Thermal Physics
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Lecture - 16
Brownian Motion: Concepts, Features, Theory of Fluctuation

Hello and welcome back to the fourth week lecture on this NPTEL course of thermal physics. Now, for todays for this week, we will be talking about Brownian motion primarily. Now, you all are familiar with the term Brownian motion. Now Brownian motion is something that we have sometimes have seen with our eyes as well. So, when there is a ray of light coming through the window, we can see that tiny dust particles.

They are making some jittering movement, random movement in this light stream. So, these are essentially the Brownian particles and they are making Brownian movement inside this, you know air molecules or in the air medium.

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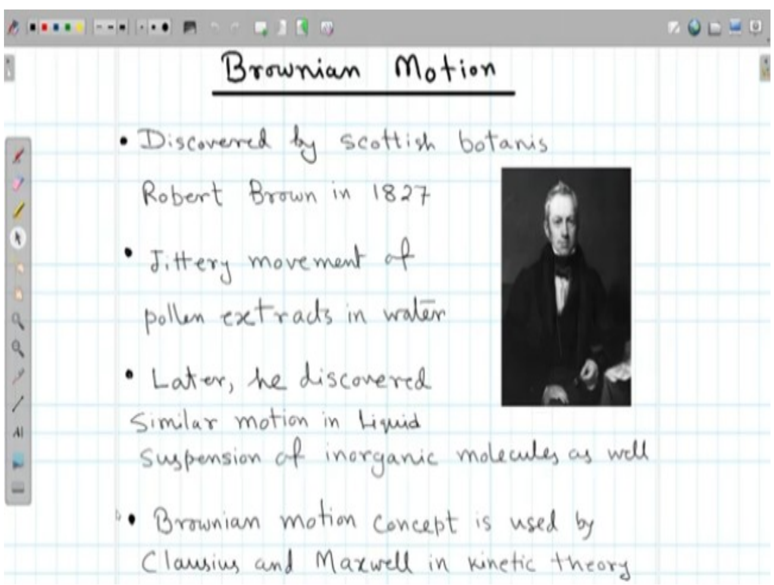

Now, Brownian motion for was first discovered by this Scottish botanist Robert Brown, in 1827. He was actually observing some, I mean he used to be a very eminent botanist of his time and what he was observing was at certain Pollen particles. Now there is a misconception that the first discovery of Brownian motion was the movement of Pollen particles inside water medium, which is wrong, it is not exactly the Pollen particles.

But some tiny extracts from the Pollen itself. Pollen is relatively bigger, but what he observed was the smaller molecules that are released by the Pollen particles. They keep moving under microscope, so it was observed under microscope. So, they know what he has observed was that the tiny particles, they keep moving or keep jittering in a very random manner inside water medium.

Now, initially it was believed that because these are pollen, I mean these are particles from the pollen extract. This movement has something to do with the life form, which was a very wrong misconception, but it was the initial belief. This is the Brownian motion is due to some biological particle and because it is a biological particle, it has some links with the life associated with it. So, later on Robert Brown discovered, himself discovered that similar movement in liquid suspension of inorganic molecules.

Or I should not say molecules, I actually issued use the word particle here, because molecule is molecule and particle is particle; that is the right word. Now, so what he actually observed was some water trapped inside some rock medium, some volcanic rock or something, I do not remember exactly but something and there are very tiny inorganic particles, that was trapped inside that water, that small droplet of water.

And he could observe the movement in that those particles as well and it was also very important discovery. So, that was maybe after few years of the initial discovery back in 1927. So, that was also very important discovery because, that discarded the theory of life associated with Brownian particles, Brownian motion. Now after almost 30 years of his initial discovery, when Clausius and Maxwell gave the concrete foundation to the kinetic theory.

Actually, the kinetic theory was first proposed by Bernoulli some 120 years back. But it was given the strong mathematical footing and the detailed theories have been worked out by Clausius and Maxwell, between nineteen, sorry, 1855 and 1860 around that time. So, they used the concept of random motion, random erratic motion of gas molecules that was directly borrowed from the Brownian movement that has been observed.

So, that for Brownian motion is a very, it has a very fundamental importance in the kinetic theory of gas as well. But of course, there is once again although it is very important, there is also a fundamental difference between the Brownian particles or Brownian motion and motion of gas molecules; so, will come to that in a moment.

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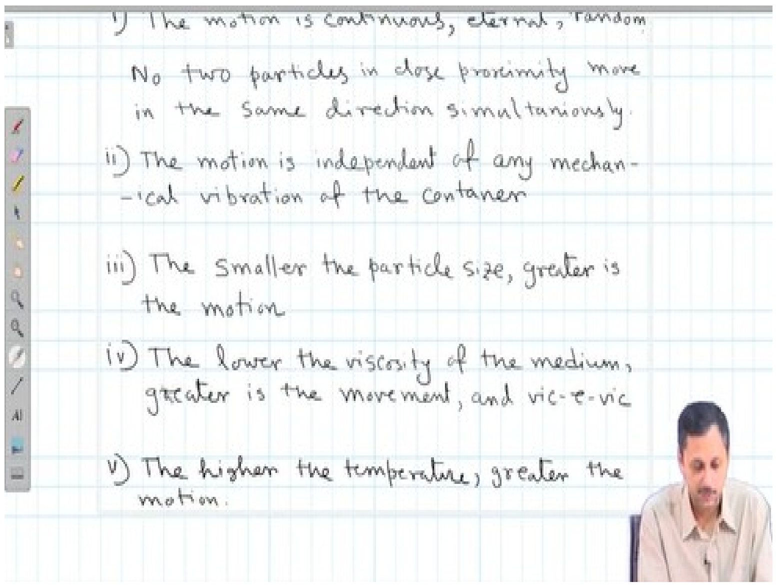

So, before we begin our discussion, we will just focus on the salient features of Brownian motion. Firstly, the motion is continuous, eternal, random and no two particles in close proximity they move in the same direction and that is also very important, same direction simultaneously. That is also very important point that we must know. So, when I say continuous eternal and random, that means the particles during their motion does not stop for a while.

They keep moving all the time for as long as you can continue with the observation and the motion is completely random. That is also very important point, that I am keep pressing on every time. And as the two particles in the same proximity does not move simultaneously in the same direction. It means, it is not due to any local force that is acting on the, I mean I should not say local force.

But there is no such region of force that is acting on these particles and making the do this movement. If that is the case, if there is a force field present in the movement, then some particles would have been moved in a group, but that we never see in a Brownian motion. Then, the motion is independent of any mechanical vibration of the container. So, even if we maintain let us say we put the container on a shape platform, you know we sometimes in biology lab or chemistry lab.

We use this shaker which keeps on moving at a constant rate for as long as we wanted to. So, that sometimes we need to you know, shake the sample overnight. So, if we place the container that contains a emulsion of a colloidal suspension, where we can observe Brownian motion and if we place that on such a platform and which it keeps moving, we still observe Brownian motion irrespective of whether this shaking movement or any other type of mechanical vibration is present or not.

And the third point is the smaller the particle size greater is the motion. That is also something very important, if we have a really tiny particle; when I say tiny, I talk about microscopic regime and smallest particle that you observe with an optical microscope is of the order of microns. Just to give you an idea our hair, human hair is typically hundred microns. And hundred microns is something that we very easily see with our naked eye.

Even half of that maybe down to fifty sixty micron also with some effort we can make out with our eyes, but beyond that down to maybe one micron, we need to have optical microscope. Even one micron is little too much maybe down to 5 microns or so we can use optical microscope to observe, no actually I am wrong, one micron can be observed with a good optical microscope and beyond that we need other techniques.

So, again there are two other observations, general observations that was made on revenue particle, that lowered the viscosity of the medium whether the movement and vice versa. I did not finish discussing this one. So, the idea was when the particle is of let us say one micron diameter, then it will move faster and in the same suspension same everything, if we have another particle of the same material, which is slightly higher in size.

Let us say 10 micron, 10 times higher in size, then it will move slowly. But it will move nonetheless, but the move relative movement will be slow. And then next comes the point that lowered the viscosity of the medium greater is the movement and vice versa. So, when we have, let us say we have same particle, similar particles suspended in water and similar particle suspended in a glycerol water mixture.

Now, glycerol water mixture as we know is more viscous as compared to pure water. I am not talking about pure glycerol, because pure glycerol is too thick and probably, we will not be able to observe any motion at all or the motion will be very slow. But if we have water, particles in water and particle in glycerol mixture, definitely the particles in pure water will move faster. The next point is the higher the temperature greater the motion.

So, if we observe the same particle at room temperature, I have let us say one solution water, particles suspended in water, I am observing it at the room temperature, which is typically 25 degree centigrade. And now if I put it on a hot plate and heat it up to 50 degree centigrade, the motion will be more, the agitation in the molecules will be more. So, these are the salient features of Brownian motion, which has been observed over and over again by many scientists in their early days.

And even now, we can always prepare a suspended particle in some liquid medium and we can observe Brownian motion and all this features we can very easily observe.

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Now, before we go any further, let me just give you a quick demonstration of what is Brownian motion. So, this is a video by IOP, institute of physics and they have used what was this exactly I do not remember, but anyway I have given the YouTube link. You can always go there and the full description is given. It was some kind of a resin particle, some polymer particle and the particles are of equal dimension, more or less equal dimension.

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So, their suspended in water. So, I like this video, there are many other videos available over YouTube on Brownian motion, but I like this video because here the number of particles are really less. There are videos where we can see basically thus tens of thousands of particle, they are moving executing this Brownian motion, but there you cannot really focus on a single particle.

But, in this video although the video quality is not very good, you can always make out, but the video is not very good. I remember, these are polystyrene spheres actually, which is some kind of a polymer material. So, these are inorganic particles essentially. So, you see you can actually focus on any of the individual particles and you can, for example if I focus on this particle, I can track its path, I can basically track its path and that is possible.

So, this gives you if you play the video over and over again, you will get a good idea what is the meaning of Brownian motion. But, at this point these are the observations and of course this is a video from not very recent but, I think it is a 2010 or 11 video, but still, it is pretty recent. So, these observations, similar observation has been made by Robert Brown and later on many other scientists.

But there was no explanation, no feasible explanation, although the similar movement has been assumed for gases in the kinetic theory, there was no solid explanation. Now people try to explain Brownian motion with many different theories, but finally it came all boil down to Einstein back in 1906.

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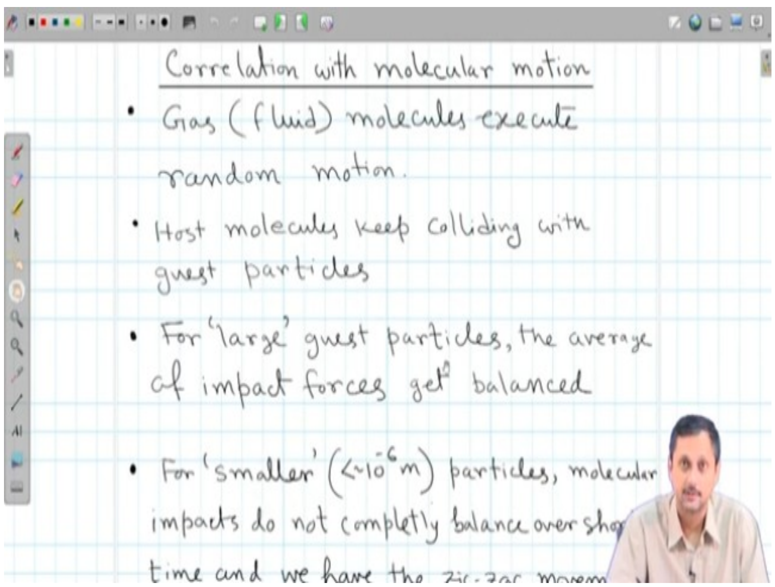

So, of course it was not developed overnight that the theory. So, we have series of observation made by different scientists and first I will brief the observation that has been made by over a long period of time as in for almost 50-60 years different observations has been met. And it was observed and so those observations are actually summarized in the when I discussed about the salient feature.

Now, what Einstein did was actually he correlated the movement of Brownian motion with the movement of underlying or the host meeting. So, let us quickly go back for one more time here.

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See here the movement is due to or movement to observe is that the guest molecules. The host molecules which are for example in this case water molecules is not seen, do you see that? No, we do not see.

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But it is present and it has been assumed that the movement of this host molecule and somehow correlated with the guest molecules, sorry, the movement of this guest molecules are somehow correlated with the host molecules and this correlation is what I have written down here step by step. First of all, the gas or fluid molecules execute random motion. That is something that was already accepted because kinetic theory has been a big success in order to explain.

Already existing experimental results, like different gas laws, pressure expression, all different types of things that we have already discussed. So, it was not very difficult to accept that the basic assumption of kinetic theory, that gas molecules make random motion, execute random motion that that has to be accepted. So, if first accept that, next is host molecule keeps colliding with guest particles.

So, let us say we have a Brownian particle, please remember as I have said in the beginning of my lecture that, there is a difference between movement of a Brownian particle and movement of gas molecules. The gas molecule at the host matrix and Brownian particle is actually a guest that is coming inside this host matrix. So, the host molecules which are Brownian particles, which are definitely load bigger.

Even a one micron particle is 10 to the power 4 times bigger than a water molecule. So, typical water dimension is of the order of Armstrong, which is 10 to the power minus 10 meters, if I am not very wrong yet 10 to the power minus 10 meters and 1 micron is 10 to the power minus 6 meters, so 10 to the power 4 times as big as the host molecule. But the host molecule they keep colliding with guest particles. And this number of collisions are really, really large.

Legitimate predicted that, it will be something of the order of 10 to the power 21 collisions per second. And this is happening from all directions, please remember. Now, for a large particle when the surface area is really large, all these forces of collision from all the directions, they average out nicely and we do not see any movement. So, for example if I have a tennis ball floating on water, that is a big object.

This is also bombarded by water molecule from all the direction, not all the directions but at least from the bottom half, where which is submerged in water. But because the ball is so large as compared to the water molecule, the effect of such collisions is not obvious in the movement of this ball. But for smaller particles which are micron, actually I should not set less than 10 to the power minus 6, I would say anything less than 10 to the power minus 4 actually.

It will execute some sort of a Brownian motion, which are considered small. So, 0.10 to the power minus 4 meters is 0.1 centimetre, so that is 1 millimetre essentially 1 millimetre particle will also execute some kind of a jittery movement, right. The molecular impact that is taking place, does not balance out completely. Of course, if I take a sufficiently long-time interval and average it over from all the directions, this will balance out nicely.

But instantaneously, as I said every second there is a large number of collision the forces are imbalanced and what we see that zigzag movement is due to that unbalanced force.

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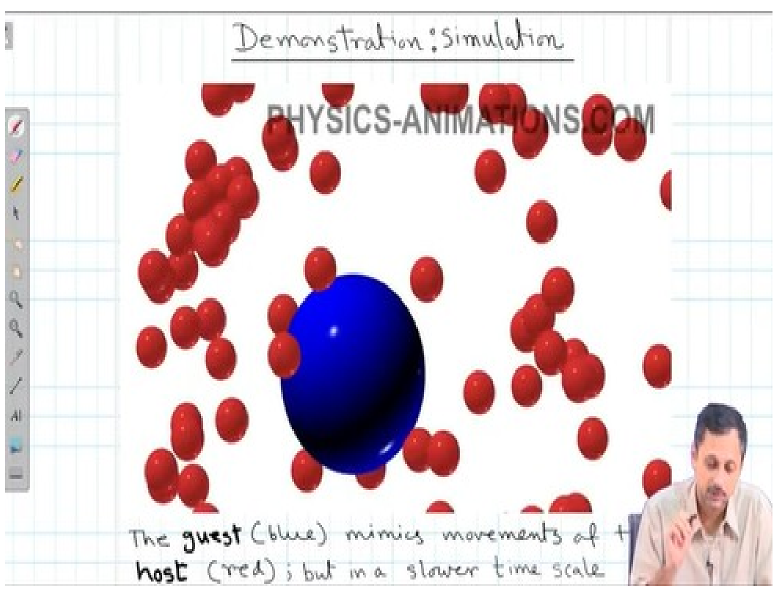

So, let us have a simulation demonstration, the blue molecule is the guest molecule, which is much bigger as compared to the host molecules which are red. So, let us see this is of course a simulation, so this is not the real life data, but let us see how the Brownian motion takes place.

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See here we just because, it is a simulation we can simultaneously observe the guest and the host particles and we can readily see that the host particle or the red particles their bombarding in the forces, the force of bombardment is unbalanced and that is why the blue particle is moving. So, but in reality, for any experimental observation, we do not see the red particles, the host matrix, water molecules we do not see.

And that is why it looks like as if, so what you mean to say is here also if you notice carefully. So, that there is a dimensional difference, but the dimensional difference is of course not of the order of 10 to the power 3 or 10 to the power 4 or 10 to the power 5. So, it is maybe 10 times in the factor of 10 or something like this. So, here the movement is you can see that the blue particle, that is actually mimicking the movement of the red particles, but in a reduced time scale.

It will be more prominent, if I increase the size of the blue particle, as in what I mean to say is then the blue particle will be moving lot slower as compared to the red particle. Here, because the size difference is not that much, they are kind of comparable.

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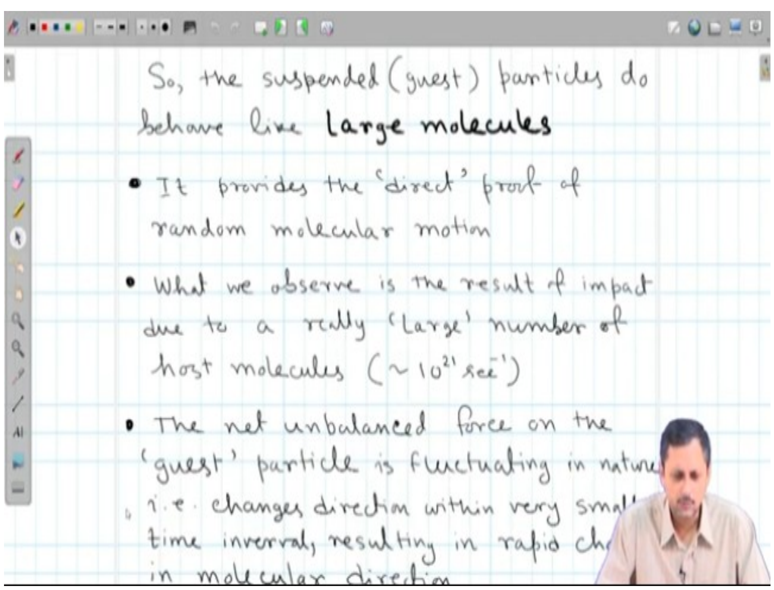

So, what we have is a suspended particle do behave like large molecules? So, what we can say that the suspended mark particle the blue particle in this case, they behave like large molecules. Which is again, you have to take it with lots of salted paper, because these are not in molecular scale by any means, but they still execute this exact motion which is characteristics of the molecule. So, I should actually put this word large molecule in quote unquote.

So, the Brownian movement actually provides direct proof of random molecular motion, because Brownian motion is a result of random molecular motion, which is basically the effect of large number of host molecules, collision with a large number of host molecules which is 10 to the power minus 21 per second as per Einstein and Langevin. And the net unbalanced force is pretty much zigzag in nature. So, there fluctuating that force, which we just discussed here, I will just play it one last time.

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You see the force; this is the force itself is changing direction rapidly with time. So, that is why we have this zigzag movement, the force is not uniform over time.

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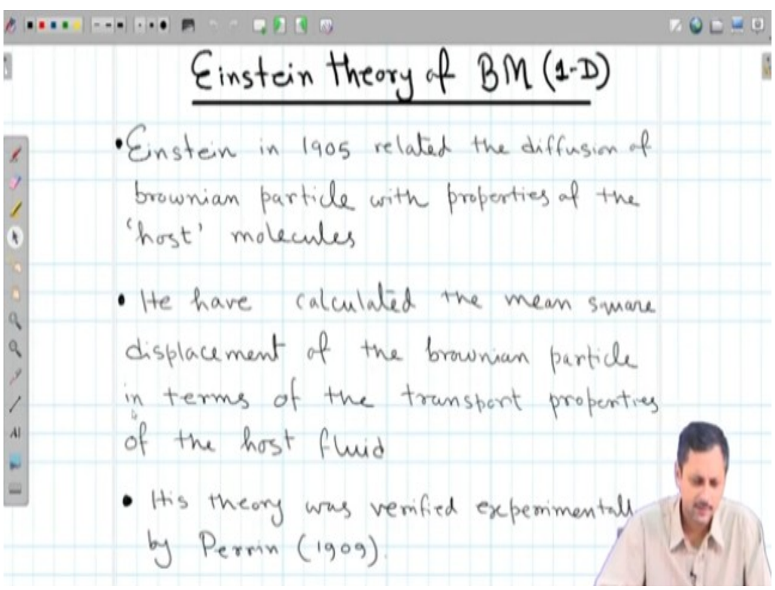

Now keeping all this in mind, Einstein came up with his theory of Brownian motion in 2005. So, basically, he related the Brownian movement of Brownian particle and of course there is a overall diffusion. If I just go back to this video is not so obvious.

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But if I go back to this video for the last time you see if I trace for example this particle. So, I will just keep my cursor on this particular, so this is my initial position, see over time it is slowly moving in certain direction. So, if I take every snap short in every 10 seconds of 30 seconds, I can actually trace out the trajectory and I can find out that there is certain diffusion actually, that is taking place.

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So, Einstein took this concept and he calculated the mu square displacement of the Brownian particle, in terms of the transport properties of the host fluid and that is a very big step. I mean, here whatever we say before that is all speculation, we said that, so these are actually the fluctuation is due to host, if that with host particle. But there is no solid mathematical theory behind it.

Einstein is the first one who came up with a solid theory in which; he could actually correlate the movement of a Brownian particle with the properties of the host matrix. And then his theories was later verified by a series of experiment by Perrin, I should not say 1909 actually between 1909 and 1915 and we will come back to that in a more detailed manner after one more lecture. So, we will have basically two more lectures on the parent experiment itself.

Which are wonderful set of experiment. But before that let us quickly look into the theory that Einstein had developed.

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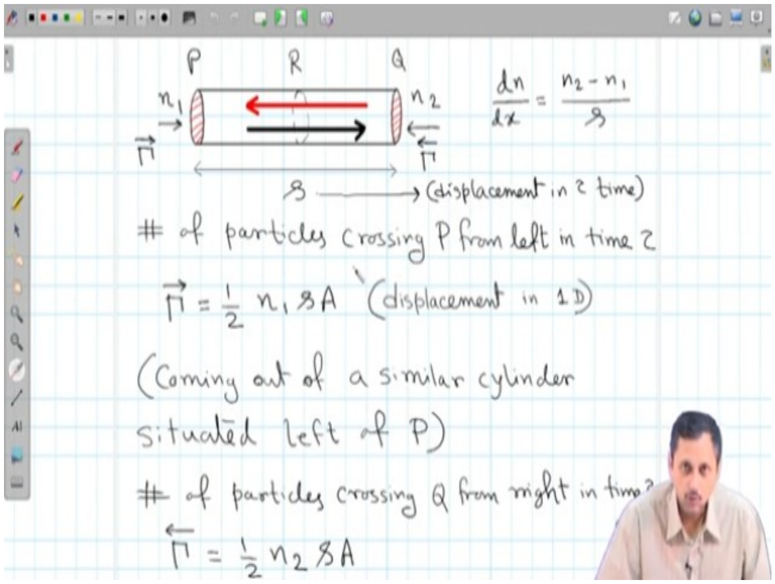

So, here assumed 1D diffusion, one dimensional diffusion and he has assume that over a time tau, so do not mix it up with the mean free time, this is nothing to do with mean free time. This time tau, the displacement, the mean square displacement, what is mean square displacement? Basically, these are, I have let us say 5 different movements in let us say basically I have 5 different random movements.

I can think of I just take the x projection of those movements then, I square it then, I divided by 5, the square of total displacement divided by 5. So, this is my mean square displacement. So, he assume the net means square displacement in time tau is given by s square. And also, for simplicity here as assume that, for all the particles in the system, they moves by at distance s over a time tau.

And please remember although we observe Brownian motion primarily in a 2D plane, so we have the field of view is a 2D view, the theory here is for one. Now, how to experimentally verify it and all? We will come back to that, when we will be discussing the experimental part. And, here assume that there is of course if there is diffusion there has to be a density gradient. So, here assume the density of the Brownian particle.

Please remember when I talk about density here on, it is all the density of the guest particle not the host matrix. So, Brownian particle is n 1 and that of Brownian particle is n 2 in the right phase. So, we call it the P and the Q, the surface area is given by A, the red surface these are marked, these are A and we have dn, dx is equal to n 2 minus n 1 divided by s. So, basically the black arrow gives you the direction of the density gradient.

So, density is increasing in this direction and of course diffusion, net diffusion is taking place opposite to the density gradient, which is given by the red arrow. So, the basic assumption, so the primary assumption has been each molecule, they move in mover distance s in a time interval tau one another. So, this is also kind of a mean field theory. Now, let us assume that there is another cylinder, exactly similar cylinder to the left of this.

Where, the surface P is the common that is the rightmost surface of the left cylinder and the leftmost surface of this present cylinder. So, whatever molecule that resides inside this P, after a time tau, it will diffuse out of that cylinder and half of that will diffuse to the right. Because, it is a 1D motion or 1D diffusion, because let us say there is a cylinder here. So, half of the particle will diffuse to the right, half of the particle will diffuse to the left. That is by 50-50 probability.

So, the total number of particle that is contained in a cylinder of this length s and with density n 1 and cross section area A is given by half n 1 s A. Then the half factor is coming because only half can come, so only half from this cylinder can come in. Similarly, that is the number of particle, that is moving towards the positive x axis. Now, for the number of particle, that is crossing Q from right in time tau is given by this gamma left arrow half n 2 s A.

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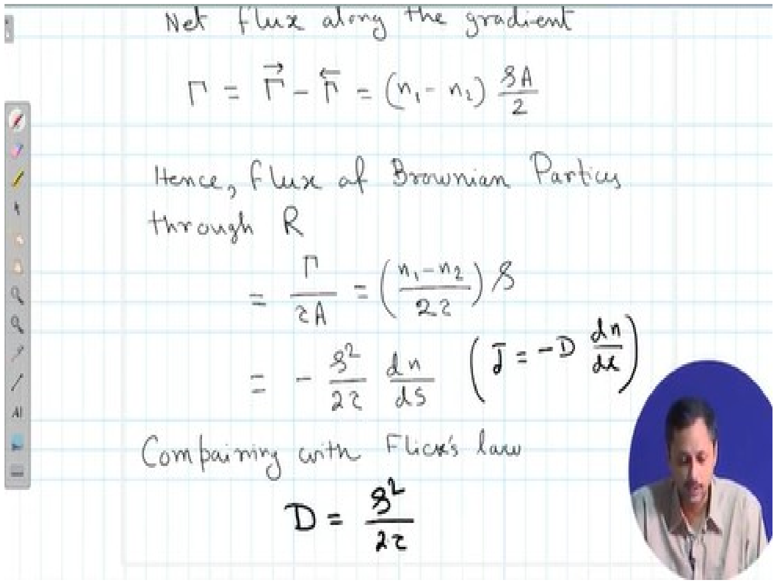

So, the net flux along the direction of the gradient, once again just the same treatment what we did during the transport studies. The net flux along the gradient will be gamma times a gamma is equal to gamma for right arrow minus gamma left arrow, which is given by n 1 minus n 2 times s A by 2. So, the net flux of the Brownian particle through R will be gamma divided by tau times A, so what is flux? Flux is unit the number of particle that is crossing unit area in unit time.

That will be given by gamma divided by tau A, which is n 1 minus n 2 by 2 tau times s. And, once again we use the relation that, dn dx is equal to n 2 minus n 1 by s, which is the linear gradient and we can write another, we can bring in another s in the denominator and we can finally write that the flux of Brownian particle through R; R being at the centre of this cylinder, the surface at the centre of the cylinder is minus s 2 square by 2 tau dn ds.

Now, if we compare this with the Flick's law diffusion, which was if you remember, the flux J is per unit area per unit time is, sorry it will be minus dn dx, so if I just compare this to, we get an expression of D, which is equal to s square by 2 tau. Now, this is one way of correlating the diffusion constant with the mean square displacement. Basically, s square is the mean square displacement in time interval tau and there has to be another way and then that can be compared.

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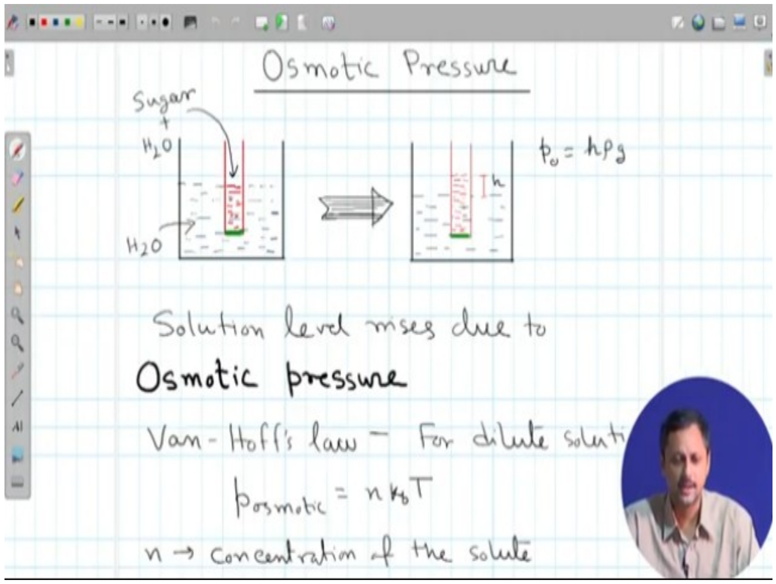

Now, it is so happen that another way is by means of osmotic pressure. Now, what is osmotic pressure? Osmotic pressure is something for example I just give you a quick demonstration of what osmotic pressure is. Let us say I have a small capillary tube with the end covered with the semi permeable membrane. Now, if we have that and if I dip it in and I put sugar solution inside this and I dip it in a beaker and if I wet for some time, what do we see?

We see that some water molecule will pass through the semi permeable membrane and the height of this capillary will be raised by h. So, this happens due to osmotic pressure. And, there is a Van Hoff's law for osmotic pressure. So, Einstein did, basically he derived the diffusion constant from two directions. One is from the osmotic pressure consideration, which will be discussing next and which the other one is from this mean square displacement.

And, finally what it did was he equated this to in order to get an expression of mean square displacement, in terms of the parameters or rather the transport parameters of the host medium. So, that is how the displacement of a Brownian particle can be compared with the properties of the host matrix, which we will continue, which will discuss and will continue from here in the next lecture, thank you.