Thermal Physics
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Lecture - 17
Brownian Motion: Theory of Osmotic Pressure

Hello and welcome back to another lecture on this NPTEL course on thermal physics. Now in today's lecture we will be continuing with the same direction. So, in the last lecture what we did was? We determined the diffusion coefficient from pressure gradient. So, basically diffusion coefficient in terms of the sorry the concentration gradient, diffusion coefficient is expressed in terms of the mean square displacement.

In today's lecture we are going to derive an alternative expression for diffusion coefficient in terms of the osmotic pressure.

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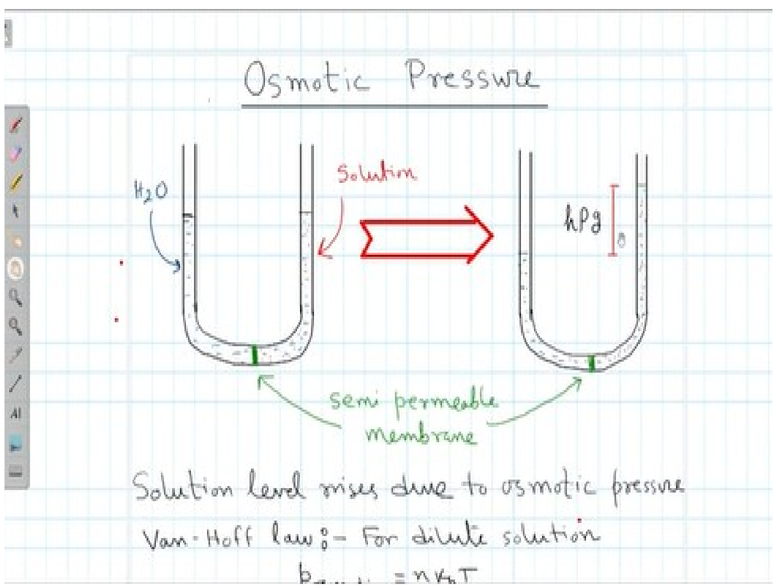

So, first up let me introduce what is osmotic pressure. Now osmotic pressure is something that is very familiar to all of us and we have learned it from our text books earlier in you know school days textbook. So, let me give you a quick example. So, let us say we have a uniform tube of equal sides and we fill it up with water on one side and a solution it could be anything a sugar solution, salt solution anything I mean water with some solute.

So, water is the main solvent. So, let us say I have in two worms I have pure water and the solution and they are separated by a semipermeable membrane. So, what do you mean by semi permeable membrane? Semi permeable membrane is basically a membrane that will have holes which will allow the solvent molecules but not the solute molecules. Now if we allow sufficient time so, we allow sufficient time it will go from this state to this state.

Where the some part of the water molecule will pass through the semi permeable membrane here and it will end up in the other half. So, effectively what do we have? We will have the liquid level on the right-hand side will be up by a height h and correspondingly we can determine a pressure which is h rho g rho being the solution concentric concentration of the solution. And this happens primarily because as always nature wants to drive things towards equilibrium.

Now if you look carefully here on the left hand side we have pure water, right hand side we have water and some solute molecules. So, the partial pressure of water the concentration of water on the right hand side is less as compared to the concentration on the left hand side. Obviously, because light right hand side is not pure water and left hand side is pure water. Now as the system drives towards equilibrium liquid molecules.

Or water molecules from the left side will go into the right hand side in order to equilibrate the solution pressure or the concentration of water on both sides and effectively the right hand side solution will be diluted and it will be rising by some amount which is given by which corresponds to a pressure of h rho times g. Now this is the concept of osmotic pressure and as we know that osmotic pressure is something that is directly measurable from this type of experiment.

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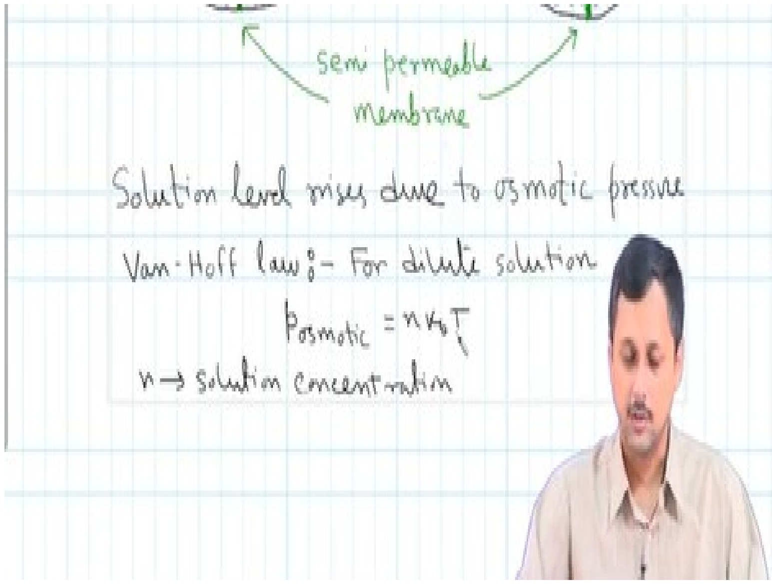

And Van t Hoff's law exists which says for dilute solution the osmotic pressure is equal to n times k b times T where n is the solution concentration. So, this is essentially the same expression written in a slightly different form. So, if we have the solution the concentration gradient in terms of this you know if there is a n being the solution concentration then we have p osmotic equal to n k b T.

Now, Einstein derived the diffusion equation or diffusion coefficient in terms of the mean square displacement as we have seen in the last class. In this class we will derive another expression which will discuss or which will determine the diffusion coefficient in terms of the osmotic pressure.

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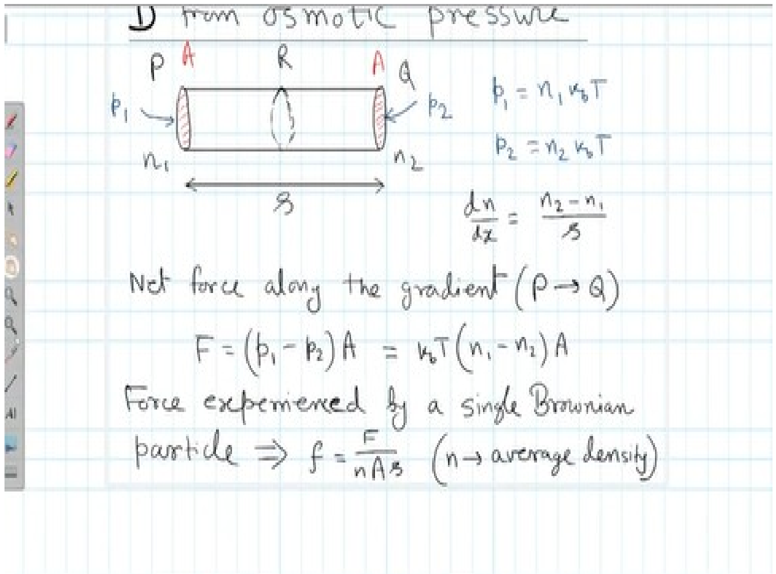

So, let us go back to the exact same geometry we have this tube PQ of length s which is the mean displacement over time tau. And let us assume we have the pressure on this side is p 1 and pressure on this surface is p 2. Now this pressure is purely osmotic pressure it is not the actual pressure of the system, because system pressure will be a you know both solute and solvent together.

This pressure is purely due to this concentration gradient which is n 1 on this face and n 2 on this face. And we have at concentration gradient d and dx is equal to n 2 minus n 1 by s. Now if I compute the osmotic pressure on pressure p 1 and p 2 from the Van Hoff's formula, we have p 1 is equal to n 1 k b T, p 2 is equal to n 2 k b T. So, the net force along the gradient now gradient is once again gradient is along this direction so, the flow of molecule will be in the opposite direction.

So, the net force along the gradient which is move from P to Q is p 1 minus p 2 times A, A being the cross sectional area of the cylinder which is equal to k b T times n 1 minus n 2 times A. And this force is acting on all the particles which is confined inside the cylinder. What is that volume? What is the volume that is confined inside the cylinder? This volume is nothing but n times A times s, s being the length A being the cross section.

So, n times s is the volume of the cylinder and n is the average density of the Brownian particle. So, force total force F that is acting across the cylinder is actually acting on n times A times s number of particles. So, force experienced by a single Brownian particle is simply the term f capital F divided by n times A times s. So, this is very straight forward up to here.

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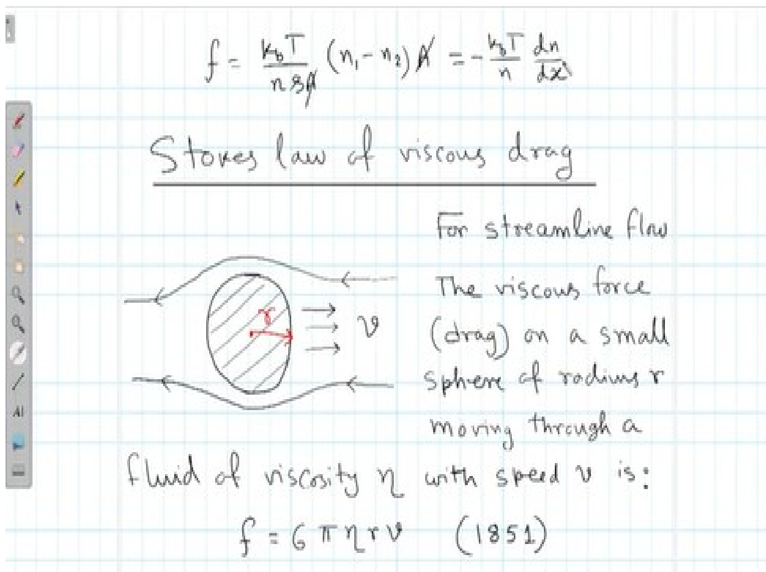

Now we can use the expression which we have just derived over here. So, we can equate this we can use this expression for F and we can write small f which is equal to F divided capital F divided by n times A times s is nothing but k b T n 1 minus n 2 a divided by n times F times s, n times A times s which is a and a cancels out which is k b T by ns n 1 minus n 2. Now n 1 minus n 2 by s is nothing but or n 2 minus n 1 by s is nothing but dn dx.

So, n 1minus n 2 by x s is equal to minus d and d x because this is an uniform gradient we are talking about and we can write this as k b T times n times dn dx where n is the average density T is the temperature of the system and dn dx is the this density gradient. Next is we talk about we discuss force Stokes law on viscous drag. Now in 1851 Stokes came up with this relation that for a streamlined flow when the velocity is relatively small.

Then if a particle is moving a spherical particle or spherical object of uniform spherical object is moving with the velocity V through a viscous medium which, has you know density or the viscosity index given by eta then the viscous force which is acting on this sphere of radius r moving through the fluid is given by small f is equal to 6 pi eta r V which is the well-known relation by Stokes. Now as I have already mentioned the Einstein formulation is sometimes around 1905.

So, approximately 50, 55 years back Stokes came up with this relation. So, now we are in a position to equate this force, this force is purely due to viscous force because the you know in equilibrium this force has to be equal with the viscous force when on the right hand side, we have the density gradient.

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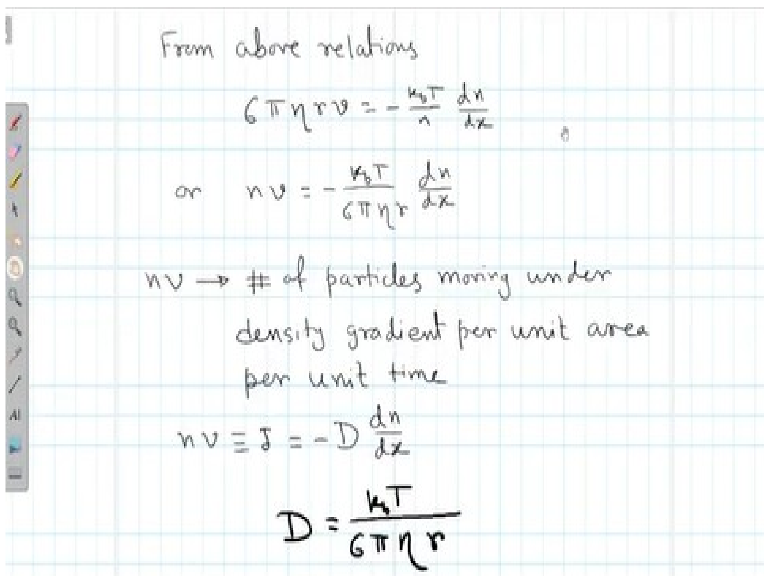

So, these two can be equated. So, we can write 6 pi eta r v is equal to minus k b T by n dn dx so, n v is equal to minus k b T by 6 pi eta r dn dx. So, this is the relation. Now let us focus on this term n v, n is the density v is the velocity and this product n v is actually the number of particles moving under density gradient per unit area per unit time. So, look at the dimension of this object, it will be number divided by length cube and we have a length and we have a time inverse.

So, the dimension will be the it is a number of particle basically it will be just a number of particle divided by area square or sorry length square which is area divided by time which is unit area per unit time. So, this is nothing but the diffusion current J we have discussed previously and I can write nV is equal to J is equal to minus d times dn dx which is nothing but the Flick's law, Flick's law of diffusion.

So, comparing we can say D is equal to this precisely this quantity which is minus k b T by 6 pi eta r. So, we have d is equal to k b T divided by 6 pi beta r. Now we have already derived an expression for D in terms of the mean square displacement. Now we have another expression of D of T in terms of the parameters which are macroscopic in nature. See assuming that r is known temperature can be measured directly it is a macroscopic variable, eta is a transport quantity transport parameter which is also measurable from macroscopic experiment.

Of course, there are ways of measuring eta and you know in by different methods like terminal velocity method capillary method which we are not going to discuss at present maybe the terminal velocity method will be discussed later but something all you know that eta is measurable directly.

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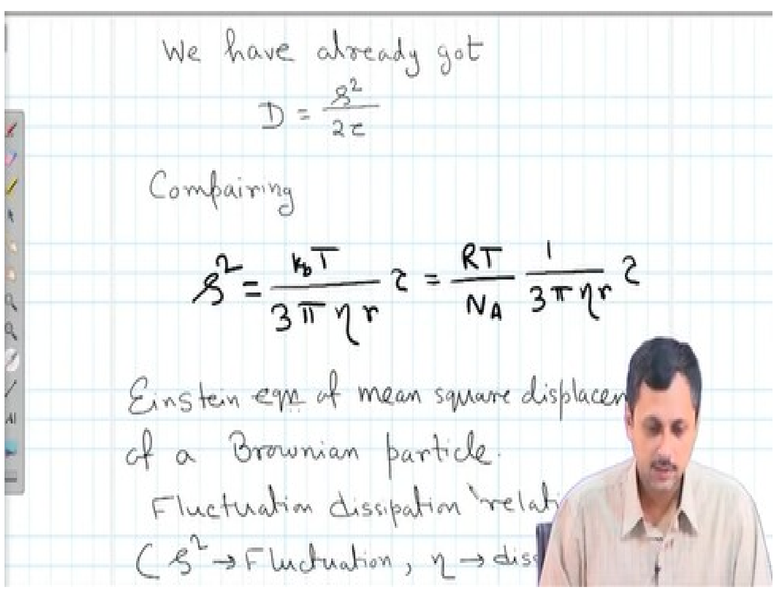

So, equating the two expressions we already as I said we already have one expression D is equal to s square by 2 tau where s is the s square is the mean square displacement in time interval tau and, if we compare these two, we get the expression that s square which is the mean square displacement of a Brownian particle is k b T divided by 3 pi eta r times tau. And we can manipulate this expression slightly by writing k is equal to r by N A.

And we can write RT divided by N A which is the Avogadro number divided by a multiplied by 1 by 3 pi eta r times tau. Now the right hand side of this expression all the terms are exactly measurable we know N A of course N A is something that we can compute T of course R is also a constant N A is something let us assume that we know it r is something that is once again a constant T is the temperature, r is the radius of the object.

If we have to measure it somehow, eta is the viscosity and tau is the time for which we have computed the mean square displacement. So, this relation actually correlates the two sides, it is called a fluctuation dissipation relation. Why? Because it correlates one fluctuating term which is the mean square displacement with dissipation term which is the viscous force which arises because of the dissipative forces present in the medium.

So, Einstein actually correlated a mean square I mean a fluctuating term with a dissipation term dissipation related term through the equation which we have just now derived. Now we will see that later on this equation was or this relation was experimentally verified by Jean Perrin through a series of experiments not only this relation there is another relation which we will talk about in a moment and in the next lecture we will be discussing on the experimental verification of Einstein's theory and subsequently the measurement of N A, that is the Avogadro number.

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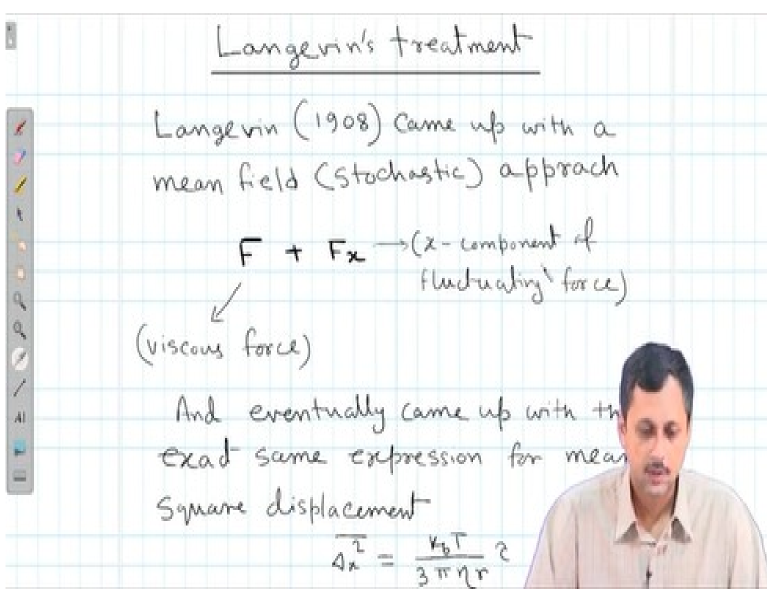

So, next up we will just briefly discuss Langevin treatment. Langevin in 1908 after almost three years after Einstein came up with his theory, he derived the exact same relation by a mean field or stochastic approach what he did was he took the total force which is applied on a Brownian particle as F plus F x where F is the viscous force which is expressed once again by the Stokes relation that is F is equal to I mean on a part sorry F per particle is equal to 6 pi eta r v.

And F x is the x component of the fluctuating force and he actually used the classical Equiv Partition theory in order to evaluate the final expression which is exactly similar to what Einstein has came up with this is that the mean squared displacement is equal to k b T divided by 3 pi eta r times tau. Now Einstein's theory is still accept I mean was readily accepted of course after subject to the experimental verification.

But there were some controversy regarding the language approach because Langevin actually com I mean took this force, force term in which we have one dissipative force which is kind of a macroscopic variable but this x component of the fluctuating force which is due to large number of impacts with the you know, host matrix particles of the host matrix. This was for a long time this was debated upon whether this it is right to take an average value of this fluctuating force.

But it turned out that the expression the final expression what he has got is exactly the same as Einstein and later on I mean initially there were like questions on whether this approach is correct but later on this approach was well established and even now for standard molecular dynamic simulations people use the starting point is the Langevin equation. So, we are not going into the details of all this I am just giving you a brief overview of what was done at the time in order to explain and Brownian particle.

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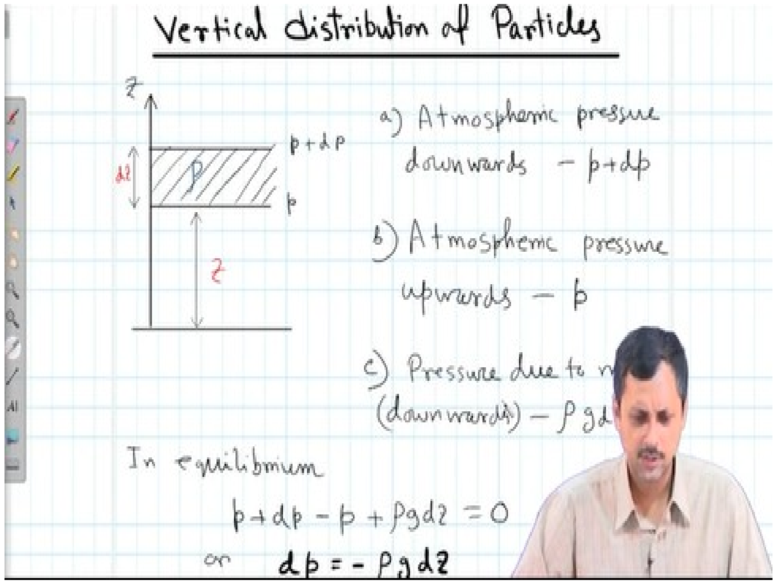

So, the next topic which we are going to discuss is the vertical distribution of particles. Now in this, this is actually the problem of sedimentation. In sedimentation what happens?

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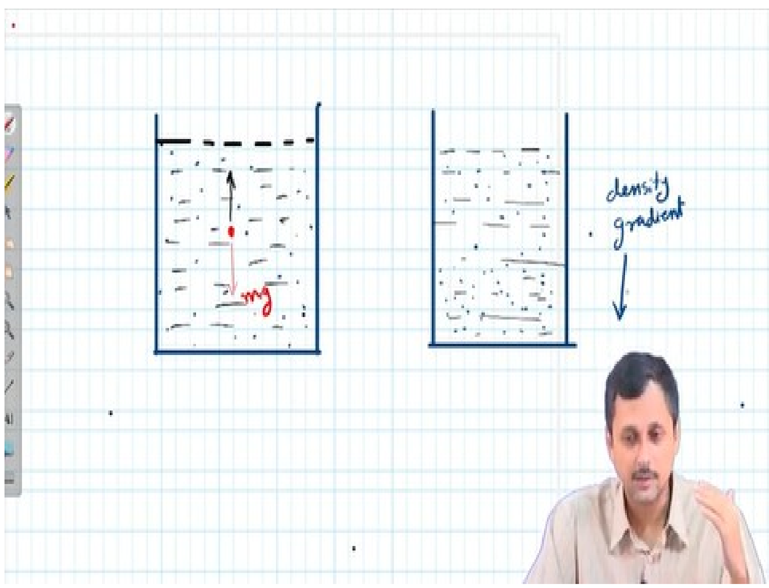

We have let us say let me just give you a brief overview of sedimentation then probably will understand what I mean by this thing. So, let us say I have one container and I pour inside this container I pour a solution in which I have a solute I mean there is a host metric that is a solution and inside we have large number of particles which are suspended. So, basically it is a colloidal solution. Now so far whatever we have discussed the geometry has been horizontal.

So, the Einstein, approach so far what we have discussed is this particular geometry in which the particle flow is along the x axis or the horizontal direction. Gravity has not been brought into this picture. Now what happens if we just take a colloidal suspension and allow it to settle for long enough time. Long enough as in sometimes days sometimes weeks so, what happens. Now if I just focus on one particle let us say this particular marked in red I am just trying to focus on this particle.

And see it will be acted upon by gravity in the downwards direction, this is the gravitational pull it will experience which is equivalent to for equivalent to mg the gravitational so we have to choose the right pen mg. And at the same time there will be a buoyancy force I think you are all familiar with buoyancy concept of buoyancy which will be given by you know, the amount of fluid it has displaced.

So, in effect there will be two I mean two opposite forces acting on this one, in effect it will eventually settle down. If we just let the container sit here for overnight or for long enough time so, we will have a distribution of particle inside this beaker in which some of the particles will be coming down and some particle will stay afloat. So, just wait so if I just wait long enough time so what happens is this?

So, more particles will come in the bottom end and as we go up the density of the sedimented particles will be less. So, basically there will be a density gradient, density gradient of Brownian particles in the downwards direction. So, I hope you understand what I mean by this; that if I allow but please remember that not all will be settling down there will be a distribution of Brownian particles.

Now let us look into it in a more formal manner and try to see what happens. So, if I just take a layer of this system at a height Z from in the horizontal line a vertical direction then this layer has a thickness dz let us say the pressure on the top will be given by p plus dp. And the pressure at the bottom will be given by p. So, all together there are three forces that is acting on this layer, one is the atmospheric pressure downwards which is p plus dp.

Atmospheric pressure upwards which is given by p and the pressure due to mass which is acting downwards which is rho times g times dz where rho is the density once again of the Brownian particle. So, the in equilibrium we have the relation dp is equal to minus rho Z dz.

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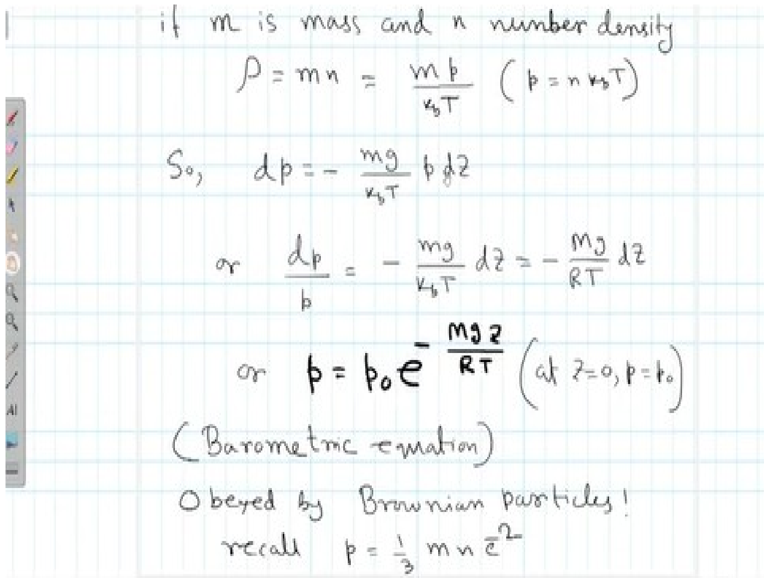

So, by writing the mass m and if m is the mass of individual particle and n is the number density then rho we can write as equal to m times n and once again n can be substituted by p divided by k b T. So, we can write rho is equal to m divided by m p divided by k b T. So, we can substitute back and we can write dp by p is equal to minus mg by k b T dz. Once again, we can multiply m with the Avogadro number, we can multiply k with the Avogadro number.

And we can write this as minus m capital Mg divided by RT where R is the gas constant and M is the you know the molar mass. So, we finally get to this equation which is called the barometric equation which is p is equal to p 0 e to the power minus m g Z divided by RT. So, what is the outcome of this? If we take the derivative dp will be equal to negative quantity, negative definite quantity where of course p 0 is the value of the pressure at Z is equal to Z 0.

So, basically what we have assumed that the pressure up here will be p plus dp and dp being a negative quantity. So, the pressure will decrease so, this will be outcome of this equation. So, anyway we get this barometric equation which is p is equal to p 0 e to the power minus mg by

Mg Z by RT and now recalling that p is equal to 1 third m n c bar square where c bar being the mean squared is mean velocity square of this Brownian particles.

And of course, we have to assume that the Brownian particles behave like ideal gas which has been the assumption more or less during the discussion for this portion.

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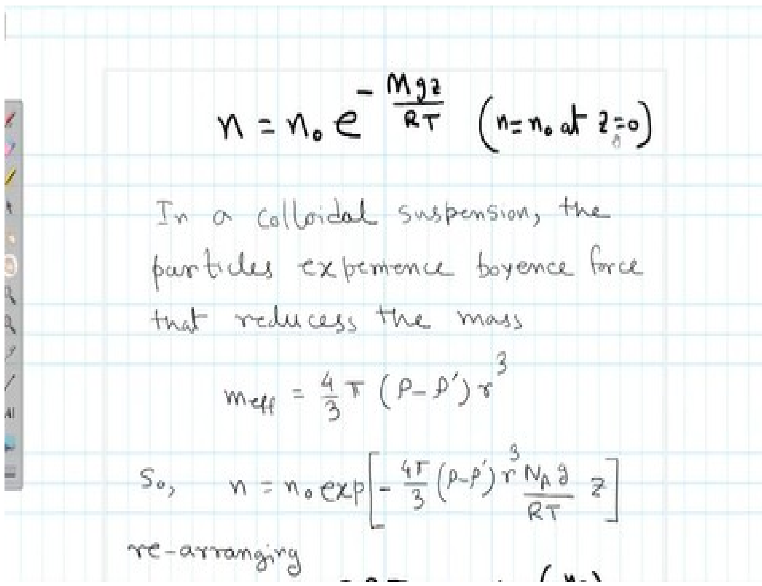

So, what we can do is? We can straightforward manner we can write n is equal to n 0 e to the power minus m g Z by RT. Once again, n at n is equal to n 0 is equal to n is equal to n 0 at Z is equal to 0. Now in a colloidal suspension the particle experiences buoyancy forces as I have discussed already. So, there are two force components one is the gravitation the other is the buoyancy.

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$$m_{eff} = \frac{4}{3}\pi\,(\rho - \rho')\,r^3$$

So, $$n = n_0 \exp\left[-\frac{4\pi}{3}(\rho-\rho')\,r^3\,\frac{N_A g}{RT}\,z\right]$$

re-arranging

$$N_A = \frac{3RT}{4\pi r^3(\rho-\rho')\,g(z-z_0)}\,\ln\left(\frac{n_0}{n}\right)$$

$n_0 \rightarrow$ number density at Z_0

And this buoyancy will reduce the mass by m effect the effective mass will be n effective is equal to 4 third pi rho minus rho prime divided by r cubed. Now rho as we have already discussed is the balance or the density of the Brownian particle and rho just a minute it should be and rho dashed is the density of the displaced liquid that means the density of the medium times r cubed r being the radius.

So, we can write this expression as n is equal to n 0 exponential minus 4 third pi rho is equal to rho dagger rho minus rho dash r cube N A g once again what we have to do is? We have to you know sorry in this equation we can write capital M as equal to small m times N A and that N A is the Avogadro number and finally, we can write N A g divided by RT times Z. And after rearranging this relation what we get is N A is equal to 3 RT divided by 4 3rd r cubed rho minus rho prime g Z lon n 0 by n.

Now n 0 is the you know density of the reference layer so, if we take, we can actually we are free to take any reference layer all we have to do is we have to replace this Z by Z minus Z 0. Actually, this will be the right expression to write instead of simple Z what we do is we simply write Z - Z 0, this will be a better way of representing this equation and so where n 0 is number density at Z 0. So, this is our equation.

Now look at this equation this is a very powerful equation because see all the quantities are directly measurable. We can measure the temperature; we can measure the radius of course I will tell you I have to tell you how to measure the radius accurately. But you know it can be measured with good accuracy rho and rho prime are the two quantity that can be measured, g is known is the gravitational I mean acceleration due to gravity Z and Z 0 are the heights that of the reference level and the level of interest.

So, basically this is the two you know heights are also known all we have to do is we have to measure n 0 and n. Then this relation can be used in order to measure the Avogadro number. In a similar manner in the previous theory or in the previous lecture in expression what we have derived if I just switch this N A over here and I can take down this s square down here. So, we get N A is equal to R T by s square divided into 1 by 1 third pi eta 1 by 3 pi eta r times tau.

So, if we can somehow measure the displacement or mean square displacement s square for a time interval tau and of course the system viscosity has to be known we can also estimate the Avogadro number. Now Jean Perrin in or I think the proper pronunciation should be Jean Perrin in a series of experiment between 1909 and 2015 used this both the expressions one is the expression of expression derived by Einstein this one or Langevin both got the same expression anyway.

And the sedimentation expression for the sediment I mean you know the vertical distribution of Brownian particles which is this one in order to measure the Avogadro number of. And also, one important point you have to note that this equation there is no mass term associated with it. Of course, there is density here but this is nothing to do with the mass of the particle. So, we will come back to that in a more details in the next lecture.

And we will try to explain how what how Perrin measured all these quantities relevant quantities of interest in order to finally get to the first experimental verification of Avogadro number. Thank you.