

**Thermal Physics**  
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**Lecture - 20**  
**Problems on Brownian Motion, Rotational Brownian Motion**

Hello and welcome back to another lecture of this NPTEL course on thermal physics. Now, for this week, the entire fourth week we have discussed about Brownian motion, we have discussed about the Einstein's theory of Brownian motion. And also, we have talked in details about the experimental work done by Jean Perrin's in order to verify those theories. Also, he barely took it one step forward.

And not only he verified the instance equations, also he has measured the, what we call their Avogadro number. And this was the first measured value of Avogadro number, first measurement that was conducted. And essentially, when he could measure the Avogadro number he could also measure or they also calculate the mass of one individual atom or molecule, because the molar masses were known already.

So, that is where Perrin's work was is of great importance in the history of modern science, related to physics, in chemistry. So, it is a fundamental importance and we have discussed it in details.

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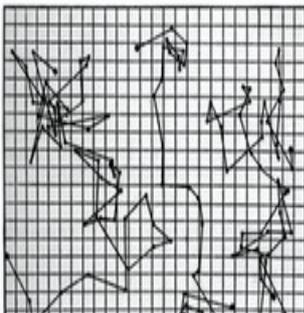
**An experiment to measure Avogadro's constant. Repeating Jean Perrin's confirmation of Einstein's Brownian motion equation**

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Note: This article is available on our website, [www.chem13news.uwaterloo.ca](http://www.chem13news.uwaterloo.ca). You might want to enter this document to copy Fig. 1 and enlarge it. See the experimental section, "Determine N for yourself".

In 1909, Jean Perrin (1870-1942), a Nobel Prize winning French physicist, reported his series of painstaking experiments to test the equations Albert Einstein had derived in the May 1905 paper that I described last month.<sup>1</sup> In this article I will describe Perrin's experimental proof<sup>2</sup> and show how you and your students can repeat Perrin's analysis as a dry lab experiment.

Early in the twentieth century Perrin had perfected techniques for producing small, spherical particles of uniform radius (in the



So, start this lecture and yesterday, I was showing you one lecture one paper or not exactly a paper, it is more of what we call a review of what paid in actually did. So, due to some technical glitch, I could not show you the entire document.

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Now, today, I can just briefly in this figure you have I have shown you, and also the equations, whatever is mentioned here, the method of data analysis that was adopted by Perrin. It is described in details in here, also, some of his original tables are reproduced. Now, there is a part where you can actually determine this end by yourself. So, you can actually repeat the analysis, not the experiment, but the analysis.

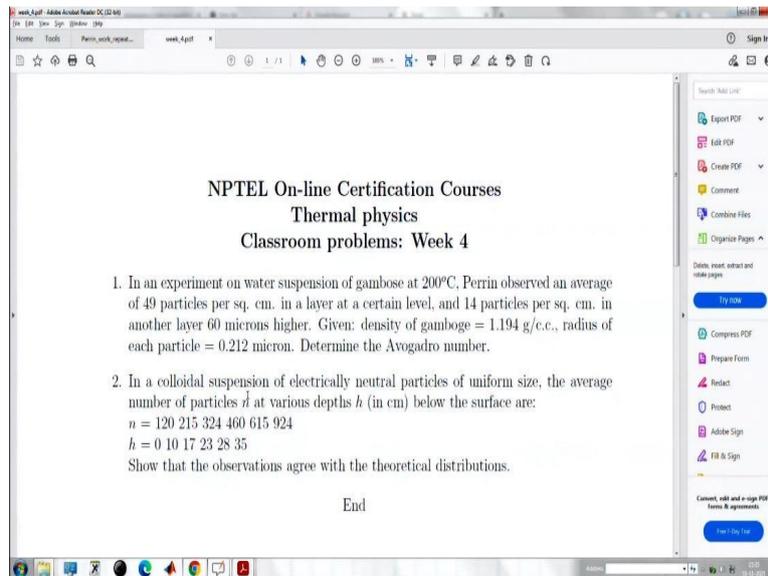
So, basically, what you have to do is? You have to take this, you have to copy this particular figure, and you can paste it on a Word document or whatever. And you can take a enlarged printout of this particular figure here were the three trajectories of what we say called A, B, and C, the last lecture who is present. And you can follow the method that has been described in this book, or in this report, actually, or article, whatever you call it.

In order to, you know, determine you analyse those data set and determine the value of the data, this one value of Avogadro number all by yourself. So, this is something that probably you can try by yourself, you do not need any additional guidance, if you can read this manuscript carefully. So, I will share all these things with you. Do not worry, you will find everything in hand. And this is also freely downloadable.

But anyway, I will give you this document itself. And I strongly suggest that you try this out. Now for this week, we will be doing mostly problems.

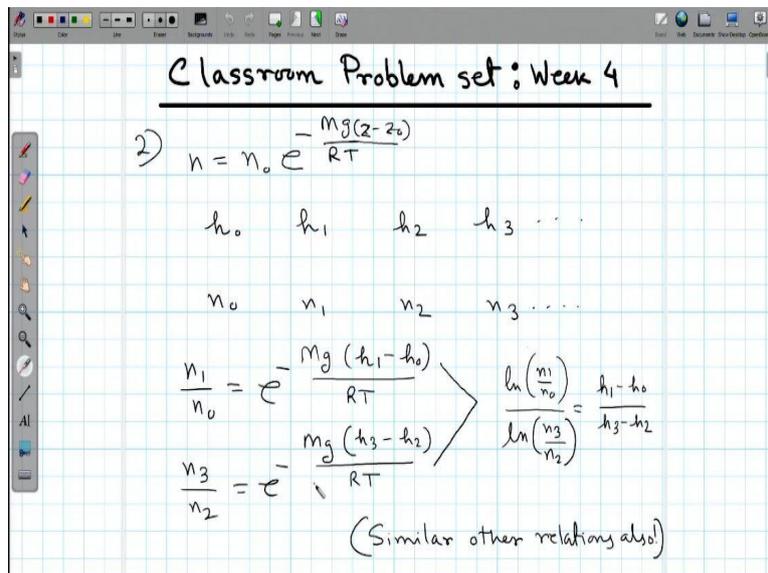
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Now it is so happened that I you know, I have only one problem here what whatever problems that I have, but I have actually formulated three more problems, which I forgot to bring the updated file. So, I will first do this first problem, whichever I have in hand and then for the other problems, we will see what can be done.

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So, let us start with the problem number 2. In a colloidal suspension of electrically neutral particle of uniform size, the average number of particles at various depths  $h$  in centimetres, any unit does not matter below the surface are at  $n$  is equal to 120. Well, so when any sorry  $h$  is equal to 0,  $n$  is equal to 120 when  $h$  is equal to 10, then  $n$  is equal to 250, when this probably did not help. So,  $n$  is equal to 215 when  $h$  is equal to 17, 17, then it is 334, when  $h$  is equal to 23, this is 460 and so on and so, these values are given.

Now, show that the observation agrees with the theoretical distribution. Now, what are we talking about here we of course, we are talking about sedimentation. Now in a sedimentation experiment, the value of or the density of molecules in a given layer, we know that it follows the parametric equation or the sedimentation equation as it called it. So, basically in this problem what you this is the sedimentation equation or the barometric equation.

Yes, we have to verify whether the given values those are provided they follow this particular equation or not. Now, there are many possible ways of doing that we can you know simply just plot these numbers and you can see if we can fit it through particularly exponential decay of any this form this can be done and alternatively what we can do is we can just focus on two you know two sets of data and few data points and see if it is valid for those data points.

So, what I did is what I have done here is actually I have just focused on this fault following four points, that is called them  $h_0, h_1, h_2$  and  $h_3$  these are the depths  $h_0$  is actually 0 and  $n_0, n_1, n_2$  and  $n_3$ . So, the equation we deal with is  $n$  is equal to  $n_0 e^{-\frac{mgz}{RT}}$  where  $z_0$  is equal to 0, but the actual equation is  $n = n_0 e^{-\frac{mg(z - z_0)}{RT}}$ .

So, for these two four data set actually, if I what we can do is we can simply group them into pairs of two. So, we can take  $n_0$  and  $n_1$  in one pair  $n_2, n_3$  in one pair and we can write  $n_1$  by  $n_0$  is equal to  $e^{-\frac{mg}{RT}(h_1 - h_0)}$ . Similarly,  $n_3$  by  $n_2$  is equal to  $e^{-\frac{mg}{RT}(h_3 - h_2)}$ . Now, if I take the Lon of both these relations, what do we get we get Lon of  $n_1$  by  $n_0$  is equal to  $-\frac{mg}{RT}(h_1 - h_0)$ . Similarly, Lon of  $n_3$  by  $n_2$  is equal to  $-\frac{mg}{RT}(h_3 - h_2)$ .

Now, just take loan of these two relations and take the ratio. If you take the ratio, you will get Lon of  $n_1$  by  $n_0$  divided by  $n_3$  by  $n_2$  is equal to  $\frac{h_1 - h_0}{h_3 - h_2}$ . Now, if we so, and we can also have many other relations, I can we can take any two pairs for example, we do not even need to consider this part here. So, we can take the ratio of  $n_1, n_0$  or  $n_2, n_1$ . So, basically this 3 by  $n_1$  will be this point to the overlapping in both the sets even that can be verified.

So, and not only that we need that does not have to be success, you know, groups or rather consecutive groups, we can take for example, h 5 and h 6 and try to compare it with h 0 and h 1, we can take any number of such combination. So, I just showed it show I am showing 1. So, I have just taken this first four points just to show you that this is valid, at least for this first 4 points.

So, all we have to do is we have to compute so n 1, n 0, n 0, n 1, n 2, n 3 all 4 are given similarly h 0, h 1, h 2, h 3 all 4 are given. So, all we have to do is we just have to plug in the values on this right-hand side expression and on this left-hand side expression and show that, they are equal.

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L. H. S

$$\frac{\ln\left(\frac{n_1}{n_0}\right)}{\ln\left(\frac{n_3}{n_2}\right)} = \frac{\ln\left(\frac{215}{120}\right)}{\ln\left(\frac{460}{324}\right)} = \frac{0.58315}{0.35048} = 1.6638$$

R. H. S

$$\frac{h_1 - h_0}{h_3 - h_2} = \frac{10}{23 - 17} = \frac{10}{6} = 1.6666$$

L. H. S  $\approx$  R. H. S (proved)

(Please check for at least 2 other depths!)

So, this is simple, we put the values of n 1, n 0, n 3, n 2 and we get and this is given in this table actually. So, these are the numbers actually which are given. So, this is n 0, n 1, n 2 and n 3 similarly h 0, h 1, h 2 and h 3. So, these are the numbers that are given and we get a ratio of 1.6638. So, it does not matter whether what are the units of n 1 and n 0 because these are ratios. Similarly, on the right-hand side, I take put these values here h 0 is equal to 0.

So, this is 10 divided by 23 minus 17, which is 1.6666. So, one side we have 1.6638 and this is one or another side we have 1.6666. So, it is in agreement within up to second decimal plus which in my opinion is pretty good. So, what you can do is you can check that agreement for

any two other combinations and at least within first few decimal places that should agree. So, that way you can find.

So, basically what we have verified here that whether the given distribution is following the parametric equation or sedimentation equation or not. Now, for the next few problems what I when I came for this recording today, I just forgot to bring the updated file, but I will anyway have this updated file in the problem set, but I always have the solution actually worked out. So, what I suggest is I mean you already have the problem set in your portal.

So, you can look into it the state statement of the problem nothing tricky. But I will try to explain as much as I can.

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3) From Einstein relation

$$s^2 = r^2 = \frac{RT}{N_A} \frac{\tau}{3\pi\eta r}$$

Given  $s = 1.13 \times 10^{-3} \text{ cm} = 1.13 \times 10^{-5} \text{ m}$

$\tau = 30 \text{ sec}$

$\eta = 1.2 \times 10^{-2} \text{ c.g.s} = 1.2 \times 10^{-3} \text{ SI}$

$$r = \frac{RT}{N_A} \frac{\tau}{3\pi\eta s^2}$$

$$= \frac{8.31 \times 300}{6.02 \times 10^{23}} \cdot \frac{30}{3 \times 77 \times 1.2 \times 10^{-3} \times (1.13)^2 \times 10^{-10}}$$

$$= 0.86 \times 10^{-7} \text{ m}$$

So, in the next problem, what we have to do is? We have to find out the radius of Brownian particle. Now, in that problem which is what we have to do, you have to start from the Einstein relation which is  $s^2$  is equal to  $\frac{RT}{N_A} \frac{\tau}{3\pi\eta r}$ . Now,  $r$ ,  $N_A$  these are constants, which are already given in the problem statement temperature is mentioned. So, all we have to do is temperature is 300 K actually.

So, all we have to do is we have to find out the value of  $r$  from this relation. So, if I just rearrange this relation, it will be  $r$  is equal to  $\frac{RT}{N_A} \frac{\tau}{3\pi\eta s^2}$ . So,  $s$  is given in centimetres, it is 1.13 into 10 to the power minus 3 centimetres. So, all we have to do is we have to convert this into meters which is 1.13 into 10 to the power

minus 5 meters. Similarly, the viscosity of water so, this is a particle diffusion of a particle in aqueous medium.

So, the viscosity of water is 1.2 into 10 to the power minus 2 c g s unit which is centipoise and the SI unit is poise which is 1.2 into 10 to the power minus 3 SI unit. So, after the appropriate unit conversion, we just have to do one unit conversion here and one unit conversion here all we have to do is and of course, tau is 30 seconds that is given, all we have to do is we have to put the numbers into this relation.

We have to put 8.31 for the gas constant 300 for the temperature 6.02 into 10 to the power 23 for Avogadro number 30 for tau 3pi eta is this and as s squared. So, you see the order of magnitude is 10 to the power minus 7. We have a 10 to the power minus 23 here, but we have a minus 10 minus 3. So, already 13 cancels out do we have 10 to the power minus 10 and 10 to the power denominator and then 1 2 and 3 3 0 cancels out.

So leaving behind 0.86 into 10 to the power - 7 meters that is the radius. Now, for the next problem, what do we have?

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4) We know  $N_A = \frac{RT}{S^2} \frac{2}{3\pi\eta r}$

We can either compute  $S_{xy}^2$  and set

$$S_x^2 = \frac{S_{xy}^2}{2}$$

Else, we may compute  $S_x^2$  directly

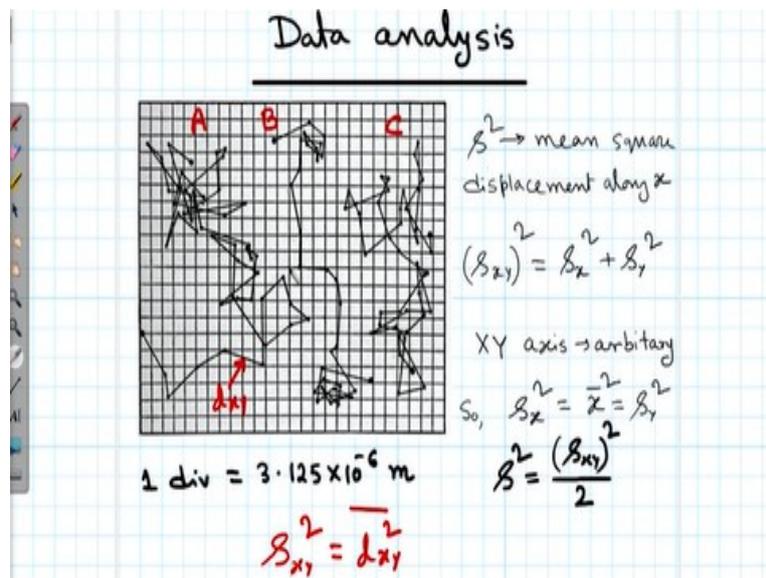
$$S_x^2 = \frac{1}{N} \left( \sum_i x_i \right)^2$$

$$= \frac{1}{11} \left( 0^2 + 5.6^2 + 4.7^2 + 10.8^2 + 6.6^2 + 9.8^2 + 11.2^2 + 4^2 + 15^2 + 19.1^2 + 16.0^2 \right) \times 10^{-12} \text{ m}^2$$

$$= 117.9 \times 10^{-12} \text{ m}^2$$

So, the next problem is slightly tricky here the displacement the x component of the displacement is given. And what we have to do is we have to compute the Avogadro number from the data. So, let me quickly go back to this figure which once again or rather I will just go back to yesterday's class note that will be easier just a minute let me just load it quickly.

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So, you see what, in this discussion of Brownian motion for the data analysis, what we did was or what Perrin originally did was he took the displacement as it is. Took the mean square displacement by computing individual displacement measuring this length between two successive points like this one or this one or this one and finally, you know, assuming that because of the randomness of the motion  $s_x^2$   $s_y^2$  will be equal to  $s^2$ .

So, if I can just measure the average displacement in the  $x, y$  plane it will be equally it will be an equal combination of  $s_x^2$  and  $s_y^2$  squared. So, he assumed that  $s_x^2$  is equal to  $s_y^2$  squared by 2 which is equal to  $s^2$ . Now, on the other hand, what we can do is we can take all these individual points this point or this point or this point or this point and we can take the  $x$  coordinate only of these points and we can just average.

Even that is a valid description given that we take large enough numbers number 1, number 2 that we anyway we are assuming that the motion is completely random. So, in the problem, problem number 3 the problem said what is given? It is given only the  $x$  displacement of a Brownian particle over time; every 30 seconds interval is given. So, for example, if I am going from here to here, the  $x$  component is changing by this much like something like this much.

But if I am going from here to here, the x component is barely changing, but when we are going from here to here x component is changing by a lot. Similarly, for example, if I look into let us say this displacement from here to here, y component is not even changing, I mean slightly changing, but very less, but x component is changing almost I mean, this is almost along the x axis similarly, this displacement is almost along the y axis.

So, the change in x component for this displacement will be 0. So, either we can take all the displacements in the XY plane average them. I mean, we take the mean square of this displacement divided by 2 this will solve for  $s_x$  or  $s_x^2$  or  $s_y^2$  or we can simply take only the x components of this coordinates of the Brownian particle and take the average and this will also serve as  $s_x^2$  which is in our case is a square root.

So, in this problem, we are going to do exactly the same there are altogether 11 displacements that has been given. And what we are going to do is we are going to write we are going to take average of these 11 displacements or rather mean square of these 11 displacements. So, we have to divide it by so, the formula for averaging is so, it is  $s_x^2 = \frac{1}{n} \sum \Delta x_i^2$ .

So, we have to take the first position which is given a zero next is 5.6, third is 4.7, 10.8, 6.6 and of course, there are certain minus quantities, but we do not consider minus, minus means, actually negative displacement. If the particle for example, if it is going from this position to this position, your x displacement is negative from this position to this position, your x displacement is negative, but we are not considering that.

So, what I meant to say when I am taking square up that it does not matter anyway, whether it is positive or negative. So, we take the square of all this, sum it over and we finally get 117.9 into 10 to the power minus 12 meter squared. So, that is the mean squared distance of the mean square displacement of the particle in the given time tau.

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$R = 8.31 \text{ S.I.}$      $T = 293 \text{ K}$   
 $\eta = 0.001 \text{ S.I.}$      $r = 1.15 \times 10^{-7} \text{ m}$   

$$N_A = \frac{8.31 \times 293}{117.9 \times 10^{-12}} \frac{30}{3 \times \pi \times 0.001 \times 1.15 \times 10^{-7}}$$

$$= 5.726 \times 10^{23} \text{ mol}^{-1}$$

5)  $s^2 = \frac{k_b T}{3 \pi \eta r}$   
 $k_b = \frac{3 \pi \eta r s^2}{T}$

The rest is very simple, what is given? We have the gas constant, we have temperature given, we have eta as given. The medium is not mentioned but the eta is mentioned. We do not need the medium actually we just need the eta value and the radius of the particle is also given. So, we plug that everything in in the original equation here, which is mentioned here N A is equal to RT by s square tau divided by 3 by eta r.

All we have to do is we have to compute this s squared which is this one and finally, we get a value of 5.726 into 10 to the power 23 molecules which is slightly on the lower side, but anyway all we have to do is whatever data we get actually paid in got a wide range of distribution and finally, his value was an overestimation. So, assuming that this is just one observation that data from one observation slightly lower value is probably.

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$\eta = 0.0012 \text{ S.I.}$  ,  $\tau = 30 \text{ Sec}$   
 $s = 6.7 \times 10^{-6} \text{ m}$      $r = 2.12 \times 10^{-7} \text{ m}$   
 $T = 293 \text{ K}$   

$$k_b = \frac{3 \times \pi \times 0.0012 \times 2.12 \times 10^{-7} \times (6.7)^2 \times 10^{-12}}{293 \times 30}$$

$$= 0.87 \times 10^{-23} \text{ J/K}$$

So, for the next problem, what we have to do is the last problem actually, we have to compute the Boltzmann constant. So, what is given? Viscosity is given, tau is given, the time interval s the mean displacement is given which is basically the root of root mean square displacement I should say rms displacement that is given which is nothing but s, radius of the particle is given temperature is now, we have to compute k b.

Now, please remember the original equation that Einstein derived it was with k b because, he just took the just let us quickly go back to his derivation here we will be, just a minute I think lecture 17, right.

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$$f = \frac{k_b T}{n s \mu} (n_1 - n_2) A = - \frac{k_b T}{n} \frac{dn}{dx}$$

Stokes law of viscous drag

For streamline flow  
 The viscous force (drag) on a small sphere of radius  $r$  moving through a fluid of viscosity  $\eta$  with speed  $v$  is:

$$f = 6 \pi \eta r v \quad (1851)$$

So, this is the original derivation. So, in here you see the diffusion constant diffusion coefficient is active diffusion constant is actually in terms of k b t divided by 6 by eta r.

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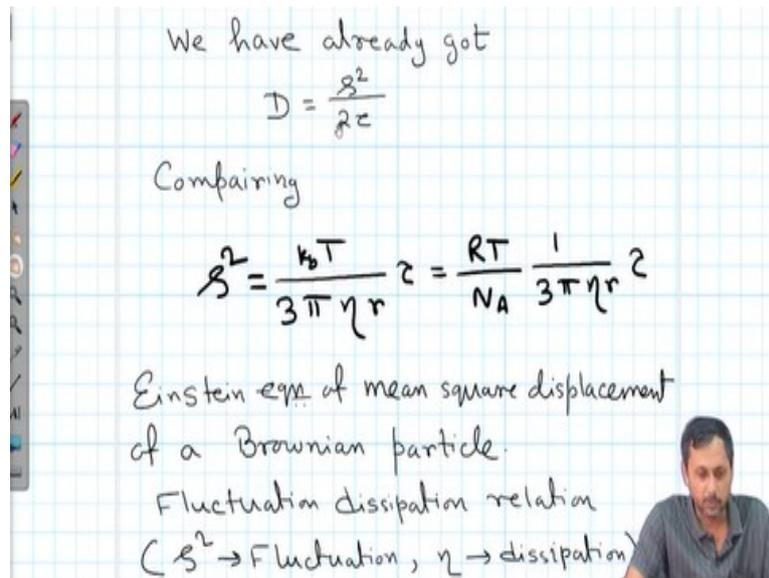
We have already got

$$D = \frac{s^2}{2\tau}$$

Comparing

$$s^2 = \frac{k_B T}{3\pi\eta r} \tau = \frac{RT}{N_A} \frac{1}{3\pi\eta r} \tau$$

Einstein eqn of mean square displacement  
of a Brownian particle.  
Fluctuation dissipation relation  
( $s^2 \rightarrow$  Fluctuation,  $\eta \rightarrow$  dissipation)



Now, the next step is he computed already he has computed the  $D$  is equal to  $s^2$  by  $2\tau$  and then he could compare these two equations and he could get this relation with writing  $k_B$  is equal to  $R$  by  $N_A$  this equation converts to this equation. So, we have to use this form of Einstein's relation in order to get to  $k_B$  the Boltzmann constant. So, all you have to do is you have to use this particular form here.

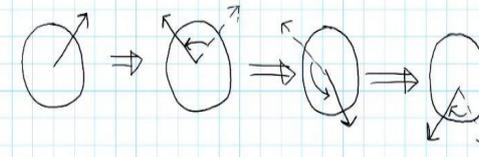
In this particular form here, where  $k_B$  will be given by  $3\pi\eta r^2$  divided by  $\tau$ . All these numbers are given when we put that in we get  $0.87 \times 10^{-23}$  joules per Kelvin. So, once again this is an underestimation, but again it is just one measurement, one measurement for this one, let us assume, so, one measurement will never give you going to give you anything close to the actual value.

Or rather one measurement will never going to give you confidence on actual value, you have to keep repeating this experiment many times only then you will get something reliable. So, this is all for the problem set problems are rather simple if we understand what we need to do. Next and for the last topic of rotational or last topic of this diffusion and Brownian motion, we will talk about rotational Brownian diffusion.

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Rotational Brownian Diffusion

Random change in orientation of a Brownian particle.



Stokes-Einstein-Debye model

$$D_r = \frac{k_b T}{8 \pi \eta r^3} \quad + \quad \left( D_t = \frac{k_b T}{6 \pi \eta r} \right)$$

finally, we may correlate random

Now, so far whatever Brownian motion we have discussed it is the translational Brownian motion. Now what happens in a translational Brownian motion? The molecules do translate from one place to another place and this translation as we have seen many times that it is completely zigzag. Now, at the same time if we are talking about a particle of finite size which the Brownian particles are they are not molecular.

But even at the molecular level we can have rotation. We have already seen that there exist rotational and vibrational degrees of freedom in a molecule and that affects the CV, so, specifically of a gas molecule of a gas assembly. So, similarly we can have random change in orientation of Brownian particles. When I say random change, I have just given you a very, I am trying to give you a very crude drawing of what can be a random change.

We are assuming spherically symmetric Brownian particles, which is once again is an oversimplified assumption. Because, unless and until it is very crucial precisely prepared you know every Brownian particle will have some sort of an asymmetry associated with it, but anyway let us just talk about spherical symmetry. Let us fix one axis in any random direction in this domain particle.

Now, when I talk about rotational diffusion what happens is? This axis changes its orientation all of a sudden. So, let us say this is the axis to begin with and it will from here it will go to here next it will go there go there go there like this. So, it will keep on moving in a random manner. So, this is observed in molecular level as well also for finite size Brownian

particle. Of course, like even for the translational Brownian particle we have already discussed.

That you know it is inversely proportional to the radius. So, higher the radius the diffusion will be less, okay. So, this type of motion this type of random orientation change is more prominent in smaller Brownian particles more prominent at molecular level. Let us for example, let us say we have protein molecules or we have some macro molecules in which can be observed with some sort of microscopy techniques.

We can actually see this execution technique less, there is a technique called dynamic light scattering, which can be used to probe this rotation for macromolecules and protein molecules. Now, it is so happens that like Stoke Einstein's relation, we have a Debye stoke-Einstein-Debye model in order to explain this rotational Brownian diffusion and the statement of this model is the diffusion constant there is also a diffusion constant associated with this rotational diffusion.

And this diffusion constant is equal to  $k_b T$  divided by  $8 \pi \eta r^3$ , which once we compare it with the minute translational very poor handwriting, it should be  $T$ . If we talk about translational diffusion, if you remember, it was  $k_b T$  by  $6 \pi \eta r$ . So, for diffusion we have similar form but instead of  $r$  here we have  $r^3$  actually I should write small  $r$  instead of capital  $R$ , just to maintain that parity.

So,  $6 \pi \eta r$  here on the right hand side for the translational diffusion and for the rotational diffusion it is  $k_b T$  divided by  $8 \pi \eta r^3$ . So, finally, it is also possible to measure the we may correlate the random change in orientation

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change in orientation with dissipation parameters and write

$$\overline{\theta^2} = \frac{RT}{N_A} \frac{1}{4\pi\eta r^3} \tau$$

$\overline{\theta^2}$  is mean square angular displacement in time  $\tau$ .

Which is due to Brownian, rotational Brownian motion with the dissipative forces and we can write finally, we can write theta squared is equal to RT by N A 1 over 4 pi eta r cubed tau, where theta squared is the mean squared angular displacement in time tau. So, this is a similar equation which is once again derived by Einstein but later modified by Debye in order to explain the rotational Brownian diffusion.

So, this sums up the discussion on diffusion and Brownian particle. So, we will stop here for this week's lecture. And I hope you have enjoyed this week's lecture. The main focus was on the experiment that has been performed a beautiful set of experiment that has been performed by Jean Perrin in order to verify this theory. And finally, we just have a very brief discussion about this rotational diffusion which we are at this point we are not going into the details of that, that theory.

But, if necessary, we will come back to that as and when required. So, this concludes the lecture of week four. We will see you in week five again, goodbye.