becomes important, ok. If it is too heavy or too big then the solvent molecules only have this thermal energy k_BT ok, they cannot move a larger stuff around, ok.

Therefore so the particles would have to be small enough that means if the if the particles are bigger, they resist the motion ok they do not move. Because the energy that the molecules have is not big enough to move the particles around ok. So, therefore the particle is too big would have very slow Brownian motion or they may not even exhibit Brownian motion, right.

So, if it is very slow, then you know you may have to do experiments for a very long time or if they do not move, you do not even have a chance of measuring Brownian motion, right. So, therefore the particles have to be of right size, ok. Now, if the particles were too small, ok, on the other hand if the particles are too small, they would move very fast ok. And if it moves too fast, ok, if you have a really good camera right you know in a which you can actually capture fast moving things you can still do experiments.

However maybe at that point in time, ok, so he could not do you know you could not get away by using to smaller size because they were moving too fast and you know and he really could not reliably track the particles ok. So, therefore if he was going to succeed in his experiments Perrin needed particles that had a precise size and of course they also have to be in the narrow size window, ok.

This again comes back something that we have discussed mono dispersity right, ok. That means, if imagine that you know I have track these particles, ok. And I have measured diffusion coefficient, ok, now if thereof different sizes, ok then I am going to get different values right. So, therefore you know or if the size distribution is too big depending upon it whether a small you know or the average or right.

So, therefore he really needed to choose particles which are of a particular size and they also have to be as you know a narrowly dispersed as possible, ok. Now, like whatever the requirements that I have said right, this is for choosing appropriate size of particles for Brownian motion experiments for example, ok. Now, if I were to generalize this for any experiment, right, can I classify whatever few point that I have mentioned into different classes.

So, what I mean by that is that, so if you look at the first part right, so there is you know it says that the particles should neither attract nor repel, ok. And they should neither stick to the walls of the container right ok, that is one requirement. The second one is you know there should be you know there should be as spherical as possible that is a requirement for this particular experiment.

And if you look at you know the density problem, ok, that mean they have to be not too big, not too small, ok and they have to be of precise size and monodispersity, ok. So, therefore I can classify these requirements into some categories ok.

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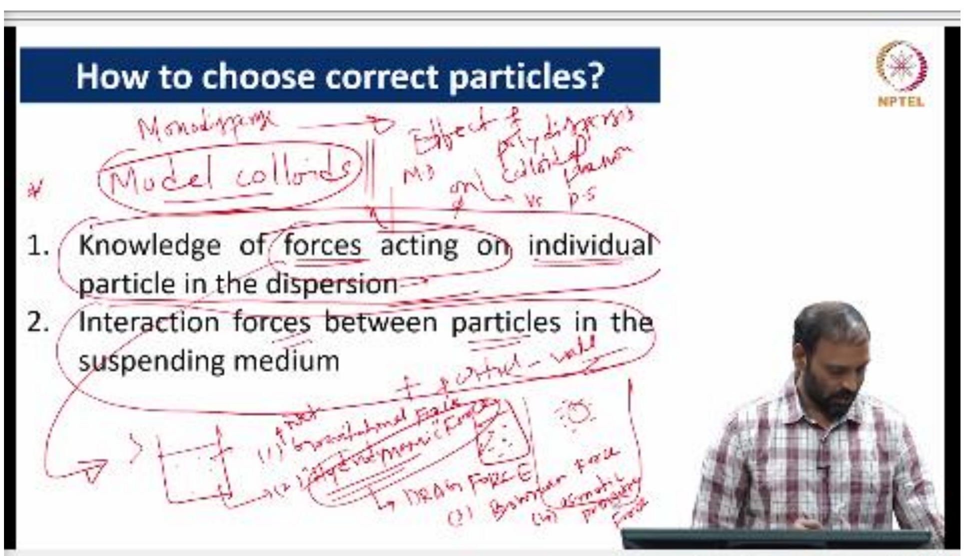

I am going to add another one here, you have to work with model colloids right, the particles of you know maybe monodisperse, known size ok known you know surface properties all of that ok. And then let us say model colloids it need not be monodisperse always ok, there are a lot of people who are trying to look at what is called is the effect of polydispersity on some colloidal phenomena ok.

Or one maybe interest to look at I want to measure what is the viscosity as a function of volume fraction, ok and I want to compare what if it is monodisperse versus polydisperse, right. In such cases you may be interested in look at you know maybe your model colloids would be both monodisperse as well as polydisperse of controlled polydispersity ok. So, therefore you know, so this model colloid requirement need not be always monodisperse ok, it depends on again what problem you are trying to look at.

So, the other point that we have discussed so far can be kind of clubbed into two main categories, you should have a knowledge of the forces acting on the particles in the dispersion ok. That was you know this gravitational settling right, so, that you know I can get an idea about whether the particles will sink or float. If I know about what is the gravitational force acting on the particle, right.

The gravitation force may not be the only force that is you know relevant in this scheme, look at a few different forces that are important. And the second thing is we should have an idea about the interaction forces between the particles in the suspending medium ok, plus of course the interaction also between maybe the particles and the container itself, right you know. For example, it could be wall or it could be if you are storing these particles in a you know in the case of you know Brownian motion experiments is the interaction between the particle and the wall.

If you have particles like say a beaker is a interaction between the particles and the walls of the beaker itself, right, these are also important, yeah. Any questions so far yeah ok, we will move on, ok. Now ok let’s talk about the forces acting on the particles, ok, what do you think are the forces that are acting on the system. So, we are talking about, so let us think about like this right. I have a container, ok, I have particles in the container and there is a continuous medium ok, what are the forces acting on the particle.

Of course one we already said right gravitation force, van der Waal forces yeah see I just want to make a distinction. So, there is now so let me put it this way let us talk about the forces on the individual particles, ok, let us put that way ok right. That is what I have written here, this is force on the individual particles in the dispersion ok. Definitely gravitation is 1, right everybody agrees, right, anything else.

Buoyancy I mean if you say a net gravitational force that takes care of buoyancy as well, right ok anything else. Viscous force ok, electrostatic charges I mean see when you talk about ok let’s say like this right. I have a particle ok, I have this is you know there is charged ok. Now the electrostatic you know interactions become important, if I have a very dilute fluid, right, you know there is absolutely nothing nearby ok.

Then electrostatic interaction you know electrostatic forces you know see you talk about electrostatic forces between 2 things right. I mean if you look at coulomb's law you have you know charge 1, charge 2, right you know this is a force of repulsion or attraction depending upon nature right. How about hydrodynamic force, you heard of this term hydrodynamic force, these forces come into picture whenever there is a flow right.

Now, if you look at particulate systems right, which if they are tiny enough, the particles are moving. Now, whenever you have a particle moving in a fluid you have what is called as a drag force ok which acts in the direction opposite to the movement of the particle right. So, the second force is a hydrodynamic force, we can also call it as hydrodynamic drag force. Third force, there was a Brownian force ok and lastly something called as a osmotic pressure force, osmotic pressure force.