Advanced Chemical Thermodynamics & Kinetics
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Lecture - 31
Introduction to solution phase reactions dynamics 01

Hello everyone, so, today we will be starting our discussion on Reaction Dynamics in Solution. So, we have given you an overview on the reaction dynamics in gas phase, what we discussed basically two models, one is the collision theory which actually covered in the earlier course, but we talked about it very briefly. And the other theory is a transition state theory which is very widely used and we showed that for very simple reactions these two theories are equivalent.

Now, those theories were developed or the way we showed it to you is for gas phase reaction, but almost all reactions in chemistry and biology that happen happens actually in solution. So, we have to understand how actually what are the mechanism and what are the dynamics of reactions in solution. So, in solution you have apart from the reactant molecules you have solvents so, the solvents actually solve it the reactants.

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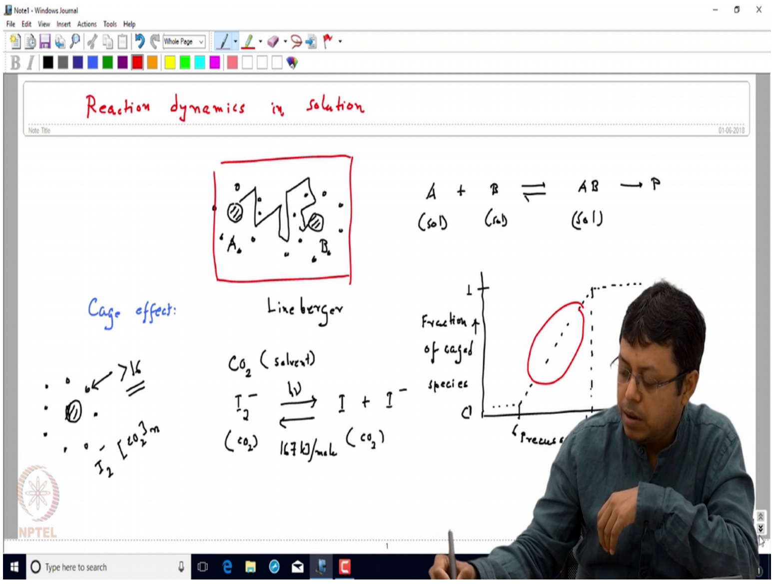

Reaction dynamics in solution

$A + B \rightleftharpoons AB \rightarrow P$
(sol) (sol) (sol)

Cage effect:

Lineberger

CO_2 (solvent)

$I_2^- \underset{167\ kJ/mole}{\overset{h\nu}{\rightleftharpoons}} I + I^-$
(CO_2) (CO_2)

So, you can actually imagine these reaction dynamics in solution, you can imagine it to begin with to something like that suppose these are the salutes and all the solids are basically surrounded by solvents. So, the solvents actually influence the rates of reactions in many different ways so, but in most of the cases if these are not ionic spaces and if there is not a large dipole which is created instantaneously we will see that the reaction rates are more or less equivalent to the gas phase reaction. The reason is these solvents does not directly participate in the reaction because, the solutes are only the participating candidates.

And secondly, the thing is that the reaction potential between the two solutes is I when they come close together. So, that is the limiting factor, meaning unlike the gas phase reaction what actually it depends on the number of collisions. What will happen in solution, you can think it conceptually that these solute molecules or the reactants will actually diffused and so they will have some trajectory.

And suppose after some time they actually diffuse this molecule let us say A actually diffuse to the molecule B and they are having now close encounters. And there can be multiple encounters between there because, now they are close and together they are surrounded by the solvent molecules. So, the solvent molecules actually effectively provide a cage around the reactants.

Now, the interesting thing is that or what I am saying if we talk about it in detail. So, I have two reactants, so A and B both are which initially were solvated. And then they should come close together so that they form a reactant pair and this entire thing together is now solvated. And within the solvent cage there they are having actually reactive encounters and they will form products, and this is the overall mechanism of the solute solvent or this interaction between solutes in a solvent.

Now, we are not considering at this moment the reaction between charged spaces we will consider it later. Now, diffusion is the key mechanism here where actually their reactants are coming closer together. Now, before that let us have a more slightly more discussion on what is this effect which I called as the cage effect.

Now, cage means it is a solvent cage around the reactants. Now, there has been a very interesting experiment by Lineberger and co-workers, and what they showed is that if they actually were taking carbon dioxide as a solvent and they took the reactant as I 2 minus and the reaction was something like that they were actually shining light and there is a photolysis or photo dissociation which actually gives you I plus I minus.

Now, the interesting thing what they observe is that when they did this reaction. So, initially I had I 2 minus which is surrounded by co 2 and the products are also surrounded by CO 2. And then when you shine light it generate I and I minus, but since they are still in the solvent cage what can happen is that they can again react back, and means actually they can actually collide again within the cage within the solvent cage and they can again from the I 2 minus.

But when you have this so the energy of the photon is actually realized as thermal energy because, you are forming a chemical bond and that energy is 167 kilo Joule per mole. Now, the interesting thing is that now it will depend on what is the size of the solvent cage? Meaning if the solvent cage is small what will happen that excess energy may actually lead you to evaporate the solvent.

So, basically it is a solvent cage will basically evaporate. And the interesting thing which you will get is that this expulsion of the solvent may not be true for actually large clusters. So, what Lineberger and co-workers did is that they were actually looking at these fraction or which is a fraction of the molecules which are caged and when the plotted this fraction of molecules. So, here I am plotting this fraction of caged species ok, cage species means this is caged I 2 minus.

So, it basically dissociates and it again reforms. So, that cage spices, so, the fraction can be minimum can be 0, maximum can be 1. And then when they plotted with the precursor of this thing like precursor I 2 minus CO 2 n because, you can actually think that there is a cluster of a suppose this is the I 2 minus and this is the carbon dioxide which are surrounding the I 2 minus initially. So, I am calling it as complex which is I 2 minus and CO 2 n. So, there are n number of CO 2 molecules around it.

So, when I plot it along this n the precursor complex and where actually I am having the n, so, n we will take of course, integer numbers. And they found the experimental data showed something like up to n equal to 6 they showed that it is basically 0, meaning the species of the fraction of the cage species they are not getting because, the cage is actually blowing apart, because this is too much excess energy this 167 kilo Joules per mole that actually helps all these small number of molecules that is basically translated into the translational kinetic energy of this CO 2 molecules. So, they fly apart so, they do not see any cage.

But then once they increase the number of CO 2 molecules and then they see that when actually this number reaches something around say 16 above that you always see the cage is for meaning if the cluster size of this co 2 molecule if it is greater than 16, the cage will be always stable. Meaning a 16, 17 or 18 those many numbers or higher number of CO 2 molecules if they are present the 167 kilo Joule per mole energy is not sufficient to break that cage.

But in between you see that up to 6 it is totally it can break, and in between 6 and 16 you have a more or less linear dependence of this of this fraction of cage species or cage I 2 minus versus the these number of CO 2 molecules that form this cage. So, this actually was a very interesting experiment that showed how the cage effect actually influences the reaction or the how the solvent actually participates in this particular reaction.

Now, moving onward, so what is a very important right now is that this was kind of a reverse experiment in the sense that you initially start with the species and you photo disassociated and you recommend that. But we are more interested in a some general considerations something like the picture I have drawn here. So, I have A and B and they are actually coming through diffusion and then they are doing the encounter.

Now, the question is for this we have to develop some diffusion control mechanism which we will be discussing now. Now, the question is so, there is a mathematical model or a physical model to describe this kind of a diffusion mediated encounters. But let us first discuss or extend our original discussion on diffusion and where actually we discussed the diffusion coefficient what are the values of the diffusion coefficient, that if you remember our previous discussion when we talked about this time dependent transport process.

We talked about Fick's law and there are two Fick's law; one was the Fick's 1st law and Fick's 2nd law. And the Fick's 2nd law basically tells you how the concentration varies with time or the or the density actually as a function of position and time we were probably using some row notation or instant notation. So, the notation can be slightly different so, as a function of time how does it changes.

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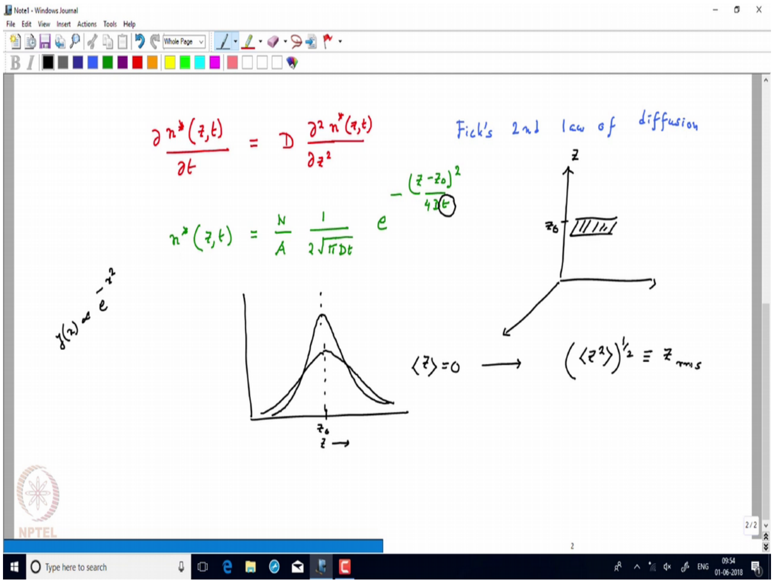

$$\frac{\partial n^*(z,t)}{\partial t} = D\,\frac{\partial^2 n^*(z,t)}{\partial z^2}$$

Fick's 2nd law of diffusion

$$n^*(z,t) = \frac{N}{A}\,\frac{1}{2\sqrt{\pi D t}}\, e^{-\frac{(z-z_0)^2}{4D\boxed{t}}}$$

$\gamma(z) \propto e^{-z^2}$

$\langle z \rangle = 0 \longrightarrow (\langle z^2 \rangle)^{1/2} \equiv z_{rms}$

And then we found that the time derivative in of the concentration of the concentration gradient how it changes over time is basically the equivalent to the spatial derivative and they are connected to a constant which is the diffusion constant. And that was if you remember that was Fick’s 2nd law of diffusion.

Now, moving on if we can actually integrate this equation I will not show you how the integration is done. So, it requires some knowledge how to integrate this kind of equation because, actually n star is dependent on both z and t. So, you have to first make you cannot do a separation of variable here. So, if we move on, so I am just writing the solution for you.

If I want to know how basically this concentration which is a function of space and time is changing as a function of space and time and particularly is a function of a time how it is changing at a particular location. So, what we will get is basically, we get something like 1 N over A and 2 square root of pi into pi Dt and then we will have e to the power of minus z minus z 0 squared by 4 Dt.

Now, what is z 0? If you remember your old model that we kind of develop we said that we are considering the flow along the diffusion I along z and then we considered plane at a location z 0. So, this was at z 0 and then we considered the flux through the surfaces if you remember that that there was an upward flux that there was a downward flux and that is how we calculated it. And we said that within the mean free path then there will be some flow of the molecules and we did all these nice calculations.

Now, what this equation shows is that at suppose some z 0 ok. So, if we consider that to be the origin and then if we just plot this quantity this n star as a function of say of course, z and suppose z 0 is the origin, now how it changes with respect to time. Now, if I plot it with the respect to z only, so it is a Gaussian as you can see it is basically y as a function of x is in this equation it is basically e to the power minus some constant into x square. Now, that is a Gaussian function.

So and which is centered around z 0 so, it will look like something like this, but with respect to time if I now plot the another Gaussian, so, as you can see the t is here. So, t is basically connected to the standard deviation or the width of this Gaussian. So, if I have more and more t what will happen here, this distribution will become wider and wider but, it will be still and Gaussian distribution.

So, as we see that with respect to time this distribution is basically spreading out which makes sense because, it is basically a time evolution of the concentration profile and eventually the concentration should become very much flat when there is no flow. Now, the interesting thing is we can actually if you ask this question what is the mean position of z or what is the like what are the if I if I just ask this quantity what is the average value of this z, so if it is a one dimensional diffusion which we considered.

And if we ask this question what is the mean position that mean position will be 0 because, they are the particles are equally provide, there is a equal probability of the particles going towards right or going towards left. So, the on average on the statistical average the mean position will always be 0.

So, if we can actually instead of the mean position we can actually calculate the mean squared position which will not be 0, and then to get an value of the mean position we can actually take the square root of that and which will be nothing but by definition is the root mean square position. Now, z and x are arbitrary, so we could have written it as x also, but I am following the older notation which we were following. And if you calculate that, so let us just try to calculate it how to calculate this z square average.

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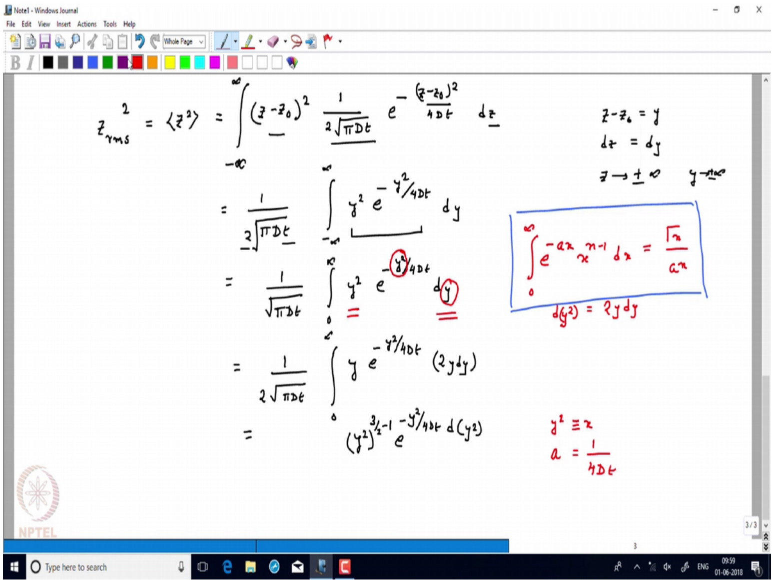

$$z_{rms}^{2} = \langle z^2 \rangle = \int_{-\infty}^{\infty} \underline{(z-z_0)^2}\, \underline{\frac{1}{2\sqrt{\pi D t}}}\, e^{-\frac{(z-z_0)^2}{4Dt}}\, d\underline{z}$$

$$= \frac{1}{\underline{2}\sqrt{\pi D \underline{t}}} \int_{-\infty}^{\infty} \underline{y^2 e^{-y^2/4Dt}}\, dy$$

$$= \frac{1}{\sqrt{\pi D t}} \int_{0}^{\infty} \underline{\underline{y^2}}\, e^{-\boxed{y^2}/4Dt}\, \underline{\underline{d\boxed{y}}}$$

$$= \frac{1}{2\sqrt{\pi D t}} \int_{0}^{\infty} y\, e^{-y^2/4Dt}\, (2y\,dy)$$

$$= \int_{0} (y^2)^{3/2-1} e^{-y^2/4Dt}\, d(y^2)$$

$z - z_0 = y$
$dz = dy$
$z \to \pm\infty \quad y \to \pm\infty$

$$\boxed{\int_0^{\infty} e^{-ax} x^{n-1}\, dx = \frac{\Gamma n}{a^n}}$$

$d(y^2) = 2y\,dy$

$y^2 \equiv x$
$a = \frac{1}{4Dt}$

So, z rms which is the root mean square position and we have to take z square and then half, but let us first calculate the z rms square and then we will take the square root. And so as you can see that you if you calculate any things average value it will be nothing but I have to take the position which is z minus z 0, and then I have to multiply by the distribution function and then integrate.

In this case the distribution function is something we already talked about. It is 1 of over 2 square root of pi Dt and then we have e to the power minus z minus z 0 squared divided by 4 Dt. And then we have to integrate this quantity which is going from now z is a one dimensional quantity. So, it can go from plus minus infinity and we will have a dz.

Now, see here first the variable here is z, but here I have z minus z 0, so you can easily do our transformation. Suppose I tell that z minus z 0 is which take some variable let us say y so, dz is nothing but d y because z 0 is a constant. So, I can just write it and also when z tends to infinity, y also tends to infinity and if it is minus infinity y also tends to a minus infinity. So, the limits are same so, I will just rewrite it like this so, I will have y square and this is a constant. So, this constant we can first take out of the integration.

So, I will have 1 by 3 inside square root I have pi Dt. So, I am actually integrating over space. So, that all the time part actually comes out so, it is a special integration and then I have minus infinity to plus infinity y square e to the power minus y square divided by 4

Dt into d y. Now this is an even function of y, so, instead of writing the limit as minus infinity to plus infinity we can write it as two times 0 to infinity. So, this integration will be 0 to infinity with an additional two and that two actually gets cancelled with these two.

So, we will have 1 over square root of pi Dt and inside bracket now I have y square minus e to the power of minus y square times e to the power minus y squared by 4 Dt into d y. Now, actually we can use the gamma function and if you remember we wrote the gamma function as a e to the power minus ax x to the power n minus 1 dx that integral between 0 to infinity is nothing but gamma n by a to the power n.

Now, here as you see that I have here y squared, but I have here y. So, I have to write this d y in terms of d of y squared and you know that d of y squared is nothing but 2 y, d y. So, I have to actually write it as 2 y, d y so, let us just write it. So, I will write it as 2 y, d y so that in the next step I can write it as a which is d of y squared. Now, if I have 2 y d y I have taken one y from here. So, this becomes the y square becomes actually y and then I have e to the power of minus y square by 4 Dt, I have integral 0 to infinity and, but I also have a two, extra two. So, to account for, that I have so I have to divide it by 2.

So, that is how the integration looks like now still, so, what I am going to do is basically this y I am going to write it as y square to the power half and y square to the power half can be further written as half is 3 by 2 minus 1. So, now, actually it forms it looks like a gamma function where you can think the x here, the y square is basically x here you look at this form of this gamma function.

So, the variable x is basically a y square in our equation and the constant a is nothing but 1 over 4 Dt. So, you can easily figure out what is the value of the gamma function. So, there is an integral 0 to infinity and constant ones 1 over 2 square root of pi Dt so, let us evaluate now the integral using the gamma function relation. So, what we got is we have 1 over 2 square root of pi Dt and then this is nothing but gamma 3 by 2 because you can easily look at the gamma function here.

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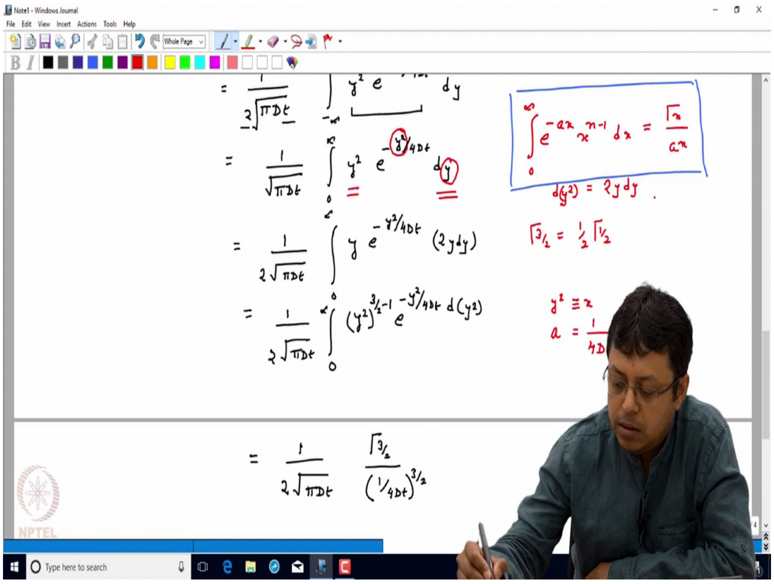

$$= \frac{1}{2\sqrt{\pi D t}} \int_{-\infty} \underline{y^2 e} \; dy$$

$$= \frac{1}{\sqrt{\pi D t}} \int_0^\infty \underline{\underline{y^2}} \, e^{-\boxed{y^2}/4Dt} \, d\underline{\underline{\boxed{y}}}$$

$$= \frac{1}{2\sqrt{\pi D t}} \int_0^\infty y \, e^{-y^2/4Dt} \, (2y\,dy)$$

$$= \frac{1}{2\sqrt{\pi D t}} \int_0^\infty (y^2)^{3/2 - 1} e^{-y^2/4Dt} \, d(y^2)$$

$$= \frac{1}{2\sqrt{\pi D t}} \frac{\Gamma 3/2}{(1/4Dt)^{3/2}}$$

$$\boxed{\int_0^\infty e^{-ax} x^{n-1} \, dx = \frac{\Gamma n}{a^n}}$$

$d(y^2) = 2y\,dy$.

$\Gamma 3/2 = \frac{1}{2} \Gamma 1/2$

$y^2 \equiv x$

$a = \frac{1}{4D}$

And it is e to the power minus a x, x to the power n minus 1. So, x is just y square so, it is n minus 1 is a 3 by 2 minus 1. So, it will be nothing but gamma 3 by 2 divided by a to the power n, now a is a as I said it is basically 1 over 4 Dt to the power 3 by 2. Now, what is a gamma 3 by 2? So, gamma 3 by 2 will be basically gamma n is n minus 1 gamma n minus 1. So, it will be half to gamma half and because actually let me actually write the value of gamma function here.

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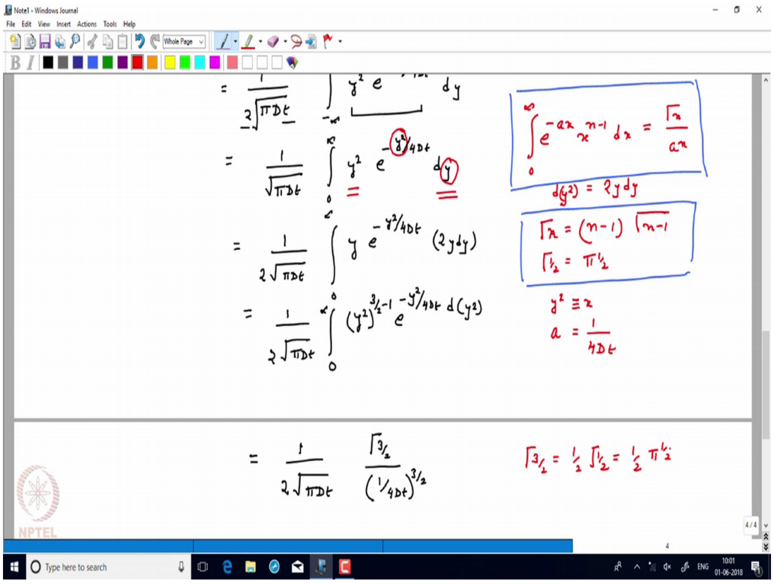

$$= \frac{1}{2\sqrt{\pi D t}} \int_{-\infty} \underline{y^2 e} \; dy$$

$$= \frac{1}{\sqrt{\pi D t}} \int_0^\infty \underline{\underline{y^2}} \, e^{-\boxed{y^2}/4Dt} \, d\underline{\underline{\boxed{y}}}$$

$$= \frac{1}{2\sqrt{\pi D t}} \int_0^\infty y \, e^{-y^2/4Dt} \, (2y\,dy)$$

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$$\boxed{\int_0^\infty e^{-ax} x^{n-1} \, dx = \frac{\Gamma n}{a^n}}$$

$d(y^2) = 2y\,dy$

$$\boxed{\begin{aligned} \Gamma n &= (n-1)\,\Gamma n-1 \\ \Gamma 1/2 &= \pi^{1/2} \end{aligned}}$$

$y^2 \equiv x$

$a = \frac{1}{4Dt}$

$\Gamma 3/2 = \frac{1}{2} \Gamma 1/2 = \frac{1}{2} \pi^{1/2}$

So, gamma n is basically n minus 1 into gamma n minus 1 that is how we have to cross it and gamma half is basically root pi.

So, now with the analogy you can show that gamma 3 by 2 is nothing but half gamma half which is half into root pi, if you put these values you can see what is the value of the integral.

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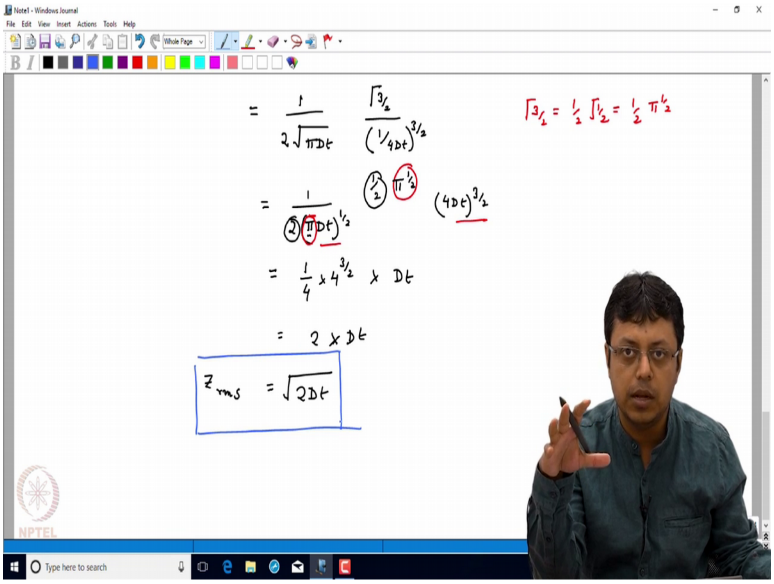

$$= \frac{1}{2\sqrt{\pi D t}} \frac{\Gamma_{3/2}}{(1/4Dt)^{3/2}}$$

$$\Gamma_{3/2} = \frac{1}{2}\Gamma_{1/2} = \frac{1}{2}\pi^{1/2}$$

$$= \frac{1}{2(\pi D t)^{1/2}} \; \frac{1}{2} \; \pi^{1/2} \; \underline{(4Dt)^{3/2}}$$

$$= \frac{1}{4} \times 4^{3/2} \times Dt$$

$$= 2 \times Dt$$

$$\boxed{z_{rms} = \sqrt{2Dt}}$$

So, as you see I have 1 over 2 pi Dt to the power half and then I have half here and I have pi to the power half. So, this pi to the power half will basically cancel out with either pi to the power half in the denominator and then what I have is 1 over 4 Dt so, I can actually take it up.

So, I will have times I will have 4 Dt to the power 3 by 2. Now so, as you can see that I have 4 to the power 3 by 2 and 2. So, that will basically cancel up 4 to the power 3 by 2 so, 4 to the power half is 2 and 2 cube is a, 2 cube divided by 2 is nothing but 4, so we will have 4 in the denominator. And what we have here there is one half here, so that 4 at that half becomes actually 2 let me actually rewrite it once again.

So, what I have, 1 and 2, so I will have basically 14th times 4 to the power 3 by 2. So, together actually I will get half because, 4 to the power 3 by 2 is nothing but 8, 8 by 4 is half and then what I will have look at the pi's, pi's will get cancelled because it is pi to the power of half and here pi to the power of half it will get cancelled.

Now I have Dt to the power 3 by 2 and Dt here, so, what I will have is just a simple Dt here. So, what we see here, so it will be not 1 over 2 it will be just 2, 2 Dt so, this is basically 4 divided 8 divided by 4. So, ultimately I am getting 2 Dt and that was basically z rms squared.

So, z rms will be nothing but square root of 2 Dt. So, this basically shows you what is the mean square displacement of the of a I mean if a particle is diffusing what is the mean square displacement. Now, this result will be very useful to discuss the subsequent discussion and which will be very important to calculate the reaction the rate law or the rate constant in solution.

Now, let us first discuss the model for suppose I have a Brownian particle, and how it is diffusing inside a solution let us first try to formulate that. Now, let us discuss what are the dynamics of a Brownian particle in a solution?

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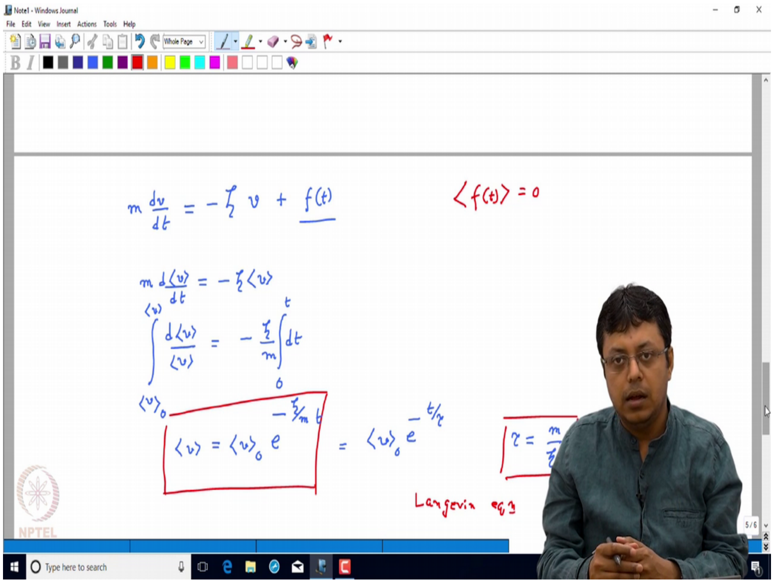

$$m\frac{dv}{dt} = -\zeta v + \underline{f(t)} \qquad \langle f(t)\rangle = 0$$

$$m\frac{d\langle v\rangle}{dt} = -\zeta\langle v\rangle$$

$$\int_{\langle v\rangle_0}^{\langle v\rangle}\frac{d\langle v\rangle}{\langle v\rangle} = -\frac{\zeta}{m}\int_0^t dt$$

$$\boxed{\langle v\rangle = \langle v\rangle_0\, e^{-\zeta/m\, t}} = \langle v\rangle_0\, e^{-t/\tau} \qquad \boxed{\tau = \frac{m}{\zeta}}$$

Langevin eq^n

Now, to approach the problem we will just apply the laws of motion and we know that the acceleration and mass times acceleration is the force. And then we can actually say, that the particle mass is m and the acceleration we can write it as dv dt that is equal to some frictional force which will be dependent on the velocity because, as it moves actually it experiences a friction from the solvent molecules and that force actually acts in the opposite direction of the movement.

So, if the frictional coefficient is constant which we write it as zeta, so I am writing a negative sign for that. And then there will be also a random force which is of course, time dependent force.

Now, this random force is very much stochastic in nature, this is basically solvent molecules are moving around and for that actually this Brownian particle receives continuous thermal peak from all the direction. Now, what we are interested in is an average force, now average means actually it is average if I talk about one particular particle it is basically average over a different position or if you can think about an ensemble of particles in that sense also it is we are taking basically average of position. And if we think that this random force is not dependent on position then we can always say this average value of this force is going to be 0.

Now, we can write over take the average of this equation and write m dv average dt is nothing but minus zeta into v average. Now, these are all identical particles, so even if I take an average so m actually comes out because, m is a constant it is mass and zeta is also a constant.

Now, we can write away integrate it is a very straightforward equation. So, it will be a dv by v will be a minus zeta let us just do it. So, dv by v the average of v is nothing but minus zeta by m into dt, and now we can actually integrate this equation and assuming that at time 0, the initial velocity or the initial average velocity was like v 0. So, it is average of v suffix 0 that it corresponds to time.

And at any arbitrary time the value is v. So, we can easily see that v will be nothing but v 0 the 0 time velocity times exponential minus zeta by m into t. So, what we see that the velocity actually drops from the initial velocity v 0 and at a infinite time it becomes 0, with the time constant if we actually write this equation as it is nothing but at some kind of correlation function. So, if we write it as t by tau then the time constant for this exponential decay as you can see is nothing but m by zeta. So, that is the with this time constant basically the initial the velocity actually drops from it is initial value to 0.

Now, the question is how do calculate the mean square displacement from this equation. Now, already we know that, so in order to calculate that we will just use the formula for the diffusion coefficient. And then we will just write the mean square displacement which we had already calculated the z rms square, but instead of z we will be using the x notation and then we will be using these connecting the mean square displacement to our to the to the time basically the with the diffusion coefficient.

Now, the problem here is that we have solved it with respect to the with respect to the velocity, but we are more interested in a calculating the position of the because what will eventually happen is that a we will calculate the what is the mean square displacement in terms of the diffusion coefficient. And then we will want to see that for a Brownian particle. And then we want to see how this particle actually changes it is position because it is ultimately the diffusion that is basically mediating the reaction in solution to happen.

Now, in order to do that instead of a writing it as m dv dt, we will just rewrite it in a slightly different way. We will just have to write it in terms of position and you already know that velocity is nothing but dx dt.

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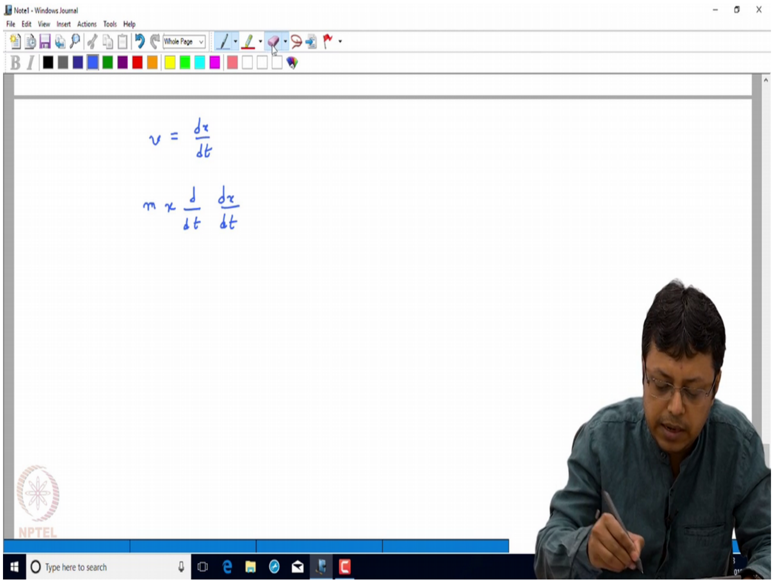

$$v = \frac{dx}{dt}$$

$$m \times \frac{d}{dt} \frac{dx}{dt}$$

So, if you follow this equation so, this is a nothing but this equation I forgot to tell them this is known as the Langevin equation, and here the assumption here is that these Brownian particles much bigger than the solvent molecules. So, that the solvent is treated as a continuum and that is why the forces which are originating in the solvent is basically stochastic and then if you take an ensemble average it is basically washes away.

However, for a if the particle is very small for example, if you have a let us say nano particle now which has a dimension of few nanometers which is diffusing in say water.

Then actually, the in your particularly in a very short time scale the diffusion or the forces will become very important to control it is trajectory and then you cannot actually average out the forces because the particle size is almost equivalent to now this solvent size. So, you cannot actually use a continuum salvation model to describe this phenomena.

Now, we are not discussing that we will we will just describe everything within the context of Langevin model. Now, I can actually write now the force equation so, that was basically if you remember it that was basically mass times acceleration, and acceleration is a nothing but we can just write it like this x into d dt of dx dt so, if you follow this one.

So, I had basically the multiply we what we did here is that we actually I am going to multiply both side by x, so, we can actually show it in the next step. So, let us first start with the original equation so, that you do not we can follow actually every step. So, we have actually a force ok, and the force was basically random. So, we can actually from the beginning ignore that force because you are anyway going to average it, but I am keeping it for the time being.

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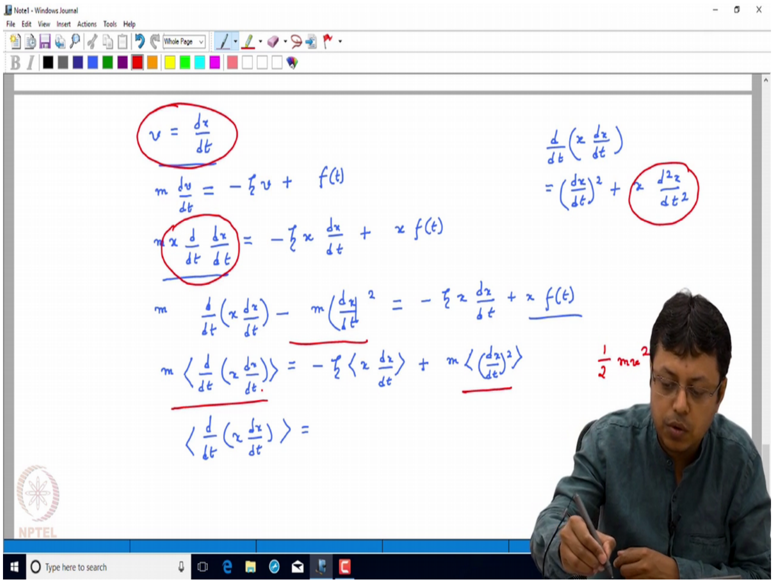

$$\underline{\boxed{v = \frac{dx}{dt}}}$$

$$m\frac{dv}{dt} = -\zeta v + f(t)$$

$$m\underline{\boxed{x\frac{d}{dt}\frac{dx}{dt}}} = -\zeta x\frac{dx}{dt} + x f(t)$$

$$m\frac{d}{dt}\left(x\frac{dx}{dt}\right) - \underline{m\left(\frac{dx}{dt}\right)^2} = -\zeta x\frac{dx}{dt} + \underline{x f(t)}$$

$$\underline{m\left\langle\frac{d}{dt}\left(x\frac{dx}{dt}\right)\right\rangle} = -\zeta\left\langle x\frac{dx}{dt}\right\rangle + m\underline{\left\langle\left(\frac{dx}{dt}\right)^2\right\rangle}$$

$$\left\langle\frac{d}{dt}\left(x\frac{dx}{dt}\right)\right\rangle =$$

$$\frac{d}{dt}\left(x\frac{dx}{dt}\right) = \left(\frac{dx}{dt}\right)^2 + \boxed{x\frac{d^2x}{dt^2}}$$

$$\frac{1}{2}mv^2$$

So, I have mass times acceleration, I am writing the old equation once again is basically related to balance by a opposing frictional force which depends on the velocity and plus a random force which is f of t. Now, I am multiplying both side by x as well as what I am doing is basically writing v as dx dt.

So, what I will have is m, I am multiplying by x and I will have d dt of dx dt and then on the right hand side I have minus zeta, and then I have x times instead of v I will write dx dt plus the random force, but I multiplied both sides by x. So, now look at this term why m why I multiplied it by x? So, if you take say x into dx dt and take the time average of that.

So, then what we will get is that x is the first function dx dt is the second function. So, the first function will be dx dt times dx dt. So, it will be dx dt squared plus I will have here x into d 2 x dt 2. Now, what we have got here you see here it is basically x into d 2 x dt 2 times an m so, this guy will be nothing but this term x into d dt of the dx dt is nothing but x into d 2 x dt 2.

So, we can actually write or replace it by you can write it as it is nothing but ddt of x into dx dt minus d 2 x dt 2. So, I am just multiplying there is an m mass so, I am just writing I am not keeping it within the bracket. So, I am just multiplying it by the mass so, it is a into dx dt whole square that will be equal to minus zeta into x into dx dt plus x into f of t.

So, what I have done I have actually cleverly use this equation because remember that what I eventually need is to get an average value of x squared. Now, let us see how we can actually proceed it, but before that let us take first the ensemble average. If you do the averaging so which you could do earlier, but I am doing it right now what we get is a basically m and then average of this quantity which is d dt of x into dx dt that will be equal to I am writing this term first the zeta the frictional term, which is zeta and then average of x into dx dt.

And then I have an additional term here I am putting it on the right hand side. So, that would be a plus sign into m into average of dx dt squared and naturally this term I know that if I take the average it will be automatically 0. So, what I what is interesting now is basically I have m times d dt of x into dx dt and now you will see that what is the dx dt squared. Now, dx dt square is a dx dt is v right, we actually wrote it very earlier, so here so, this term is nothing but mv squared.

Now, mv square is a nothing but again it is a kinetic energy, and for a particle the kinetic energy expression is half mv squared. And we know that half mv squared according to the equi partition theorem for a one dimensional particle, it will be nothing but basically equivalent to the thermal kinetic energy which is the half cavity.

So, mv squared will be nothing but k B T. So, I am going to replace that term by k B T, I can make further simplification I have m times and ensemble average of d dt a time derivative of x dx that quantity. So, then actually I can do the time derivative later and I can first take the average because, these average is basically a special averaging. So, what I can write is instead of writing this term like this, I could have actually written it as m times I can actually divide both sides by m. So, the m I am not writing right now.

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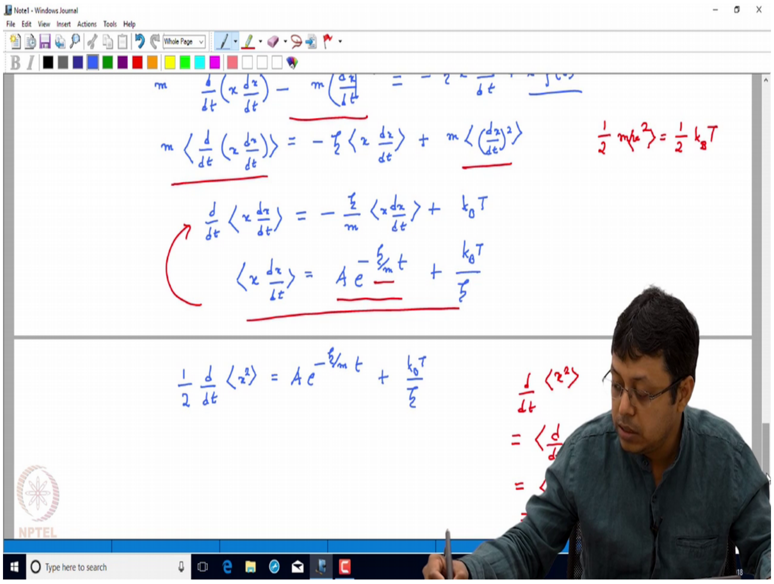

$$m \frac{d}{dt}\left(x\frac{dx}{dt}\right) - m\left(\frac{dx}{dt}\right) =$$

$$m\left\langle \frac{d}{dt}\left(x\frac{dx}{dt}\right)\right\rangle = -\zeta\left\langle x\frac{dx}{dt}\right\rangle + m\left\langle\left(\frac{dx}{dt}\right)^2\right\rangle$$

$$\frac{1}{2}m\langle v^2\rangle = \frac{1}{2}k_BT$$

$$\frac{d}{dt}\left\langle x\frac{dx}{dt}\right\rangle = -\frac{\zeta}{m}\left\langle x\frac{dx}{dt}\right\rangle + k_BT$$

$$\left\langle x\frac{dx}{dt}\right\rangle = Ae^{-\zeta/m\, t} + \frac{k_BT}{\zeta}$$

$$\frac{1}{2}\frac{d}{dt}\langle x^2\rangle = Ae^{-\zeta/m\, t} + \frac{k_BT}{\zeta}$$

$$\frac{d}{dt}\langle x^2\rangle$$

So, what I am saying is that it is a d dt of average of x into dx dt that quantity is basically minus zeta by m and I have x dx dt plus, I have m I divided both sides by m and I know that dx dt whole square is nothing but v square and the average kinetic energy I should have actually used average sign here. So, the average kinetic energy is a half k B T. So, the twice the kinetic energy which is basically mv average v square average is basically k B T and I am not writing the m because I have divided both sides by m.

Now, this equation we can actually solve and then what you will get is a basically if you just right this x into dx dt part which we actually solved earlier. So, that will be already we what we figured out from the Langevin equation. So, that we can actually write as e to the power minus if you remember correctly; so x into dx dt was basically your v.

Now, we can integrate this equation because, as you can see here it is a time derivative of some quantity which is x into dx dt is equal to some constant times that quantity plus k B

T. And if you write the solution it will be basically x into dx dt the average quantity of that is nothing but A times e to the power of minus zeta by m into t plus k B T by zeta.

Now, you can always check whether this equation is correct or wrong by just differentiating this equation with respect to time. So, if we take the time derivative as you can see here, so I will have and just basically pull out 1 zeta by m at the front and that will be minus zeta by m into A into e to the power minus zeta m by t.

But and then I will have actually a time derivative so this part will be 0, the second constant and then you can write this A into zeta minus zeta by m into A into this e to the power minus zeta m by t, again as the old function and you can easily get back to it. So, this is just to check whether this integration is correct.

Now, what we have we see I mean what we have done so far is basically you can just write now write x into dx dt, as now this is very easy to rewrite because, remember that all we wanted to do is get an expression for x square the mean square displacement. Now, if I take a time derivative of that so what I will get is so, if I take a d dt of this quantity. So, that will be nothing but d dt of x square I can write it because, it is just a spatial averaging and then that is nothing but as you can see it is 2 x dx dt. So, it is nothing but 2 times x into dx dt.

Now, this is exactly what we have solved for. So, I can actually write this quantity x into dx dt as nothing about half times d dt of x square average and that is what we are going to evaluate, the mean squared displacement if the choice of the axis is x e to the power minus zeta by m into t plus k B T by zeta.

Now, I have already kind of solved it. So, what we could write actually now, you can actually to make things a little bit simplified, as you can see I have actually A into so we can actually make first the initial conditions here, in the sense that I can say that when t equal to 0 I can actually choose an initial position. In the sense that if you remember our original description of diffusion what I wrote this figure that I have my initial initially actually I am starting from z 0.

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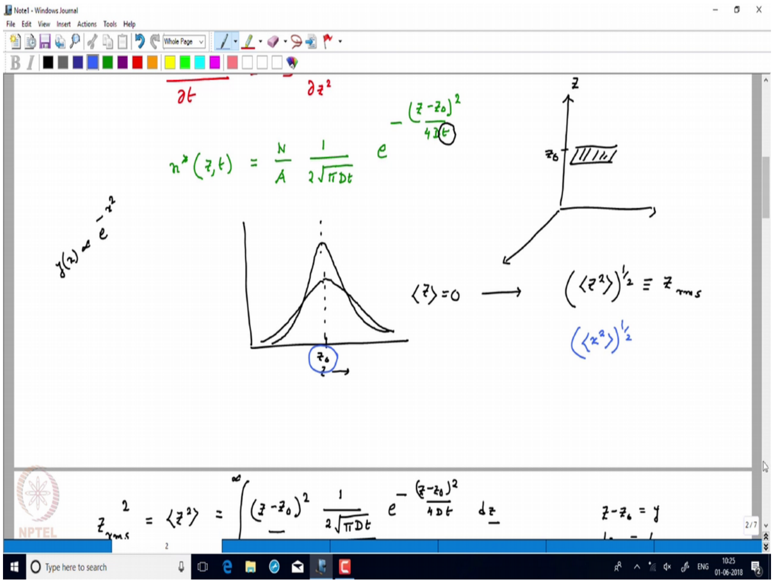

$$n^*(z,t) = \frac{N}{A}\frac{1}{2\sqrt{\pi D t}}\, e^{-\frac{(z-z_0)^2}{4D\boxed{t}}}$$

$$y(x) \propto e^{-x^2}$$

$$\langle z\rangle = 0 \longrightarrow \left(\langle z^2\rangle\right)^{1/2} \equiv z_{rms}$$

$$\left(\langle x^2\rangle\right)^{1/2}$$

$$z_{rms}^{\;2} = \langle z^2\rangle = \int^{\infty} (z-z_0)^2 \frac{1}{2\sqrt{\pi D t}}\, e^{-\frac{(z-z_0)^2}{4Dt}}\, dz \qquad z - z_0 = y$$

Similarly, if I take here actually I was using a z notation right now I am using x notation. So, x square average, so that quantity we are we are going to actually calculate eventually. Now, instead of a choosing the origin to be x 0, I can actually set x 0 to be 0 because that is purely arbitrary so, if I do that which means actually at t equal to 0 x is equal to 0.

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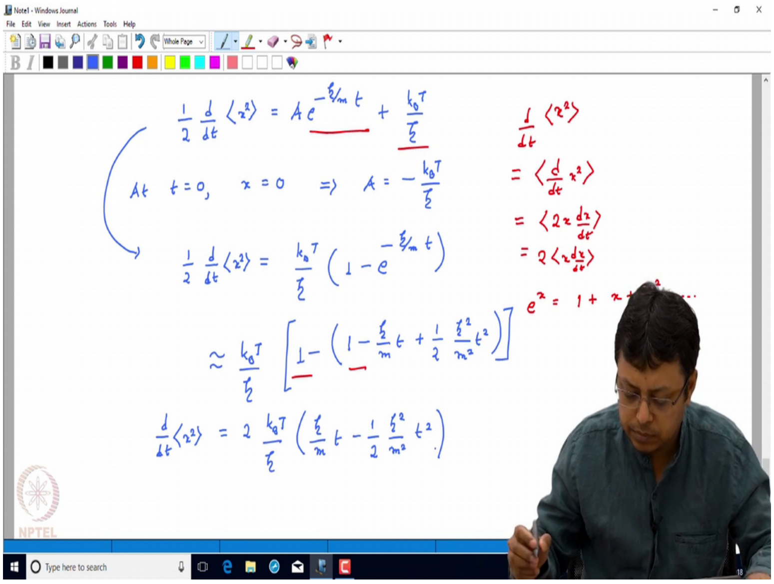

$$\frac{1}{2}\frac{d}{dt}\langle x^2\rangle = A e^{-\xi/m\, t} + \frac{k_B T}{\xi}$$

$$\text{At } t=0,\quad x=0 \Rightarrow A = -\frac{k_B T}{\xi}$$

$$\frac{1}{2}\frac{d}{dt}\langle x^2\rangle = \frac{k_B T}{\xi}\left(1 - e^{-\xi/m\, t}\right)$$

$$\approx \frac{k_B T}{\xi}\left[1 - \left(1 - \frac{\xi}{m}t + \frac{1}{2}\frac{\xi^2}{m^2}t^2\right)\right]$$

$$\frac{d}{dt}\langle x^2\rangle = 2\frac{k_B T}{\xi}\left(\frac{\xi}{m}t - \frac{1}{2}\frac{\xi^2}{m^2}t^2\right)$$

$$\frac{d}{dt}\langle x^2\rangle = \left\langle \frac{d}{dt}x^2\right\rangle = \left\langle 2x\frac{dx}{dt}\right\rangle = 2\left\langle x\frac{dx}{dt}\right\rangle$$

$$e^x = 1 + x + \ldots$$

Now, we can actually put back in your original equation. So, the left hand side becomes 0 and this becomes basically e to the power minus z time by t that becomes 1, so it is e to the power 0. And then what I will I get is nothing but I will get from here A is nothing but minus k B T by zeta. So, I can actually rewrite this equation now as half times d dt of x square average is nothing but I can take k B T by zeta common and I will have 1 from this term and there is A minus sign for A. So, it will be minus e to the power minus zeta by m into t.

Now, exponential terms I can further approximate like you know e to the power say x is 1 plus x plus x square by 2, that way I can actually expand it. And I can think that it is mass of the particle is if it is much heavier then actually I can truncate this series up to few terms. So, I am considering it up to the second order term which is the x square term. So, let us just write it so, I will have k B T by h 1 minus.

Now, the first term is 1 and then it is e to the power minus zeta n by t. So, we can actually take the take the variable itself to be minus zeta m by t. So, the next term will be nothing but x, and x is nothing but minus zeta m into t and then I have x squared by 2. So, I will have half x square is minus zeta m by m into t whole square so, the minus will be plus.

So, I will have basically zeta square, m square into t square, and I am basically truncating it so this is a basically an approximate value for this, and what I get here is after as I can see here this 1 actually. So, I had an 1 here, so this is 1 minus this thing So, let me actually rewrite it once again. So, I have 1 minus and this is the exponential series and I had k B T by zeta.

So, what I see is that this 1 will cancel with this 1. And then I have the second term it is basically minus zeta by m, but I also have a zeta here, so overall what I will get is as you can see here So, let me just rewrite it. So, I will write it as d dt of let me actually write it like this d dt of x square average is nothing but 2 times, I have k B T divided by zeta and inside I will have zeta over m into t and then I have minus and minus so this will be plus, and I have 1 minus and 1 plus this will be minus half and then I have zeta square divided by m square into t square. And then what you can do?