Thermal Physics
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Lecture - 18
Perrin's Experiment on Brownian Motion – Part 1

Hello and welcome back to another lecture of this NPTEL course on thermal physics. And for today's lecture we will be discussing about experimental verification of different theories on Brownian motion.

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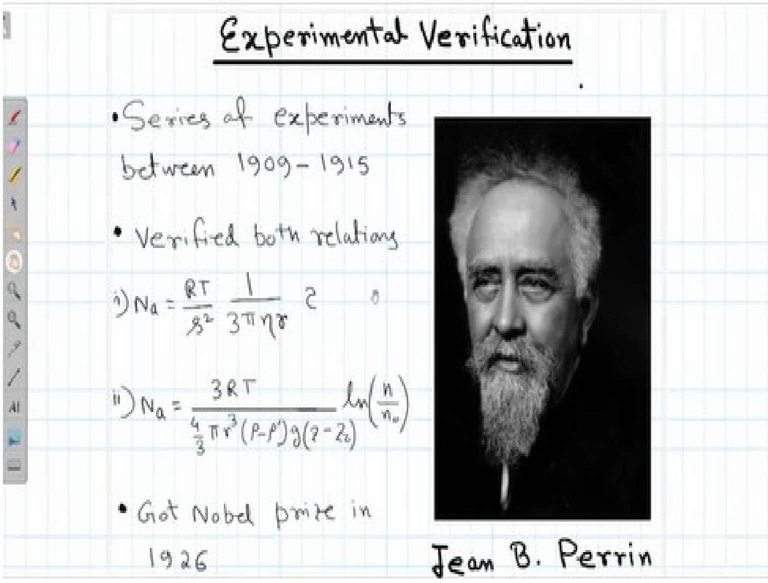

Now, we have in the last two lectures, we have discussed about Einstein's theory on Brownian motion that is translational Brownian motion. How this particular diffuse? I mean the diffusion of a Brownian particle in one dimension can be correlated with the system viscosity and see that coefficients like the parameters like system displace the coefficient of viscosity temperature and density of the medium.

Also, we have found out that there is another relation or another effect of Brownian motion in terms of sedimented particles. So, if we have a layer of or if we have colloidal suspension kept in a vertical column, then due to the action of gravity. So, basically gravity wants to pull everything downwards and diffusion wants to keep everything upload diffusion and buoyancy.

So, there this or basically buoyancy I mean diffusion is a result of bow and so I should not mention it separately. So, as a competition between these two, some particle will settle I mean the number density of Brownian particle will be highest at the lowest level and as the height increases the density of the Brownian particles will be diminished. So, this is the then we basically have two sets of equation.

One is the sedimentation equation and the other one is the Einstein's equation I mean Einstein's relation of means square displacement in terms of the system host the you know characteristic parameters of the host matrix. So, in a series of experiment the French physicist Jean Perrin 1905 and 1915 he verified both relations. So, essentially what it did was what do you mean by verification?

So, basically, he calculated the mean square displacement or he calculated the number of Brownian particle in different heights. So, he measured these things directly and from there he has computed the value of the Avogadro number. So, one set of Avogadro number I mean the sets the values he has computed these are the values were pretty accurate. We know what the modern value is, I mean modern the accepted value of the Avogadro number.

This is 6.023 to 10 to power 23 per mole and his values where I should not say very close to that but within 10 15% of that number. So, for his and please remember it is not a single observation, he has computed a series of observations all together. I do not know how many experiments but it is a very large number and he got Nobel Prize in 1926, Nobel Prize in physics in 1926 for his really, really, really rigorous set of experiment.

So, in this lecture and in the next lecture, we will be talking about Perrin’s experiments. First, we will consider the Perrin’s experiments on sedimentation the second equation and how he has prepared the sample how he has verified, you know how he has conducted his measurement everything will be discussed in details. And in the next lecture we will be talking about the tragic, I mean the you know the first equation where he essentially tracked each particle by hand in order to compute the mean square displacement.

So, why I am I will go into the details of this experiment? Because sometimes as the student we do not realize how difficult it is to conduct experiment. I mean I am not taking anything away from the theoretical phase I have in theoretical scientists. They are also doing their doing really great work but sometimes we do not realize that experimental verification even of the simplest nature how many parameters has to be optimized.

And we really do not have any idea we need to do not know how many failed attempts are there between every successful attempt. So, let me just take you through step by step through in the through the Perrin's experimental method on how to measure Avogadro number using the law of sedimentation.

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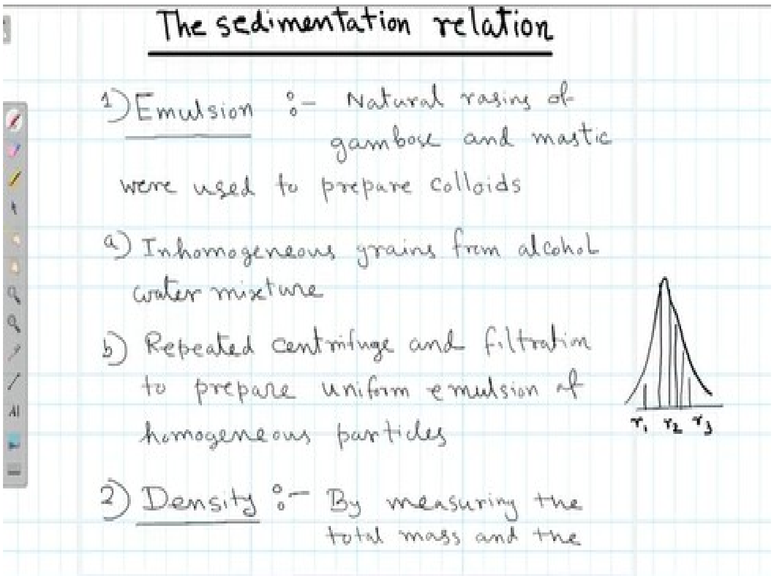

So, the first thing is preparation of the samples. So, we need Perrin needed some sort of an emulsion that will sustain and most importantly please remember that these you know the basic assumption we do in these two equations are that R is constant the radius of the particle radius of the particle in question that diffusing Brownian particle they have a constant radius. Mass is not there.

So, in both this relation, there is no, you know, it does not matter whether the particle is small or big but it has to have a uniform radius. So, the first and the foremost you know important thing was to get a very uniform distribution of radius. Of course, it cannot be like any two particles in the same even the same Brownian mode in the same experiment will not have exactly the same radius.

But it was absolutely necessary to keep the radius distribution very strict what I mean to say is, so these are more or less the experimental term I will use it anyway. So, let us say I have this is number and so let us say if I can draw a histogram if I have radius like r 1, r 2, r 3 okay, so these are the numbers and if I can draw a histogram, so the histogram should look like this. So, what I mean to say is the number distribution there should be a distribution definitely.

But the distribution has to be very narrow. So, in narrower is better so if I can make it even narrower if I can make it something like this, it will be even better. So, that is what Perrin did. Now how did it do that? So, I will try to explain so he first shows the sample which are two naturally occurring resins, one is called the gambose and the other one is called the mastic. So, both are plant extracts we know what is resin.

We have some crease, we must have seen that for example, if there is a cut in the people tree some resin some solid material will come and you know segregate there, we sometimes use those at the as gums as well. So, these are actually naturally occurring dressing. So, what it did was it took two such resin samples, he used a mortar pestle to grind them and once their properly grind he has dispersed them in a alcohol solution.

Now inside this alcohol solution when you put water in and when you put water inside this alcohol solution, the there was a emulsion of this resin inside this alcohol water mixture. Now he has used a technique of repeated centrifuge and filtration to prepare uniform emulsion of homogeneous particles and that is extremely important. So, I hope you are familiar with the term or word centrifuge.

So, that is basically a machine through which you can separate out particles of different masses and filtration is of course you know what is filtration. Next so let us say after as after certain repeated effort, he could actually get the particles to be of very uniform radius distribution sized distribution. Next is the density has to be optimized. So, density has to be measured.

Please remember in the second experiment there is a term that is rho and there is a term that is rho prime. Rho is the density of the Brownian particle and rho prime is the density of the host matrix. So, rho has to be measured.

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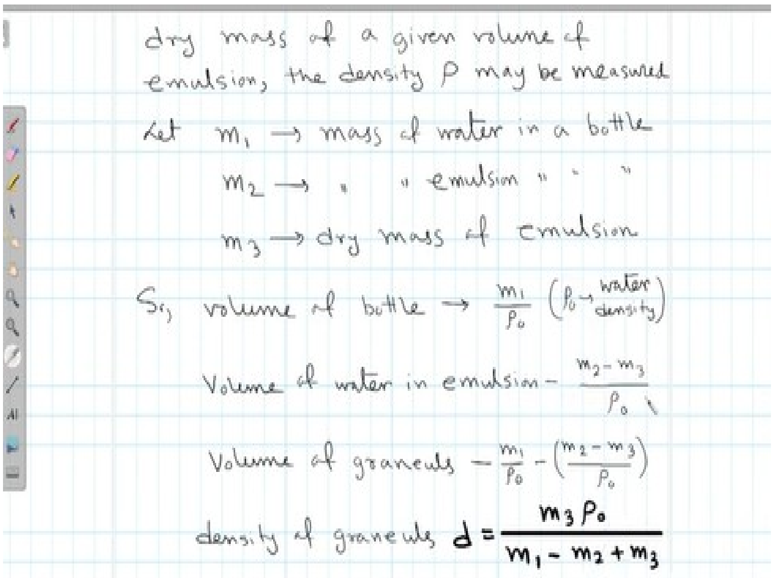

So, he measured the density by measuring the total mass and the dry mass of a given volume of emulsion. So, let us assume that initially he took in a specific gravity bottle he took m 1 amount, I mean he filled up the bottle with water, so the mass of the water in the bottle is m 1. And next if field it up with the emulsion syllable solution or that emulsion of this gamble or mastiff whatever he had and the mass of the bottle with emulsion solution filled is m 2.

Then he poured out the entire mass of the entire emulsion from that bottle and dried it in an oven. Now what happens? When we dry an emulsion solution emulsion, total solvent is lost only the solute molecule will remain as a dry powder. So, let us say the mass of the dry powder is m 3. So, the volume of the bottle is m 1 divided by rho volume of the water inside of the bottle rho being the water density.

The volume of the water in emulsion will be m 2 minus m 3 divided by rho 0 because m 3 is the dry mass, so m 2 minus m 3 is the amount of water that is present inside the same volume and the mass of the water present in the same volume and then volume is given by m 2 minus m 3 by rho 0. And then the volume of the granules will be simply m 1 by rho 0 minus m 2 minus m 3 by rho 0 and the mass of this granule or the finally the density of this granule will be m 3 rho 0 divided by m 1minus m 2 plus m 3.

So, this is the relation that we have in order to compute the density. So, even if you know sometimes, we just accept that so density is given to us but measuring a density itself is a painstaking job.

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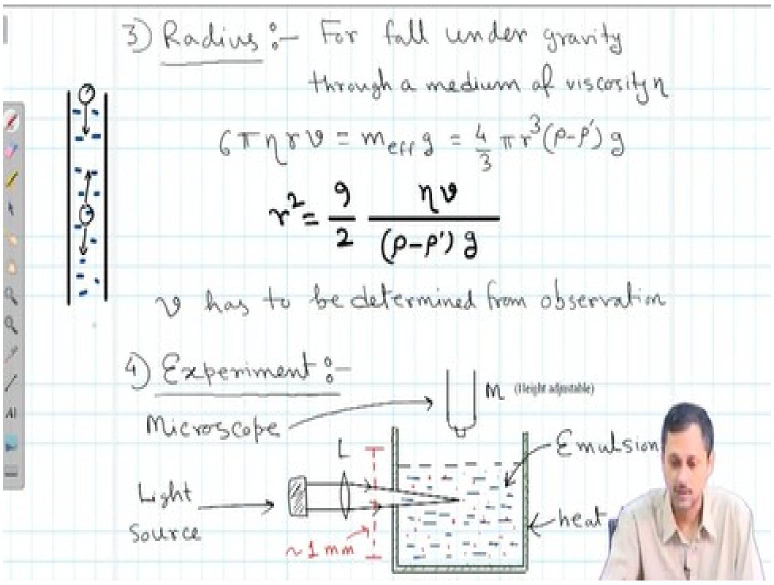

Next comes the measurement of the radius. That is even difficult because in order to measure the radius he had to use apply the Stokes relation. Now Stokes law we have seen that the viscous drag is given by 6 pi eta r v, we have discussed it in the previous lecture which is equal to and in case if you know, particle is falling through let us say we have capillary tube inside which there are some liquid water present.

And a sphere of non-radius r is moving falling through this. So, what happens when the sphere is here there is a viscous drag that will take it ups. I mean, it will be opposite to the motion and there is the mass movement or the motion due to gravity. So, these forces should balance in case of terminal velocity so it will be 6 pi eta r v is equal to m effective times g, now m effective will be 4 3rd pi r cube rho minus rho dash where, rho dash is the density of the water or whatever medium it is falling through.

So, using that relation so he could actually take the emulsion inside beaker and after shaking it if he just allows it to settle so he can see the downwards movement of this particles and he can calculate the radius using this relation. So, once again it is not a very simple procedure, he had to do many repeated measurement to get to this exact number. But he could finally get the radius of this emulsion or radius of these Brownian particles with good accuracy.

And so, you understand that v has to be determined from observation. There is no other way than just observation with naked eyes. Now it is we can use movie cameras and all but in his time the concept of movie camera was not that prevalent not in a scientific lab. Finally, then comes the experiment. So, he took a very shallow, you know container. So, I am just drawing it like this but the typical height of this liquid column is one millimetre.

So, inside that you know, and it this shallow bowl or shallow container whatever you call it is placed inside a heat path so that the temperature is evenly maintained. Because if we go back here, you see the temperature is a constant. Here also the temperature is a constant put the experiments has to be performed at uniform temperature. And then the emulsion is poured in inside this there is a source of illumination where we have a lens arrangement for example.

So, that light can be you know focused inside this container and then there is a microscope from the top we can use he has used a microscope in order to observe the particles. Now let us go back to this relation once again what we need to do is? We need to count the number n and n 0. Now this counting is something that we do not do instantly I mean; we can observe using this microscope we can probably observe but we cannot really count the numbers.

Also, there is a problem that this see we have to calculate, for example, if I take two slides, I have to calculate the numbers in this layer and I have to calculate the number in this reference layer and then only we can compare them to calculate the Avogadro number. Now in order to overcome this problem he has modified this microscope by the way, the microscope is high height adjustable.

So, we can I mean, he could have moved it up or down in order to observe different layers. So, what he did was he used a microscope with a very shallow depth of field.

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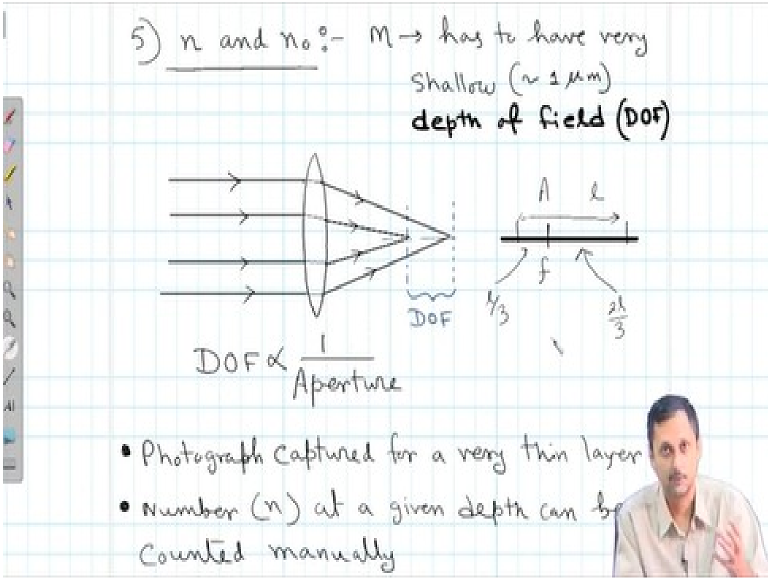

What I mean by depth of field? Let us say there is a lens assembly and it is focusing the parallel set of rays in one particular place. Now in an ideal case in an ideal world a thin lens should you know converge all the light rest to a single point that is the focal point. But in reality, what happens? In reality typically the central part of the I probably the drawing is not correct typically what happen, is I mean the focal plane or focal point is not unique.

But there is a finite you know finite length or finite depth over which the focus is sharp. So, typically I am just giving you once again rule of thumb. I hope you know there are ways of proving it I do not know exactly how to prove this but I am sure it can be done. So, if let us say if this is my focal point f, let us call it point A so and the total depth of field is l. So, the total depth of field is given by l so this rule of thumb is this portion will be l by 3.

And this portion will be 2l by 3. So, basically what I mean to say is there is a finite depth by on in which the microscope can focus anything beyond this depth. So, if one particle is so what I mean to say is if the particles are here, the Brownian particles are lying inside this depth. That can be in the sharp focus and that can be seen through the microscope. If it is there or there so basically this is the z direction the microscope you have to assume that the microscope is from the top.

So, this is the z direction so if it is below or above then the focus will be really blurred and Perrin did not consider. So, this is the concept of depth of field and once again, it is possible to prove the depth of field is inversely proportional to the aperture. So, in photography whenever the lens is has, you know, higher aperture that means you know it is the opening is more the depth of field reduces.

If the opening is less the depth of field comes more and that is absolutely understandable because in a pinhole camera if you remember pinhole camera has an infinitive depth of field. And what other modification he did? The one modification is he had a microscope with a very shallow depth of field and the other modification is he has heated a camera with this microscope. So, he could actually take the photograph of this layer.

So, now from this photograph, he can actually you know adjust the depth of field within in the range of one micrometre. So, basically when he was observing this once one millimetre length, which is approximately thousand micrometre. So, he was observing it into the as if these are slices thousands slices each of one micrometre thin. So, he could eventually count take the photograph and later on he can count the sharp points.

The hollow or the blurred-out points or blurred Brownian particles these are actually either higher or lower as compared to that particular layer. So, all he had to do was from this photograph here to count the sharp points which are sharp dots which are present and that will give him an idea of n 0 and n.

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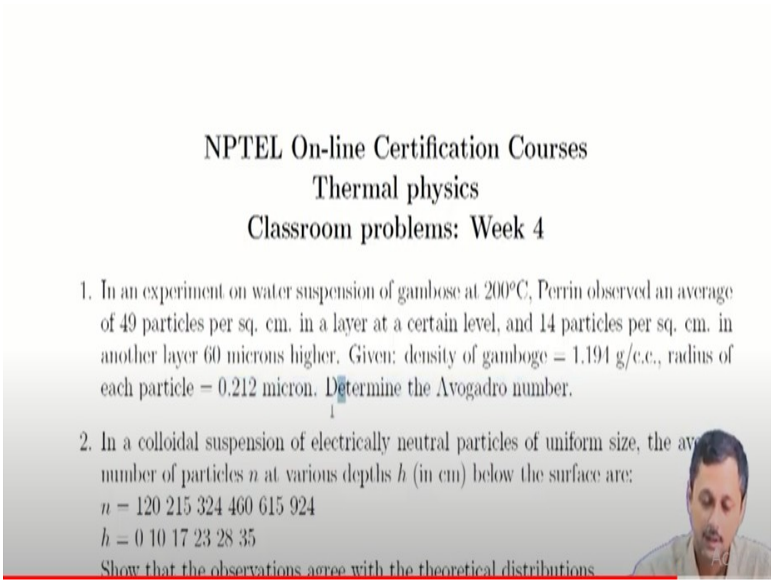

Now just to give you an idea of, how his result used to be just found out this problem. In an experiment of water suspension of gambose layers, it should be 20 degree centigrade not 200, 20 degree centigrade Perrin observed an average of 49 particles per square centimetre in a layer at a certain level and 14 particles per square centimetre in another layer 60 microns higher. So, he could actually focus on two layers which are divided, separated by 60 microns and that travel can be adjusted so there the as I said, this is the height adjustable microscope.

There will be a scale here through which the travel of the microphone can be adjusted. So, once it is focused on a particular layer now it can be moved after upward down by a certain amount measured amount using this scale. So, basically two-name n 0 and n is given and the delta z, the z displacement is 60 microns. Given the density of gambose is 1.191 grams per c c the radius of each particle is 0.212 microns. So, we have to determine the Avogadro number.

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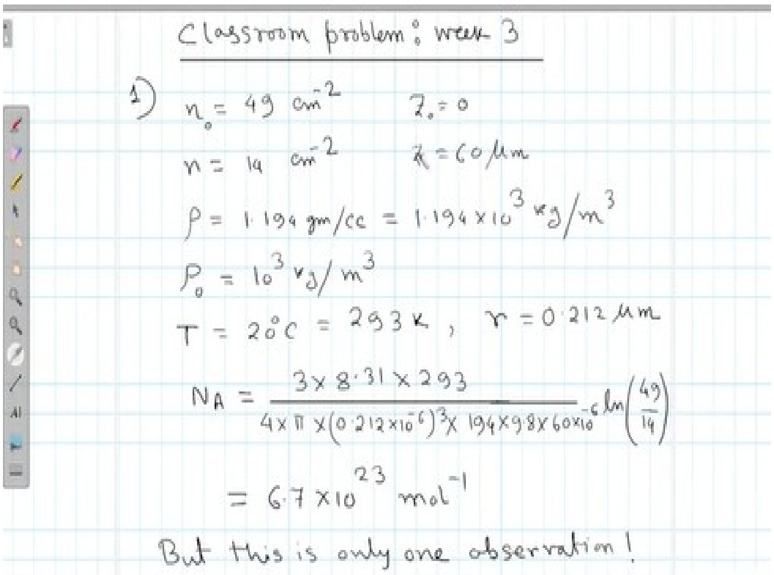

So, let us look into this problem in an elaborated way. So, let us say that we have n 0 which is 49 per meter square at 0 equal to 0, it does not matter we can take basically what matters is z minus z 0 is equal to 60, so n is equal to 14. So, in this expression we have z minus z 0, n and n 0. So, n by n 0, it does not matter whether it is in centimetre square or meter square or whatever unit as long as there in the same units n by n 0 will be just the ratio.

So, we already have this ratio and this number, g is already known temperature is already given. So, what next what do we have? So, rho is already given which is 1.194 into 10 to the power 3, rho 0 is of course the density of water which is 10 to the power 3. So, it actually should be rho prime not rho 0. So, we have T 0 is equal to 293 Kelvin, r is equal to 0.21 to micrometres. So, we will see once all the data is given it looks very simple.

Because all we have to do is if we have to plug in the numbers in this relation and we get an Avogadro number which is 6.7 into 10 to the power 23 mol units. So, we have to remember two things first of all the effort, one had to Perrin had to give in order to compute this number or this number is enormous I mean we have probably no idea on how much effort so this is not even the actual observation actual experiment. It was just to get to this numbers.

So, how many observations and how many items he had to make we have no idea. So, this are there and also please remember this is only one observation, single observation and that gives a value of 6.7 into 10 to the power 23.

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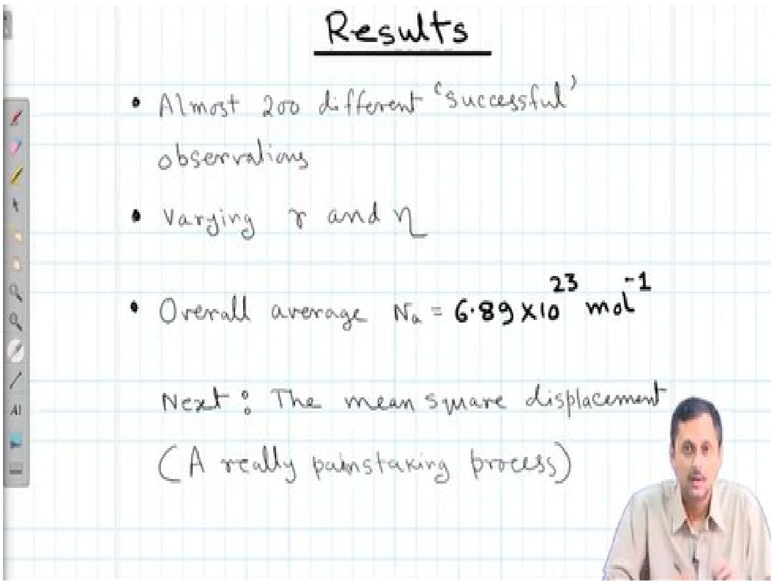

So, this is just an example of how Perrin measured Avogadro number using the sedimentation relation and he has almost 200 different successful observations and we never talk about the unsuccessful observations. Behind every successful observation I would say the ratio is typically 10 is to 1. So, if we have 10 success permanent 10 total observations, you get one successful observation on an average.

Sometimes it changes if you are lucky and sometimes you can have you know, hundreds of 10s or thousand hundreds or sometimes 500 observations without success. So, that is why when we talk about 200 successful observations, we do not know how many successful observation was there and he also did the set of experiment by varying r and eta. So, he used different mediums, different medium as in used water, he mixed alcohol with it, he mixed glycerol with it.

So, basically the viscosity was changed for I do not remember the numbers but it was some you know tens or hundreds or factor of 10 or factor of hundred. Similarly, r I think it was also varied for a factor of 1500 that is a large number 10 to the power 3 orders of magnitude. So, overall average and after all these observations so here this is one set of observation we are talking about, he actually have two sets of our observer.

I mean made as I have already mentioned that there are this is one type of experiment, he helped has all together another type of experiment. Now the overall average of N a is 6.89 into10 to the power 23 mol inverse. And this will come back once again to this number and next we will discuss the mean square displacement with is a really, really, really painstaking process. That will be the subject matter of the next lecture.

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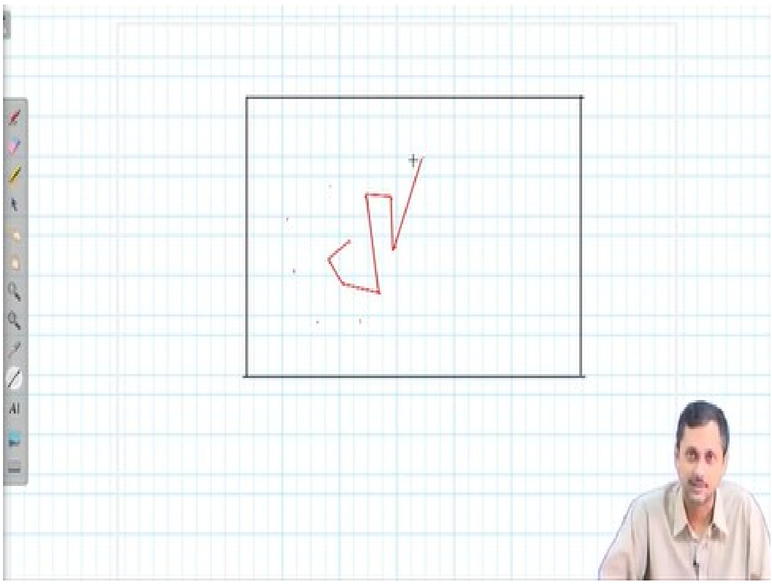

But in today's lecture what I will do is I will give you a brief account of what we are going to discuss in the next lecture. So, what Perrin did was he somehow managed how and all I discussed it in the next class only. He let us say this is a photography plate or let say there not a photographic plate that actually sorry this is a graph paper and he could actually keep marking the trajectory of a Brownian particle by hand in a random manner.

Wherever the particle was going he could mark a point after a certain time interval he could mark a point on this graph paper. And then later on he joined these points using straight line segments like this. So, I am just doing it randomly I do not know which one is were. So, you could actually see the trajectory of a Brownian particle and draw it by hand and from there he could you know, use the mean square displacement he could calculate the mean square displacement.

And then calculate the Avogadro number from this. So, this is an experiment which is even more painstaking as compared to the one I have just discussed. Because here the observation I mean at least here in this experiment he had the liberty to take a photograph and count it as per as per his convenient time. But in this set of experiment, he had to essentially you know, sit in front of the microscope and track it by hand the track the project trajectory of a particle by hand.

So, this is another example of what dedication it needs to perform a really good experiment although very simple but really good experiment and we will discuss that in the next lecture. Thank You.