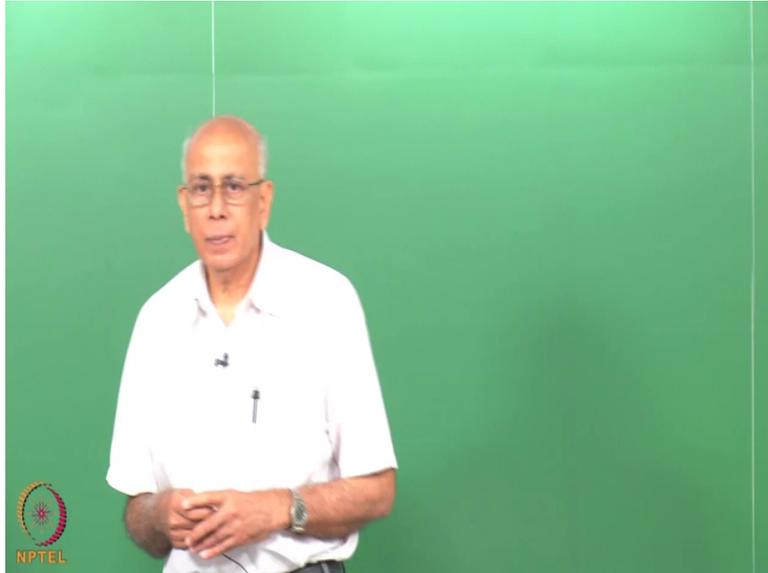


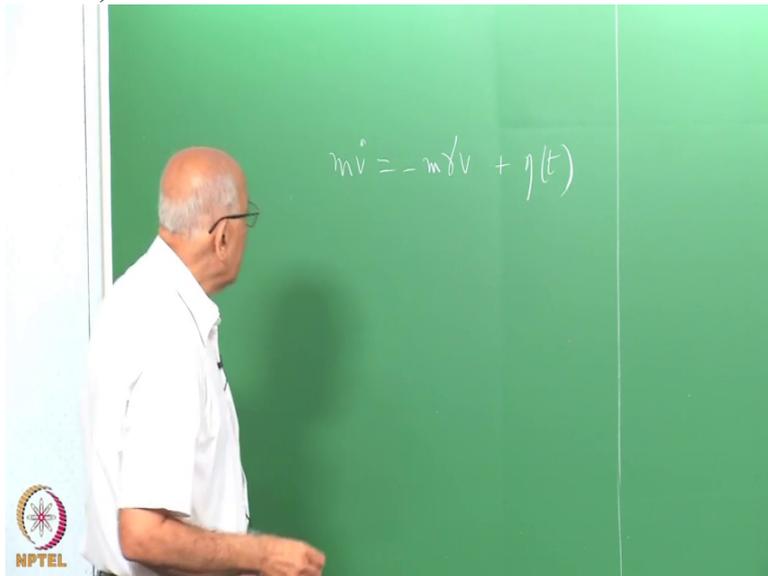
Nonequilibrium Statistical Mechanics
Professor V. Balakrishnan
Department of Physics
Indian Institute of Technology Madras
Lecture No 03
The Langevin model (Part 2)

(Refer Slide Time 00:17)



Right, so we had got to the stage last time where I had mentioned that if you took a more realistic equation of motion for the Brownian particle, namely the equation of motion $m \dot{v}$ equal to minus $m \gamma v$ plus $\eta(t)$ where this was noise,

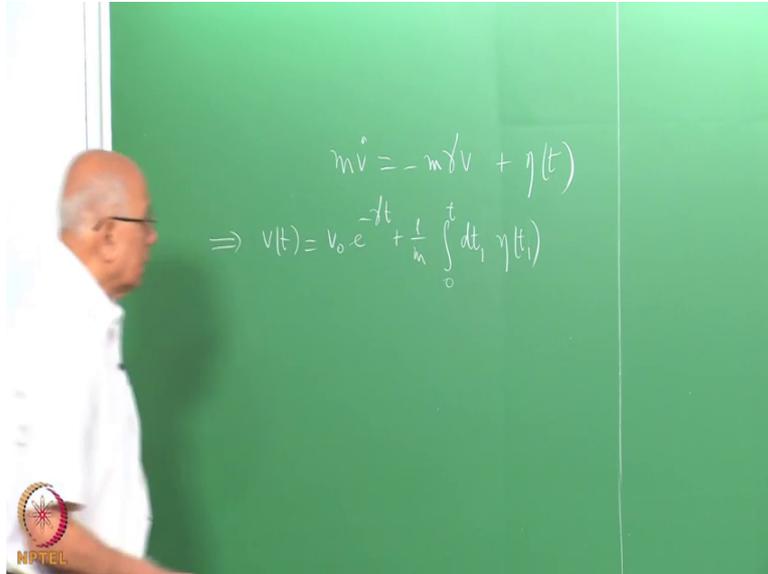
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then we might get a more physical result for the mean and the mean square which is as follows.

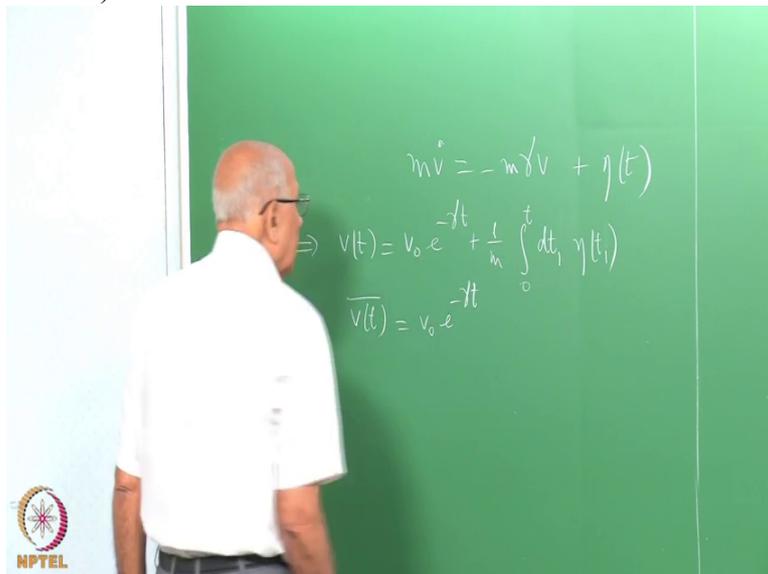
You solve this equation and this implies of course that v of t is v naught e to the minus γ t plus 1 over m and integral from zero to t $d t$ prime η of t prime. Or let's write it as t 1. So

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that's the formal solution to this first order differential equation with the initial condition that v of zero is v naught, some prescribed v naught and then we took the average. So v of t average was v naught e to the minus γ t which was very

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good because it says if you wait for long enough after the initial instant then the mean value does indeed, the conditional mean does indeed vanish as the equilibrium mean already, we know, vanishes. Ok.

The more important test was what happens to the mean square. So we computed v square of t and that was v naught squared e to the minus $2\gamma t$. Let's just compute the average value v square plus the cross term vanishes because the average of η is zero plus 1 over n square and integral from zero to t dt_1 zero to t dt_2 and then the average of η of t_1 , η of t_2 .

Now this quantity we assumed was delta correlated because the time scale on which its correlation decays

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$$m \dot{v} = -m\gamma v + \eta(t)$$

$$\Rightarrow v(t) = v_0 e^{-\gamma t} + \frac{1}{m} \int_0^t dt_1 \eta(t_1)$$

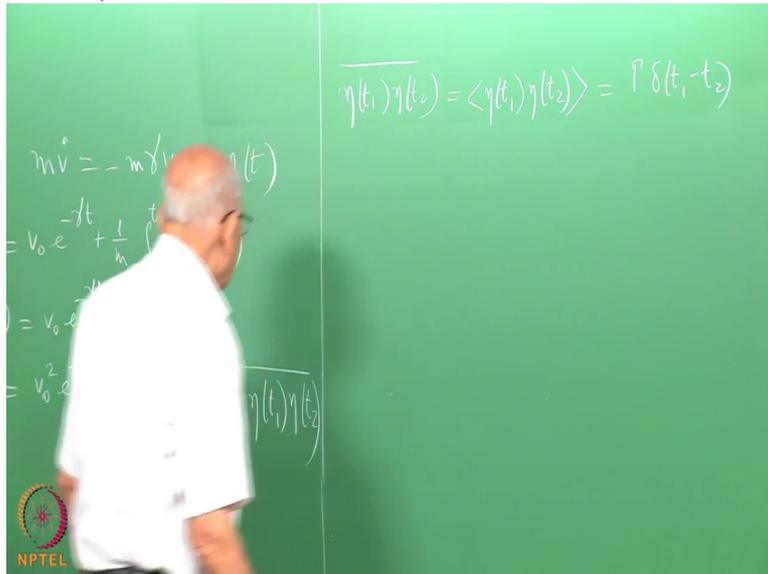
$$\overline{v(t)} = v_0 e^{-\gamma t}$$

$$\overline{v^2(t)} = v_0^2 e^{-2\gamma t} + \frac{1}{m^2} \int_0^t dt_1 \int_0^t dt_2 \overline{\eta(t_1)\eta(t_2)}$$

is much, much smaller than the time scale on which this object is moving. By the way there is a dissipation time scale already introduced into the problem by introducing the constant γ , γ inverse has the physical dimensions of time. So it is roughly representing, already we can see from the structure of the equation that its representing some kind of dissipative time scale, the time scale on which the motion of this particle relaxes. But we are going to make that concrete. So if I put in the fact that η of t_1 , η of t_2 average is same as the equilibrium average of this quantity and this is equal to some γ delta of t_1 minus t_2 .

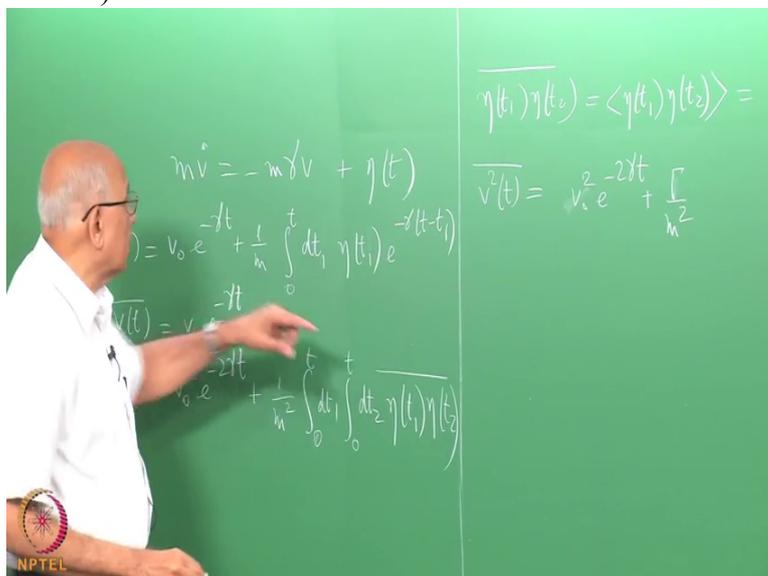
If I put that

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in here and do this integration, then you immediately see that v square of t is equal to v naught square e to the minus 2 gamma t plus 1 over gamma over m squared and then I do the delta function integration here and I just t 1, t 2 equal to t 2 except that, ah this is a wrong solution, this is e to the minus gamma t minus t 1. You have the integrating factor here

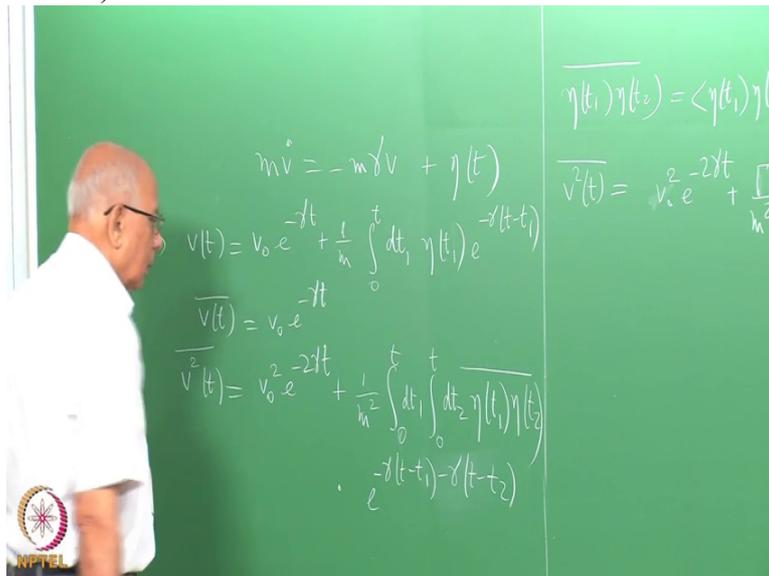
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because of the differential equation here.

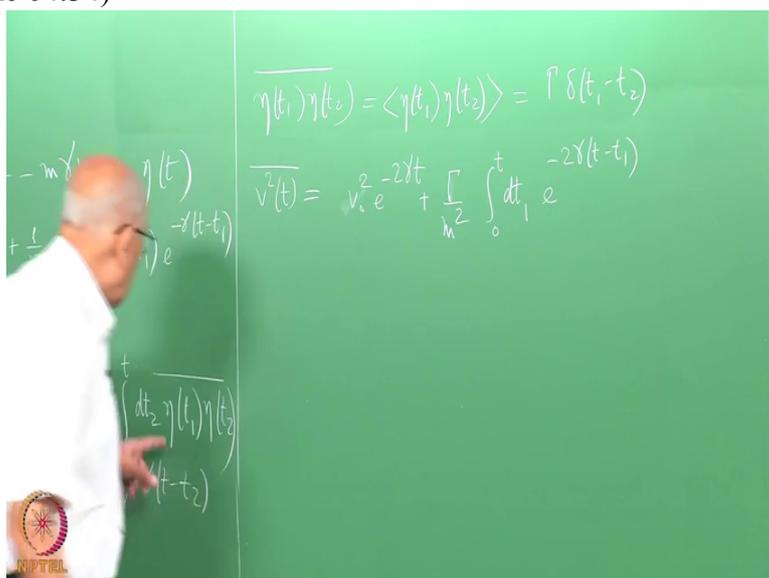
So that sits in here, time is e to the minus gamma. This multiplied by e to the minus gamma t minus t 1 minus gamma t minus t 2, that's sitting in here,

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Ok. So if I keep track of that this is gamma over m squared and integral from zero to t d t, d t 1 e to the minus 2 gamma t minus t 1 because the

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delta function fires and puts t 2 equal to t 1 and this factor gives you a factor 2 here, yeah

(Professor – student conversation starts)

Student: 0:04:44.1 Sir, what is the dissipation time...?

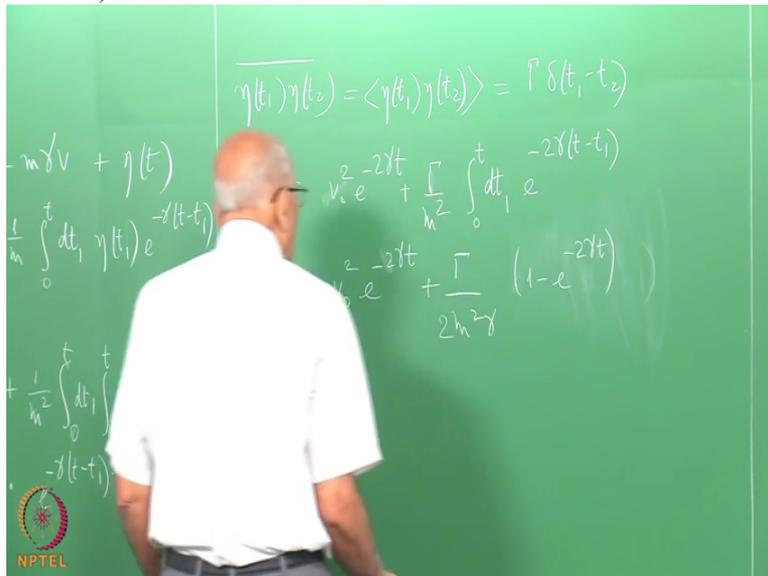
Professor: Yeah I have got to come back to it. So I am saying that the moment I put in a friction like this, a term like this here then we see this, this is d v over d t, so this immediately means that this gamma inverse has the physical dimensions of time. And this is a damped oscillator in the oscillator case if you did it for x, except here it is for v, here. You are already

familiar from the equation of motion for the damped Simple Harmonic oscillator that a first order term will represent some kind of dissipation. The coefficient here will represent some relaxation time.

(Professor – student conversation ends)

We are going to make that concrete here, Ok. So this is what the equation, the solution is out here and what we have to do is to do this integral so this is v naught squared e to the minus $2\gamma t$ plus γ over m square and there is a $2m$ squared γ because this factor comes down and then you have e to the minus $2\gamma t$ times e to the $2\gamma t$ minus 1 , 2γ right. And if I put this, take this factor in then it is 1 minus e to the minus $2\gamma t$. Or if

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I combine the t 0:06:13.7 here, this is equal to v naught square minus γ over $2m$ squared γ , little γ e to the minus $2\gamma t$ plus a constant. So that's the

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The image shows a green chalkboard with handwritten mathematical equations. A hand is visible on the left side, pointing towards the equations. The equations are as follows:

$$\overline{\eta(t_1)\eta(t_2)} = \langle \eta(t_1)\eta(t_2) \rangle = \int \delta(t_1 - t_2)$$

$$\overline{v^2(t)} = v_0^2 e^{-2\gamma t} + \frac{\Gamma}{m^2} \int_0^t dt_1 e^{-2\gamma(t-t_1)}$$

$$= v_0^2 e^{-2\gamma t} + \frac{\Gamma}{2m^2\gamma} (1 - e^{-2\gamma t})$$

$$= \left(v_0^2 - \frac{\Gamma}{2m^2\gamma} \right) e^{-2\gamma t} + \frac{\Gamma}{2m^2\gamma}$$

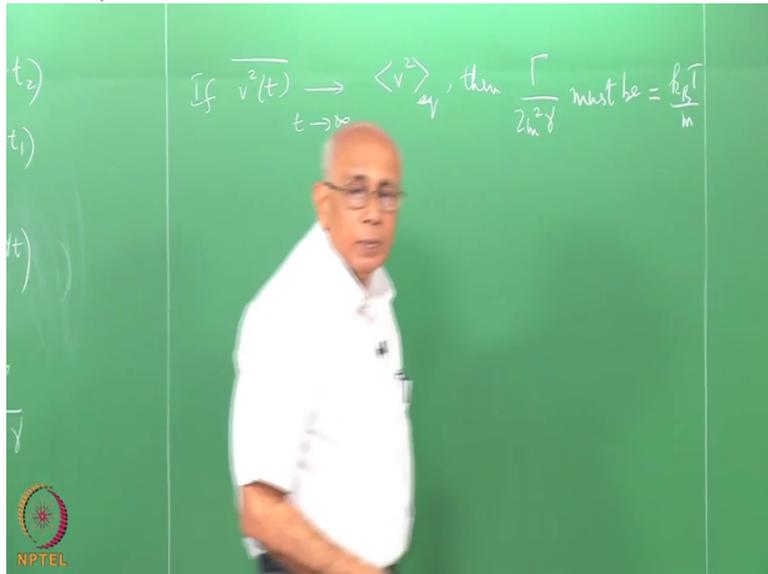
value of the conditional mean square of the velocity of this particle which starts out with the deterministic velocity v_0 at t equal to zero and this is what happens to the average velocity as t , for any arbitrary t greater than zero, Ok.

Now 2 things can be done. One of them is to say this particle, this Brownian particle which started off with some given fixed initial condition which I imposed on it, so what I did was to pick out that particle or that set of particles which had initial velocity v_0 and I am following the path of one of these particles, the subsequent history and I average over all such particles and this is the answer here.

Now one possibility is to say, if t becomes very large compared to zero, much, much larger than zero, t tends to infinity, then this term drops out and this goes to a constant. And the expectation would be it should go to that constant which is what the equilibrium of the mean square velocity is. So if you expect, if mean squared of t tends as t tends to infinity to v^2 in equilibrium, the whole thing is in equilibrium in any case here, then if you let t go to infinity, it is clear that this portion goes away and you get this answer here, right.

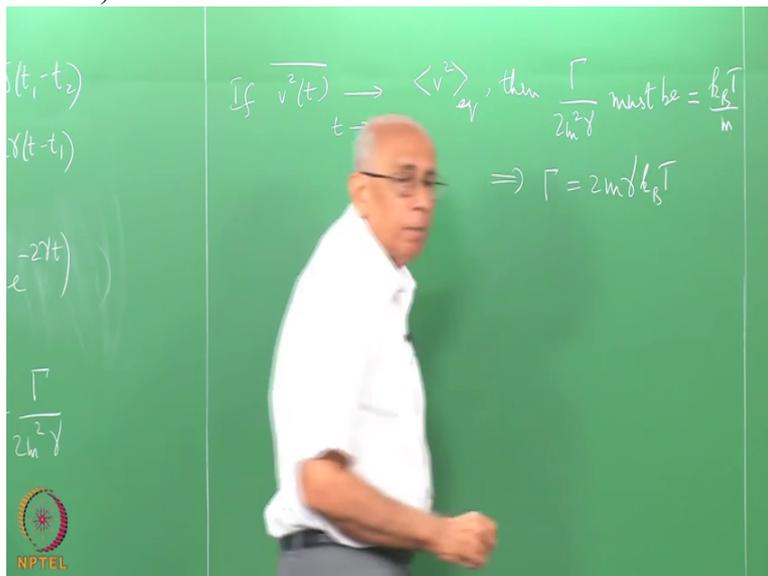
So this must be equal, this would imply, then $\frac{\Gamma}{2m^2\gamma}$ must be equal to the equilibrium value of this mean square value in one dimension which is $\frac{kT}{m}$, from the Maxwell distribution of velocities. So I would expect this must be equal to $\frac{kT}{m}$, Boltzmann T over m ,

(Refer Slide Time 08:39)



Ok which would imply that capital gamma is 2 m gamma k Boltzmann T.

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So it gives you a relation between capital gamma which is the strength of this white noise if you like, the delta correlated noise because we said this is some gamma times delta of t 1 minus t 2 on the one hand, so this eta is driving fluctuations into the velocity of this Brownian particle and this gamma measures the strength of these fluctuations in some sense, Ok.

That gets related to this constant gamma which represents the systematic part of the random force on this particle here. This part is also random because v is a random variable. And that systematic part has a constant m, gamma sitting here and the two are related to each other, Ok. And you can see for instance, that this v square of t is relaxing with this time constant

here. So it is related to gamma, the gamma inverse is related to the relaxation time of this average, to whatever value it attains in equilibrium.

So there is a relation between the fluctuations on the one hand and the relaxation on the other hand, or the dissipation. And this is called as the fluctuation dissipation relationship.

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$$\text{If } \overline{v^2(t)} \xrightarrow{t \rightarrow \infty} \langle v^2 \rangle_{eq}, \text{ then } \frac{\Gamma}{2m^2\gamma} \text{ must be } = \frac{k_B T}{m}$$
$$\Rightarrow \Gamma = 2m\gamma k_B T$$

It is the simplest of the fluctuation dissipation relationships. We will come across several more. It is sometimes called the fluctuation dissipation theorem but we will see in what sense this is, yes

(Professor – student conversation starts)

Student: Sir when you are assuming that your 0:10:21.8 average on the left hand side, the v square of t is tending towards the full average, the right hand side, you are assuming kind of 0:10:29.5

Professor: I am assuming that the system remains in equilibrium, yes definitely. I am assuming that the system remains in equilibrium and there is an unique equilibrium state which is what I started with. And I haven't done anything to the system. I haven't perturbed it in any way. It is just a beaker containing some colloidal particles, beaker of water and there, so whole thing is in thermal equilibrium. It is just that I started by looking at a sub ensemble of particles with some given initial velocity v_{naught} and I am asking what is the history of these guys as time goes on. And since the system remains in equilibrium throughout, this conditional average must tend to the equilibrium average.

(Professor – student conversation ends)

But if you don't like that argument, there is even better argument which is let's average this fellow over v naught. So let's find, so that's the alternative. Or let's take v squared of t and find this quantity which by definition is equal to the integral over rho equilibrium of v naught v squared of t , conditional average $d v$ naught from minus infinity to infinity; by definition.

Now

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$$\text{If } \overline{v^2(t)} \xrightarrow{t \rightarrow \infty} \langle v^2 \rangle_{eq}, \text{ then } \frac{\Gamma}{2m\gamma} \text{ must be } = \frac{k_B T}{m}$$
$$\text{OR } \Rightarrow \Gamma = 2m\gamma k_B T$$
$$\langle v^2(t) \rangle = \int_{-\infty}^{\infty} \rho_{eq}(v_0) \overline{v^2(t)} dv_0$$

I go from conditional average to the full average. So I complete the procedure by integrating over all possible initial conditions v naught, remember this is a function of v naught here. So all I have to do is to take this fellow and use the Maxwellian distribution of velocities for v naught and average, and do the average here. So this will then give you automatically, there is a v naught sitting here and that gets averaged and the answer is $k T$ over m . So this is equal to k Boltzmann T over m minus γ over $2 m$ squared γ e to the minus 2γ T plus γ over $2 m$ square γ .

(Refer Slide Time 12:37)

$$\Rightarrow \Gamma = 2m\gamma k_B T$$

$$\langle \overline{v^2(t)} \rangle = \int_{-\infty}^{\infty} p_{eq}(v_0) \overline{v^2(t)} dv_0$$

$$= \left(\frac{k_B T}{m} - \frac{\Gamma}{2m^2 \gamma} \right) e^{-2\gamma t} + \frac{\Gamma}{2m^2 \gamma}$$

But this cannot depend on time, because the system is in equilibrium. You have done the full average. It has to be the Maxwellian distribution once again. So you are compelled to say that this must be equal to $k_B T / m$. There is no choice.

(Refer Slide Time 12:56)

$$\langle \overline{v^2(t)} \rangle = \int_{-\infty}^{\infty} p_{eq}(v_0) \overline{v^2(t)} dv_0$$

$$= \left(\frac{k_B T}{m} - \frac{\Gamma}{2m^2 \gamma} \right) e^{-2\gamma t} + \frac{\Gamma}{2m^2 \gamma}$$

$$= \frac{k_B T}{m}$$

There is only one way in which that can happen, in which this time dependence vanishes and this becomes $k_B T / m$ and that is if this condition is satisfied. So you have no choice.

Consistency demands, the only consistent solution is that the capital gamma, the constant capital gamma is related to the little gamma by this relationship. There is no alternative, Ok, that the noise is thermal, yes absolutely. We are looking at the problem where the noise is entirely thermal fluctuations, yeah, no other external source, experimental error, none of

those things. We are just looking at a system in which the temperature, the fact that the system is at finite temperature is what is driving fluctuations into the system, absolutely. No quantum fluctuations for example here at all.

We will, at some stage if time permits, talk about the quantum Langevin equation and see what happens there but this is at this very elementary level of just thermal fluctuations. Mind you, we haven't addressed anything which is truly non-equilibrium because we are still talking about a system in thermal equilibrium but we are asking some time dependent questions of this system here.

(Professor – student conversation starts)

Student: But in a sense, the conditional average is still answering one time, simple time independent. If you make a measurement at some instant of time...

Professor: Yes

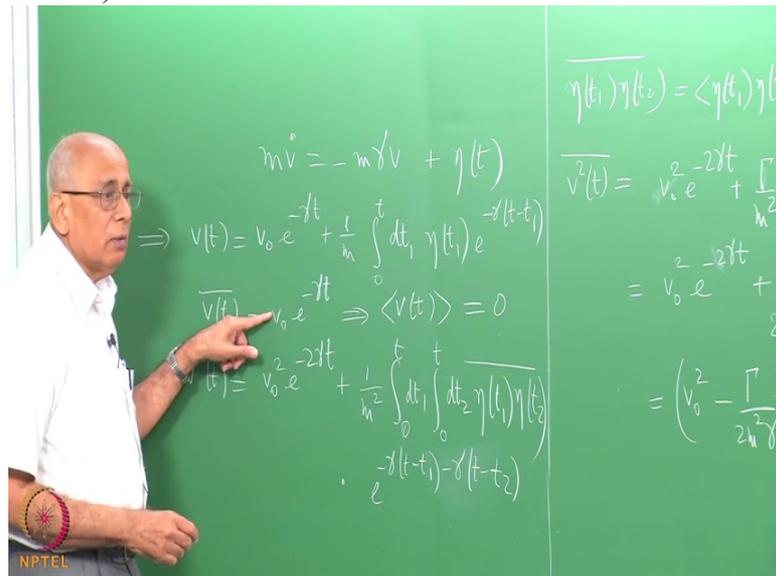
Student: of that particle, how that is going to...

Professor: How is it going to reach the equilibrium case? You get hold of one particle. It is moving with velocity v_{naught} . That of course is drawn from the Maxwellian distribution, some number v_{naught} but now I follow that particle and ask what happens to it, this velocity of this particle as time goes on. Well it merges into the distribution and the way it does it is by this, relaxes in this fashion, Ok.

(Professor – student conversation ends)

So now this is completely consistent. What we found is that this will automatically imply that v of t ; full average is equal to zero because I average over the Maxwellian in v_{naught} .

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By symmetry this vanishes. This is an odd function and the mean square comes out to be the right answer here provided this consistency condition is met.

Now what we are saying is, I take one particular particle, any particle, they are all equivalent to each other. I take one of these particles and I discover that its velocity initially is some number v naught. I make this measurement. And then I ask what happens to this as I follow it and so on. Well it gets hit by the other particles etc etc and if I take an ensemble average over all these objects and wait long enough, you are going to get the equilibrium values for the average. So this is all I am saying. Or better still, I do a second average over the initial conditions and I get the same equilibrium average. That's the meaning of an equilibrium average in any case, right?

So this is now, as you can see, you can appreciate now the fact that this is the consistency condition. Otherwise you run into inconsistencies. Earlier we ran into a very bad inconsistency which said that mean square value of the velocity is spontaneously increased linearly with time. We fixed that problem by saying, no, no there must be some kind of damping term here, systematic portion which on physical argument to say there must be a term of this kind.

But the moment you put in the term of this kind, that problem that this runs away as a function of time doesn't happen anymore. It tends to a constant but then what constant can it tend to? Consistency demands that it tend to the equilibrium constant, right. So I would like

to say this is a very important relationship. It is a consistency condition and it is called the fluctuation dissipation. We will come across many of these

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$$\langle v^2(t) \rangle = \int_{-\infty}^{\infty} P_{eq}(v_0) v^2(t) dv_0 = \left(\frac{k_B T}{m} - \frac{\Gamma}{2m^2\gamma} \right) e^{-2\gamma t} + \frac{\Gamma}{2m^2\gamma} = \frac{k_B T}{m}$$

$\Rightarrow \boxed{\Gamma = 2m\gamma k_B T}$
consistency condition
(Fluctuation-dissipation relation)

such relationships, yeah.

(Professor – student conversation starts)

Student: Why is the noise, the strength of the noise should depend on the mass of the particle? 0:17:20.3

Professor: The strength of the noise, as in acts on this particle. It is not some absolute...

Student: I think instead of the definition gamma you could have eliminated the definition

Professor: You could have, in principle, done that. But that's a good, nice question. Why should, its, why should the strength of this noise depend on the particular particle? If I change that particle, I get another value of this strength of this noise. Good question, but it is not, strength of noise on what; strength of what noise?

Student: Thermal noise of the particle 0:18:05.7

Professor: Ok, strength of the noise on that particle, right. So it is not surprising that it has some dependence on that particle. I change the mass of the particle, I get a different strength. Of course because this is the strength of, the effective noise due all the other molecules as it acts on that large particle. So there must be some dependency on that particle and there is, in this case. But we will see, some similar magic is going to happen very soon when we talk about the diffusion coefficient.

Student: Can't they rescale and if 0:18:39.9 we go back to the original equation....

Professor: Right

Student: And divide everything by n and then you define $\tilde{\eta}$ which has no 0:18:47.1.

Professor: Yeah, in principle you could do that.

Student: In that there will be, in that relation there would be...0:18:49.0

Professor: Yeah, in that case there will be. But like in the question, it is essentially the same thing. It is finally the same. The physical answer is simply that this is the force as it acts on that particular particle, right? Ok. But having done this, now let us go on and ask, what happens to the velocity correlation time? That is crucial. So let's see.

(Professor – student conversation ends)

At the level of the mean square we are all happy but let's see what happens if we did this? I want to now compute, I would like to now compute what is the average value of v of t , v of t prime where t prime is not the same as t in general and let's find the average value of this quantity here. Eventually I want to take the full average but let us find the average value of the conditional average first.

This is v naught square e to the minus γt plus t prime, that's the first term, the cross term vanishes as before but then plus γ over m square integral zero to t $d t$ 1 zero to t , $d t$ 2, t to the minus γ times t minus t 1 minus γ times t minus t 2, t prime minus t 2, well it is a t prime here and then a delta function of t 1 minus t 2.

But this time I can't close my eyes and write t 2 equal to t 1 inside the integration because the limits of integration over these 2, this is t prime, the limits of integration are different for the 2 integrals,

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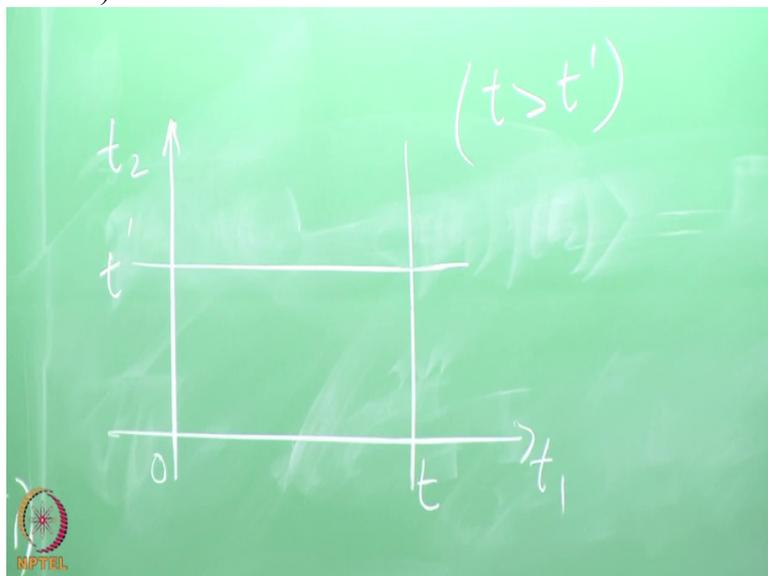
$$m\dot{v} = -m\gamma v + \eta(t)$$

$$\Rightarrow v(t) = v_0 e^{-\gamma t} + \frac{1}{m} \int_0^t dt_1 \eta(t_1) e^{-\gamma(t-t_1)}$$

$$v(t)v(t') = v_0^2 e^{-\gamma(t+t')} + \frac{1}{m^2} \int_0^t dt_1 \int_0^{t'} dt_2 e^{-\gamma(t-t_1)-\gamma(t'-t_2)} \delta(t_1-t_2)$$

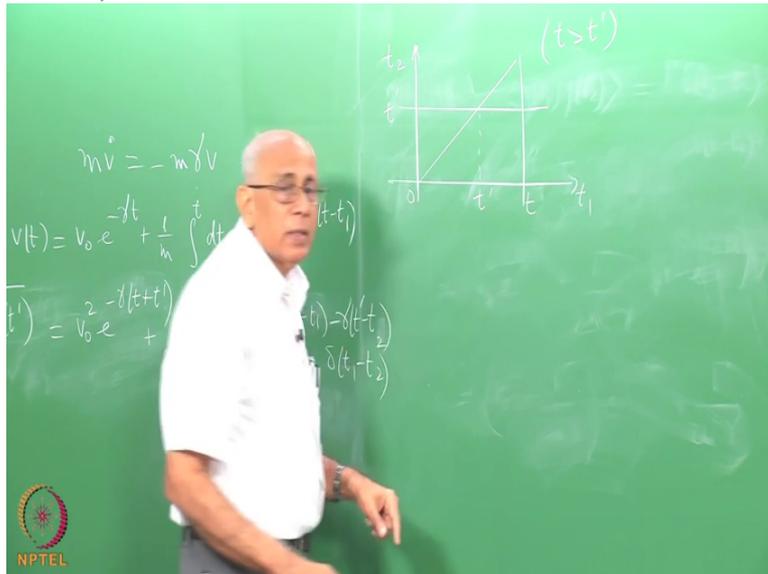
right? So if we draw a little picture, here is t_1 and here is t_2 . I am integrating t_1 up to the point t but t_2 only up to the point t' in the case when t is greater than t' . If t is less than t' the rectangle height is greater than the width.

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So without loss of generality let's take t' to be less than t , the other case is trivial by interchanging t and t' in the answer. And what's the delta function constraint? It says t_1 is equal to t_2 which is a 45 degree line, in this fashion. So as you integrate, for a fixed value of t_1 , as you integrate t_2 , the delta function fires as long as t_1 is, as long as t_1 is restricted to

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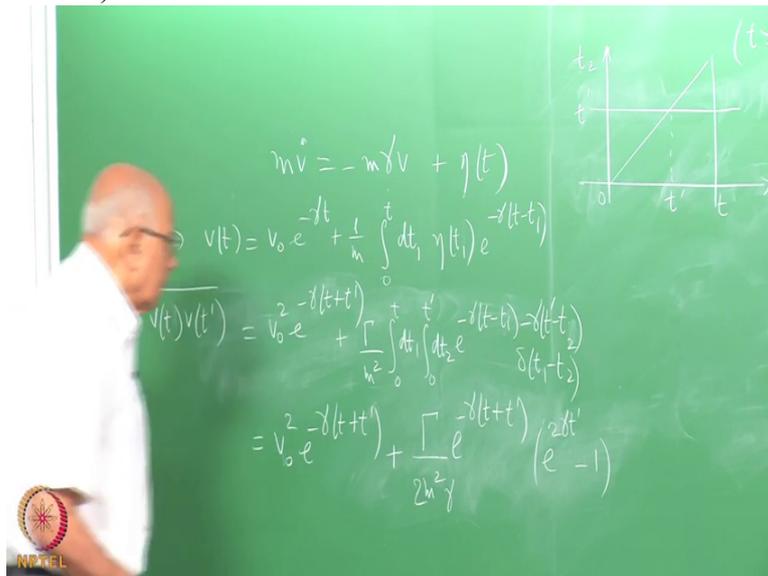
the range zero to t prime. The moment it goes outside, there is nothing to integrate.

The delta function doesn't fire because t prime, t_2 is cut off at t prime, Ok. So this means that you can replace t_2 by t_1 but the t_1 integration is now restricted to the range 0 to t prime, the lesser of the two, right. So this is immediately equal to v naught square e to the minus γ t plus t prime plus γ over m square integral zero to t prime, smaller of the two and then this goes through.

So this is e to the minus γ t plus, let's take that out of the integral, e to the minus γ t plus t prime and integral zero to t prime $d t_1 e$ to the power γ t_1 γ t_1 , 2γ t_1 . I do the integration again, $2 m$ square γ comes down and then it is e to the 2γ t prime minus 1. That's the integration, right.

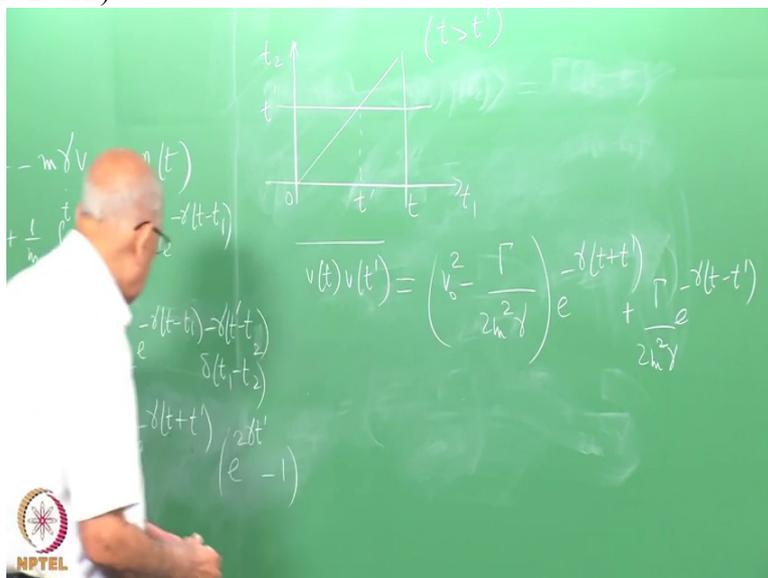
So

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as you can see the first term is going to be e to the minus gamma t and then e to the plus, plus t prime because there is a plus twice here. And the second term is going to be e to the minus just this fellow here, same thing. So therefore v of t, v of t prime average is equal to v naught square minus, take this guy here, by the way, Ok let's write it in two steps, gamma over 2 m square gamma, e to the minus gamma t plus t prime, that takes care of the second term and the first term is plus gamma over 2 m square gamma e to the minus gamma t minus t prime,

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that is this portion out here.

But we already know capital gamma over 2 m square gamma must be equal be to k T over m. That was our consistency condition. So we have to put that in and if you do that, this

immediately gives you $v_{\text{naught}}^2 - \frac{k_B T}{m} e^{-\gamma t} + \frac{k_B T}{m} e^{-\gamma t'}$,

(Refer Slide Time 24:49)

The image shows a green chalkboard with handwritten mathematical equations. The top equation is:

$$v(t)v(t') = \left(\frac{2}{v_0 - \frac{\gamma}{m}} \right) e^{-\gamma(t+t')} + \frac{\gamma}{2m\gamma} e^{-\gamma(t-t')}$$

The bottom equation is:

$$= \left(\frac{2}{v_0 - \frac{k_B T}{m}} \right) e^{-\gamma(t+t')} + \frac{k_B T}{m} e^{-\gamma(t-t')}$$

There is an NPTEL logo in the bottom left corner of the chalkboard image.

Ok.

Now what do you expect? Once again if I argue that I let t become infinite, t' become infinite such that the difference $t - t'$ is finite, any finite value this term goes away and that survives. On the other hand, if I do an average of the initial value of the velocity, average over v_{naught}^2 , then the average of v_{naught}^2 is in fact $\frac{k_B T}{m}$, and this cancels. And there is nothing to average there because v_{naught} , this term is independent of v_{naught} here.

So whichever way we look at it, it gives you an answer for the correlation time. So now we immediately follow v of t , v of t' is equal to, this therefore is equal to $\frac{k_B T}{m} e^{-\gamma t}$ and we did this for $t > t'$. Had we done this for $t < t'$, t and t' would just have been interchanged so this is simply replaced by the modulus, Ok which is a very important result.

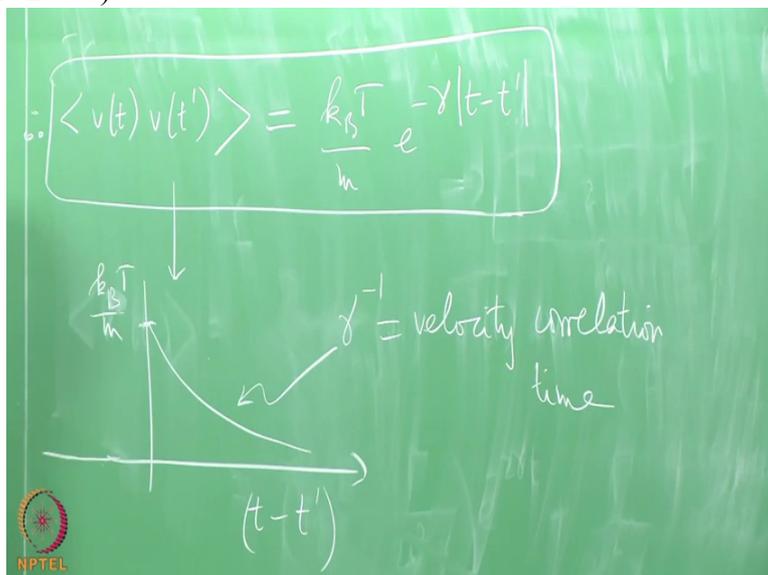
So now we understand finally what I meant by the relaxation time.

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A green chalkboard with a white rectangular box containing the equation $\langle v(t)v(t') \rangle = \frac{k_B T}{m} e^{-\gamma|t-t'|}$. The NPTEL logo is visible in the bottom left corner.

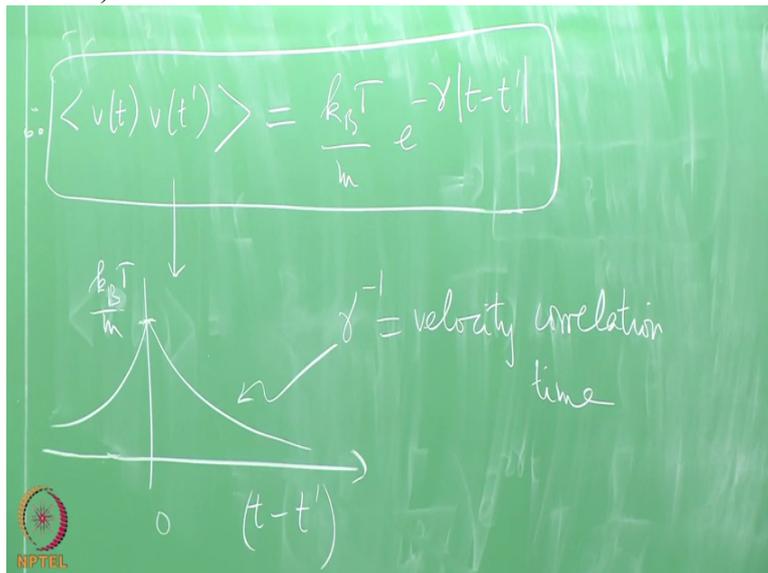
It says the velocity correlation time is gamma inverse. Because it relaxes to zero, this thing becomes zero if t minus t prime tends to infinity, it gets de-correlated starting from if t equal to t prime, you set this equal to zero. e to the zero is 1; it is k T over m which is what you expect. So this quantity here as a function of t minus t prime has this following behavior. It starts at this k T over m which is the mean square value and it decays exponentially to zero with a characteristic time scale gamma inverse,

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Ok. Of course since we have a modulus here, we can also ask what happens for t minus t prime less than zero and it does tell this. It is a symmetric

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function, right?

Well that's a very important result. It is saying something very crucial about this velocity process which we haven't talked about yet, about its distribution. We will discover later that this velocity process under the assumption that this η of t is a Gaussian white noise namely a noise which has got equal power in all frequencies, delta correlated Gaussian Markov process stationary etc then under those conditions this equation actually implies that the driven process v , the velocity process remains Gaussian in nature. It is Markov, it continues to be Markov, it is stationary, but it is not delta-correlated, it is exponentially correlated.

So the driving noise is delta correlated. It is no correlation at unequal times. It just, correlation function vanishes. But the driven process is much slower than that in the sense that it retains of some memory of where it was by this formula here which tells you exactly how it de-correlates as time increases, Ok. That's a crucial lesson. We will see that this v is, satisfies, its probability distribution satisfies that of Ornstein-Uhlenbeck process but it is the very, very paradigm of a Gaussian stationary Markov process, Ok.

(Professor – student conversation starts)

Professor: Pardon me?

Student: Markov ... 0:29:26.0

Professor: I have not said any of those things yet. I am just using those words. I haven't established any of those things yet but we will do so, Ok. In fact the only Gaussian stationary

Markov process that is exponentially correlated is called the Ornstein-Uhlenbeck process. There is no other such process at all. So it's sort of fundamental process, random process. It is kind of continuous process.

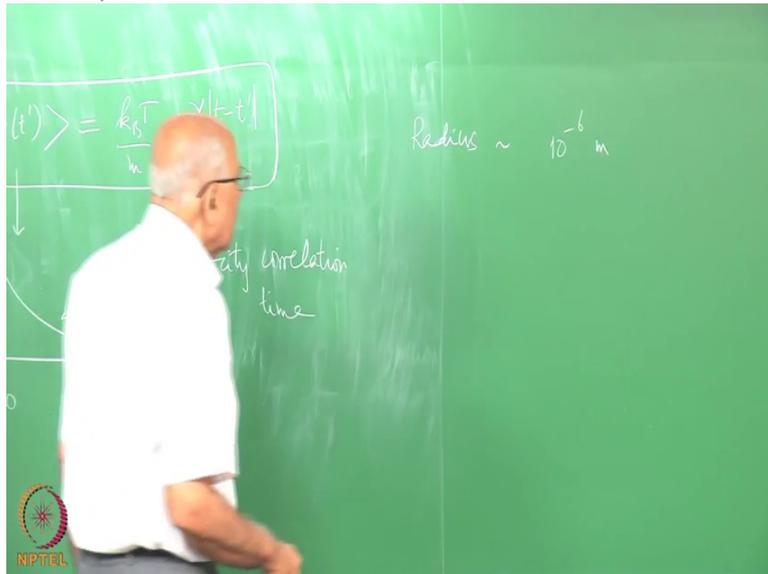
(Professor – student conversation ends)

Yeah you should also add that. It's the way it is the continuous process because this is continuous, noise and not a jump process. So the only continuous, stationary, Gaussian Markov process which is exponentially correlated is Ornstein-Uhlenbeck process, Ok. So we have some powerful results here. Let us put in some numbers and see whether this whole thing makes any sense or not, Ok.

Now I said that these particles are much bigger than the molecules themselves, Ok. So let's assume they are spherical particles, the simplest assumption. They are like pollen grains or rather the original experiments were done on Brownian motion where Robert Brown 1827 or something like that, and he actually used crushed pollen grains. So if you take pollen grains and you crush it to fine powder, then you get micron sized particles of some kind and then they float around in water, they do a jiggle dance called Brownian motion and they are described by this model very adequately.

Let's see that makes any sense, what the time scale this γ is going to be turn out to be like. Well, if you put this in water and let's assume that the radius of the particle is of the order of the micron, so 10^{-6} meters

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and let's assume that its mass is the same density as water, so we can compute water's masses. Water has a density of 10 to the 3 kilograms per meter cube. I find these Standard International units rather inconvenient to use for such small objects but anyway, so the mass of this particle is of the order of 10 to the 3 kilograms per meter cube so that's the density multiplied by the volume which is a cubed, so times 10 to the minus 18, is of the order of 10 to the minus 12 kilograms.

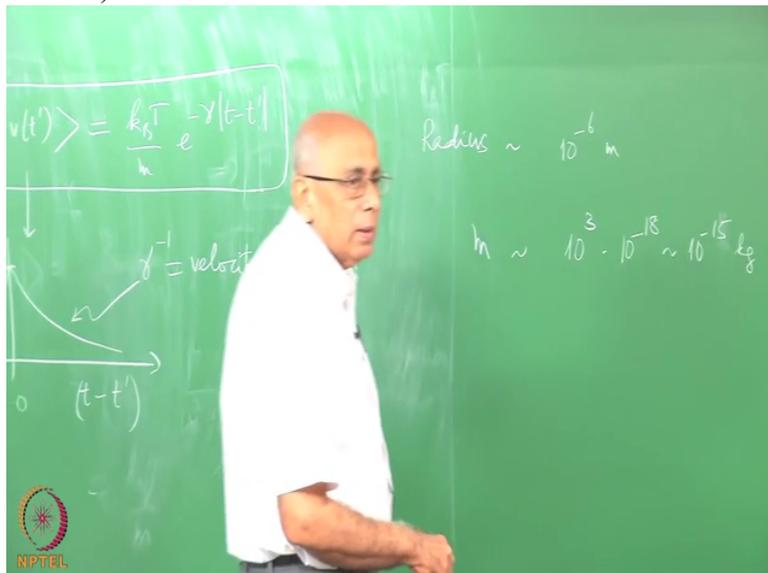
Actually it is even smaller.

(Professor – student conversation starts)

Student: Minus 15

Professor: 10 to the power minus 15, yeah which is Ok, reasonable

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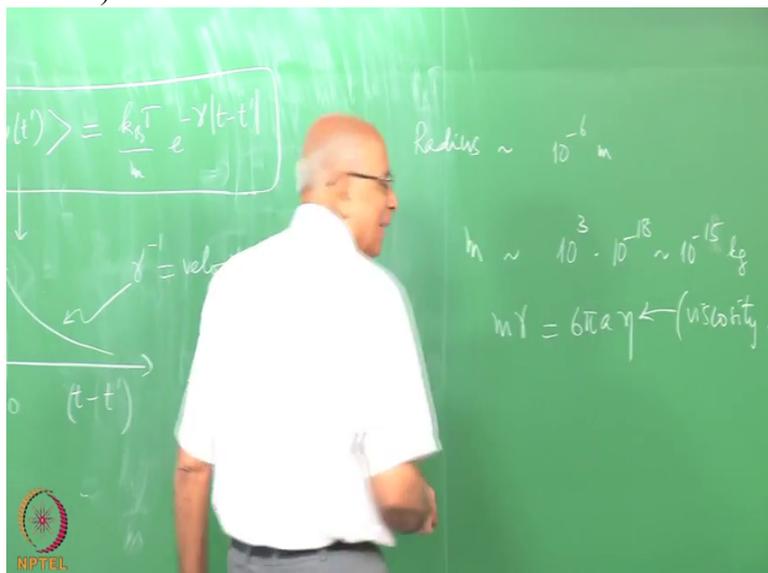


thing, Ok. Now we need to find out what this gamma is, right. Since these are particles which are suspended in water and they are floating around, we said the effect of gravity is essentially nullified by the viscosity; they are at terminal velocity in that sense. So we have Stoke's formula for the terminal velocity of a spherical particle dropping under gravity and whose gravity, the force of gravity is exactly balanced by the viscous drag. So what's that formula?

Student: $6\pi a \eta$... 0:32:50.5

Professor: Yeah, so it says $m \gamma$ is equal to $6\pi a \eta$, by the way this is viscosity. It is not that η , Ok,

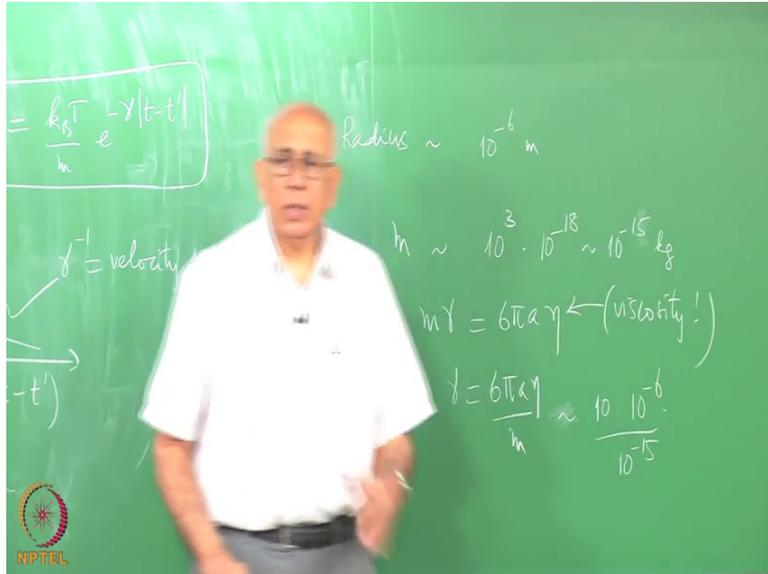
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sorry for this notation. It is not this noise here, it is the viscosity of water, the dynamic viscosity, not the kinematic viscosity which is this divided by the density, Ok. So that tells

you that gamma equal to 6 pi a eta over n which is equal to, which is of the order of 6 pi is of the order of 10, and then a which is 10 to the minus 6, 10 to the minus 6, divided by 10 to the minus 15, right and then eta, what is the viscosity

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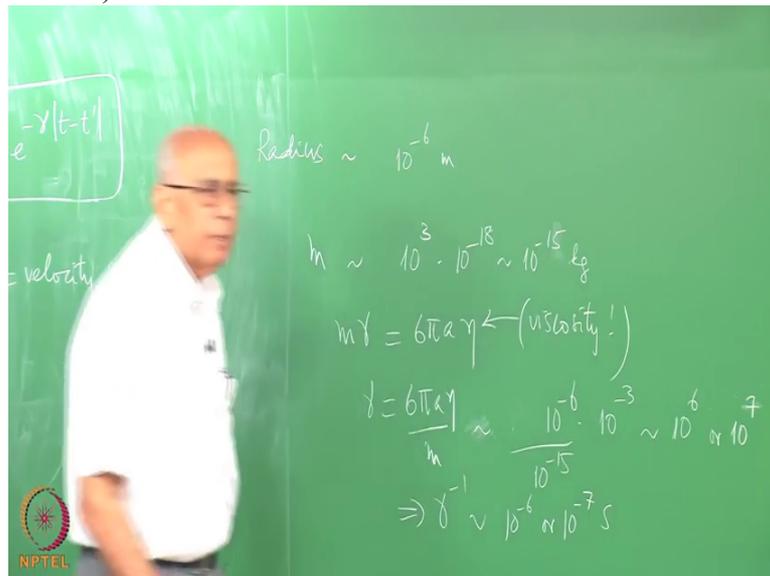


of water like?

(Professor – student conversation ends)

Newton's law of viscosity, what one normally uses, and viscosity is measured in, the C G S unit is poise but this Standard International unit is pascal second, newton second per meter square, Ok. And for water at room temperature it is easy to remember, at 20 degree Celsius or something, gamma is of the order of 10 to the minus 6 or 10 to the minus 7 seconds,

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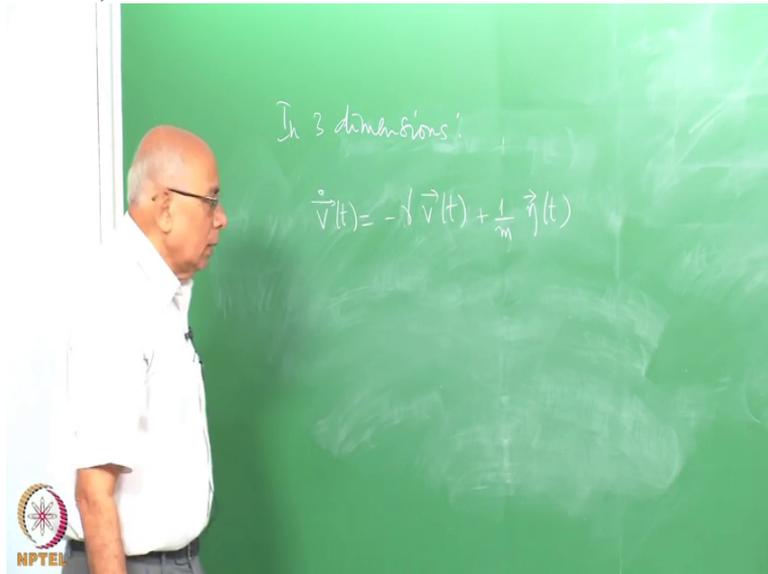
microsecond.

So you see we started out with something which had motion on the order of picoseconds, the molecules themselves, the atoms and all of a sudden out has come this time scale which is much, much larger and it is of the order of microseconds. So that is the time scale on which these Brownian motion's particles velocity, memory of the velocity will be lost. Many orders of magnitude greater than the molecular motion time scales, Ok.

So that's one of the reason why I said, this theory does not apply to individual molecules themselves. There are several reasons why that fails at that level starting with correlated motion but this is now in the right ballpark, at least in the right ballpark, Ok.

So what next? We could ask we did it this one dimension, what happens in three dimensions, that is something we can straightaway take care of, so let's do that. So in 3 D, what we need to do is to write $\mathbf{v} \cdot \mathbf{t} = -\gamma \mathbf{v} + \frac{1}{m} \boldsymbol{\eta}(t)$, vector of t .

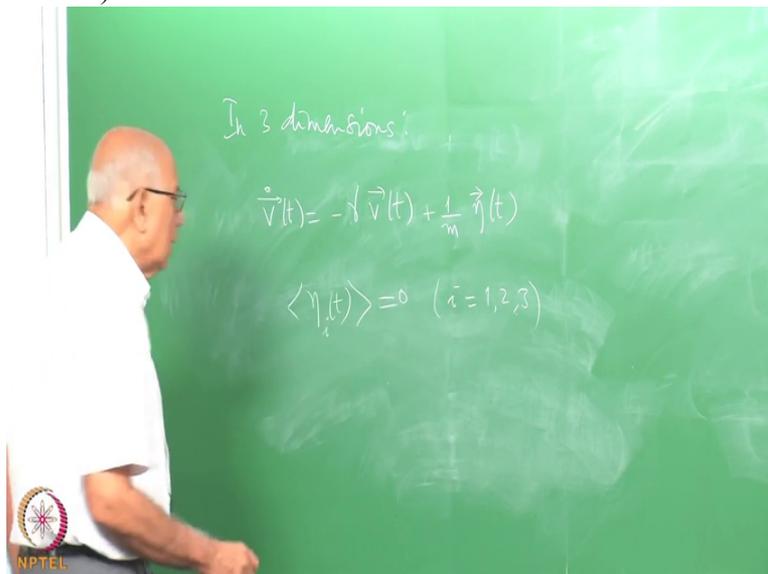
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Now all we need to ask is what are the statistical properties of this vector noise here.

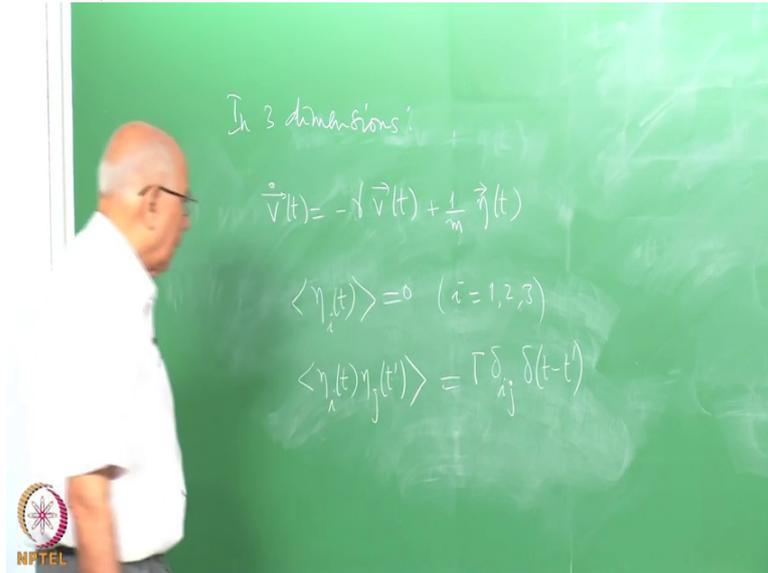
Well we resolve it into Cartesian components. The fluid is a homogenous fluid, isotropic fluid in all directions. So it is very reasonable that each Cartesian component satisfies exactly the same equation with the different noise but essentially the same statistical properties, right? So now what you would do is to again assume that η_i of t average equal to zero, i equal to 1, 2 or 3 for the Cartesian components

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and η_i of t , η_j of t' , the correlation between these two fellows equal to γ times δ of t minus t' but the different Cartesian components are completely uncorrelated with each other, so all you need to do is to put a δ_{ij} ,

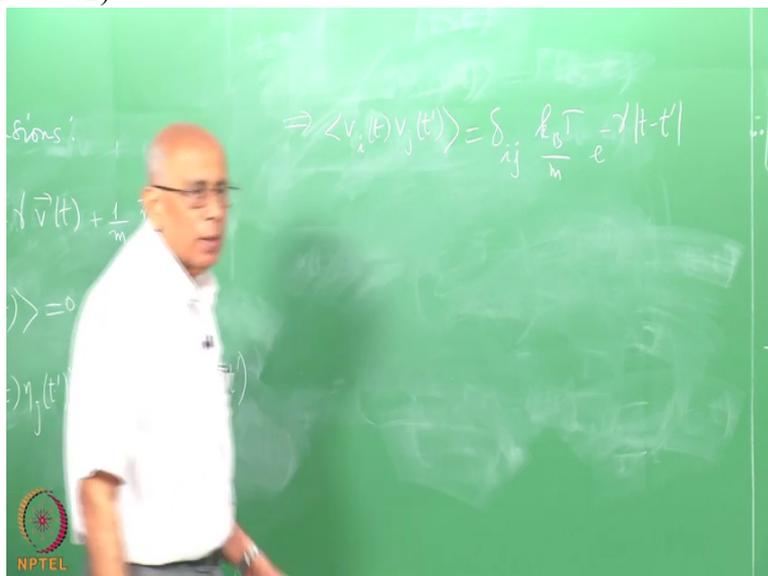
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achronic delta.

And you go through exactly the same thing as before, you will get precisely the same results. Nothing will change. What will happen to the velocity correlation time? Well now I have to write v_i , v_j and there is going to be δ_{ij} sitting out there. So this will imply that v_i of t , v_j of t' equal to $\delta_{ij} k_B T$ over m into minus γ $t - t'$, that's all it that's going to happen.

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If the different Cartesian coordinates were correlated with each other for some reason, then this would no longer be true at all. They are completely independent, so. Mind you, we are talking about Cartesian components, Ok. If I were talking about more complicated objects

like what's happening, what's the kind of stochastic equations satisfied by the magnitude of the velocity or the speed; that is a more difficult problem. We will say little bit of it when we, about it, when we come to Brownian motion but this is what this thing does. Or if you like, write it in simpler language, $\langle v_i(t) v_j(t') \rangle = \delta_{ij} \frac{k_B T}{m} e^{-\gamma |t-t'|}$

(Professor – student conversation starts)

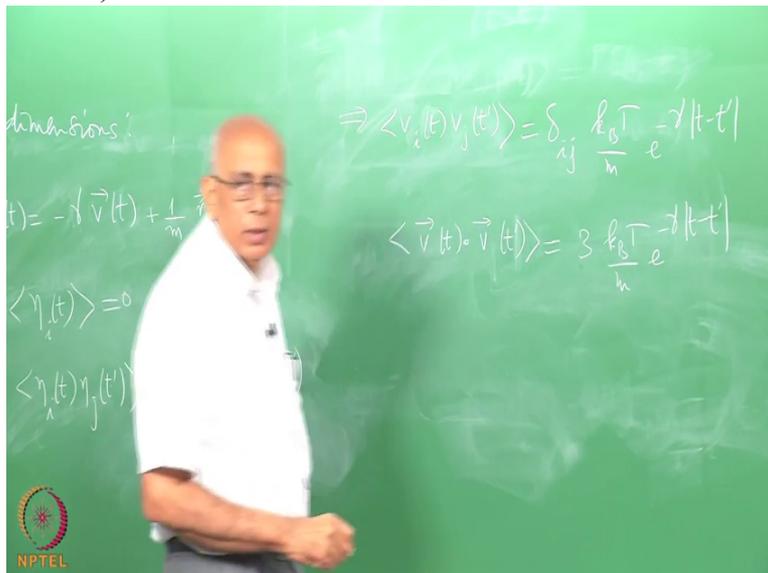
Student: Times

Professor: times what?

Student: 3... 0:38:40.0

Professor: Times we have to take the trace of this tensor, so it is in

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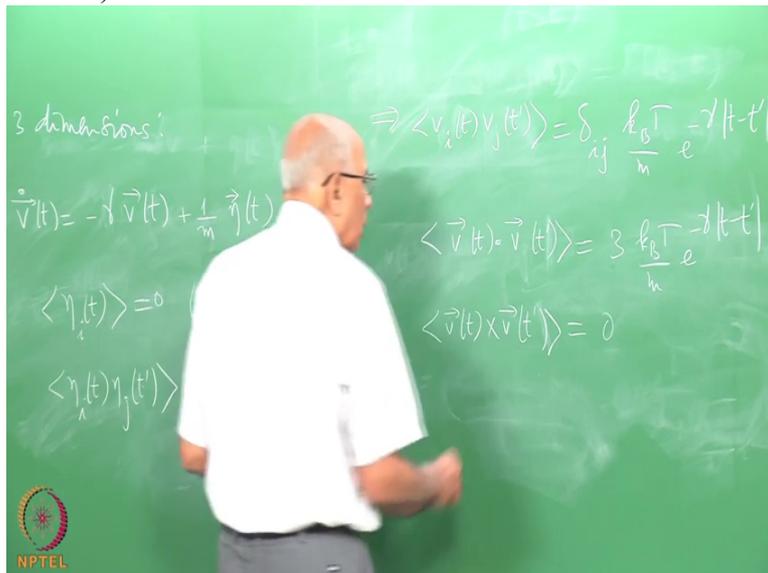


times 3. And what is this equal to?

Student: It is equal to zero 0:38:57.8

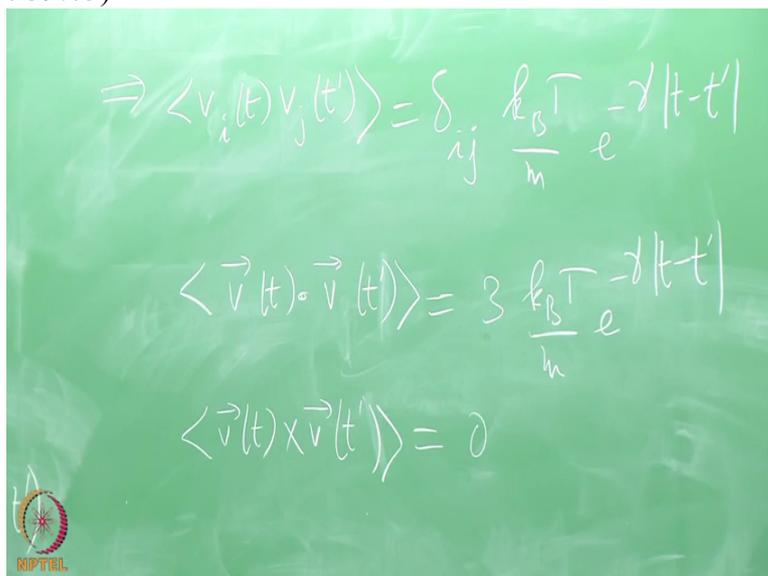
Professor: Equal to zero, unequal components are

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uncorrelated, right?

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Can you think of a situation where the different velocity components get correlated, I mean that has to show up here itself, something that says the acceleration in the direction 1 is related to the velocity in direction 2.

Student: Magnetic ... 0:39:21.3

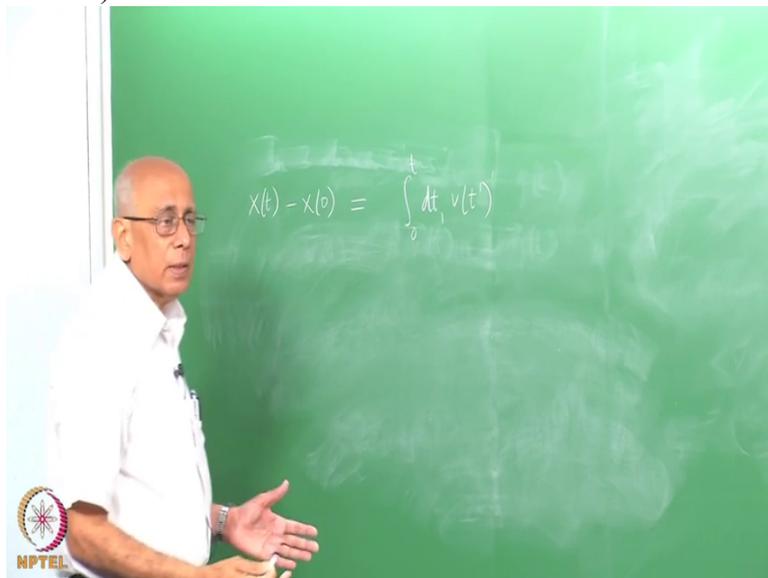
Professor: If I put a magnetic field that is going to happen. That is going to be immediately the Lorentz force on it, and this part of it will depend now on the other components here. Now you can see what will happen is that there is going to be some correlation between the different components of the velocity and you have to solve this problem all over again. So, however certain things will not change.

(Professor – student conversation ends)

Certain things won't change at all because the magnetic field doesn't change the energy of the particle, just causes the path to curve around, it does not do any work on this particle at all, doesn't change the energy. So interesting thing that will happen is that while diffusion in direction perpendicular to the magnetic field will be inhibited simply because system starts moving in circles before it is disturbed by thermal noise. Certain other things won't change like the velocity correlation, this relation here and so on. We will see what happens to it, Ok, alright.

Now since I talked about displacement, let's compute that too. We need to do that as well. So again for simplicity let's go back to our one dimensional case. Well I can always compute the displacement by simply using the fact that x of t minus x of zero is by definition, integral zero to t of v of t' , that's it.

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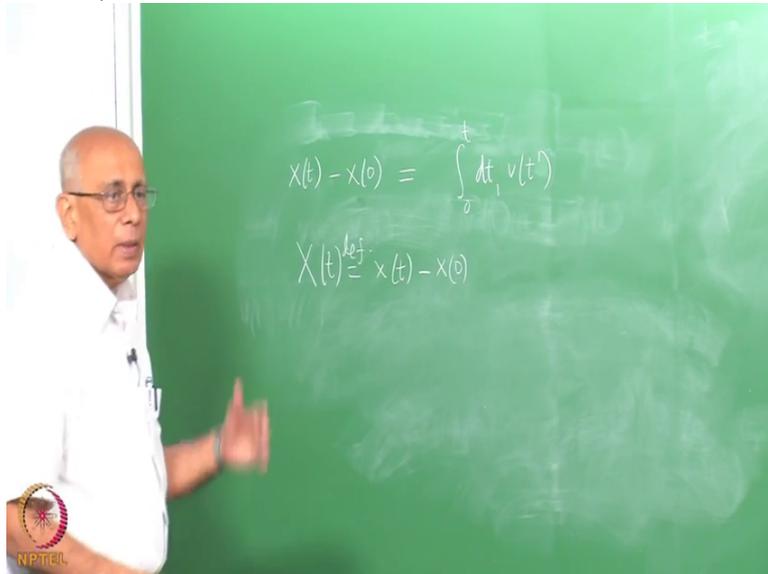


So the statistical properties of this displacement from whatever initial value the position had are given by the statistical properties of this integral.

Well this is a random variable, here. And we know everything about this. At least we know reasonable amount about it, such as its equilibrium correlation function. So let's try to compute what happens to this displacement as the function of t . So let me use another

symbol, let's call x of t equal to little x of t minus x naught, wherever it was. This is the definition, with

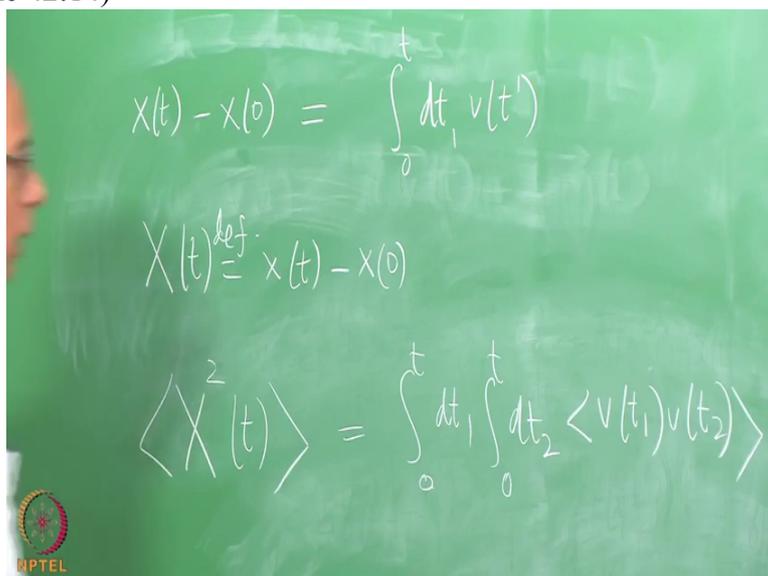
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displacement Ok. x is the position and that's the displacement, right?

And then let's compute x squared of t and take its average. Ok. So this is equal to integral zero to t dt_1 integral zero to t dt_2 times the average of v of t_1 , v of t_2 . Well I am going to go straight for the full average. I could do the conditional average first, write down the formulas and then do this, but we are interested in this thing here, full average. We need

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to compute this quantity. Some simplification can be done directly, immediately because this quantity we already know its value.

We already know that this is equal to $k_B T$ over m e to the minus gamma modulus $t_1 - t_2$. We already know that.

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$$x(t) - x(0) = \int_0^t dt_1 v(t_1)$$

$$X(t) = x(t) - x(0) = \frac{k_B T}{m} e^{-\gamma|t_1 - t_2|}$$

$$\langle X^2(t) \rangle = \int_0^t dt_1 \int_0^t dt_2 \langle v(t_1)v(t_2) \rangle$$

So all we need to do is to put this in and do this integration. And integration is over a symmetric region zero to t , it's a square. So if you go back here, here is t , t_1 , here is t_2 and the integration is over this, over this square. So we are integrating over this full square.

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$$-x(0) = \int_0^t dt_1 v(t_1)$$

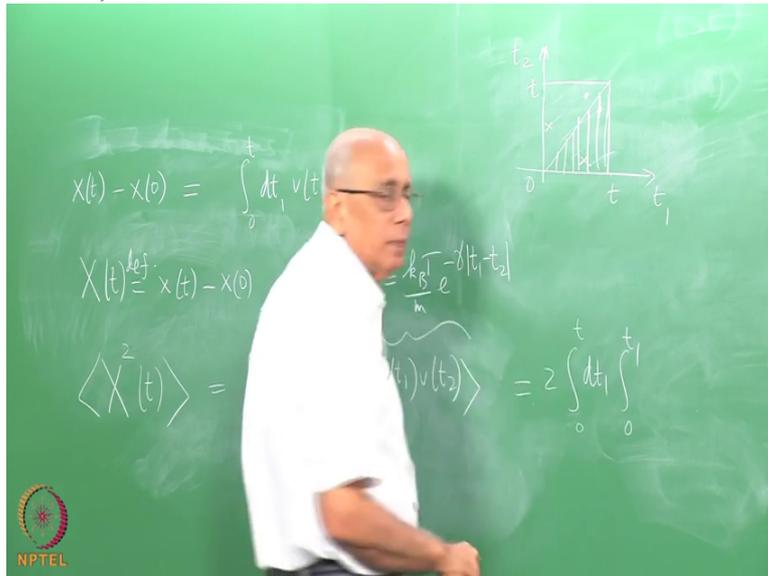
$$X(t) = x(t) - x(0) = \frac{k_B T}{m} e^{-\gamma|t_1 - t_2|}$$

$$\langle X^2(t) \rangle = \int_0^t dt_1 \int_0^t dt_2 \langle v(t_1)v(t_2) \rangle$$

But this is a symmetric function under the interchange of t_1 and t_2 which means if I reflect about the 45 degree line, then the integrand's value doesn't change. In other words, here is the 45 degree line and the value of the integrand here is the same as the value at this point. The value at this point is same as the value reflected at that point and so on.

Now in this triangle t_1 is bigger than t_2 and in this triangle t_2 is bigger than t_1 . It doesn't matter which triangle I choose so thing here is twice the integral from zero to t dt_1 , from zero to t_1 , so I integrate here, I am going to choose this integral. I start with the value t , t_1 between zero and t , it starts with this value but t_2 is integrated only up to that point and I am going to scan this in this fashion,

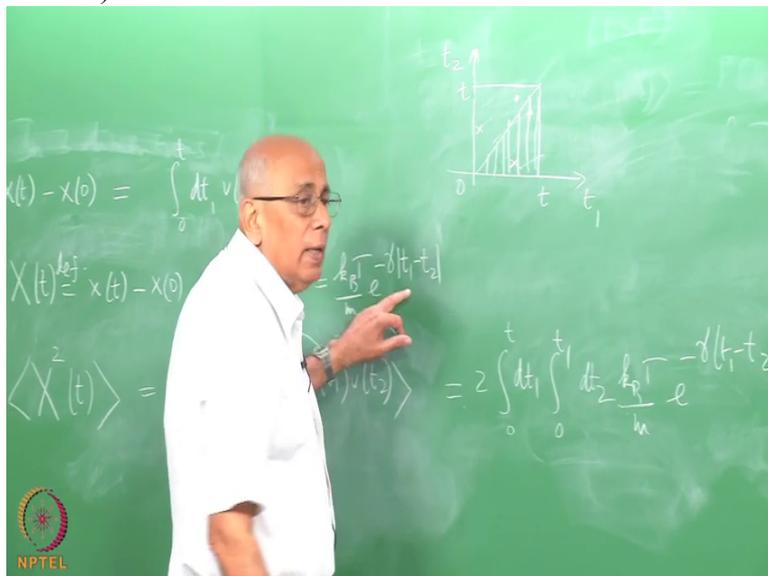
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right. So zero to t_1 , I stop at t_1 for the integration over t_2 . dt_2 $k_B T$ over $m e^{-\gamma(t_1 - t_2)}$.

I can get rid of the modulus sign

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because t_1 is bigger than t_2 , in this integration. What is this equal to? This is $2 k_B T$ over m integral zero to t dt_1 $e^{-\gamma t_1}$ times $e^{-\gamma t_2}$ from zero to t_1 , right? That's equal to $e^{-\gamma t_1}$ over γ .

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I am integrating that. That's a trivial integral. So this is equal to, it says that the displacement x square of t is equal to $2 k_B T$ over m γ times this integral is the integral of 1 which is just t itself, t and then the integral of $e^{-\gamma t_1}$ which is equal to $-\frac{1}{\gamma} e^{-\gamma t_1}$, so it is equal to $-\frac{1}{\gamma} e^{-\gamma t_1} - \frac{1}{\gamma} e^{-\gamma t_1}$, Ok

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which is equal to $2 k_B T$ over m γ^2 and then inside you have γt minus 1 plus $e^{-\gamma t}$.

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$$\langle X^2(t) \rangle = \frac{2k_B T}{m\gamma} \left[t - \frac{1}{(-\gamma)} (e^{-\gamma t} - 1) \right]$$
$$= \frac{2k_B T}{m\gamma^2} \left[\gamma t - 1 + e^{-\gamma t} \right]$$

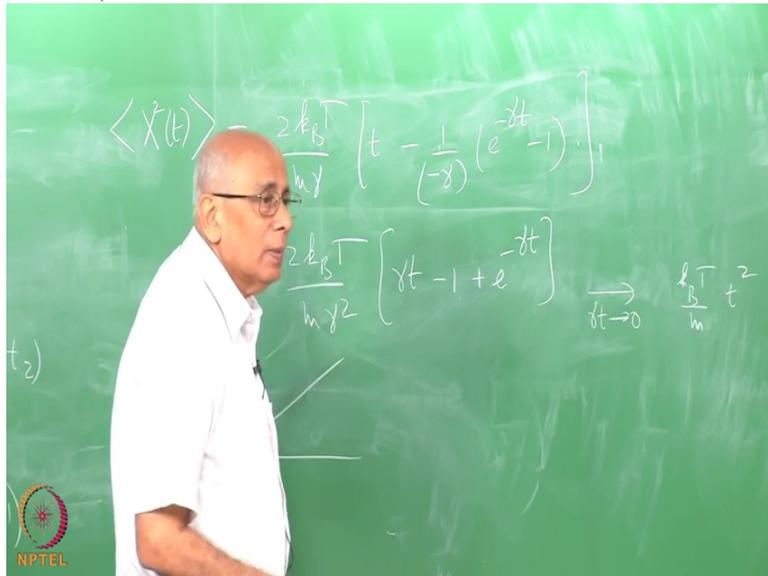
The image shows a green chalkboard with handwritten mathematical equations. The first equation is $\langle X^2(t) \rangle = \frac{2k_B T}{m\gamma} \left[t - \frac{1}{(-\gamma)} (e^{-\gamma t} - 1) \right]$. The second equation is $= \frac{2k_B T}{m\gamma^2} \left[\gamma t - 1 + e^{-\gamma t} \right]$. In the bottom left corner of the chalkboard, there is a small logo for NPTEL.

This one 3 minus is minus 1, yeah so that's the answer. I have taken the gamma out, so that thing becomes dimensionless, everything inside is dimensionless, Ok. That's the mean square displacement. And you can see this has got the physical dimension which I write, this has got to be the square of a length and indeed that's energy divided by mass that is t to the minus 2, so it's just square of a length, Ok. Well that's the exact expression.

Now notice that as t becomes very small, now we can ask what do I mean by small time and large time? There is a time scale in the problem which is gamma inverse. So when I say small time, I mean t much, much less than gamma inverse, and large time is t much greater than gamma inverse or gamma t tending to infinity, Ok.

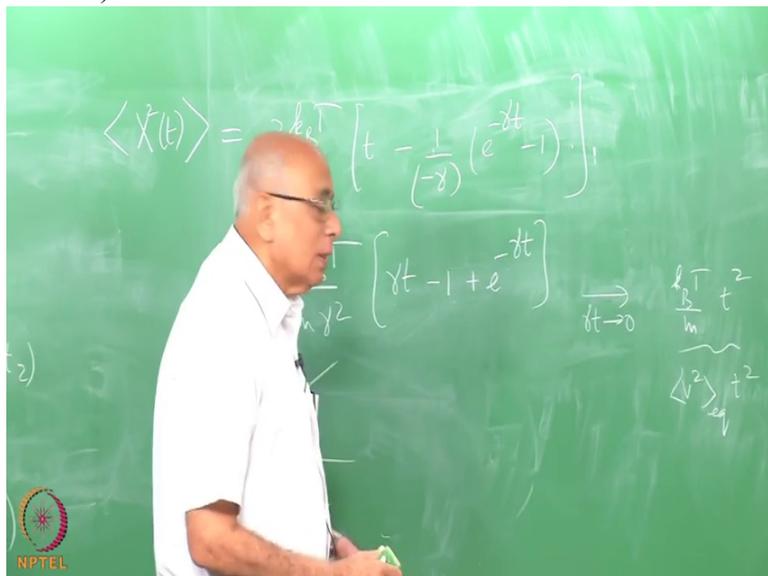
Now what happens is that there is some slope and this term dominates at very long times and at very short times, if I expand this, the 1 cancels, the gamma t cancels, it starts with gamma square t square. In fact what does it do? This goes as gamma t tends to zero, this fellow tends to, there is a gamma square t squared so that cancels, 2 and 2 cancels, so k Boltzmann T over m times t squared

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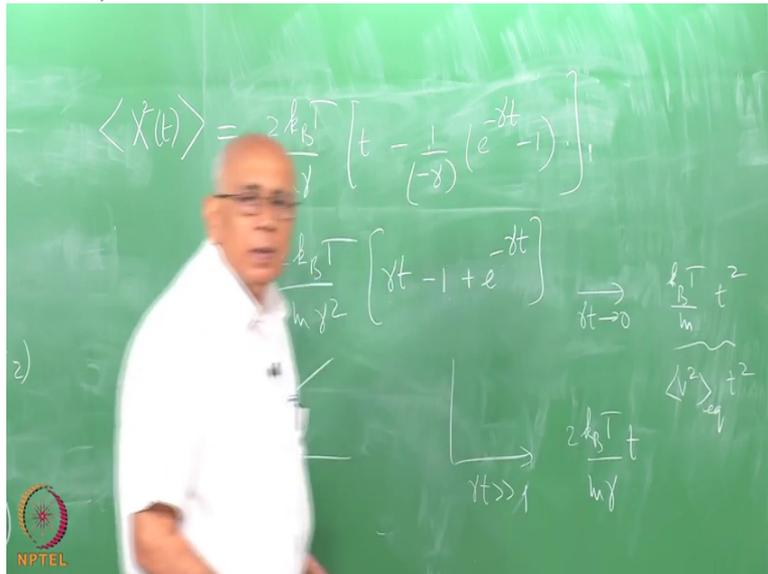
but remember that this fellow here is v square of, v square equilibrium times v square t square.

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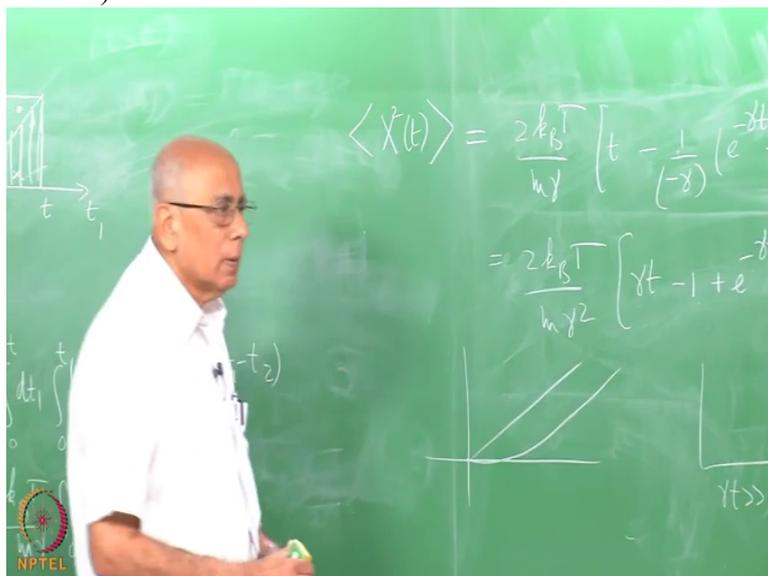
So it is as if this Brownian particle is undergoing ballistic motion but with the velocity which is the root mean square velocity. But more significant is here what happens at very long times. So at very long times, γt much, much greater than unity, this goes to $2 k_B T$ over $m \gamma$ times t .

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It goes linearly with time. So if I plot it, this fellow is going to do something like this.

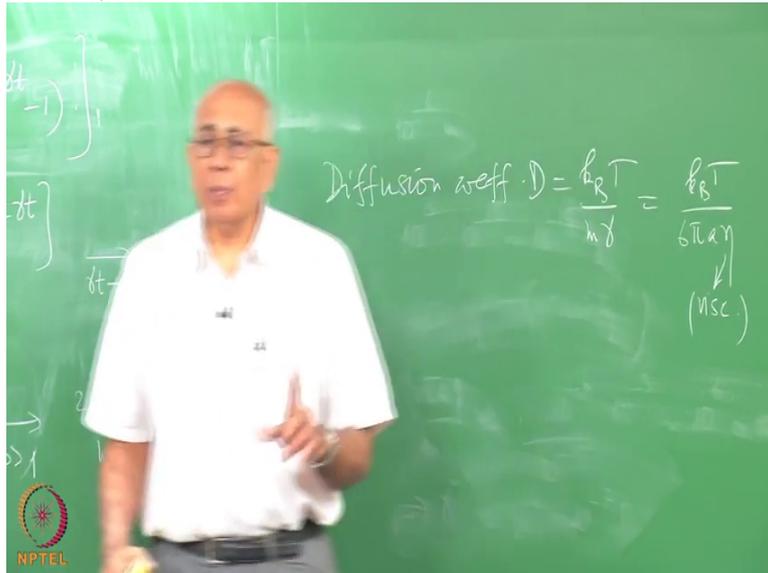
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And the asymptotic slope is twice this constant. And that is called the diffusion constant. Because as you know in diffusive processes, the mean square displacement goes linearly with time, twice $d t$ and coefficient D , $N i$'s dimension 0:49:03.0 is the diffusion coefficient. In 3-dimensions r squared will go like 6 times this coefficient. So we have actually ended up with a formula for the diffusion coefficient and if you put $m \gamma$ equal to $6 \pi a \eta$, then you have a relation which says this diffusion coefficient is $k_B T$ over $m \gamma$ equal to $k_B T$ over $6 \pi a \eta$, this is the viscosity.

So independent

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of the Brownian particle there is nothing in the last formula which has any reference to the Brownian particle at all, you are finding the diffusion coefficient of this particle. This was Einstein's great achievement. This formula is due to Einstein and of course it uses the Stoke's relation so it is called the Stokes-Einstein formula and Einstein brilliantly derived this by very different argument altogether. It is part of his thesis in the famous papers in 1905 but coincidentally a couple of months earlier, this physicist called Sutherland from Australia also derived the same thing, published it so I should really call it Stokes-Sutherland-Einstein relation.

But it is a very famous one and it helped Einstein compute now the size of a molecule, the size of a Brownian particle from here. In fact what I didn't mention was that, essentially it tells you what is the value of Avogadro's number, which I will mention how that comes about little later. But this was a fundamental relationship which was found by different argument but we will see how this emerges at this stage. I will stop here today and next time, we will take up a little deeper, we will go further into whether this model can be generalized, whether you can look at more complicated systems and how they relax and what is the relation between the relaxation and the response of the function. So let me stop here today.