Thermal Physics
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Lecture - 19
Perrin's Experiment on Brownian Motion – Part 2

Hello and welcome back to another lecture on this NPTEL course on thermal physics. Now, for today's lecture, as promised, we will be discussing the other experiment that was performed by Perrin in order to determine the movement of Brownian particles. Now, he not only tracked the movement of Brownian particles in real time in this particular experiment, but also used this diffusive motion.

In order to estimate the Avogadro number; which turned out to be the first ever reliable estimate of that Avogadro number which is now known to all of us. So, without further delay, let us look into the Perrin's work in more detail.

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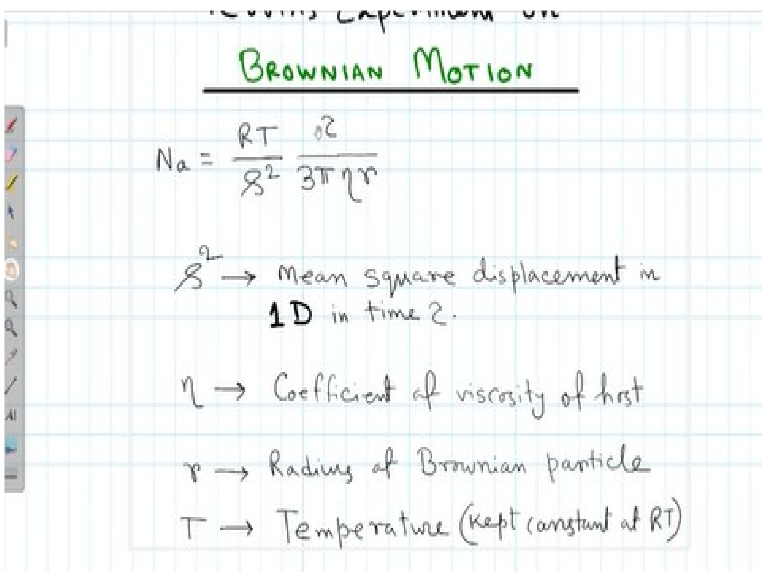

So, in the last lecture, we discussed about Perrin's experiment on the sedimenting particle. And, we have found out that there was a working formula that was derived based on the constant, I mean, or that the competitive forces of gravitation and buoyancy acting on a particle or acting on a Brownian particle that is moving in a vertical direction. But for horizontal movement, Einstein came up with this theory through which this particular relation N a is equal to RT by s square tau times 3 pi eta r was derived.

And this was derived thoroughly in previous lectures. So, I am not going into the details of this. Just for a quick recap, what do we have here? We have s square is the mean square displacement in the time interval tau. Eta is the coefficient of viscosity of the host metric that is the liquid through in which the Brownian particles are moving, diffusing. r is the radius of the Brownian particle and T is the temperature which is kept constant at room temperature for the course of this experiment.

So, what are the unknown quantities here? The unknown quantities here are the temperature, the mean square displacement tau. Tau and mean square displacement, they are correlated with each other and eta and r.

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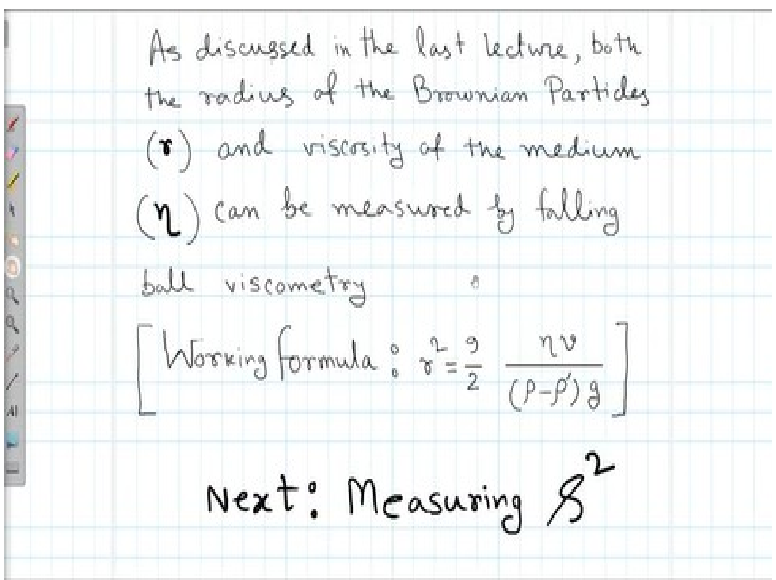

Now out of this unknown parameters eta and r, it was already discussed in the last lecture that how to measure the radius of this Brownian particles. So, what Perrin did was he actually, just a quick recap this is, he actually took the emulsion of gambose and there was another mastic so, these 2 natural resins. So, he took the powder of those, dispersed those powder into an alcohol water mixture and using repeated centrifuge and filtration he came up with a set of particles which has a very defined range of radius.

So, that is why so, he used kind of uniform Brownian particles. That was very crucial, because for both the working formulas for both of his method r is a constant. So, once if there is a distribution of r there is a good chance that his results would have been not reliable. So, it was very necessary that r the radius of these particles were accurately measured. So, we have discussed how he measured the radius.

He basically used falling ball viscometry in order to measure the terminal velocity of these particles and through this particular formula, which is given by r square is equal to 9 by 2 eta v by rho minus rho prime times g, where rho and rho prime are the density of the Brownian particles and the density of the medium respectively and eta is the viscosity, he could calculate the value of r. Now, in the same method, if we take a finite size sphere like, let us say, metallic sphere of known radius that means r will be known.

So, in a similar manner eta can be calculated. So, falling ball viscometry is a very standard technique to calculate eta which Perrin used in a slightly different way. Even that the eta is known, he used it to determine the value of r. So, both can be measured, both eta and r can be measured with a slight modification of the experimental setup using the same working formula. Now, temperature is probably the easiest thing to monitor, maintain and monitor in this set of experiment.

Because this Brownian suspension is actually very tiny. We have discussed some dimensionality while in one of the previous lectures. The measurement actually carried out well, for the sedimentation experiment the measurement was carried out over a depth of 1 millimetre. So, we can understand, you know, the length scale of this experiment I mean the actual sample holder in which this emulsion of uniform diameter is kept.

So, that small sample holder has to be put inside a heat bath, so that the temperature of the whole system is maintained at a constant value T. So, that is very easy to do. The major challenge comes in the measurement of this S square that is the mean squared displacement. So, how to measure that? And that is why I mentioned this particular set of experiment as painstaking, you will understand in a moment.

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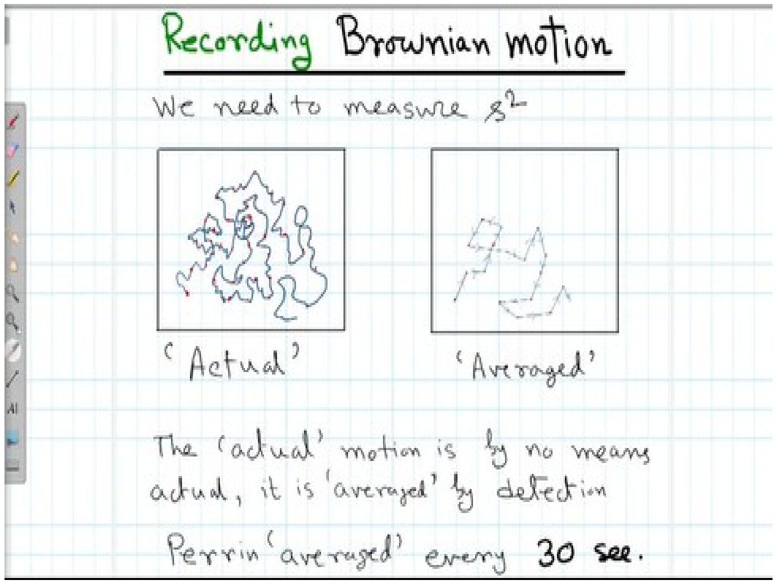

So, now, we come to the question of recording Brownian motion in particle. So, basically, we need to measure S square that is the mean square displacement. So, let us first look into these two trajectories one to the left, one to the right, of course, these are trajectories which I have drawn by hand. I am just selecting a random area and let us say the blue particle is the actual motion. Now, this actual motion, but when I say actual motion, this actual motion is not exactly actual because it is actually averaged by the detection method.

If we are observing this Brownian particle with our naked eye so basically, we have, let us say, we are just looking through the eyepiece of the microscope and so that we can see these Brownian particles moving okay. So, then we are limited by the frequency of our eye. So, detection frequency of our eye and which is typically, you know, one 30 of a second. So, there are very nice experiments, school level experiments;

Which demonstrates detection frequency of our eyes, just to give you a basic idea on how to do it. See, for example, movies are typically, you know, on the olden days, when there used to be films, if I am not very wrong it was 25 frames per second or so, for the motion picture. Yes, or maybe 30, I do not remember. And, I remember watching a beautiful experiment where I have, you know, lights simple light bulbs.

The filament light bulb connected with a frequency knob through which we can vary the frequency. So, when we are in the DC region, the bulb is constantly illuminated. And as we increase the frequency, what is happening? It is slowly turning on and off. So, when we start altering the direction of the current by increasing the frequency, we can actually see that bulb is momentarily turning off and then turning on, turning off and turning on.

As we increase the frequency after a certain while, it looks like all the time the bulb is illuminated. But in reality, the bulb is being, you know, it is glowing for a certain period and switching off for a certain period. So, that experiment shows how our eyes are limited in the timescale of detection. Similarly, every camera, for example, in a modern-day setup, if we use a camera in order to record the movement of Brownian particle, that camera also has a temporal resolution.

So, if the movement is let us say, you know, faster than this temporal resolution, let us say the temporal resolution for a very good camera is 10 to the power of minus 8 seconds, which is very high almost, so 10 nanoseconds, almost. So, 10 nanoseconds resolution ultra high definition camera but if the particle movement in reality if it is moving at a timescale of 10 to the power of minus 12 seconds that is one picosecond.

So, what happens is, we observe the particle once in every 10 nanoseconds. In between whatever happens to the particle we have no information. So, I tried to describe the same concept through this diagram. This blue one is, let us for a second assume that this is the actual trajectory of the particle. So, I am just trying to put my, you know, pointer over this. So, let us say that this is more or less the trajectory of the particle which is kind of so many points that we cannot really you know, observe it carefully.

Now, what we can do is? We can choose a certain time interval tau and we can mark the position of this particle on each such interval. So, these are represented by these red dots here one dot here one dot here, here, like you can see all these red dots. So, I took my time to mark some of these dots on the actual trajectory. And on the right-hand side, what I did is, I just took this set of red dots and I have drawn it on the same scale on the right-hand side diagram.

So, what do we see here? We actually see the averaged version of the actual movement of the particle where each point is averaged over a time interval tau. And this is exactly what Perrin did. He actually averaged over a timescale of 30 seconds, how?

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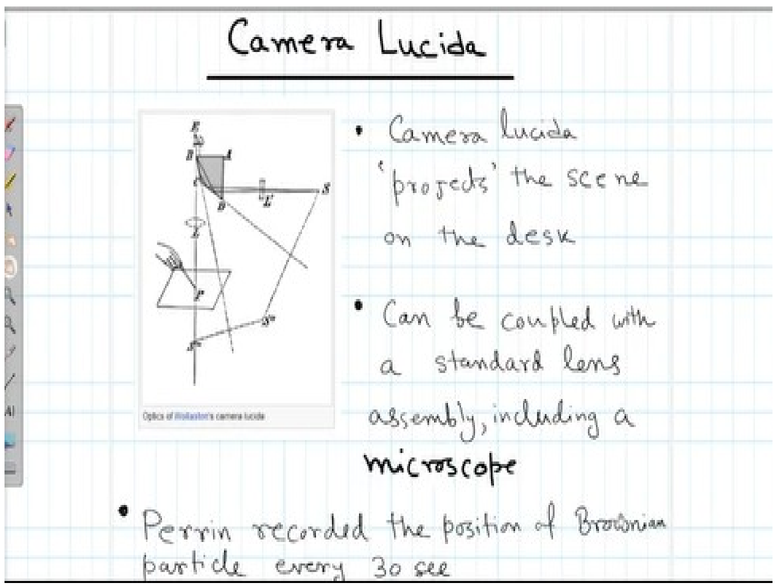

He used a setup called the camera Lucida. Now, camera Lucida is even nowadays people use it. It is primarily an artist tool. So, what can you do using a camera Lucida? This particular picture, whatever I have taken, I have taken it from Wikipedia. So, there are companies which still, I mean, produces this something like this camera, Lucida but of course, now it is the age of digital imaging. So, the entire technology is slightly different.

But what I have drawn here is actually the old school Camera Lucida which is nothing but a lens arrangement it is kind of a projector arrangement. So, let us quickly look into this picture. So, let us say S is the actual source. Then, let us say there is a point source somewhere. And this S through a lens and prism management is projected downwards, such that the actual image and it is projected on your table.

So, I have a camera Lucida placed in front of me, and whatever is seen, you know, whatever is there in front of me, can be projected using this camera Lucida onto the table on which I can put a piece of paper. Let us say this one, this piece of paper. So, this source S is projected as a virtual source S triple prime actually. So, it is slightly complicated. I mean, we do not want to go into the optics here. But the observer's eye is here.

So, basically, what can be done is one can observe the image whatever object is there the image of that on this piece of paper and can use a pen or a pencil in order to trace the outline. Now, this is for the microscopic world. This is primarily as I have said it is an artist tool. So, artists have used to, you know, recreate the scenery or recreate the faces of certain person using this camera Lucida for many years. I do not remember exactly the dates.

But it is already known in the time of Perrin. It is already known for over 100 years. Then also for the scientist community, it was a known practice to couple this camera Lucida with a microscope. So, once you couple it with the microscope, you not only see the microscopic picture or whatever scenery or whatever object to place on a study table, but you can also see tiny particles, microscopic particles through Camera Lucida.

So, Perrin recorded the position of Brownian particle every third, so, what Perrin did actually I could not find out the exact, you know, ray diagram of Perrin's actual experiment. But I can assume that he has some sort of microscope arrangement and the eyepiece of the microscope was modified. Such that this will be, you know, whatever we see through the eyepiece of the microscope, it will be projected by using a camera Lucida setup on the table.

And on the table, he used a graph paper where the grids are present, like exactly how you see it on the screen on my writing. So, I am using a software of course, this is digital. But it is something like this type of grids here, like we have here. So, and then, he calculated the exact resolving power of the microscope and the magnification he achieves by projecting the microscope view onto this port.

And, he could find out the exact, you know, now exact length that each of this small segment on this board corresponds to. And then so, basically using this camera Lucida arrangement, he can actually project the movement of Brownian particles on a piece of paper, a piece of graph paper, kept on the table and he using a pencil, he can mark the position of individual particle every 30 seconds.

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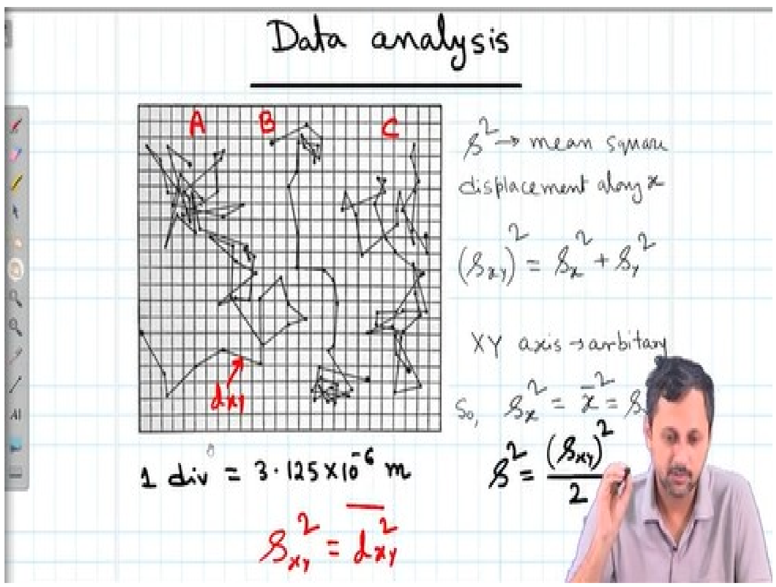

So, what he has got, and then comes the question of data analysis. So, let me start with his data. So, this is basically the original data by Perrin and this is taken from his book. He has published it, his works, in two books, I will give you the reference later. And two books, I mean, he was a French so, his primary publication was in French. And later on, he has published couple of more books in, I mean, sorry some of his books were translated in English.

So, that it is there for the world scientific community. Now, this picture is adapted from one such book, where we see the trajectory the real time trajectory of three particles taken at 30 seconds interval marked as A, B, and C. So, if I just follow just to give you an example, so let me follow the path of A. And then what he did was? After joining, so, I also followed the same thing, so after putting this you know, points so every two points I mean, successive points will be connected by a straight line.

So, this is an average trajectory, and I have also put the arrows so that you get an idea of which direction the particle is moving. But anyway, might whatever I have drawn here is actually I mean, it is not any trajectory of any real particle, I just give you a representative idea. And these are the trajectory of the real particle. So, let us say the real particle, I do not know whether this trajectory should start from this point or this point.

But let us assume from this point, so these, these, these, these, these, these, these, like this, I mean, it becomes more complicated. Similarly, for B, it is like this something like this for C, I do not know where to start, maybe here. So, it moves around here, then goes here, then goes here, moves, you see it there. It is total random and finally ends here. So, C is actually, I mean, all three of them, they are very random.

And it turns out that there is no overlap between A, B and C and I would say this is just by accident. I think out of so many such graph paper I mean, so many such traces, Perrin presented this particular one, because there are no overlap and looks somewhat neat. Now, the next question is how you calculate the S square which is mean square displacement along x. Please remember Einstein's relation which was derived was, this is for 1d Brownian diffusion.

So, every calculation or every assumption that in the motion is along one direction is of course not valid because we see in reality the motion is 2d could be 3d as well could be because, we have no data on the z direction displacement. And assuming that, you know, when the particle is moving along the z direction by certain degree, I mean, some good amount it will go totally out of focus and this trajectory will end.

Because if you remember in the previous lecture; I talked about the depth of field. And Perrin used very shallow depth of field in order to keep this, you know, so that he can only monitor particles, which does not change, you know, the position of the z direction does not change much. Because moment they go slightly higher or slightly below the focus level, they will go out of focus anyway. So, this is purely x y motion. What we need to do is?

We need to compute the displacement only along x or only along y, one of the directions. Now, because these motions are completely random, and also the choice of the XY axis is totally arbitrary, what do I mean, of course, there is a grid. So, it is very tempting that I choose, you know this as my X axis and this as my Y axis. But think of it, I can just let us, by some digital means, I can just take this.

Right now, it is easy, actually, because there are lots of, you know digitization software through which we can digitize the data. So, think of it this way. In case, if I have this paper tilted slightly the trajectories will not have changed. What have changed was the respective coordinate, because the choice of XY axis is totally arbitrary. In case, we have these two reference points, we can choose them as X and Y.

But if I tilt this graph paper and we will still get some random trajectory and then our XY axis will be different axis. So, it does not matter. So, keeping those arbitrariness of the, you know, XY axis and the confinement of this motion in 2d, what we can say this is the total displacement in the x y plane, let us call it S xy square is actually S x square plus S y square. And this is true for individual line segments as well.

So, if I just focus on this one line segment, let us call it d xy. So, this is a combination of d xy square is equal to d x square plus d y square. So, same holds for the average and we can write that S x square, which is actually x square, average my arrow is not in the right place, sorry, my y is not in the right place, it should be x square, average which is also equal to S y square, because x and y axis, they are identical, they are basically identical.

So, S x square, which is present in the Einstein's equation, which is nothing but S x square is also equal to S y square. So, we can write S x square is equal to S xy square divided by 2, where S x square is all the d xy. So, I have just given you 1 representative d xy. So, what Perrin did was, he actually measured all the length of, I mean, length of all the straight-line segments. So, let us say 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, like this.

So, he physically measured, he knew exactly how much of this one division correspond to the actual movement, I mean, how much actual movement corresponds to one of this divisions. So, first, he calculated this, you know, he took this lens just by using a simple ruler, or simple scale, he could measure this lens. He then took this average, I mean, he squared those lens and took the average of all those lens in order to compute S x square xy.

Which is nothing but basically sorry S xy square, which is nothing but S x square sorry, which is nothing but S x square times 2 divided by 2 he got this displacement in one direction, average, mean square displacement in one of the directions and then all you have to do is to convert this into this actual displacement by this conversion factor. All this process is summarized beautifully in this paper.

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It is not exactly a paper because I do not know. It is not an original work, it said. So, we cannot call it a research paper anyway. But this is basically a popular science article where the actual data of Perrin is presented and also the details of the analysis has been discussed. So, you know, you can find how to compute this scale factor. And then, there is a chapter, just a minute some technical error just give me a second and I will come back to it.

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We will come back to this, no problem. So, basically this S x square can be measured by taking average of all these line segments. And this average divided by 2 will give you the average mean square displacement along the x direction or y direction, whichever way you look at it.

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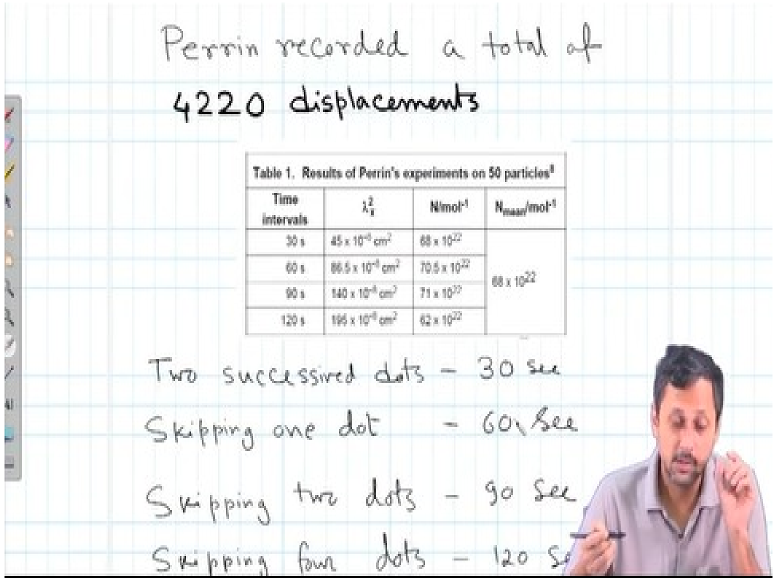

So, Perrin recorded all together 4220 such displacements. And that paper I have just showed or that popular science article I have just showed you, it actually summarizes Perrin's work nicely and this is there in this table. So, he not only did took 30 second interval, but later on in the same data, he made you know, he recalculated using 60 seconds interval, 90 seconds, 120 seconds interval.

And the average value of this Avogadro's number from 1 set of such observation is 68 into 10 to the power of 22 which is 6.8 into 22. When I say 60 second basically this means skipping one data point in between. Let us say some from here to here is 30 seconds, here to here is 30 seconds. So, 60 seconds is from here to here. So, you have to draw a straight-line segment between these two points. Similarly, a 120 second interval will be 30 plus 30 plus 30 plus 30.

So, jumping from here to here. I do not know for whatever reason, he thought, you know, recalculating using 60 seconds or 90 seconds or 120 seconds interval will give probably a more accurate result. I do not know exactly, because I am yet to read his original book, but this is what I have learned from this paper.

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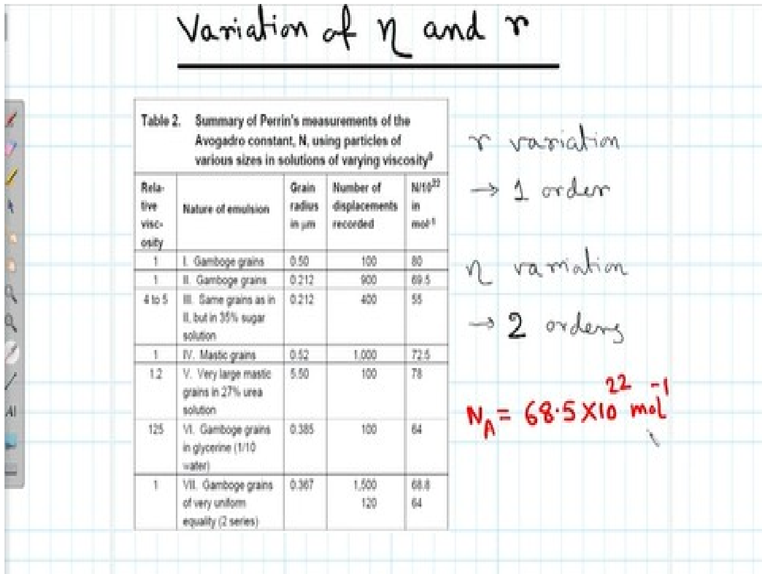

Table 2. Summary of Perrin's measurements of the Avogadro constant, N, using particles of various sizes in solutions of varying viscosity[9]

Relative viscosity	Nature of emulsion	Grain radius in μm	Number of displacements recorded	$N/10^{22}$ in mol^{-1}
1	I. Gamboge grains	0.50	100	80
1	II. Gamboge grains	0.212	900	69.5
4 to 5	III. Same grains as in II, but in 35% sugar solution	0.212	400	55
1	IV. Mastic grains	0.52	1,000	72.5
1.2	V. Very large mastic grains in 27% urea solution	5.50	100	78
125	VI. Gamboge grains in glycerine (1/10 water)	0.385	100	64
1	VII. Gamboge grains of very uniform equality (2 series)	0.367	1,500 120	68.8 64

And finally, he also varied eta and r. That is very important, because if we go back to the original equation here, we see there is a combination of eta r, eta times r which is present which is the only characteristics of the medium and the Brownian particle given the temperature is constant. So, there is no question of mass and the relation should hold for any arbitrary value of eta and r. So, it was very important that values of eta and r is chosen over a wide range.

So, that is why, that is exactly what he did he varied. This is basically the summary of his table, where the relative viscosity of the medium is reported in the first column. Look at this number there is 1, 1 is to 10 dissolved water mixture, which has almost 10 to the power you know, 3 times higher concentration, I mean, sorry 125 times higher concentration as compared to his previous report.

So, I should not, actually, I mean, I have read in some other books, that he actually varied the viscosity by a factor of 1500, which I fail to locate the actual data, but that is what I have read. So, I have written here 3 orders of magnitude. And same goes for the radius, at least in this report, whatever I can gather is the variation of radius is from 0.5 microns to 5.5 microns. So, 1 order of magnitude.

So, actually, I should write 2 orders here, because that is what we have in hand. But anyway, does not matter and he got an average value of 68.5 into 10 to the power of 22 mol inverse which is 6.85 into 10 to the power of 22 mol inverse. So, in this table basically we summarize Perrin's experimental work on Brownian particle. Of course, he has carried out experiments on sedimenting particles and altogether the average value of the Avogadro number is somewhat similar.

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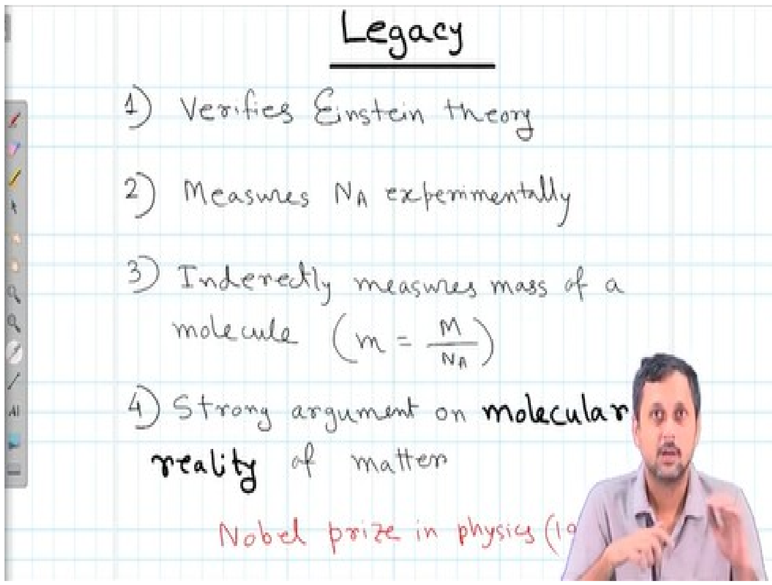

Now, let us talk about the legacy of Jean Perrin. So, these are the points that we have discussed over last few lectures. But let me just summarize, what did he achieve? He verified Einstein's theory of course, which was a very unique theory at that time, because it is the first theory of its kind that is to say fluctuation dissipation kind, where a fluctuating phenomena and a diffusing phenomena are correlated. So, that was verified.

Also, he measured, he was the first person to measure N A that is the Avogadro number experimentally. And when he measured the Avogadro number, he has indirectly measured the mass upon individual atom or molecule, because molar mass is something that was already known. This quantity was already known. So, mass of each individual molecule is nothing but molar mass divided by the Avogadro number.

So, this in effect gives a very strong argument regarding the molecular reality of the matter. But when I say molecular reality, I mean, that you know, at that time 1909, when Perrin started his experiment, there was, I mean, of course, a group of scientists strongly believed that molecules exist, molecules and atoms they exist. But at that time, there was no direct experimental evidence present that the molecules do exist.

Of course, lattice was known, crystal lattice and all these things were known. But there were a group of scientists or a group of philosophers who actually always used to present a counter argument saying that none; of these are not actually molecules but something, something. So, Perrin's experiment kind of proved beyond doubt that molecules do exist. Because Einstein gave a theory assuming that the molecules I mean, theory that actually describes the microscopic world.

Which Perrin could actually observe and give estimation of a number, which is microscopic by nature. Not only that, because, I mean, his work was so meticulous and so rigorous. Before that, or even after him, people used to use microscope as a tool of qualitative measurement. Perrin was probably the first one who has actually quantified the measurement, the microscopic measurement. And, he is considered the father of quantitative microscope.

So, this is the legacy of one of the greatest experimentalists of all time that is Jean Perrin and, he won the Nobel Prize in Physics in 1926. Now, we will just quickly review.

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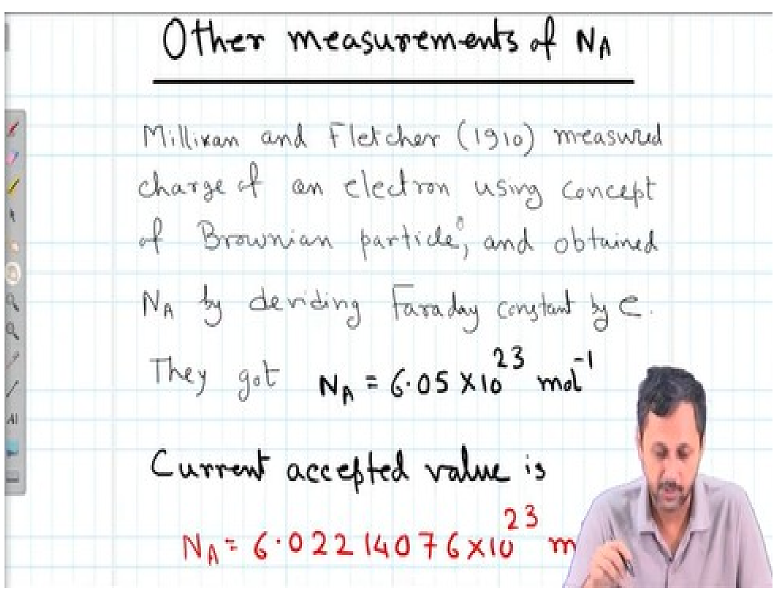

I have one more slide to show you. What are the other measurements of N A? Around the same time, when Perrin is working on these Brownian particles, Millikan and Fletcher in 1910, measured the charge of an electron using this famous Millikan oil drop experiment. And then what he did, I mean, after the charge was accurately measured by Millikan it was only a matter of decision.

So, Faraday constant which is one mole of the charge of one mole of electron which was already accurately measured the value of the Faraday constant was known. So, Faraday constant divided by e gives another estimate of Avogadro number which is 6.05 into 10 to the power of 23 per mole which was of course more accurate than Perrin. And it was also a beautiful experiment and I am pretty sure you are all familiar with it.

But because Perrin did it at least one year before this Perrin gets the credit of measuring the first measurement, first accurate measurement on Avogadro number. Now the current file end this lecture by giving you the current accurate value or an accepted value of the Avogadro number. It is not an approximate number anymore in 2019. It has been agreed in the international bureau of standard on this particular number which is 6.02214076 into 10 to the power of 23 mol inverse as the accurate measure of Avogadro number.

So, that is where we stop in today's lecture. On tomorrow, and of course, I will share this particular document which I could not show it to you because of some technical issue. I will share it with you. You can always have a look at it. If you have any questions or comments, you can always mention that in the discussion forum. And in tomorrow's lecture, on the next lecture, on this series, we will be solving problems related to Brownian motion. Till then thank you.