Nonequilibrium Statistical Mechanics
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Lecture no 27
Module no 01
The Boltzmann equation for a dilute gas (Part 5)

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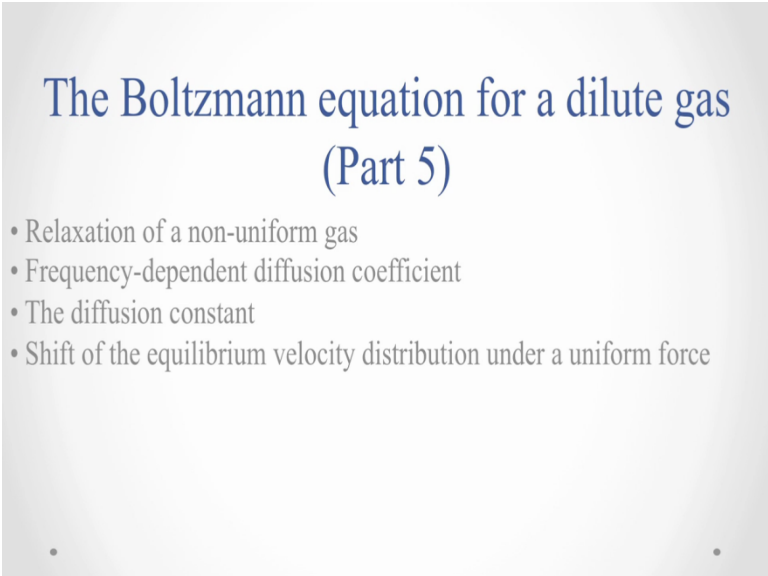

Right so we started looking at the way in which non-uniform distribution equalises becomes uniform as a function of time, essentially the diffusion problem in the context of the Boltzmann equation and we have whole lot of symbols on the board, but let me go over it again and then we will complete where we were getting at. So if you recall, we want to look at the distribution we want to look at f of r, v, t on the timescale where the velocity has essentially formalised that is where the diffusion regime is okay, although we are not explicitly saying so.

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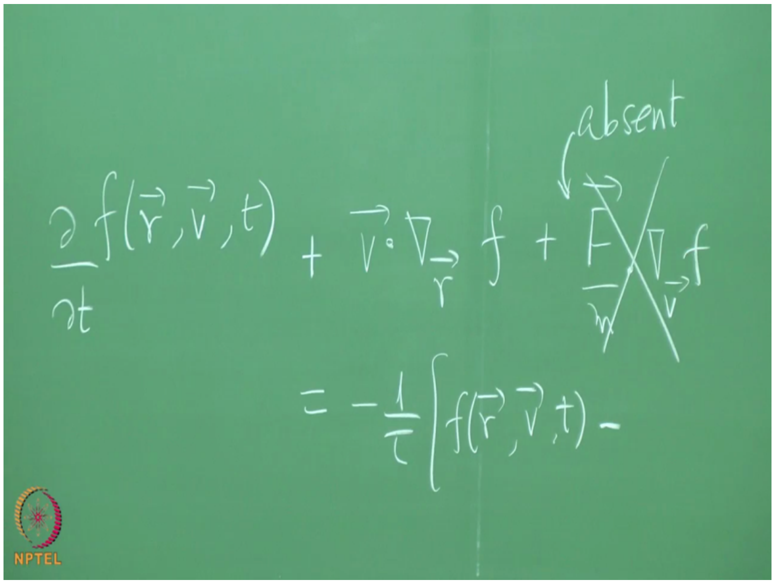

So we would like to ask what happens if the velocity distribution is Maxwellian essentially but the positional distribution is a function of time, starts with some initial given prescribed distribution and then it obviously is a function of time, due to diffusion it equalises. We are trying to understand that process and understand the timescale which appears in the problem when you try to find out how it goes to this equilibrium situation. So the equation we wrote for f was Delta over Delta t + there is a v dot Del and that is definitely present, this term Del r is definitely present because we are trying to find out how this function of r changes okay.

So this time f + an external force but that is 0 there is no external force so F over m dot grad v this term acting on it, this term is absent. And this is equal to on the right-hand side – 1 over Tau times f of r, v and t – whatever it relaxes to, whatever the system relaxes to. Remember that when we look at the Langevin problem in phase space one part of phase space, I said that beyond the diffusion time the joint probability density in phase space factorises into a portion which was essentially Maxwellian times the portion which satisfied the diffusion equation. I did not said it is equal to constant, it satisfies the diffusion equation we are trying to see that emerges here okay.

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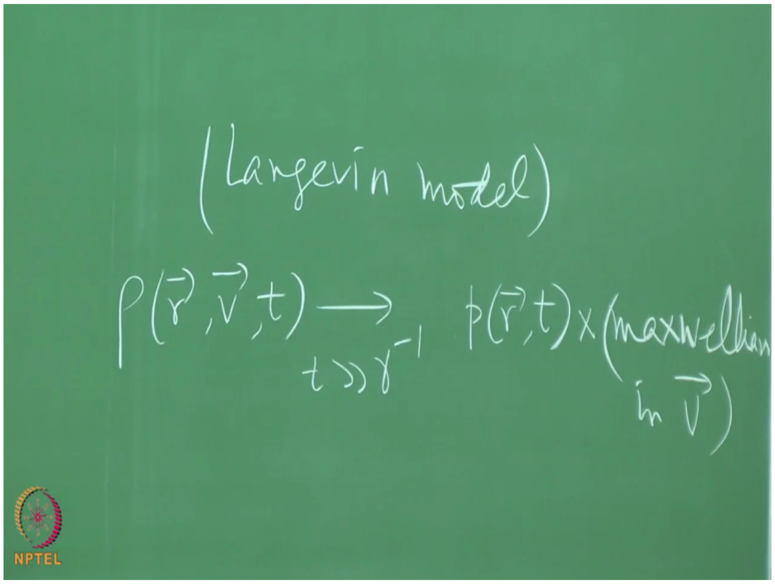

So that is the point that you raise and that is what we are looking for, we are trying to find out what happens. Just to recall to you we had a row there we had a row of r, v and t and we said that when t much much much greater than Gamma inverse in the Langevin model in this case, this went to some probability distribution r, t times Maxwellian so in the velocity. That is that is the one that that is what we discovered in the diffusion limit and then we found out what the equation satisfied by this quantity, so it is in that way that this is being done.

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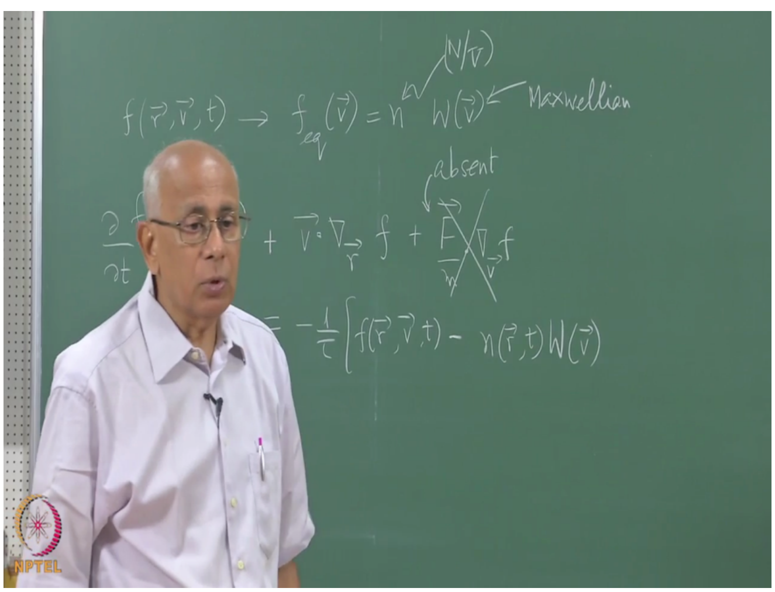

So what we need here is an n of r, t times W of v which is the Maxwellian distribution. So just to set your normalisations remember that f uhh of r, v, t, if you integrate this over r and v, you end up with the number density finally. So this quantity here f equilibrium this goes to f equilibrium of v that is the absolute uniform distribution in space, so this is equal to n a constant just the number density at constant times W of v which is the Maxwellian, the Gaussian distribution in v with a variant which is proportional to k t okay. So that is what is setting here except that it is not the equilibrium distribution we are going to, we try to find out what is this distribution, so target is actually to find out what this point is.

Student: (())(5:21) if t tending to infinity.

Well if t tends to infinity in the solution of the diffusion equation, everything becomes 0 in an infinite volume. Here everything will become uniform distribution, 1 over the volume it is not very interesting uh. We are trying to find out what is the mode by which what is the timescale that is really what we are trying to do. So we put in a timescale here and we are trying to see how this timescale is going to play a role in controlling the timescale on which things equalises okay. But of course we must also look at another fact which is that when you have a nonuniform distribution and you do a Fourier transform in space, you have all wave numbers so you can resolve it into sinusoidal fluctuations on all link scales on all wave numbers, right?

Now the question is, how does that play a role? So clearly the relaxation time is going to depend on the wave number itself, so there cannot be one relaxation time right. There is going to be a dependence on the wavelength, so a disturbance which is very long wavelength disturbance is going to take different time to relax then one which is a very short (())(6:40) that is what should come out. So although we put in one constant here, we are going to get a whole family of constants, a continuous family of constants so it is going to depend on the wave number of the fluctuation and the question is how okay yeah.

Student : (())(7:00) velocity reaches the equilibrium distribution position.

That is right, exactly.

Student: We can always (())(7:09)

Yes absolutely yeah. We already saw what is the timescale in which this one, in this single mode thing we already saw that this Tau is the velocity relaxation. So now we are looking at timescale much bigger than that Tau but it will depend on what k is what the wave number is, so this is what we are going to discover right. Essentially we are going to find the whole family of relaxation time one for each k, but how does it depends on k is a question okay. So this is the target and now we are in business, so let me go through it quickly since we did this already last time.

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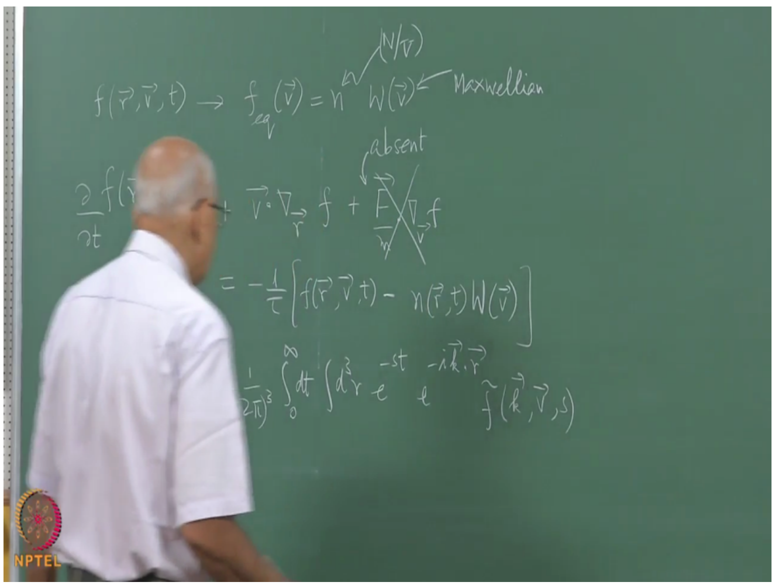

I do a Fourier transform with respect to space and Laplace transform with respect to time so essentially we are going to write f of r, v, t equal to well 1 over 2 Pie whole cube integral 0 to infinity dt integral d 3 r e to the – s t that is the Laplace transform. And then the Fourier transform was e to the – i k dot r f tilde of k, v and s. Oh (())(8:39) d 3 k and our Fourier transform convention was Laplace sign for this case. I should write inverse transform, we should not do that way.

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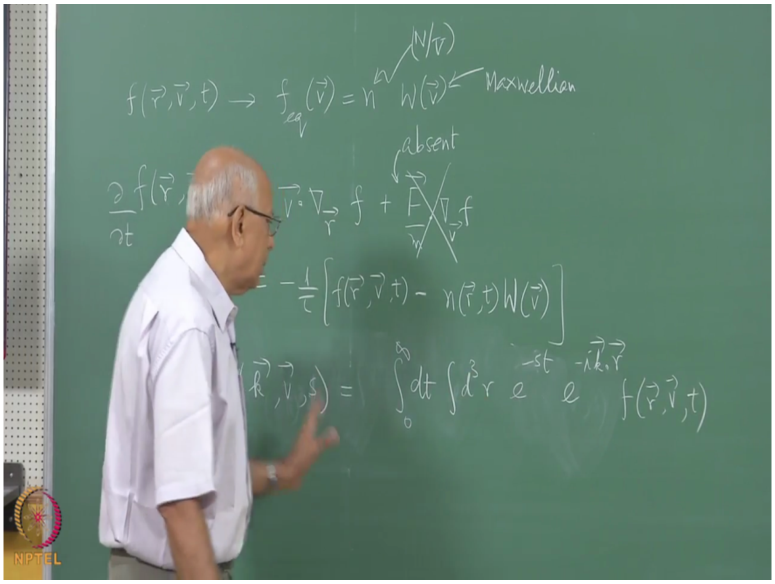

So let us write f tilde of k, v and s equal to integral from 0 to infinity dt integral d 3 r e to the power – s t e to the power – i k dot r f of r, v and t okay. And inverse transform will have a 1 over 2 Pie cube v to + i k dot r and this is going to become + st over (())(9:40) whatever. So what is going to happen here, d over dt of this guy but this fellow if I write it down it is going to pull on i k dot r so let us write this down.

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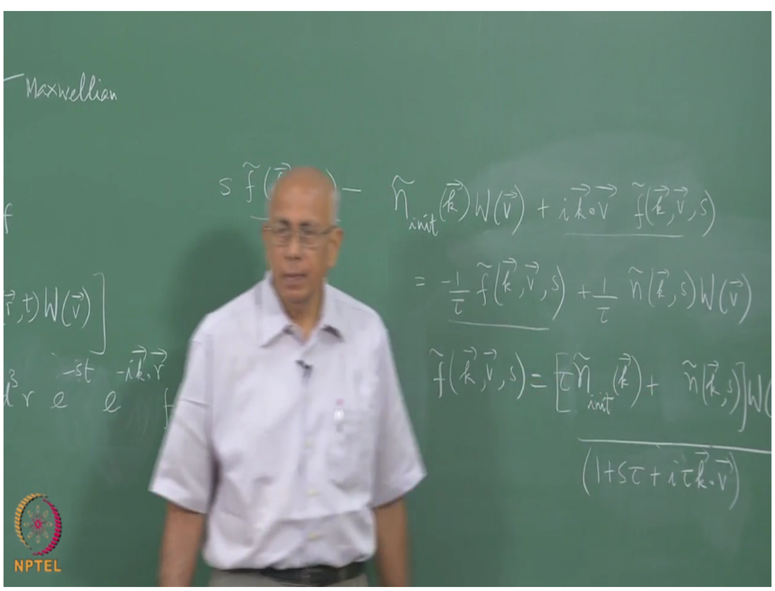

So we have s time f tilde of k, v, s – the initial value. Now we made that the assumption that the initial distribution f of r, v, t this is going to be is equal to some initial some initial distribution in r at 0 multiplied by w of v that is the assumption we have made right. So – if I take the transform, n initial tilde of k W of v that is the value of this guy after Fourier transform in space. And then there is this term is going to pull v dot whatever Del r acting on this fellow is going to put + i k dot v on f tilde of k, v and s. And this is equal to – 1 over Tau f tilde of k v, and s on this side + 1 over Tau n tilde of k and s times W of v okay we got all the factors right now.

So I bring this, this and this to the left-hand side and I have s + i k dot v + 1 over Tau I think on f tilde of k v, and s equal to so this term has been taken into account so has this and so has this and move this to the right-hand side, this is equal to n initial tilde of k + 1 over Tau n tilde of k and s times W so that they can solve this term and this term. Should not there be what?

Student : (())(13:03)

We are finding the Laplace transform of the derivative time derivative so it is the transform of this function – the value of the function in time at t equal to 0 which is all I have written, but then I did a Fourier transform in space and so let us move this fellow down here this thing divided by s + i k dot v + 1 over Tau, let us multiply both sides by Tau so that it is Tau times this + just that equal to 1 + s Tau + this i Tau k dot v and this goes that is it. Now of course we need to close this set of this equation, so what we do, we integrate over v, we integrate over v and I get precisely v n tilde of k and s once I finish integration over v because f of r, v, t if I integrate over v I get n of r by definition.

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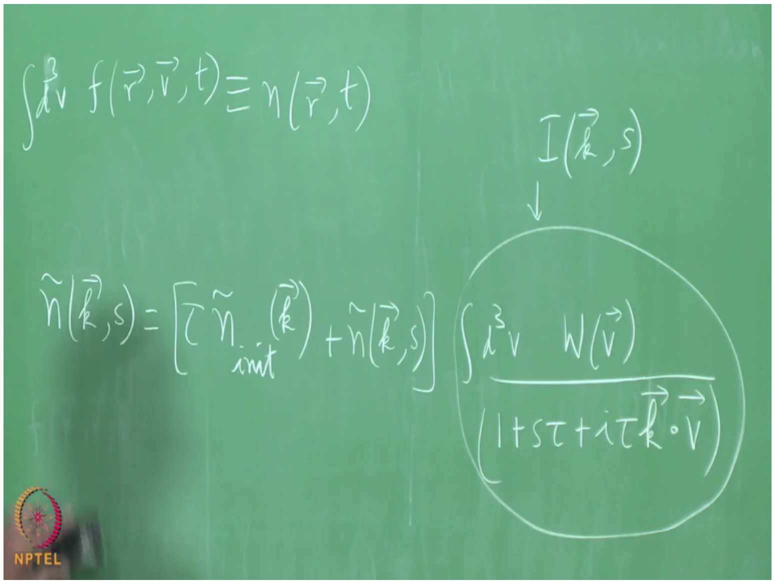

What we have is integral d 3 v remember that, so I integrate and Fourier transform so I am going to get f tilde of K is n tilde of k, s if I take Laplace transform. So this tells you that n tilde of k and s equal to Tau n initial tilde of k whatever that be + n tilde of k and s here in the bracket times integral that integral is integral d 3 v W of v divided by 1 + s Tau + i Tau k dot v. I have to integrate this over v along with that and it comes out.

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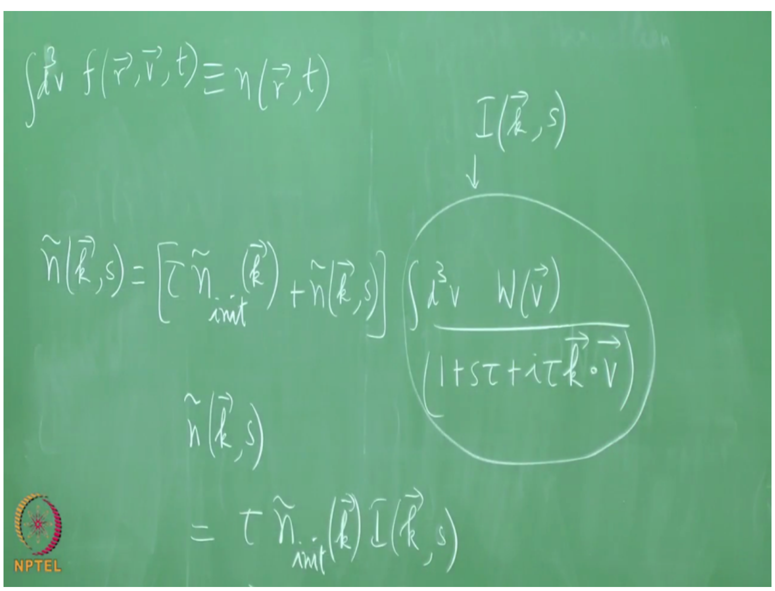

So let us call this integral something, let us call this uhh integral i some integral and it is a function of k and s, the v is gone. So I have 1 – I k and s times n tilde of k s equal to Tau n tilde initial of k let me write it properly equal to Tau n initial tilde of k times I of k and s, divide by the factor 1 – I of k and s that is the solution okay. Now everything is known, we know this is a Maxwellian, in principle if something the denominator (())(17:20) so once you do this integral you know this function explicitly, it in both places and you know this from the initial distribution so therefore I know the Fourier Laplace transform of n of r, t of this one and it is the one I am trying to find out.

Of course it cannot be inverted and analytically, this is a terrible mess, this itself is bad and then on top of it you are going to put that here and then invert both the Fourier and Laplace transform, it is not a possible task okay. But what are we trying to get? We are trying to find out what happens at long times and what happens on long length scale, the scale on which diffusion occurs, the modes the longest wavelength the shortest wavelength the largest sorry the smallest k which means longest wavelength, k is the wave number okay which is why the diffuser modes are.

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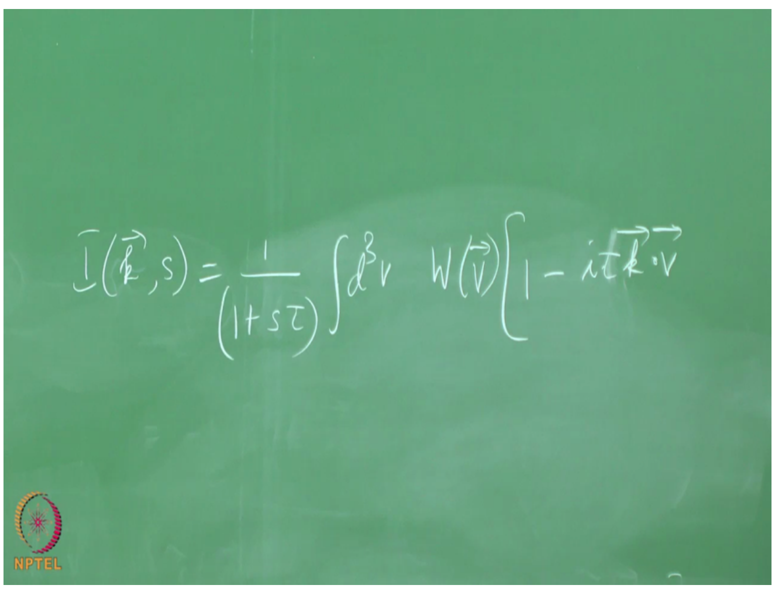

So one way to do this is to expand this whole thing in powers of k, this is 1 + something and you say k is going to be near 0, so expand this systematically in powers of K using the binomial theorem and do the 1^{st} order, 2^{nd} order, et cetera terms. Now when you do that, you can see immediately what is going to happen here so let us try to expand i of k and s equal to let us pull this out of the denominator and then do a binomial expansion in powers of k. So that is independent of v so this is 1 over 1 + s tau and then an integral D3 v W of v times one I am going to pull this out and take this denominator here, so it is 1 + something inverse and therefore it is 1 – i k dot v i Tau yeah.

Student : (())(19:41) so we can choose a particular k.

Absolutely

Student: And then (())(19:51)

Oh yeah yeah yeah precisely, what you are saying is the first-order term in table will vanish, all other things will vanish yeah, I just want to show you explicitly how that happens as you can see. So this divided by 1 + s Tau, we must keep the next term because that is not going to be 0 so it is 1 + x inverse which is 1 – x + x square but then there is – sign here because of this guy so – Tau square k dot v the whole square divided by 1 + s Tau square + dot dot dot.

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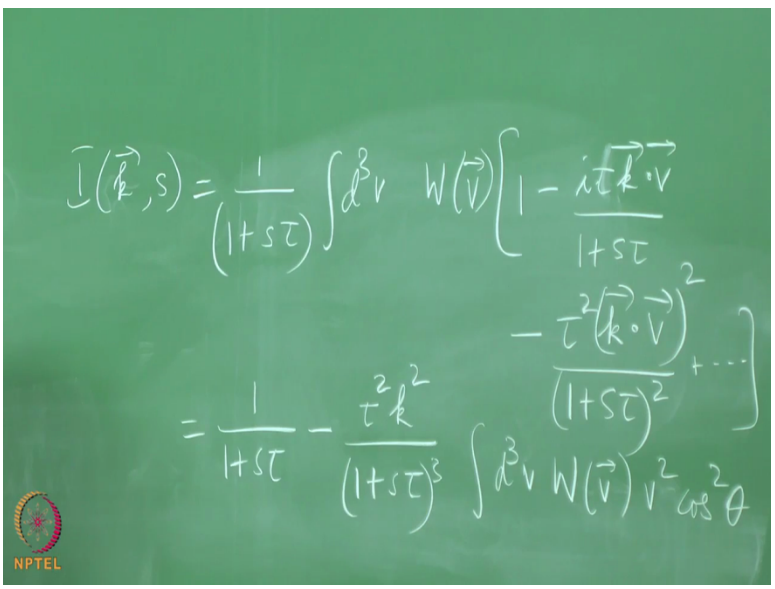

Now integral D3 V W of v is 1 because it is a normalised Maxwellian already so the 1st term is 1 + now this term here has a k dot v, obviously you should use polar coordinates such that polar axis is along v, then this becomes k v Cos theta and you do an integral on Cos theta from – 1 to 1 d Cos theta so that is an odd function and it vanishes, it is obvious from isotropy here. So the first-order term is 0 and then this one is the first non-zero term uh and that is easily evaluated so you have 1 – 1 over 1 + sorry, so this is equal to 1 over 1 + s Tau – Tau square k square divided by 1 + s Tau the whole cube is 1 factor here and 2 more there times and integral D3 V W of v and then v square out here times Cos square theta where theta is a polar angle.

I have assumed that we are going to polar coordinates spherical polar coordinates in these space and chosen the polar angle polar direction along that of k because that is the vector that is sticking out right, so you are going to get v square here and then a Cos square here + higher orders.

Student : Anything better to do this (())(22:49)

Yes yeah I just want to do it in spherical polar coordinates because I do not want to get into Cartesians and count different kinds of integral, there is only one integral to be done here right. In fact, I am not even going to do the integral, I am going to leave it to you as a homework problem it is a trivial problem, but what I want to do is to extract the temperature dependence of this term that is crucial. There is temperature sitting there in W of v on the Maxwellian, I want to know what it looks like that is the main point I want to get at right. So we should keep this, but you see this term here what is it going to be?

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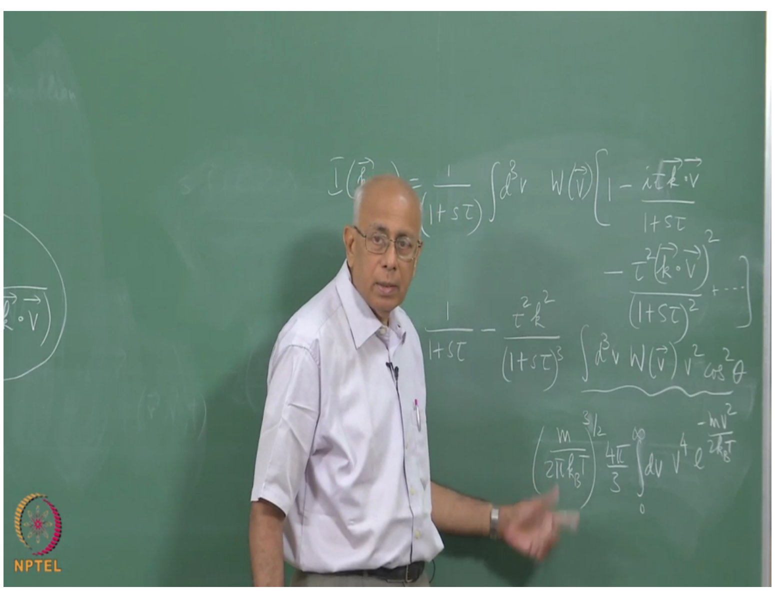

There is first of all in the Phi direction there is 2 Pie, so first of all this fellow is n over 2 Pie k Boltzmann t to the 3 halves that is the normalisation of this W of v – and then there is v square dv and then there is 2 Pie from the Phi integration, this is v square and Cos square theta and Cos square theta is integrated from – 1 to 1 so it is twice the integral 0 to 1 and then it is twice integral from 0 to 1 divided 3 so it is 2 over 3 times 2 pie is 4 Pie over 3 that is why I mean it is obvious you are going to get 4 Pie over 3 and all that is finishing then you are left with an integral 0 to infinity d v there is already a v square and v square so it is v 4 e to the – m v square over 2 k Boltzmann and it is a Gaussian integral with B 4 here so it is a trivial thing to do.

Change variable so m b square over 2 k t then you are going to get if you call that u or something like that, there is going to be 1 over square root of u and then a u square so u to the 3 halves so there is going to be Gamma of 5 halves but you can scale this fellow out completely, v square scales like k t so this will go like k t whole square and then there is 1over square root of k t here and there is this fellow sitting here, so (())(25:22) there is going to be a k t finally whatever be that constant from k t over (())(25:31) okay I leave that to you as an as an exercise.

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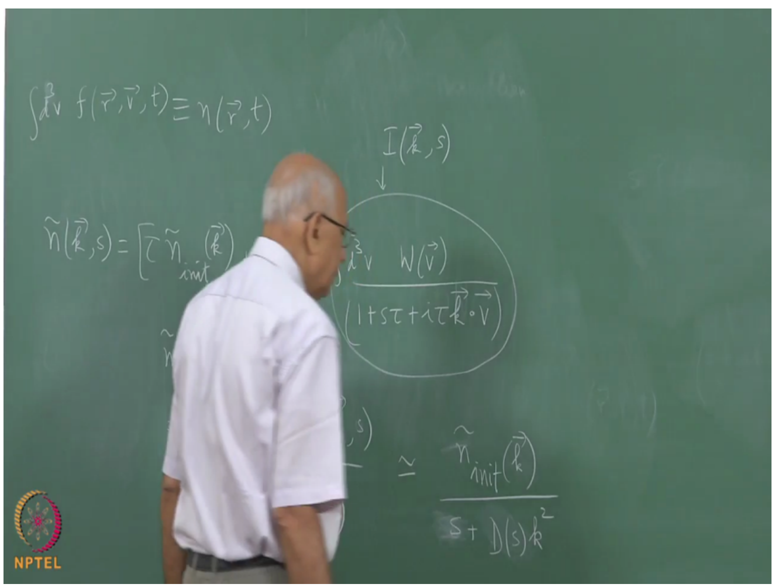

Whatever it is, finally let me write down the final answer down, is a very well-known answer let me write this down. This fellow after you put that in here and here and then keep to order k square because it is the order to which you cut it off everywhere except this. So the coefficient of whatever this is correcting this initial distribution has a term which is of the order 1 and in order k square and so on and so. So if you do that, this term here becomes equal to it looks like the following n initial tilde of K divided by s + function of s and we call it D of s times k square.

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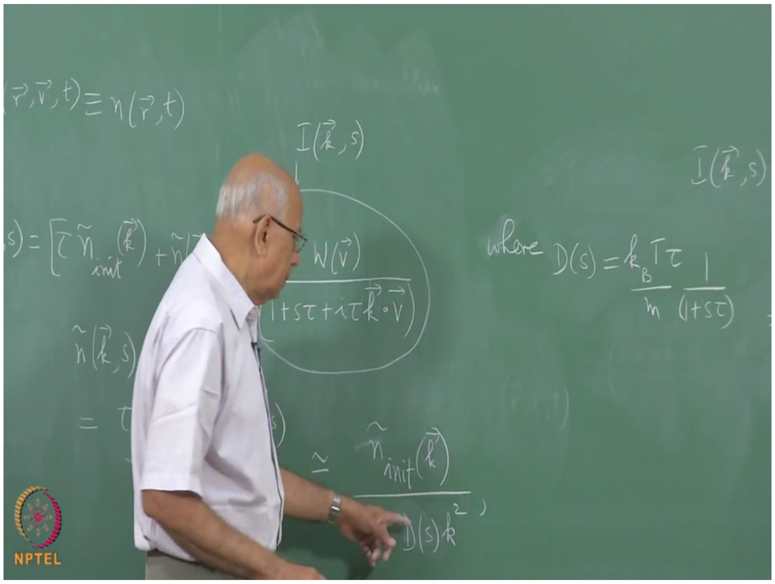

Where I have used this D of s deliberately because it has dimensions of the diffusion coefficient, this fellow has got dimensions of time inverse and this fellow is linked to the – 2 so this whole thing this therefore must have dimensions L square over t, which is the dimensions of the diffusion constant so I call it D of but it is a function of s where D of s equal to and now it is not surprising, you are going to get the temperature dependence from here so it turns out to be k b T Tau over n 1 over 1 + s Tau. You could have sort of guess some of these things, 1 over 1 + s tau because that is appearing here goes with the k square so that is the solution.

Now you have to tell me about what this is, and then I have to invert it with this weight and this weight here. But now let us see, we are trying to ask how does the initial distribution whatever it is how does it defuse out? Okay. It depends on the poles of this okay because when I do inverse Laplace transform, 1 over s + Lambda has inverse transform e to the – Lambda t right, so it is going to depend on k square. Therefore, the leading relaxation is going to be of the form for s Tau much much less than 1 because we want long time or small s going to 0, you can neglect this term.

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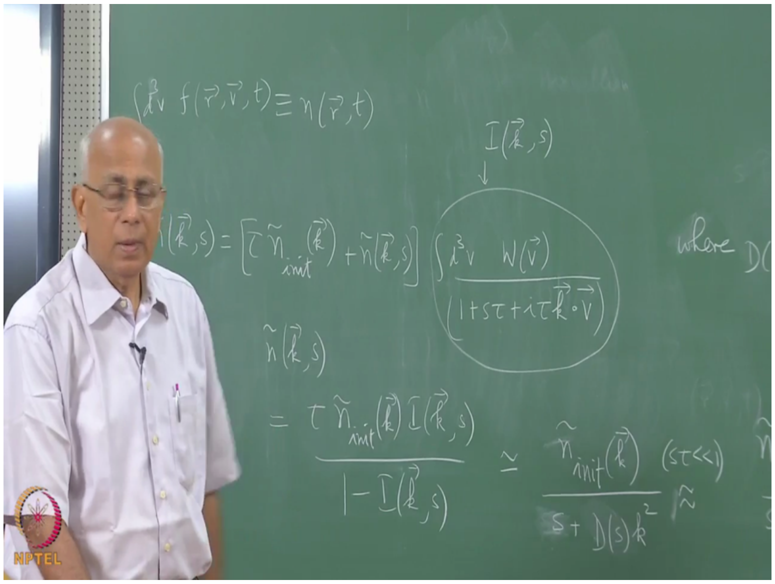

So this is going to look like n initial of K tilde divided by s + d of 0 k square. And now you know exactly how it is going to relax because I can invert the Laplace transform it is therefore trivial and it says finally, so it says n tilde of k and t let me leave the k still, it is equal to n tilde initial of k e to the – D k square t, where D is k Boltzmann T Tau over n, so you see it is typical of what it is exactly what we expect. Remember, in the Langevin model we have got k t over m Gamma and the velocity correlation time was Tau Gamma inverse. Well, here the velocity correlation time is Tau in this model and m is the mass of the molecule.

So the approximation has been sort of gross in that sense that it has become essentially the mass of molecule, but this Tau is completely arbitrary completely arbitrary, we just put that in mayhem. So that is the diffusive mode as you can see and you can see it is a Gaussian solution because what is the inverse of Fourier transform of just this guy, if you make this it will give me start with a Delta function for instant, then this fellow here is a constant. If you give me Delta function in r, this m Tilde of k is a constant. So and then the inverse Laplace transform of e to the – k square a Gaussian is of course e to the – r square again a Gaussian.

Now this Gaussian has a variance 1 over dt and in r it will have a variance proportional to d t, so you have exactly the diffusive behaviour with this diffusion constant d okay. But it is giving you a lot more information, this thing is telling you much more it is telling you how other modes relax in principle. So even though it is a single relaxation time approximation, because of this complicated way in which k appears and s appears, it is actually telling you much more, it is going beyond this diffusion approximation okay. So this is how space dependent relaxation appears.

So first we said the velocity itself how does it relax given a uniform distribution, we found that was rather trivial it was like a Kubo Anderson process. Then we said what happens if we have nonuniform spatial distribution, well it is diffusive this is called diffusive mode. Now let us ask another question, suppose the distribution in space is uniform and I start with the equilibrium distribution but now I switch ON an external force, then what is going to happen?

And let us in the simplest case let us switch ON the force, which is time-dependent but uniform so that the uniform distribution in space does not change however, you put on a force external force and these particles are going to get dragged, so I expect that the Maxwellian distribution will be disturbed. And if the force finally goes to a constant force as a function of time then the Maxwellian certainly will be distorted, sort of intuitively in the direction of that force right, so that direction should be singled doubt, let us see how that happens okay.

Now we will play the same game, and it is quite an easier thing so let us do that. So till now we were looking at problems where you were little away from equilibrium, you relaxed equilibrium, but now I start with the equilibrium and I push it out of it and ask what is the new distribution to which it goes?

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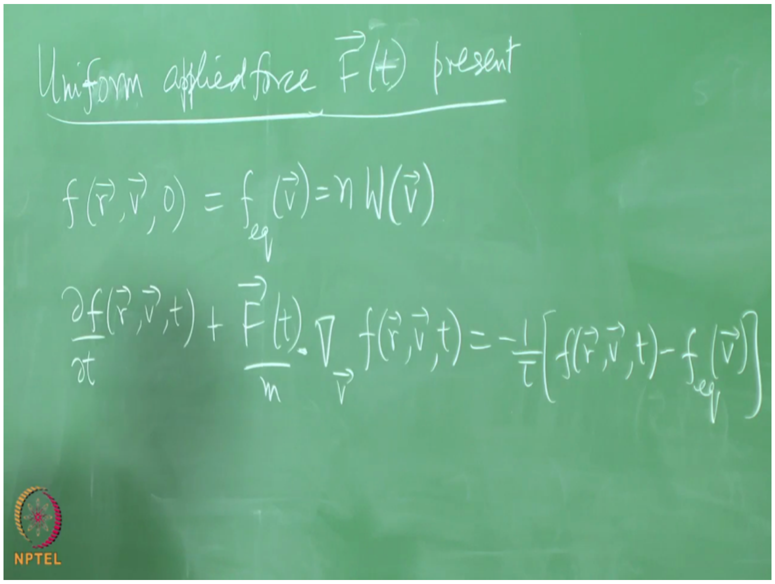

So constant uniform, so I have f of r, v, 0 the initial things is the equilibrium distribution which is equal to n times W of v okay and it is a uniform force. So uniform force is not going to destroy in initially uniform spatially uniform distribution, it is going to remain spatially uniform, so I do not have to worry about the gradient term with respect to r acting on this thing at all. Then what happens to the equation that we have, it has some force F of t, no r dependency.

We have data f over Delta t and there is function of r, v and t + F of t over n dot gradient with respect of the velocity that is important of f of r, v, t, this guy is equal to – 1 over Tau f of r, v, t – f equilibrium of v, so I want to know how f is moved away from equilibrium distribution because that is what I started at t equal to 0 this is the difference in the single relaxation time approximation, so this is the equation I have to deal with.

Now clearly it is sensible to call this something else, equal to some g of r, v and t. In particular I want to compare the answer we are going to get here with whatever we know from linear response theory, remember in linear response theory we found the average velocity divided by the applied force with constant applied force per unit applied force was the mobility. And in the case in which the force was constant timing dependent, we got static mobility so we want to see what happens now in this case, but this is completely kinetic. We do not need to carry the r dependency because there is no term with respect to this guy so we forget about it completely, it is uniform everywhere.

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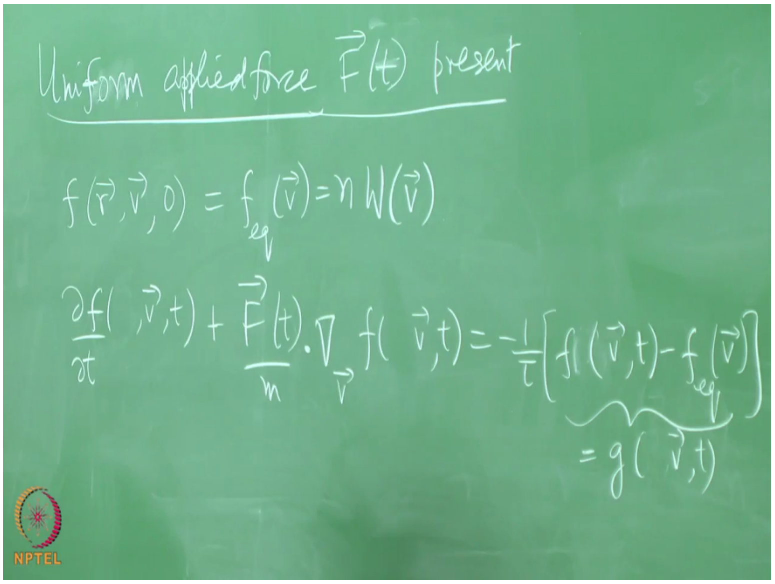

So let us make this f of v, t and that is it, no r dependency. The statement is, you have a force which is uniform time-dependent but uniform, you start with a initial uniform distribution, there is nothing which is going to make that distribution non-uniform in space okay, so this is what we got to work out this fellow here. And now let us put that in here so you get Delta g over Delta t + f of t over n dotted with gradient with respect to v of f equilibrium that is equal to f equilibrium v + g of v and t because f is f equilibrium + g (())(37:40) okay. This is equal to – 1 by Tau g of v, t.

We want to compare, now that is an exact equation right, however we have to compare with what happens when the external force is weak that is the whole idea that you want to compare with linear response theory. Now it is clear that this g is going to depend on the external force, there is no force, this g is 0 identically, will remain in equilibrium. So g is going to have a 1st order term then have second-order, 3rd order, et cetera, et cetera, but if you are going to work to linear response level then this term f times g is already of 2nd order in g right, this is a correction which is proportional to f and higher powers.

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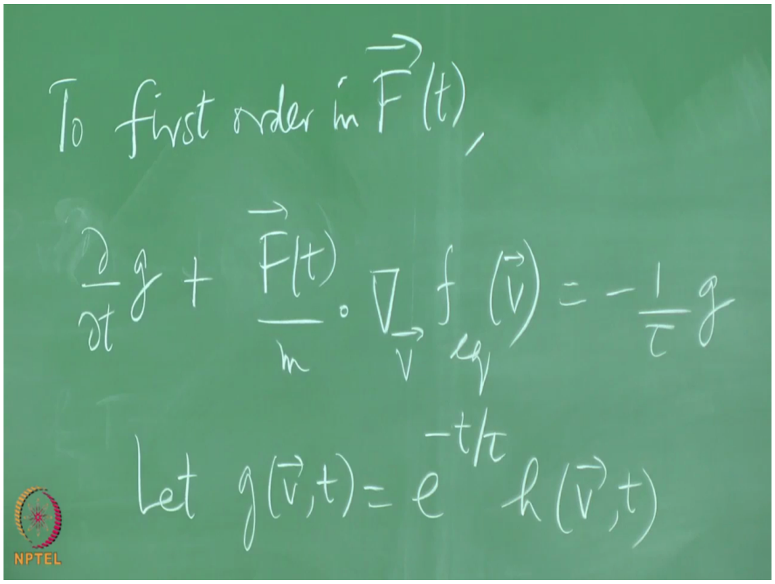

And this is already an f here so I am going to drop this with respect to this okay and then we get Delta g to first order in F of t, where equation is Delta over Delta t g that is this term + F of t over m dot gradient with respect to V of f equilibrium of v equal to – 1 over Tau. Now of course one brings this to this side and that is the same as saying that g of v, t equal to e to the – t over Tau times something else let us call it h of v, t let... Just removing this integrating factor. So the first term is – 1 over Tau times g itself and that cancels and then you have e to the – e over Tau Delta h over Delta t equal to – F of t over n dot gradient V f equilibrium v.

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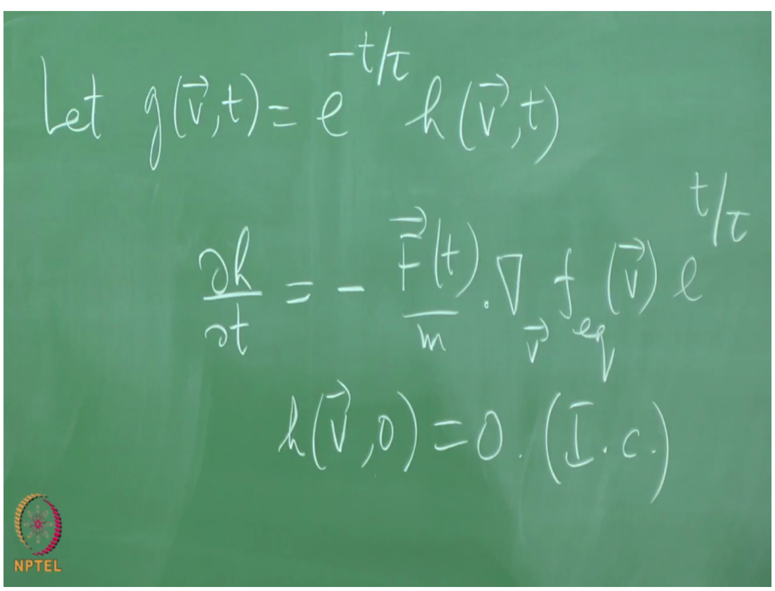

So move e to the t over Tau to the right-hand side, now what is the initial condition? Well the initial condition on this f was that to start with it was not the equilibrium distribution so g of v, 0 is 0 therefore, h of v, 0 is 0 this is the initial condition and we have a formal solution. What is the formal solution now?

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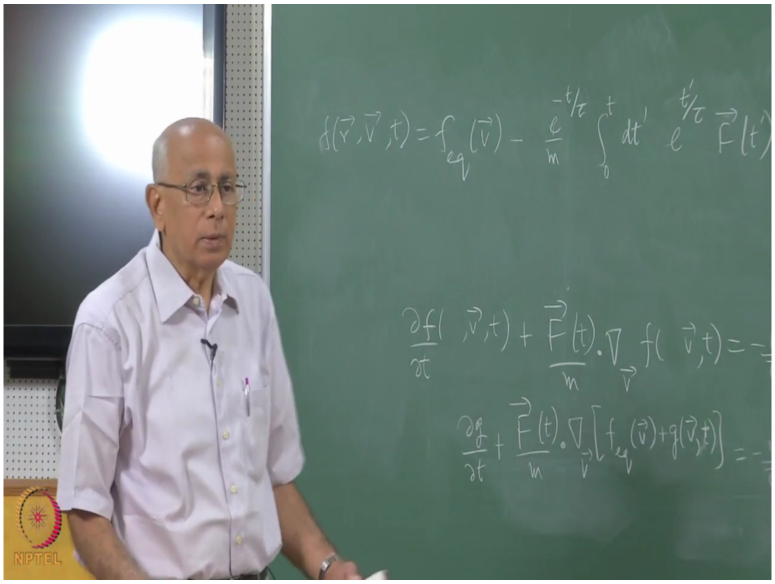

It says h of v, t equal to – 1 over m integral from 0 to t dt prime F of t prime dot gradient V oh (())(41:25) e to the t prime over Tau times F of t prime dotted with gradient with respect to V f equilibrium of v that is h, so it says g therefore, is e to the – t over time Tau times is that so this is e to the – t over Tau times and that is the formal solution for g, F however is f equilibrium + g, so it says f of r, v, t equal to f equilibrium of v – this thing and that is the solution.

We would like to see what happens at longtime if I put a constant force, so what I need to do is switch on the force by whatever means I like and a typical way to do this just to get an idea what asymptotic behavior is, is to do the following, it is called antibiotics switching and you do this in quantum mechanics for example. When you do participation theory, you switch ON the force slowly and not suddenly so that all the energy levels do not get giggle up but the same spectrum remains but gets slowly perturbed okay.

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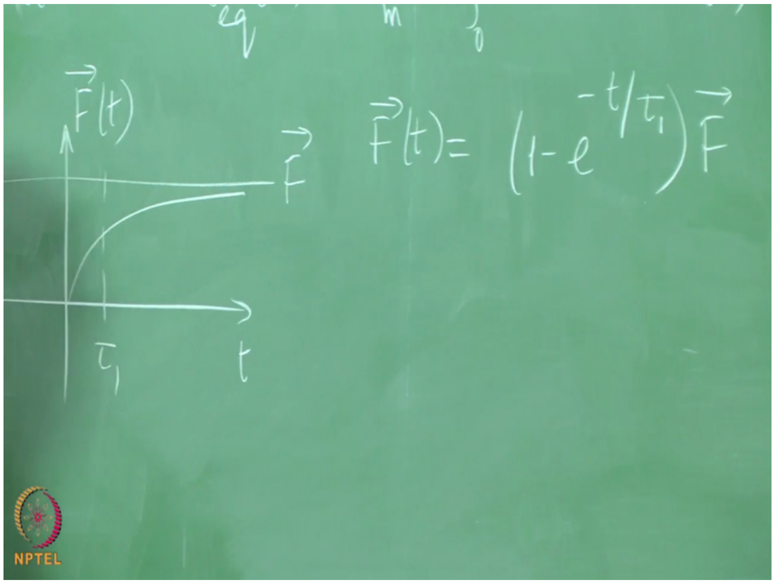

In the same way, here is the way to switch ON the force. So let us suppose that was the time axis you have here F of t magnitude of whatever, you want to make it go to a constant value, this value is f and let us say you start switching it ON at t equal to 0 because we took at t equal to 0 the system to be in equilibrium. And typically what would happen is that you would switch it ON, it would do this, you can choose any forces you like, but I would like to see what happens at longtime. So a simple model would be to say that F of t equal to it should start at 0 and should end up with capital F which I have to put in the end, so 1 – e to the – t over some time scale whatever you call let us Tau 1 F okay.

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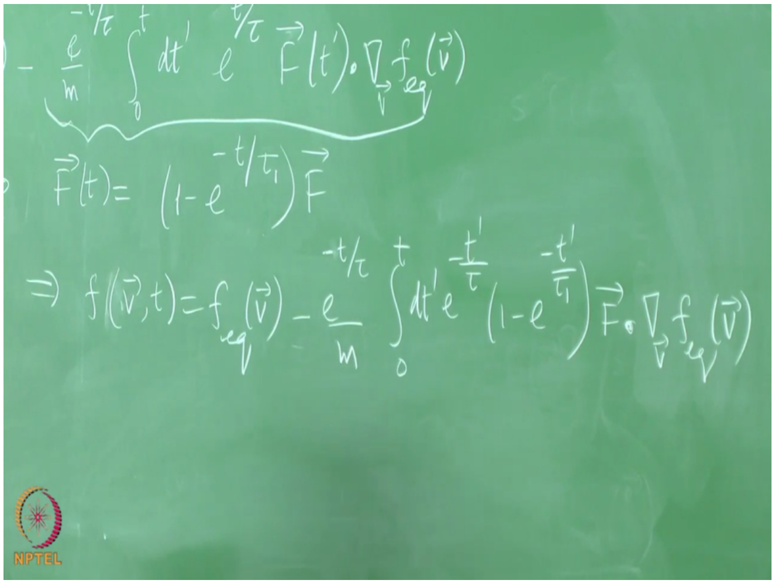

I mean this is typically Tau 1, the time scale on which this fellow essentially reaches 1 over its saturation value or something okay. So that is one way to do this, you put that in here when you integrate okay. So this fellow here becomes this term this term alone, let us look at what happens to this, let us look at the whole thing so this implies that f, there is no r... f of v, t equal to f equilibrium of v and then what? – e to the – t over Tau that was the relaxation time over m and then the time integral is a essentially integral 0 to t dt prime e to the – t prime over Tau 1 – e to the – t prime over Tau 1 and then there is outside there is an F dot grad v of f equilibrium of v, this fellow is independent of time just comes out and it is a trivial integral this whole business.

First is e to the whatever, it is the + I mean this is the + sign. So the 1st term is going to give you e to the t over Tau – 1 and when you multiply by this, it becomes 1 – e to the – t over Tau, the second term has got a smaller term which is a positive term, so it is 1 over Tau – 1 over Tau and if Tau 1 is much bigger than Tau for instance then this term is going to be positive 1 over Tau – 1 over Tau 1 but smaller than 1 over Tau. Therefore when you hitted with this, this integral that part will vanish exponentially. So the someone substances the only thing that remains for t much much greater than Tau and Tau 1 is f equilibrium of v – what remains?

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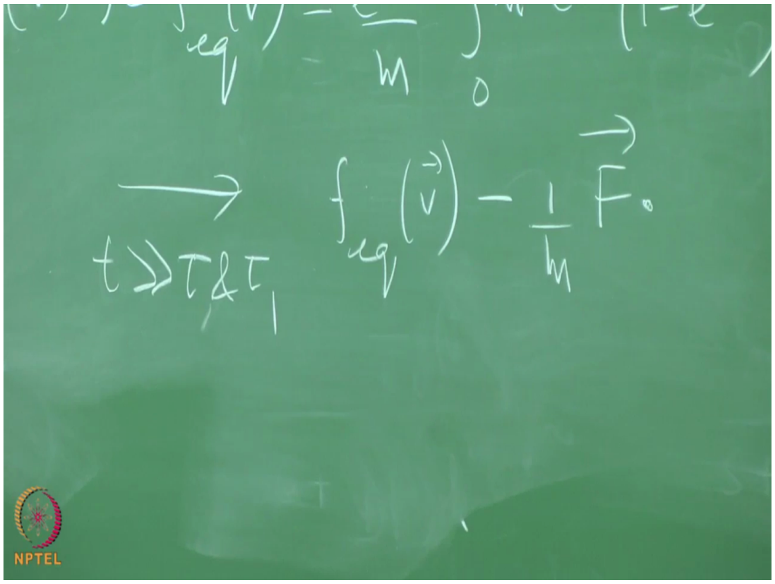

This is going to give you an e to the t over Tau leading term and it is going to kill this, so you are just going to get 1 over m F constant dot grad v of as equilibrium of v, what is that going to be?

Student: f equilibrium.

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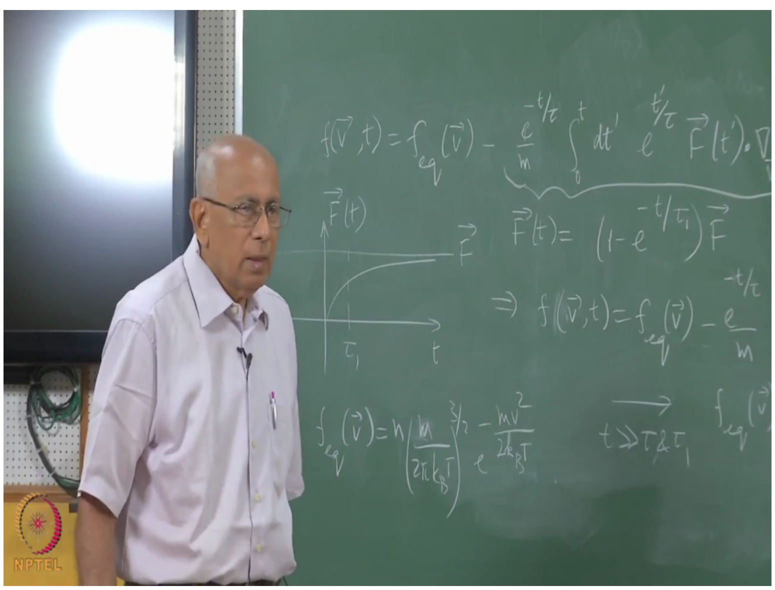

Because remember that f equilibrium of v equal to n times this m over 2 Pie k t stuff multiplied by e to the – m v square over 2 k Boltzmann T. Now what is the gradient of e to the – r square in physical space in three-dimensional space? Just d over dr is going to appear and in the direction of r, so the gradient of r square it is essentially r vector twice or whatever it is. Now when you differentiate this, it is going to give you twice and that twice would cancel here and you get to m over k t in the denominator looking starting to look like mobility as you can see and then there is going to be a space which is essentially v right.

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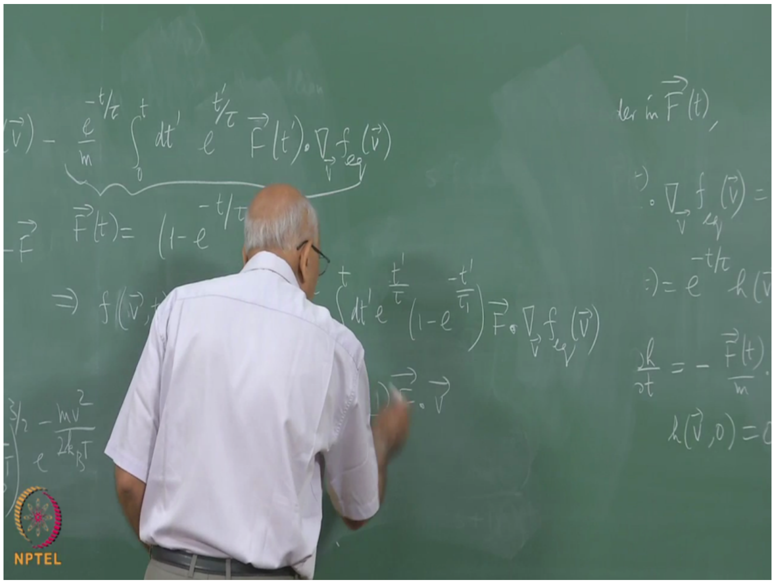

So this whole thing is going to look like f dot v apart from some constants, there are some constants which I leave you to figure out and then f equilibrium v, so it is going to become proportional to this.

Student : Constant is m by k v.

Constant is m over k v yeah, so there is 1 over k Boltzmann t and a ‘+’ sign because I am differentiating a ‘–’ here, so and a ‘+’ so we can even write this down + so constant is m over k v t, so this m goes away, but remember that when I integrate it to the t prime over Tau, I get a Tau on top. So yes, so there is going to be Tau over k Boltzmann t let us write it properly, so that is how it gets dragged in the direction of force okay, leading correction to 1st order in F. We know the answer should be proportional to it is going to be a scalar and the only other velocity you have is v itself, it is going to be proportional to f dot v and times this, this gives you the constant of proportionality okay.

Exactly, precisely F dot v is the rate at which power is supplied to the system, if a rate at which energy is supplied to the system, a work is done on the system by the force, so that is the sort of very straightforward interpretation. Now what is done in transport theory is apart from publications of solving the Boltzmann equation in various situations is you remember the collusion in variants we talked about, 1 and then the velocity itself which gave the momentum current and then the energy to current itself. So what one does is to take each of these currents and from that one can extract transport coefficients such as the shear modulus, the thermal conductivity, the electrical conductivity, et cetera, diffusion coefficient is already extracted.

So you have to construct, you can even construct heat current, the thermal conductivity because there is mechanical portion which is the moment of all these things depend on taking this follow here an integral of v times f of r, v, t times some something here some function of v as I put it, these are the current and if this follows 1 you got the momentum current, if this was Kinetic energy half m v square, you got the energy current and so on. So you take half m v square – the average value 3 halves k t or something like that and that gives you the heat current.

You can go one step further and say, I will find out what thermal conductivity is, what is the heat conduction equation, you can derive Fourier law for heat conduction equation here with a linear response by using this local equilibrium approximation. We say that the temperature is different at different places, but in a very mild way so you write t as a function of r itself, then the derivatives are going to special derivatives will act on that t and in that manner you will end up with Fourier law of heat conduction, which essentially says Delta capital T over little t partial little t is – thermal conductivity times Del square of t, we will get the t.

You will get of, actually we will get the formula for the heat current, which says it is proportional to the temperature gradient that is what will emerge automatically from this okay and so on. So I am going to call halt from this portion of it which is Kinetic theory really and we go on now to the current topic that is being current for a while, but it is still a very crucial one namely we will do Dynamic critical phenomena next. For that we will start with some notions of equilibrium critical phenomena, 2^{nd} with Continue phase transitions, talk about Mean field to worry and then we will see how time dependence comes in, so that is the next thing we take.