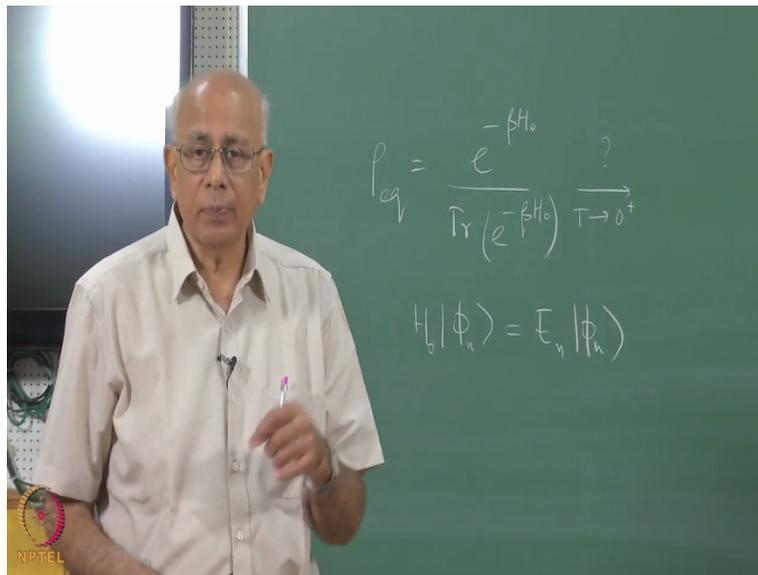


Nonequilibrium Statistical Mechanics
Professor V. Balakrishna
Department of Physics
Indian Institute of Technology Madras
Lecture no 28
Module no 01
Quiz 2 – Questions and answers

Right, we will today discuss the answers to this quiz that we had last week. And what I like to do is to also make comments, ideally I should have given you the answer sheets so you could check against it, but I will read out the questions and then you would be able to recollect what the question was about and we will try to give justification for the various choices. So the 1st question was in true or false was that as follows. Consider a quantum mechanical system with Hamiltonian H_0 , its normalized density operator and the canonical ensemble is given by either the $-\beta H_0$ over the trace of the same thing.

(Refer Slide Time: 1:01)

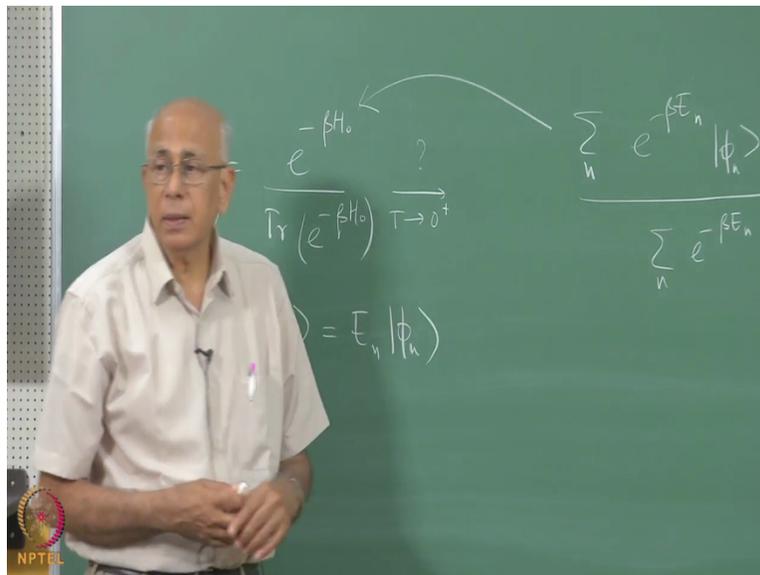


So you have given this, ρ_{eq} is $e^{-\beta H_0}$ divided by the trace of... And the question asked is what does this tend to as T tends to 0 from above of course as it goes to absolute 0. The statement is that it tends to the unit operator, is that true or false? It tends to the unit operator as T tends to 0. What happens to the state as T tends to 0 that means β tends to infinity, this thing goes to infinity here right. So you cannot just put β going to infinity because in this βH_0 goes to 0 directly, but then this denominator has to be taken into account. So if

you took this system to have a discrete set of energy levels E_0, E_1, E_2, \dots with corresponding eigenfunctions.

So if you said that $H_0 \phi_n = E_n \phi_n$, if you get this then this state normalised states form a complete set in orthogonal set, not a normal set of eigen vectors, n now labels all the possible states, stationary states of the system, all the eigen states of the Hamiltonian. There could be degeneracy in which case n will be more than one label, it will have more than one quantum number and we are just schematically writing everything down as with an n here. So this trace is over all the states diagonal elements over all the states clearly.

(Refer Slide Time: 3:25)



Now in this representation of this ϕ_n , it is clear that this operator itself has a representation which is summation over n of $e^{-\beta E_n}$ times the portion that projects onto the ground state to the state end. So this is $\phi_n \phi_n$ divided by summation over n of $e^{-\beta E_n}$, this is over the states n , and out here when you take $\phi_n \phi_n$, it normalise to unity and you get this. So the question is what happens to this? Now we can say what happens to this as β tends to infinity. Clearly, if all the E_n are positive then the numerator also is 0 and denominator is also 0, but if E_0 is finite, we do not care if it is positive or negative, we really do not care where you start measuring this spectrum from, wherever is the ground state, it should not be $-\infty$.

(Refer Slide Time: 5:01)

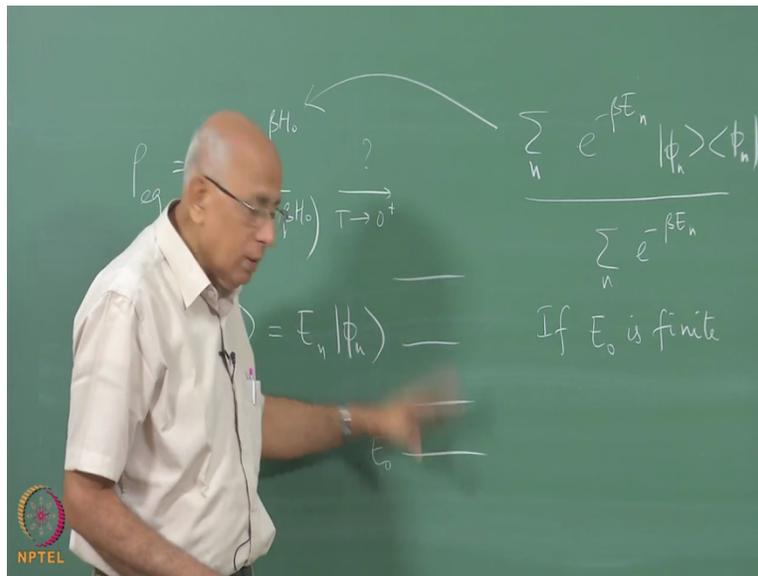
The image shows a green chalkboard with handwritten mathematical expressions. On the left, the expression is $\frac{\sum_n e^{-\beta E_n} |\phi_n\rangle\langle\phi_n|}{\sum_n e^{-\beta E_n}}$. An arrow labeled $\beta \rightarrow \infty$ points to the right. On the right, the expression is $\frac{e^{-\beta E_0} |\phi_0\rangle\langle\phi_0|}{e^{-\beta E_0}}$. Below the right-hand side, it says "If E_0 is finite". In the bottom left corner of the chalkboard, there is a small circular logo with a star and the text "NPTEL".

Wherever you have this ground state, you can pull out E_0 as a common factor and then whatever is inside, all the other exponentials will be the difference of $E_0 - E_n$ and they will all go to 0 as β tends to infinity. So this thing will tend as β tends to infinity to just the contribution from the lowest energy level the ground state, which is equal to of course $e^{-\beta E_0} |\phi_0\rangle\langle\phi_0|$ divided by $e^{-\beta E_0}$ because all the other terms will have decaying exponentials, will all go to 0 and this cancels out. So it tends not to the unit operator but to the projector of the ground state as it should because the system goes to its ground state at absolute 0 temperature right.

The probability of it being in any higher state is 0 essentially and it is with probability 1 in the ground state therefore, the density operator is not any longer there is no uncertainty thermal uncertainty, here it is this the ground state of the projector that is it, which is not the unit operator which is not the unit operator because recall that it is this quantity, this is equal to the unit operator.

Student : At T equal to infinity.

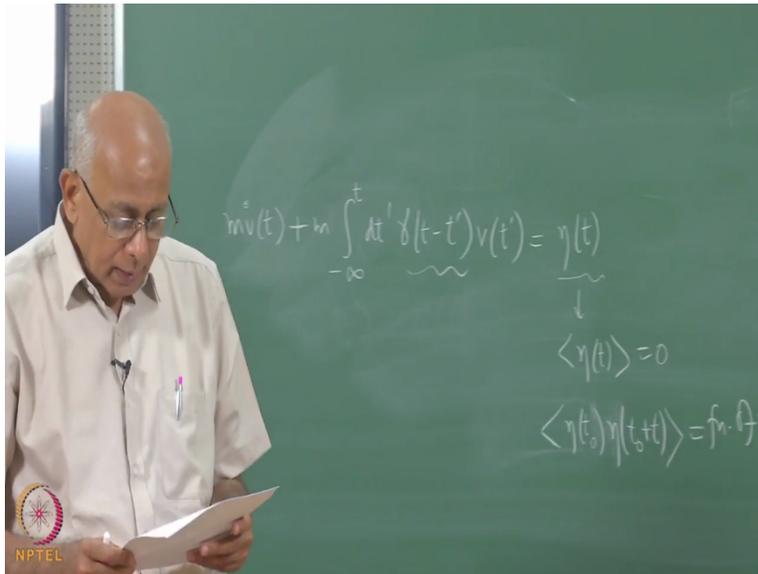
(Refer Slide Time: 6:58)



At T equal to 0 infinity you can ask, what happens if temperature becomes finite, then all these Boltzmann factors $e^{-\beta E_n}$ essentially all of them go to 1 , everything becomes equally probable and then the system will run and up with this density operator. You see, if these are the energy levels of the system they do not have to be equally spaced and this is the ground state E_0 . What statistical mechanics is telling is that once you have a certain finite temperature then there is an average energy and there is a variance scattered about it okay.

On the other hand, if the temperature becomes infinite then kT which is the thermal noise the quantum of thermal noise becomes much larger than the gap between energy levels, so these gaps are irrelevant completely and the system will just freely move around from state to state and therefore there is no bias at all in this case and every state is equally probable essentially in the limit. But as the temperature is lowered, the bias comes more and more strongly towards the ground state till T equal to 0 everything sits in the ground state. So that is the fundamental property of equilibrium statistical mechanics and the answer therefore is false, it says the projector of the ground state okay.

(Refer Slide Time: 7:56)



The next statement is, given that the x component of the velocity of a particle of mass m fluid satisfies the generalised Langevin equation with memory kernel which is the decreasing function of its argument and η is the stationary noise. All you are given is that this is the stationary noise, you are not given anything more so the statement is, $m \dot{v}(t) + m \int_{-\infty}^t dt' \gamma(t-t') v(t') = \eta(t)$ and this is stationary. So we are told that this quantity here as 0 means at any time and $\langle \eta(t_0) \eta(t_0 + t) \rangle = f(t)$, the origin does not matter, that is all you are given.

And you are also told that this is that this quantity γ is a decreasing function positive decreasing function of its argument for all positive values of its argument right, so that is all you are told nothing more. And then the statement is, $v(t)$ is a Markov process and its density function conditional density period satisfies the Fokker Planck equation, this is true or false?

Student : False.

It is false because there is incredible memory is sitting here, this is an integral differential equation, it is not a Langevin at all, usual type of Langevin equation, if you insist on writing this as a differential equation you will have derivatives of all orders in the time variable so there is lot of memory in this business and it is not a Markov process. So there is no chance that the

probability density function period satisfies the Fokker Planck equation then whatsoever, it is not a Markov process.

But there is actually an interesting theorem which says that if this is stationary and Gaussian, which you have not said in this problem but if this is stationary as well as Gaussian then it turns out that the density function period p of v , t , v_0 this is the conditional density, turns out in that case when this is also a stationary Gaussian process to obey an equation which looks very much like the Fokker Planck equation but it is not a genuine Fokker Planck equation. In particular in particular you have to recognize that if it is not a Markov process then this 2 point conditional density alone does not determines the rest of the process, you have got all the joint densities on top of it.

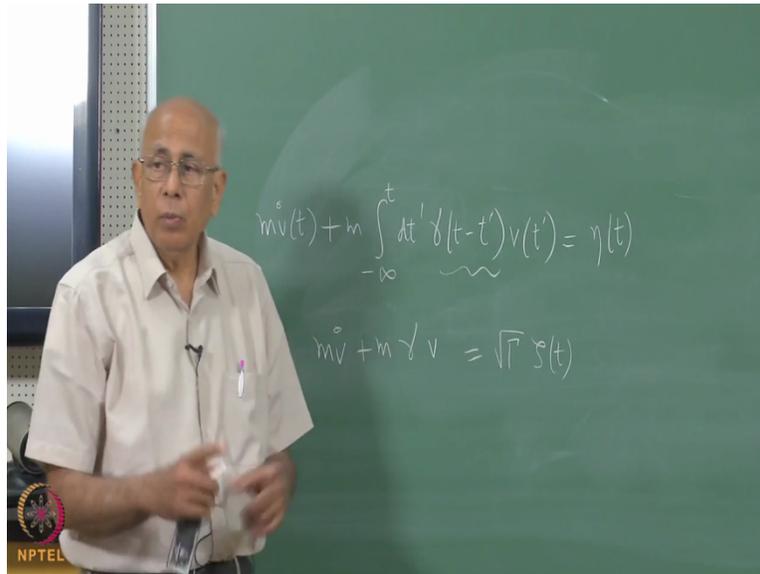
So the fact that this satisfies a certain Fokker Planck like equation might help in calculating this quantity and therefore the autocorrelation, but it does not help as far as understanding the nature of this stochastic process that is much more integrate than this.

Student: Irrespective of the nature of Eta it is Markovian?

Well, one of the question says that this is inconsistent for Eta to be Delta correlated that we can see right away, we will see in a minute that it is not this cannot be Delta correlated. So the question is, suppose I tell you this is a stationary process, it is not Delta correlated, it has got some finite correlation time, what is it you can say about output process here. For that you got to take this close to this fluctuation dissipation theorem, which will talk about in some detail.

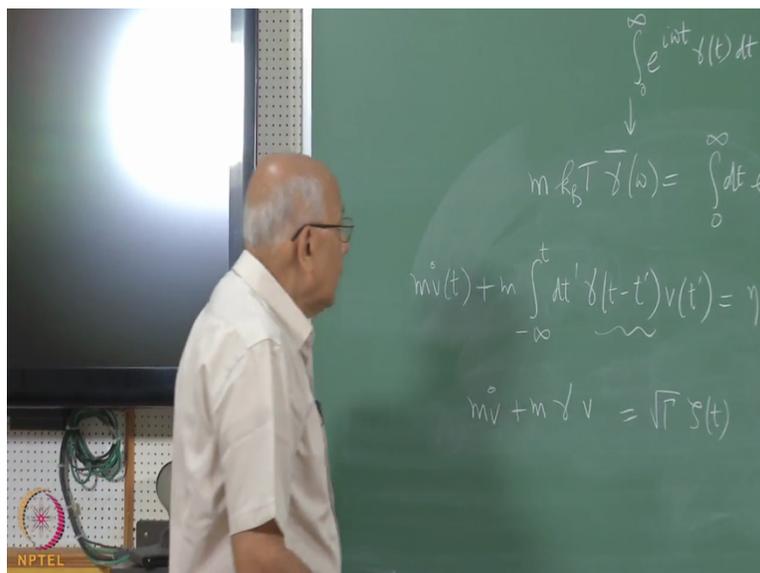
So you can make some statements about the autocorrelation of v of t computed, but in general to find out what is this process, what is its probability density function exactly that is not doable from this and it stands okay. We need to know all the properties of Eta of t and K_s by K_s you have to analyse it which is not a trivial task, so the statement is false this statement is false.

(Refer Slide Time: 12:26)



Next thing says, the assumption that the autocorrelation of Eta of t is proportional to Delta function leads to an inconsistency, is that true or false? That is true, it definitely does as follows so we can see what the problem means, you see all you have to do is to ask what is the 2nd fluctuation dissipation theorem in this case. Recall that the original Langevin equation which had this $m \dot{v} + m \gamma v$ just a local function with a constant Gamma the ordinary Langevin equation, this was set equal to square root of Gamma times Zeta of t. This was the Gaussian white noise with 0 mean and with Delta function autocorrelation right.

(Refer Slide Time: 13:38)



Then consistency required that $2 m \Gamma k_B T$ had to be equal to capital Γ that was the 2nd fluctuation dissipation theorem relating the dissipation in this equation with the strength of the fluctuation driven by the noise okay. The question is, what is that for this process? Not very hard to do, all you have to do is to find out what is the correlation here and how does it get related to this quantity here. The corresponding relation here turns out to be $m k_B T \bar{\Gamma}(\omega) = \int_0^\infty dt e^{-i\omega t} \langle \eta(t) \eta(0) \rangle$ that is the Second fluctuation dissipation theorem in this problem okay.

Now you can see how this is going to reduce to this okay because in the case where this quantity is integral $e^{-i\omega t} \Gamma(t)$ from 0 to infinity, one sided Fourier transform. Now to go to the ordinary Langevin equation you have to assume this to be a Delta correlated quantity. So with capital Γ times Delta function we put Delta of T when T equal to 0, this goes away and with capital Γ which is on this side and on this side we are going to get $m k_B T \bar{\Gamma}$. Now the way to go to a constant is to put this memory kernel $\Gamma(t)$ little Γ of t to be equal to constant Γ times Delta function.

(Refer Slide Time: 15:35)

$$m\dot{v} + m\gamma v = \sqrt{\Gamma} \zeta(t) \quad 2m\gamma k_B T = \Gamma$$

$$\gamma(t) \rightarrow \gamma \delta(t)$$

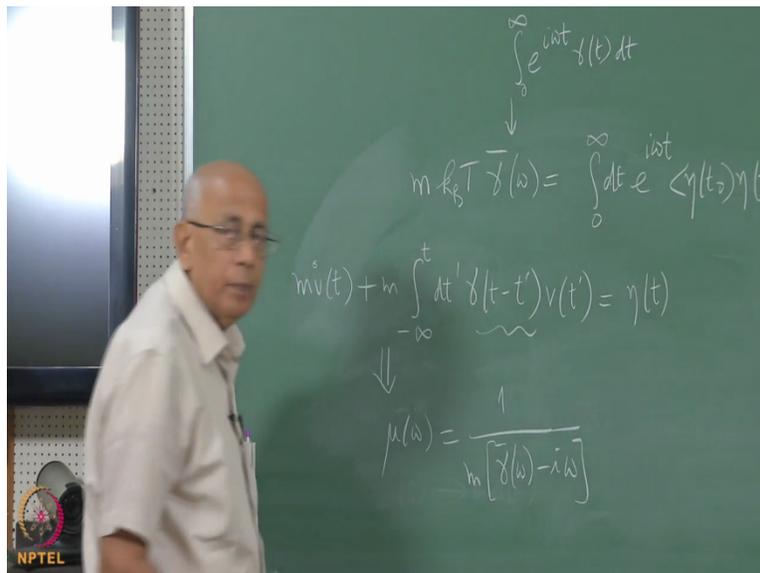
So when $\Gamma(t)$ goes to $\Gamma \delta(t)$ no memory, then you get the ordinary Langevin equation from the generalised Langevin equation. If you put that in, this term here becomes Γ but with a factor missing because this quantity here when I say Delta, it got run from $-\infty$ to ∞ to pick up the full contribution of the Delta function, otherwise you

pick up half the contribution and when you put that back here you get this relation. So that is how from the general 2nd fluctuation dissipation theorem you end up with the special case for the ordinary Langevin equation.

Now the question asked is, it is inconsistent in the general Langevin equation generalised equation to have a Delta function as the correlation of the noise to have this Delta correlated. Yes indeed because we put in Delta function of t here times the constant, this integral becomes just that constant but on this side it has got a function of Omega and there is an immediate inconsistency, you cannot have a function of Omega equal to a constant because certainly we know that if this is not trivial, this is some function of Omega and that is Gamma bar, so on this side you got a function of Omega, on this side you have got a constant which is inconsistent.

So this is how we see that Delta correlated noise is inconsistent with the generalised Langevin equation. This is got to have a finite correlation time, in fact that is the reason for introducing the Langevin generalised equation in the 1st place because we said look in real life no noise is Delta correlated, is always some finite correlation time so that is the reason why we had to introduce a memory kernel for consistency so the statement has a stance and it is true okay.

(Refer Slide Time: 17:18)

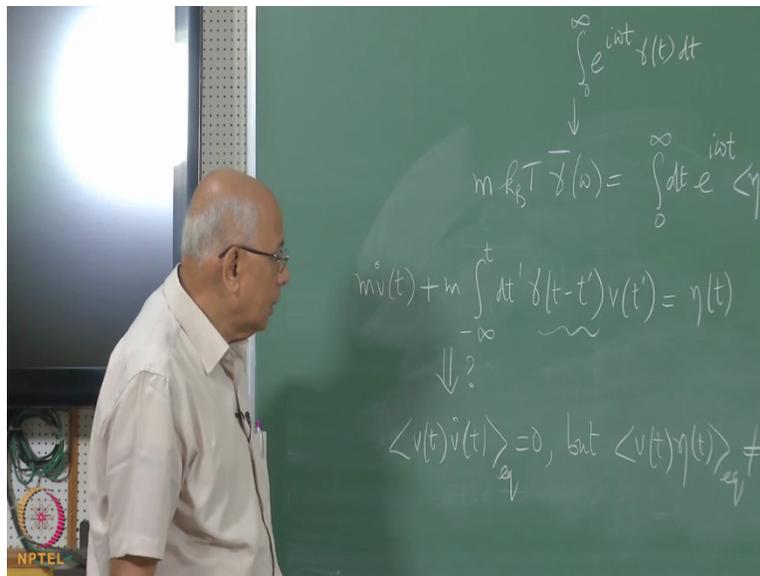


The next question says, the dynamic mobility of the particle vanishes for infinite frequency as Omega tends to infinity, so this too is a very straightforward question because from this equation we derive the fact. This equation implies that the dynamic mobility in this problem is 1 over n

times Gamma bar of Omega – i w. Whatever be this, it is clear that this quantity here becomes infinite as Omega tends to infinity and it just vanishes. And physically it is expected because the dynamic mobility gives you the average velocity amplitude for a given amplitude of some sinusoidal frequency Omega.

As Omega tends to infinity, this becomes so large that the system cannot respond, it does not get (17:52) from responding therefore it should go to 0 which is what is happening, with or without this term it still goes to 0, so this statement is certainly true.

(Refer Slide Time: 19:01)



The next one is a little tricky, it says; in this model the generalised Langevin equation model, the equal time correlation between the velocity and Eta the noise Eta is not equal to 0 but the equal time correlation v of t with the acceleration v bar of t is equal to 0 and the question asked is whether this is true or false. So again between the context of this equation, the question asked is does this imply that v of t v dot of t in equilibrium equal to 0 but v of t with Eta of t in equilibrium is not equal to 0 and you are asked if this is true or not okay.

Student: It is true.

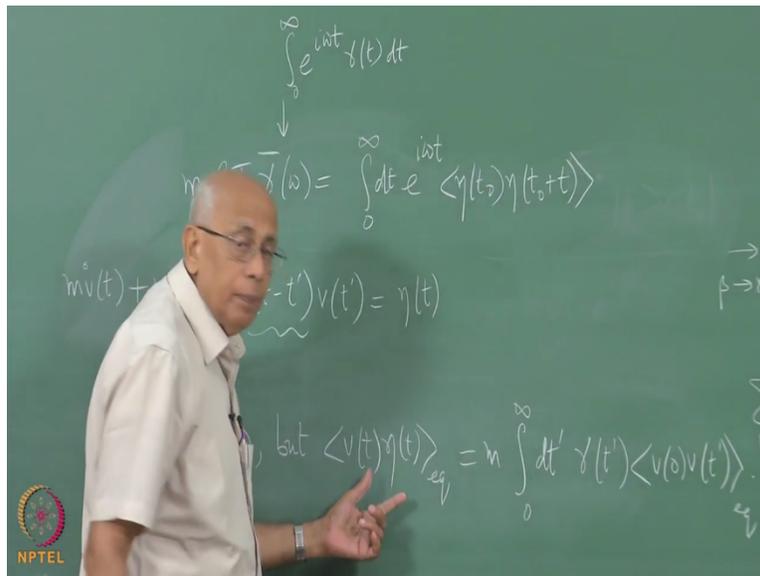
It is true, it is true because the whole point about fixing the whole point about causality and the stationarity conditions in this problem. Well, the 1st problem was in the ordinary Langevin equation while we discovered that the correlation of the velocity is stationary and the velocity is

stationary random process that v of 0 , v of t in equilibrium e to the $-\Gamma$ modulus t , we ran into the difficulty that stationarity was apparently violated. Because if you took v square of t average that is equal to $k t$ over m Maxwellian and you differentiate both sides, the right-hand side has no dependence on little t , the left-hand side you differentiate and then said t equal to 0 or something like that.

When you immediately discover that this must be equal to 0 , for a stationary process any stationary process Z_i of t , Z_i of t Z_i dot of t must be equal to 0 that is the meaning of stationarity, but the Langevin equation violated it. The question is whether it is true in this equation and the answer is yes it is true, this thing can be established rigorously this is certainly true. But is this true or not? Now in the ordinary Langevin equation we took this quantity the force on the right-hand side to be uncorrelated to the velocity at the same time arguing that the force determines the acceleration at any given time and the velocity comes a little later after integration, so this quantity is certainly 0 by causality.

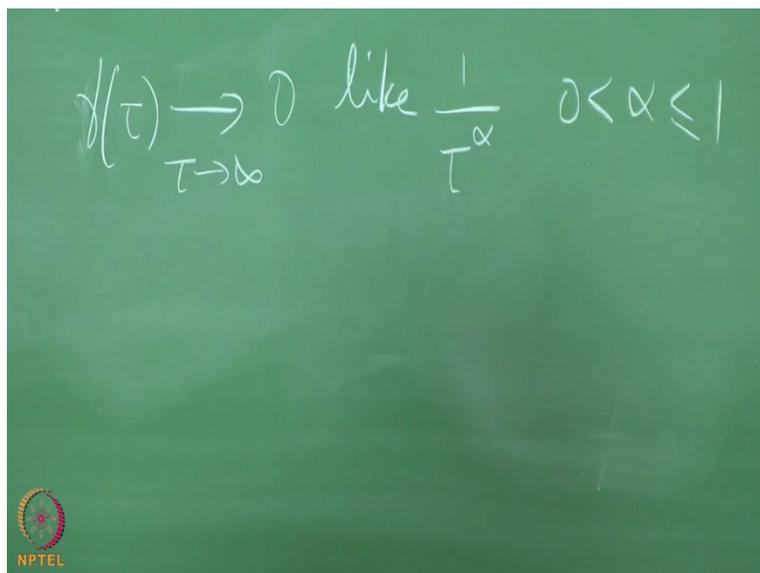
But that lead to a problem, that lead to an inconsistency with stationarity. To fix that we took this problem and said look, stationarity has to be rigorously obtained here because equilibrium tells you that this velocity is stationary but causality has to be written more carefully that the effective random force is not this, but a portion of it which comes from the history here. And the assumption of causality was that the velocity is uncorrelated with that effective force at a later instant of time. When you did that carefully, then it turns out this quantity is not 0 at all, but rather it has got a finite value which also we computed I think.

(Refer Slide Time: 22:14)



So somewhere along the line we had this here, so it turns out that in this model if you compute this thing here, this turns out to be equal to n times an integral from 0 to infinity dt' γ of t' v of 0 v of t' in equilibrium. So at a given instant of time, this correlator is not 0 but rather it depends on the memory kernel in this fashion. So it is in integral over the velocity correlation at all previous instance from 0 to infinity weighted with this memory function and it is not identically 0. So the statement as it means is actually true but this is a little tricky to evaluate, but it is straightforward to evaluate it after you make proper causality assumption.

(Refer Slide Time: 23:27)



Then finally the last one on this set of questions is; in the same generalised Langevin equation as Tau tends to infinity suppose the memory kernel γ goes to 0 like some power of Tau inverse power of Tau. So you have given you have given that Gamma of Tau goes to 0 as Tau tends to infinity like $1/\tau^\alpha$ where $0 < \alpha \leq 1$, we believe it is less than or equal to 1. The statement is, does the starting mobility of the particle vanish in this case? So the question asked is, is $\mu(0)$ equal to 0 as a consequence of this? Yes or no?

Student: Yes.

(Refer Slide Time: 24:28)

$$\mu(\omega) = \frac{1}{m[\bar{\gamma}(\omega) - i\omega]}$$

$$0 < \alpha \leq 1$$

$$\mu(0) = \frac{1}{m\bar{\gamma}(0)} \rightarrow 0$$

$$\int_0^{\infty} d\tau \gamma(\tau) \rightarrow \infty$$

Yes it is true, the reason is very straightforward. We know that $\mu(0) = 1/m\bar{\gamma}(0)$ and this integral is $\int_0^{\infty} d\tau \gamma(\tau)$. If this dies down like $1/\tau$ or $1/\sqrt{\tau}$ or any power of Tau less than 1 in the denominator then of course its integral blows up. So this tends to infinity and therefore $\mu(0)$ vanishes, this quantity therefore tends to 0 because its memory is so strong, its dissipation is like the effective drag is so strong that the system does not move okay, that is what is meant by slowly decaying memory okay.

(Refer Slide Time: 25:48)

The image shows a green chalkboard with handwritten white text. At the top, there is a question mark above the equation $\phi_{AA}(\tau) = -\phi_{AA}(-\tau)$. Below this, a downward-pointing arrow leads to the expression $\langle \frac{[A(0), A(\tau)]}{i\hbar} \rangle$. In the bottom left corner of the chalkboard, there is a small circular logo with the text 'NPTEL' below it.

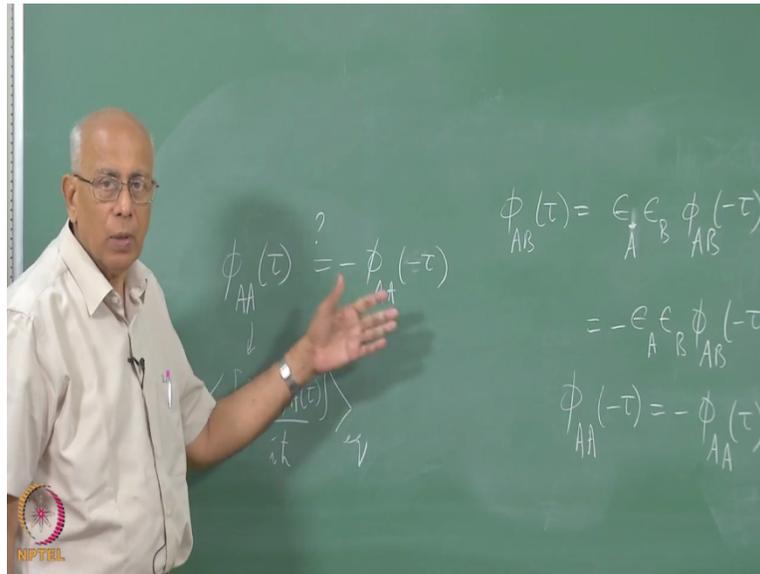
So much for the generalised Langevin equation, the next set of questions has to do with linear response theory. Given that A represents a physical observable of a quantum mechanical system and you are asked, the statement made is ϕ_{AA} of τ equal to $-\phi_{AA}$ of $-\tau$ okay, where he called at this quantity stands for the expectation value in quantum mechanics of A of 0 , A of τ over $i\hbar$ cross in equilibrium over the canonical sum here okay, so true or false?

Student: True.

The statement is true and why do you say that?

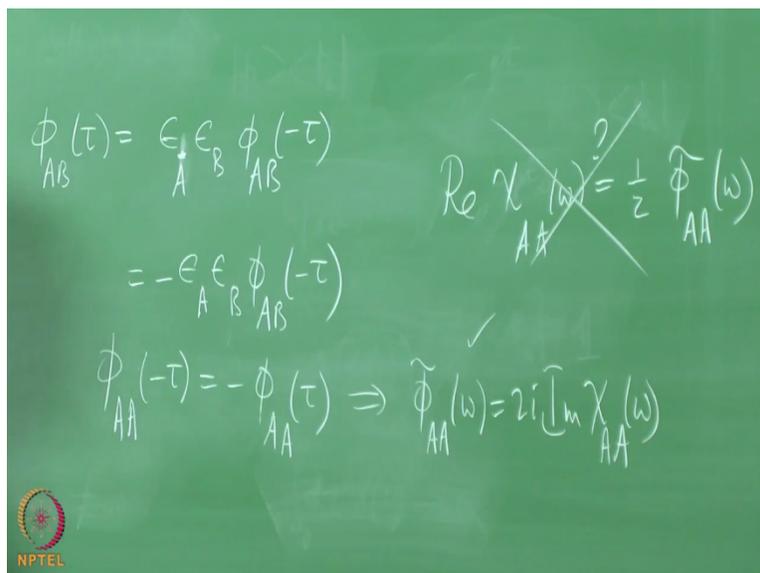
Student: (0)(26:09)

(Refer Slide Time: 27:34)



Because under time reversal you are asking what happens under time reversal and we know in general you have ϕ_{AB} of τ in general is equal to $\epsilon_A \epsilon_B \phi_{AB}$ of $-\tau$, where ϵ_A is a time parity $+1$ or -1 , which is equal to $-\epsilon_A \epsilon_B \phi_{AB}$ of $-\tau$ because ϵ_A and ϵ_B have opposite time parities like position and velocity or velocity and acceleration. So in this case $\epsilon_A = \epsilon_B$, ϕ_{AA} of $-\tau$ equal to $-\phi_{AA}$ of τ because ϵ_A^2 is 1 , whether it is $+1$ or -1 does not matter, ϵ_A^2 is always 1 .

(Refer Slide Time: 28:28) 29:05



So this response function is an odd version of Tau okay and that helps us answer the next part of it. It says that the corresponding generalised susceptibility and spectral function are related according to real Kai AA of Omega is equal to half Phi AA tilde of Omega. So you are asked is real Kai AA of Omega equal to 1 half Phi AA tilde of Omega, is this true or false? Well, because of this, this thing implies that it is Phi AA tilde of Omega is actually 2 i times the imaginary part of Kai AA of Omega. Had this been a symmetric function, this should have been twice the real part but because it is anti-symmetric, it is twice the imaginary part.

(Refer Slide Time: 29:36)

$$\text{Re } \chi_{AA}(\omega) = \frac{1}{2} \phi_{AA}(\omega)$$

$$\checkmark$$

$$\Rightarrow \tilde{\phi}_{AA}(\omega) = 2i \text{Im} \chi_{AA}(\omega) \Rightarrow \tilde{\phi}_{AA}(-\omega) = -\tilde{\phi}_{AA}(\omega)$$

But now we know that the imaginary part of the susceptibility is an odd function of Omega while the real part is an even function of Omega and in this case the spectral function is proportional to the imaginary part, so it is clearly an antisymmetric function and it is therefore this statement that this is not true, instead you have this statement here, so that is the correct statement okay. So the spectral function is therefore an odd function because it is proportional to the imaginary part of i, so this of course immediately implies Phi AA so that takes care of this part right.

And then there are set of questions on Boltzmann equation, the 1st of which says let f of r, v, t denotes the phase space density in the 1 particle phase space new space of a dilute classical gas. We will assume that the molecules of gas will only undergo binary collision with each other, then the statement is at every instant of time the gas can only be in a state in which f satisfies the Boltzmann equation, is this true or false?

(Refer Slide Time: 30:39)

The image shows a green chalkboard with the following handwritten text:

$$f(\vec{r}, \vec{v}, t)$$

↓

$$f_{eq}(\vec{v}) = n W(\vec{v})$$

The NPTEL logo is visible in the bottom-left corner of the chalkboard image.

They are not saying that the gas is in equilibrium, they are saying that it satisfies, they are not saying... there is f of r , v , t and in the absence of an external force this thing goes in equilibrium to f equilibrium of v which is independent of time. And in the absence of external force this quantity is equal to n times the Maxwellian W of v we have seen that. Even if there is an external force present, which is dependent only on the position of the particle the conservative force then this quantity here goes to the Maxwell Boltzmann distribution.

(Refer Slide Time: 31:34)

The image shows a green chalkboard with the following handwritten text:

$$f(\vec{r}, \vec{v}, t) \longrightarrow n e^{\frac{-\phi(\vec{r})}{k_B T}} W(\vec{v})$$

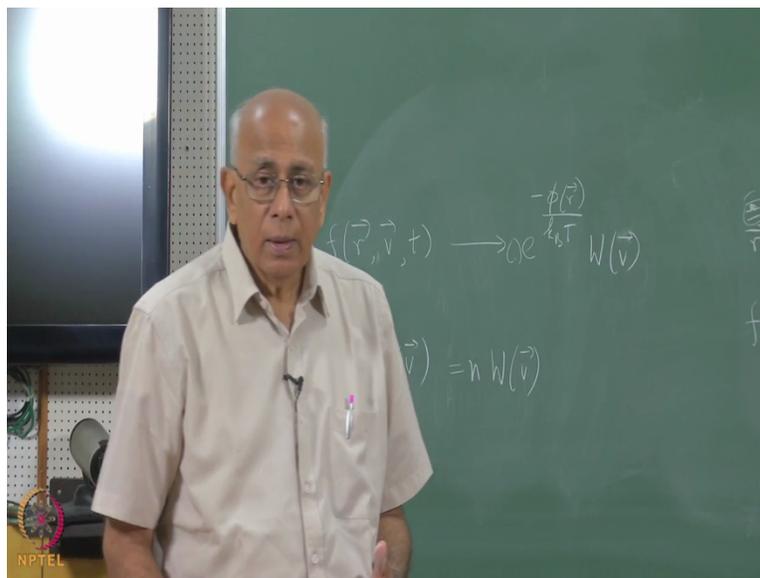
↓

$$f_{eq}(\vec{v}) = n W(\vec{v})$$

The NPTEL logo is visible in the bottom-left corner of the chalkboard image.

So this will go in equilibrium as t tends to infinity to $e^{-\phi(r)/k_B T}$ times $W(v)$ right, apart from some normalisation factor such that the whole thing is normalised okay. The integral of this over d^3r should be equal to the number density and so this fixes this constant will fix that normalisation okay. Now the question is, at every instant of time is the Boltzmann equation satisfied or not? We are not saying that at every instant of time the phase space density is the equilibrium density, we are not saying that at all. The equilibrium density could happen in between, it could occur it is one of the possibilities, the gas could be in the state where this density is exactly the way we density and as T tends to infinity we know that it attains that okay.

(Refer Slide Time: 33:18)



Now the question is, at every instant of time is the Boltzmann equation itself valid or not? Well, no in general no because you see the Boltzmann equation is valid if and only if the assumption of molecular chaos is valid. If and only if in new space we said that at some point r inside the cell, the centre of a cell in new space, we have assumed that the probability that you have particle in this r with velocity v_1 and t , probability density is this and the probability density that you have 2 of these guys with velocity is r velocity is v_1 and v_2 is the product of these densities. What does that mean? It means that there is no correlation in velocity space at all okay.

This would certainly not be true if there are recollisions, something hits against its particle, it goes and hits another particle and comes back to and hits this then this kind of assumption is not

valid anymore. You can easily see that it builds up a correlation between these 2 particles okay that is immediately clear. Take the simplest possible example, put everything on a line let say the particles are equal mass and put a wall at one end. Particle A sitting here, particle B comes and hits it bounces back hits the wall comes back and hits it.

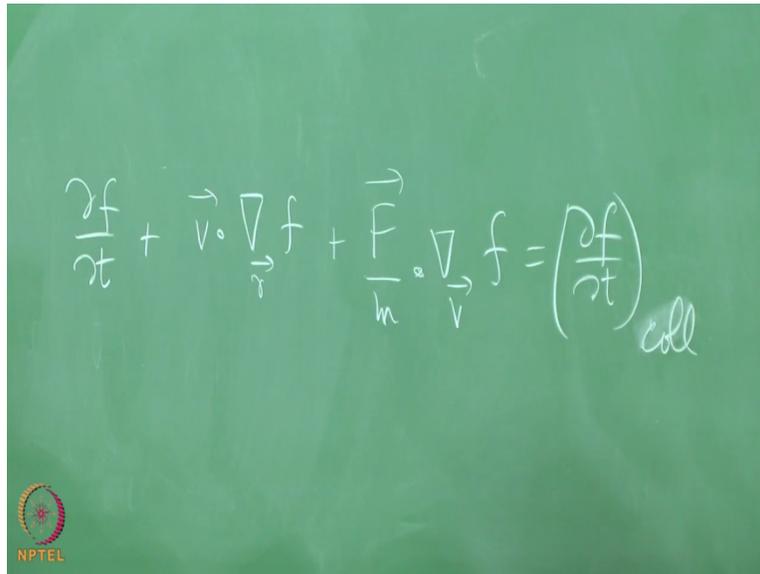
Surely the velocity of the the projectile 2nd time is dependent on what happened the 1st time okay, so this is no longer true, it is only true at some instance of time and at those instance the Boltzmann equation is valid. So the answer is false, the Boltzmann equation holds good only at those instance where the molecular chaos assumption is valid, in between there are all kinds of states possible, which do not satisfy the assumption okay.

Student : It specifies that the molecular chaos in binary collision (())(34:32)

No. It says let f of v, r, v, t denote the phase space density, in one part it is phase space or new space of a dilute classical gas. We assume that the molecules of the gas only undergo binary elastic collisions with each other that is it that means no energy is lost. Then the statement is, at every instant of time the gas can only be in a state in which f of r, v, t satisfies the Boltzmann equation and that is not true okay.

The next statement says, since the Boltzmann equation is the 1st order partial differential equation in $T \Delta f$ over Δt equal to something or the other, it follows that r and v comprises 6 dimensional Markov process. Because as you know for Markov process the master equations says that the density whatever be the conditional density satisfies the 1st order the differential equation in time, what that equations is depends on actual process, the transition rates and so on but it satisfies the 1st order process in time.

(Refer Slide Time: 36:04)


$$\frac{\partial f}{\partial t} + \vec{v} \cdot \nabla_{\vec{r}} f + \frac{\vec{F}}{m} \cdot \nabla_{\vec{v}} f = \left(\frac{\partial f}{\partial t} \right)_{coll}$$

Not only that, it satisfies the chain condition, so it is even if you like a non-linear integral equation just like the Boltzmann equation, but is the Boltzmann equation a Markovian master equations? What do you think? So if you recall, Δf over Δt + there are terms like \vec{v} dot gradient with respect to \vec{r} here, that does not bothers us because this sort of term appears even when you write down the Langevin equation in phase space, when we wrote down the (36:14) equation for instance we got terms like this, these streaming terms + $\frac{\vec{F}}{m}$ dot gradient with respect to \vec{v} of f , this is equal to over right-hand side Δf over Δt collision.

And if you recall, this was a complicated integral which involve quadratic squares products of $2f$ set... $2f$ – final – initial and so on, we had a very complicated collision term here. So this is by no means a Markov process of any kind, it is much much more complicated thing like that. Finding what the correlation is between the auto correlations and so on this case is very tricky because you have to essentially solve this Boltzmann equation and notice this there is no explicit randomness which is bought in anywhere here, you have in principle you are supposed to know this on the right-hand side and solve with self consistency, so it is certainly not a Markovian master equation by any means.

However, if you recall, when we looked at the so-called single relaxation time approximation, in the case when you linearise the Boltzmann equation we did not really explain what are all the assumptions which you need to the linearisation, but if you did, it is a small departure from

equilibrium and on top of it you make the single relaxation time approximation than under suitable cases the velocity relax like like a Kubo Anderson process, it relax like a Markov process. So that is a special case of a special case, in that case you can mimic it but that is a crude approximation to the actual Boltzmann equation, this is not a Markovian master equations.

And it does not say how strong the collisions are, it just says v_1 and v_2 go to v_1' , v_2' , it does not say put any bounce on how big this quantity should be, it does not put any bounce on how big the relative velocity $v_1 - v_2$ should be at all, could be drastically written.

Student: (0)(38:29)

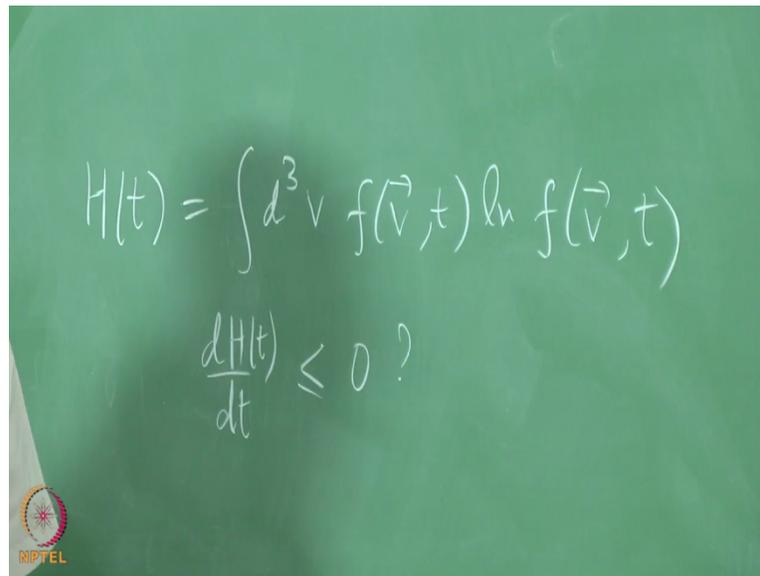
Yes yes.

Student: (0)(38:34)

No, detailed balance only involved time reversal in variant for the dynamics right. So in general what you do is, for Markov processes if detailed balance obtains then you can write down the equilibrium distribution by using the detailed balance condition just as we could do so here too by inspection of that collision integral, but there is nothing which says detailed balance should be there because in the Markov process I can specify the transition rate probability is between different states of the system quite arbitrarily subject to some ordinary conditions. But the fact is they are completely arbitrary, there is no reason why detailed balance should apply at all for general Markov process okay.

Whereas here the Physics is saying that it does apply because ultimately the collisions the dynamically process of the collision is time reversal in variant, whatever is happening there is assumed to be time reversal invariant okay. So that means some physics has been put in about the molecule level process of scattering and then you get this detail balance coming out popping out okay. And finally consider the gas in the absence of external force, the statement is for any given distribution f of v , t there is no dependency on r , the Boltzmann h function is defined as $f \log f$ integrated over v statement.

(Refer Slide Time: 40:37)

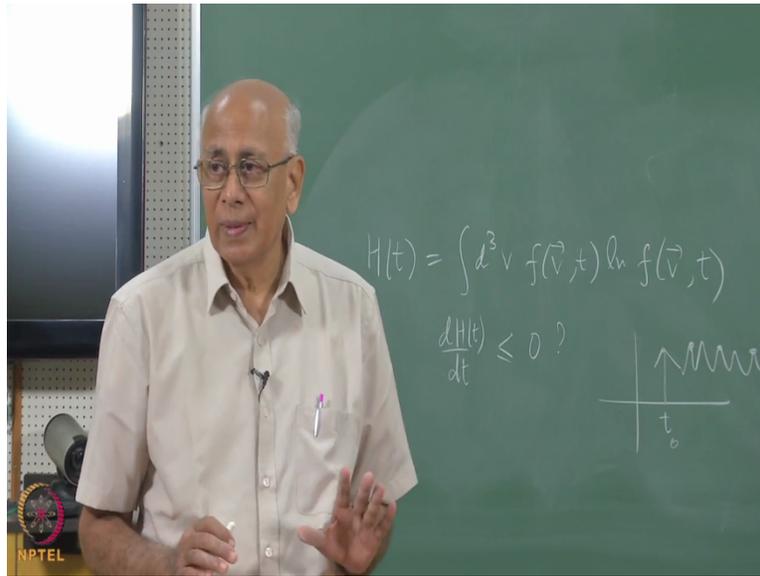

$$H(t) = \int d^3v f(\vec{v}, t) \ln f(\vec{v}, t)$$
$$\frac{dH(t)}{dt} \leq 0 ?$$

H of t is a monotonically decreasing function of t, true or false? So let us be careful, you define the Boltzmann function as integral $d^3v f(\vec{v}, t) \ln f(\vec{v}, t)$. And is it true that this quantity satisfies $\frac{dH}{dt} \leq 0$, is this true?

Student: () (40:53)

Exactly, you see definition this quantity, you give me any distribution and I will define this quantity the H function, what we have proved is that if this satisfies the assumption of molecular chaos and therefore satisfies the Boltzmann equation then you can show this. So what it is saying is that if at instant of time t, if at this instant of time some particular instant of time say t_0 the Boltzmann equation is satisfied when the slope, local slope at that point is negative, so its H function will go like this. But it is not saying that at all these instances of time the Boltzmann equation is valid, the local instantaneous slope to one side is made.

(Refer Slide Time: 42:38)



And then you can also show by clever argument that if at this instant of time the Boltzmann equation is going to be satisfied then at an immediately preceding instant the slope is positive okay. So this function actually fluctuates in this crazy fashion, it is not monotonic at all. So what we do and what we can establish is that at some of these peaks at local peaks at points where the Boltzmann equation is satisfied, the H function is at a local peak, the converse is not true, we are not saying that at all such peaks the Boltzmann equation will be satisfied. And certainly it is not satisfied here or here or here, so it is only satisfied in a statistical sense.

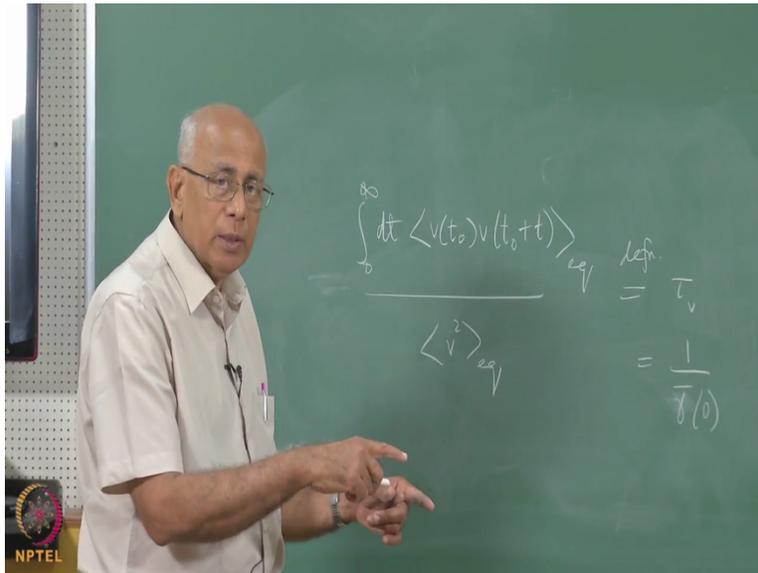
Then there are others questions about how frequent are these points, how much dense are they and so on, those are certain questions okay, there is lot of integrate stuff involved there. So the theorem is very clear and the statement has (())(43:02) H of t is not monotonically decreasing function of t, it is rapidly fluctuating function of t. Then finally consider the gas in absence of an external force, let f equilibrium be the equilibrium phase density and $v_1 + v_2$ goes to be v_1' v_2' as usual, it is an elastic scattering process between 2 molecules.

Then statement, f equilibrium is unique and satisfies a detailed balance condition such that f of v_1 , f of v_2 is equal to the product f of v_1' f of v_2' , true or false? True, this satisfies by the system is in equilibrium okay. So at this stage detailed balance is valid and it is necessary and sufficient condition for equilibrium. So that condition actually as we saw determines the

equilibrium distribution completely because what you do is to take logs and then it says $\log f$ of $v_1 + v_2$ is $\log f$ of v_1 prime + v_2 prime.

So $\log f$ of v must be something which is a function of all the quantities that are conserved in the collision process such as constant, the velocity itself of equal mass particles, some of initial velocities and some of the Kinetic energies, so that is what necessary and sufficient condition. For proving the necessary part of it we have to go through the H theorem, sufficient was inspection just by looking at the fact this condition satisfies the (44:40) and in the absence of external force f is time independent exclusively, so that part was straight forward, so the statement is true okay.

(Refer Slide Time: 45:38)



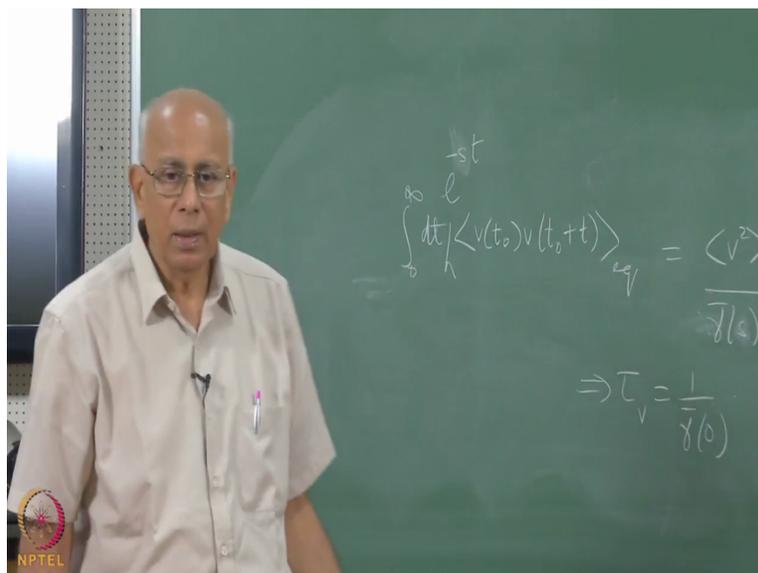
Then we have a few Fill in the blanks, the 1st of its said that we have a system satisfying the Langevin equation and you are asked to find the velocity correlation time in terms of the memory kernel. So what is... integral 0 to infinity dt $\langle v(t_0)v(t_0+t) \rangle_{eq}$ divided by $\langle v^2 \rangle_{eq}$, this quantity has dimensions of time, this is by definition τ_v the velocity correlation time. And the question is in the ordinary Langevin equation this was Γ^{-1} . The question is, what is it in the generalised Langevin equation? Pardon me...

(Refer Slide Time: 46:44)

$$\int_{-\infty}^{\infty} dt e^{i\omega t} \langle v(t_0)v(t_0+t) \rangle_{eq} = \frac{\langle v^2 \rangle_{eq}}{\gamma(\omega) - i\omega}$$
$$\Rightarrow \tau_v = \frac{1}{\gamma(0)}$$

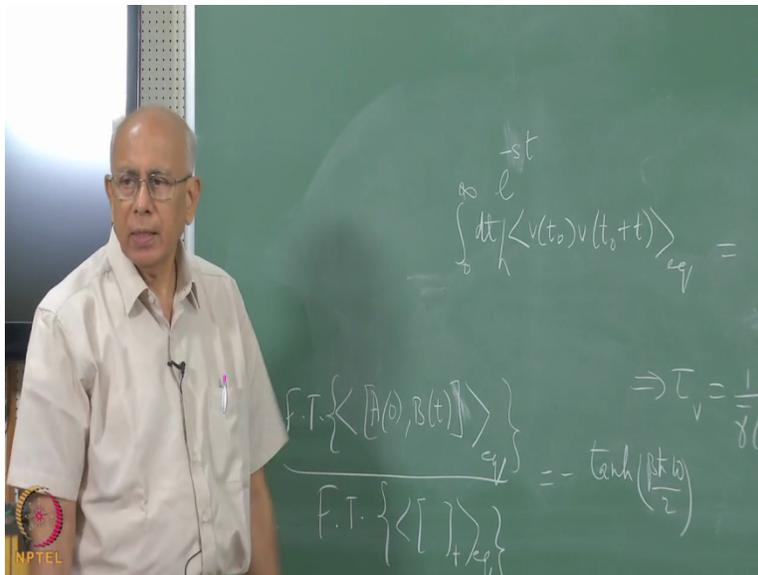
Yeah this quantity is equal to 1 over Gamma bar of 0, and the way you establish that is to go back to the 1st fluctuation dissipation theorem which essentially says that if you multiply this by e to the i Omega t then you get this quantity is equal to v square equilibrium which is K t over m as usual divided by Gamma bar of Omega – Phi Omega, all you have to do is to set Omega equal to 0 and divide by this quantity so that immediately tells you, this implies the Tau velocity is 1 over Gamma 0. As indeed you can see that in the case of constant friction this will go to 1 of over Gamma.

(Refer Slide Time: 47:41)



But again I repeat, in the generalised Langevin equation this quantity is not an exponential decaying exponential, something much more complicated. You can easily see what it will be instead of this $e^{-i\Omega t}$ imagine this to be the Laplace transform so certainly this is true, e^{-st} of this is $\Gamma(s)$ where this is the Laplace transform $+s$. Therefore this quantity is the inverse Laplace transform of this expression, had this been a constant that was just $e^{-\text{constant} \times t}$, but this is some complicated function of s we do not know what it is in general. So the correlation function can be very messy very very messy indeed, you have to invert this Laplace transform, it is not a rational function of s in general okay.

(Refer Slide Time: 48:36)



Then the next one was to find the Fourier transform of A of 0 , B of t commutator equilibrium the Fourier transform of this fellow divided by the Fourier transform of the same thing but with anti-commutator. Now we know that this thing here was equal to the spectral function on the right-hand side $\tilde{\Phi}$ of $A B e^{-i\Omega}$ whatever it is. So the Fourier transform was essentially $i\hbar$ cross times the spectral function. The Fourier transform of this had the same thing except there was a quart hyperbolic with a ‘-’ sign. So this ratio will become – and hyperbolic $\beta \hbar \text{ cross } \Omega$ by 2 that is it. All you have to do is to read of the Fourier transform in each case.

(Refer Slide Time: 50:18)

The image shows a green chalkboard with a handwritten equation. The equation is:
$$\langle A^2 \rangle_{eq} = \frac{i\hbar}{2\pi} \int_{-\infty}^{\infty} d\omega \frac{\tilde{\phi}_{AA}(\omega)}{1 - e^{\beta\hbar\omega}}$$
 The chalkboard also features the NPTEL logo in the bottom left corner.

Then the equilibrium mean square value of A square is related to integral of the spectral function according to what? Now you have a formula for A of t B of t prime or A of t prime. B of t whatever it is expectations in terms of the spectral function spectral representation. Only got to do in that is to put A equal to B and t equal to t prime right, so you end up with A square equilibrium therefore cannot be dependent on time, this is equal to i h cross I do not know if there is a 2 Pie there must be a 2 Pie somewhere yeah over 2 Pie integral – infinity to infinity d Omega Phi tilde of AA of Omega for 1 – e Beta that is it.

Student: (())(50:19)

Yeah, you get an apparently different expression so what happens? If you use A of t so you have one expression for A of t prime B of t, then you have another expression for B of t A of t prime then you have a third expression for some of the 2 which is really the Fourier transform, which is this type right? In everyone of these except in the commutator where if you put A equal to B and t equal to t prime you get 0 equal to 0, except for that all of them will give you expressions. There is only one expression right, so what is happening yeah they will all give you exactly the same if you simplify this. If you simplify this thing here this, I pull out a half h cross Omega here and then this becomes – sign hyperbolic or whatever it is this side right?

So they will all give you exactly the same expressions. One of them has an e to the Beta h cross Omega on top, this one does not have it at all but you can convert one to the other, you have to be little careful. You also have the d to the i Omega whatever it is right, so in doing this conversion you may have to change Omega to $-\Omega$ okay, so it is just a little piece of algebra that you have to do but you should satisfy yourself that all of them will give exactly the same expression, I can write that in several ways.

(Refer Slide Time: 53:25)

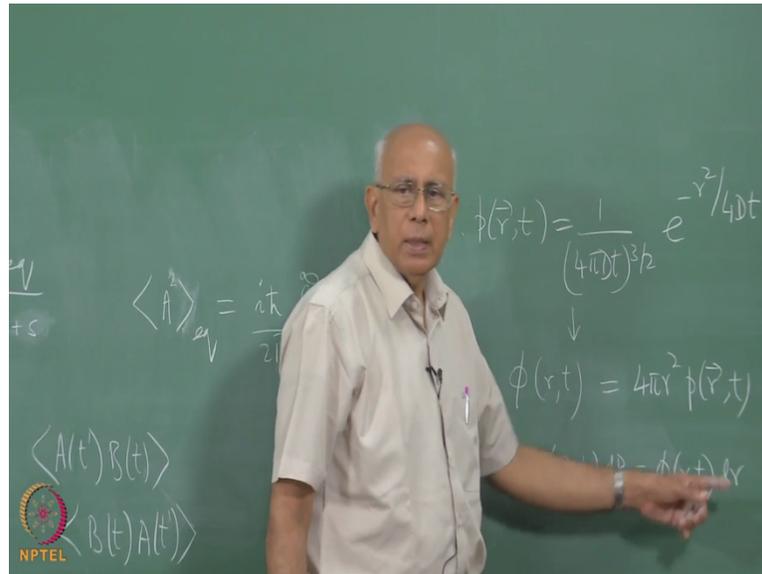
$$p(\vec{r}, t) = \frac{1}{(4\pi Dt)^{3/2}} e^{-r^2/4Dt}$$

$$\downarrow$$

$$\phi(r, t) = 4\pi r^2 p(\vec{r}, t)$$

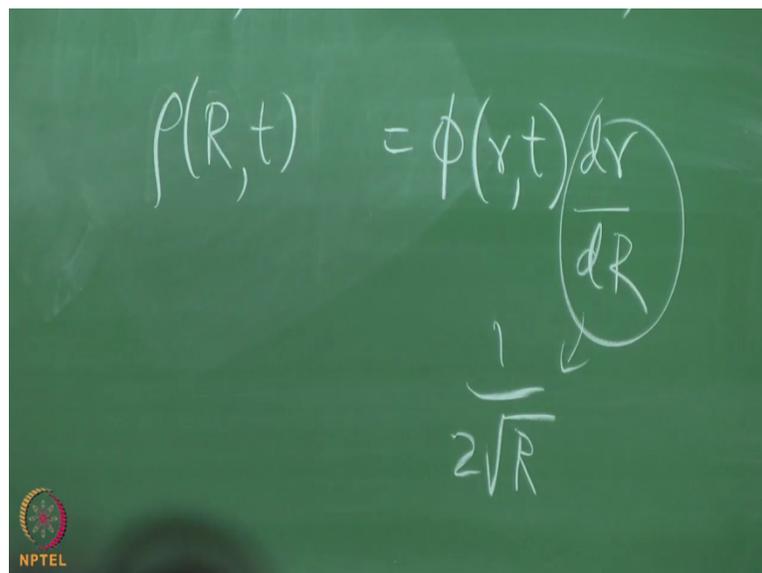
When they came these questions on diffusion which I think could uhh might have been little tricky because we did not spend too much time on this when I discussed this topic. So the 1st question says, uhh to find diffusion in 3 dimensions we have the Gaussian fundamental solution of diffusion equation and then you want to find the probability distribution of r square which is also random variable. Now that is straightforward because all you have to do is 1st you find the probability distribution of little r , which is $4\pi r^2$ times the fundamental distribution and then so let us suppose that you have p of r, t equal to $1 / (4\pi Dt)^{3/2}$ $e^{-r^2 / (4Dt)}$.

(Refer Slide Time: 54:13)



From here you go to let me call it Phi of r, t with distribution of r itself, this is just equal to 4 Pi r square P of r and t. It is density, you integrate over angles and you get (PDF of the radial distance okay. Then you want to go to Rho of R but we know that Rho of R dR – Phi Rho of R and t. If the little r is between R and r + v r, capital R is between r and capital T r then this equation obtains in this case, both are positive so we have no problem, it is being mapped only once. So if you plot r and R it is a 1 to 1 map okay and then therefore there is no complication about folding and things like that.

(Refer Slide Time: 55:00)



So this immediately implies that this quantity, so it says, take this quantity, eliminate little r and write it in terms of capital R and put this Jacobean factor in which is equal to 1 over 2 root R, we should not forget that, then you get something like square root of capital R e to the – capital R by 4 Dt so that is the density that part is still here. The next question is what is the Fokker Planck equation satisfied by it? And the last part of its says what is the Langevin satisfied by? Now there you have to be careful, to find Fokker Planck equation is not very trivial, what would you do? We will discuss the answer, after I have gone through the answer books just to find out what people have done. What would you do?

Student: We know the Fokker Planck equation (55:39)

(Refer Slide Time: 56:12)

$$\frac{\partial p}{\partial t} = D \nabla^2 p$$

$$p(\vec{r}, t) = \frac{1}{(4\pi Dt)^{3/2}} e^{-r^2/4Dt}$$

For what? We know the Fokker Planck equation for this that is just the diffusion equation. What should you do to get the Fokker Planck equation for this? So this quantity is Delta p over Delta t equal to D del square P that is the Fokker Planck equation, just the diffusion equation. What should I do to get the Fokker Planck equation for this?

Student: (56:15)

In this equation put P equal to Phi over 4 Pie r square and then solve, write it as an equation for Phi, so that is the Fokker Planck equation for Phi. What should you do for Fokker Planck equation for this?

Student: (56:38)

Change variables once again, do the same thing. Now use this use this relation here and then get.

Student: You can do it in one step.

You can do it in once step, of course you can do both these in one short okay. Crucial point is each time you have to keep track of the Jacobean, this one is the phase space factor and this one is the Jacobean factor you got to keep track of that. So you got the Fokker Planck equation for Rho and then you got to use this correspondent backward in order to get the Langevin equation for capital R okay. That will have a drift term and it will have multiplied noise so it is not the ordinary diffusion equation.

(Refer Slide Time: 58:41)

$$\dot{r} = \dots$$
$$R = r^2 \Rightarrow \dot{R} = 2r \dot{r}$$

(V²)
eq 1

Could I have just done this starting with Langevin equation for little r and then going to capital R? After all if I get some equation, do not ask me how, equal to something or the other, can I simply say R equal to r square implies... Can I put this and get the Langevin equation for this? No, no, this is where the tricky part of white noise or the wiener process comes in okay, when you have multiplicative processes.

Whereas going through this route of this correspondence between the Fokker Planck and the Langevin equation systematically is a shortcut okay to get the Langevin equation for capital R or

little r for that matter which are non-trivial statements because this so-called white noise that we talked about is not a well-defined object mathematically, you have to use what is called Wiener process and then you have to use (Ito) (58:33) calculus which is somewhat different from normal calculus, so you will not do that but I will mention after I go through your answer books, we will come back and I will mention what the right answer here is okay.

So that this last portion would have been a little time-consuming, the rest I think was very straightforward. Okay, so we will start next time with critical phenomena.