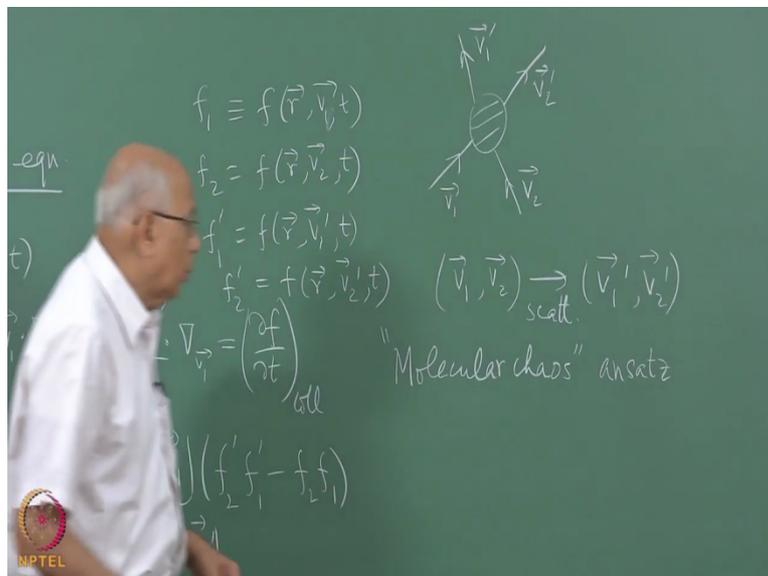
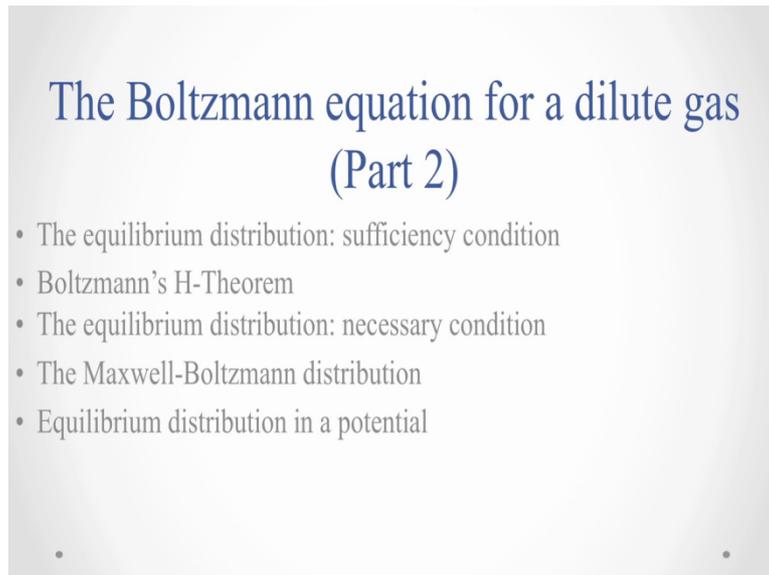


Nonequilibrium Statistical Mechanics.
Professor V. Balakrishnan.
Department of Physics.
Indian Institute of Technology, Madras.
Lecture-24.
The Boltzmann Equation for a Dilute Gas (Part-2).

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Right, so we had discussed last time the Boltzmann equation, very crucial equation and I will like to talk today about some consequences of it, specifically a very important consequence namely the equilibrium distribution. We have not taken this for granted that in equilibrium for a dilute gas, classical gas, the distribution is Maxwellian in the velocity. But now would like to see how that is rigorously derived from the Boltzmann equation itself. There are also

couple of points regarding the question itself, regarding the assumption which had like to reiterate, although I have mentioned this earlier.

So if you recall, just to refresh your memory, in the Boltzmann equation, for the one particle density, number density f of r, v , it is possibly time, due to Collisions and external forces it is evolving in time, this quantity f of r, v, t , under the assumption that the gas is dilute and only binary collisions are included, the details of the collision have not been specified, they have been kind of encompassed in cross-section, differential cross-section, for which there is a separate technology to compute that. But given a cross-section, a nonzero cross-section and some arbitrary external slowly varying field, this f satisfies the following equation.

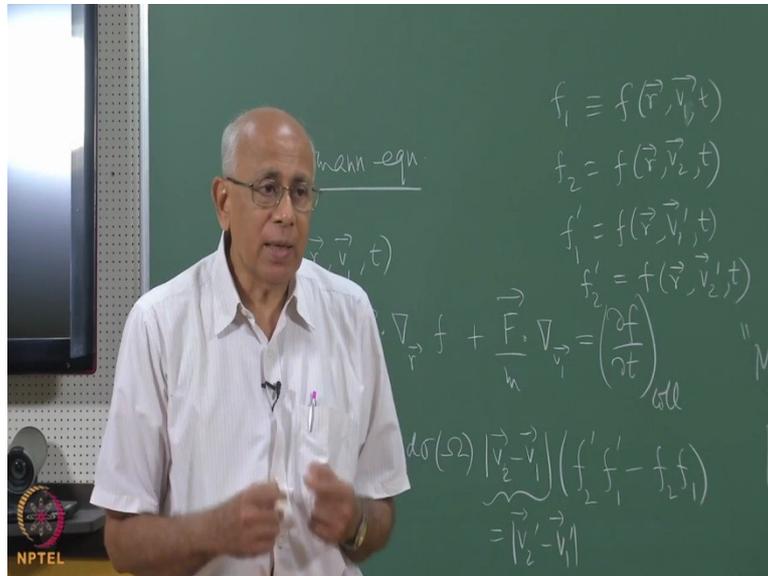
$\Delta f / \Delta t + v \cdot \text{gradient with respect to } r f + \text{any external force divided by } F \cdot \text{gradient with respect to } v$, let us let say v_1 , so v_1 here, this quantity here. This is equal to on the right-hand side by definition the collision integral, is equal to this quantity here. And for this Boltzmann derived formula, okay and that formula was, this is $\int d^3 v_2 \int d\Omega \Sigma$, this depends on which angle you are looking at times modulus of $v_2 - v_1$ times this factor, yes, times $f_2' f_1' - f_2 f_1$ in this fashion where these are the same functions f but under the following conditions. f_1 is shorthand for f of r, v_1, t and f_2 is shorthand for f of r, v_2 and t , where for any given v_1 , any v_1 that you specify on the left-hand side, v_2 is such that it undergoes scattering.

So here is v_1 coming in, here is v_2 , and then v_1 goes out, this particle goes out with a velocity v_1' and that goes out with the velocity v_2' and the scattering occurs inside. So these quantities $v_2, v_2', v_1',$ etc., they refer to what happens before and after the scattering. So f_1' is f of r, v_1', t and f_2' is f of r, v_2' and t . So once you fix v_1 , whatever be v_1 , then you integrate all, overall v_2 with these weights factors, such that v_1 and v_2 after the scattering process go to v_1', v_2' with all the consideration that this implies. Namely that $v_1 + v_2$ vector is equal to $v_1' + v_2'$, the squares of all, the sum of these 2 fellows is equal to the sum of those 2, etc. Etc.

This is the relative velocity and we also know that this relative velocity does not change different after scattering. So we know that this is identically equal to, by consideration this is $v_2' - v_1'$. I call this U last time and this is U' . So it is a non-linear equation with different arguments here, except for the positional argument which is the same, different velocity arguments for the 4 quantities, these 4 have different velocity arguments in them. Now crucial assumption that went here was that the distribution of the position is

independent, the position of the particle molecule is independent is of, it is not correlated with velocity, instantaneous velocity.

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That was crucial and it is called the assumption of molecular chaos. That was an ansatz which Boltzmann used in order to derive this equation, this set, this set of, this equation here. So the idea is that the velocity and position are not related to each other, so recall that f of r , v_1 , t times $d^3 r$, $d^3 v_1$, this quantity has a physical significance of being the number of particles with, at position r , in the cell located at the position r , with a velocity v_1 , this quantity here is the number, number density multiplied by the volume element in phase space.

And since this is appearing always in this pairwise form, the assumption of molecular chaos is equivalent to saying that this quantity multiplied by f of r , v_2 , t , $d^3 r$, $d^3 v_2$, this gives you the number of pairs of particles in a cell centred about the point r , such that the velocity of one of them is v_1 and the other one is v_2 . Okay.

(7:43) you actually write 2 particles.

Yes, if this was not true, this is where the dilute gas approximation went in. If this was not true and it was dense and there were recollisions being considered all the time, then you cannot have this completely independent of this, this probability, these density functions would not factorise, because whatever happens, we would say are how many pairs are there such that one of them has v_1 and are the other has v_2 , if they are correlated, then it is not just a product of the density here times the density there. There could be correlations, there could be memory of collisions and so on.

It is because you are avoiding, you are ignoring that, you are neglecting that, that you are able to derive this formula at all. Okay, this is crucial and of course now the question is can one prove this, can one prove this from dynamics, etc. A lot of effort has been expended in trying to find out whether Boltzmann, he called it molecular chaos, this is not although that is literal translation of the little phrase used. This is not quite the same as chaos in the modern dynamical system sense, although it is related, closely related to each other. The gas in this room for instance is certainly chaotic, it is badly chaotic.

It is Lyapunov exponent, namely the number which governs how quickly the errors get amplified, how quickly the initial conditions separate out as a function of time, that is of the order of number of degrees of freedom of the gas in the room itself. So you have Lyapunov exponent which is itself of the order of 10 to the 23, it is incredibly chaotic. But that of course, if you now speaking about the exact dynamical state of all the molecules in this room, then if you have 2 of them, I mean if you have 2 configurations which are infinitesimally close to each other, it would essentially double, this error would essentially double in time which is a Lyapunov time, the inverse of the Lyapunov exponent.

So it is just incredibly chaotic. Even in a few particles, you put in this room and they have a scatter of each other, dynamical chaos takes over almost immediately, it is not integrable. So all those this is related to it, this chaos is not the chaos, yah...?

So we write an expression like this $(10:15)$, is there a bound for this expression which says that below this there is a dilute gas $(10:24)$.

Yes indeed, so you got to now ask what is the correction to it. After all if I write the 2 particle density, then the leading term is this quantity and then the question is what is the correction. So one can make a systematic density expansion, for instance, in the simplest instance, if you take a gas, real gas, you would do what is called the virial expansion, that will immediately tell you what are the corrections to this leading approximation here. + there are various other ways of doing this, there are cluster expansions and so on. When we talk about nonideal gases, one essentially uses these facts.

There is a rigorous way of asking what are the, if this was not true, then what would be, what would appear here on the right-hand side in the collision integral would be the 2 particle distribution function and then you wrote in the equation for that, what would appear would be 3 particle distribution function and so on. So you have an infinite hierarchy. So in principle

you have an infinite hierarchy, but the point I am making here is that even in the simplest instance when you have got, when you have neglected all such correlations, you still have a terrible equation to solve, we have a non-linear integrable differential equation to solve in general.

So that is something I wanted to call your attention to. Namely this assumption is crucial assumption to do whatever we have done, to do this derivation, okay. Now the question is having got the Boltzmann equation, can we say something about what happens at t equal to infinity, then we say something about the equilibrium distribution? By definition equilibrium exhibition would be one which does not depend on time explicitly. So we would like to have $\Delta f / \Delta t$ to be 0 and then let us see what this distribution is.

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Equilibrium distribution

$f_0(\vec{v})$

$\frac{df_0}{dt} = 0$

~~$\frac{df}{dt} + \vec{v}_i \frac{d}{dv_i} f + \frac{F_i}{v_i} \frac{d}{dv_i} = \left(\frac{dI}{dt}\right)_{coll}$~~

Now if you have any equilibrium distribution $\Delta f / \Delta t$ must be equal to 0, okay. Alternatively as we have seen from all over the best experience, you could ask, if I take f of r, v, t and let t tend to infinity, then I expect to get, if it all equilibrium exists, I would expect to get the equilibrium submission. So let us impose that and for simplicity let us put the external field to be 0 for the moment. We will come back and see what happens if you apply and external force to the system. So once this is gone, the external force, what breaks translation invariance in the system is the external force. Otherwise the thermodynamic limit, you have translation invariance.

So we can assume f , if there is an equilibrium distribution, to be independent not only of time in this fashion but also of r . So I expect that the equilibrium distribution, if such a distribution

exist would be independent of r . So what happens then, in this equation this term is not there, f equilibrium, let me call the solution to this equation δf_0 , so the standard notation for an equilibrium distribution is f_0 , or f equilibrium, so f_0 is a function of v alone. No t dependence, no r dependence, then this term goes away because it is a gradient term on r , acting on f is 0 of course and there is no external force, so this is 0. Okay.

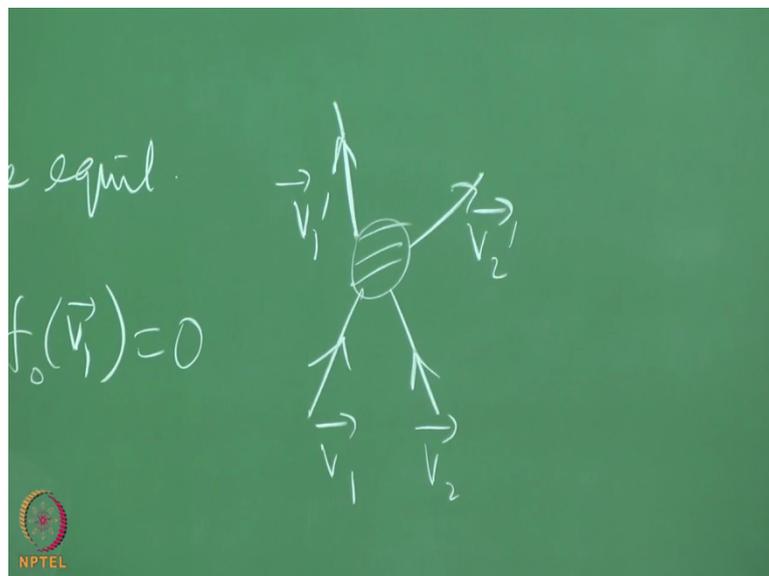
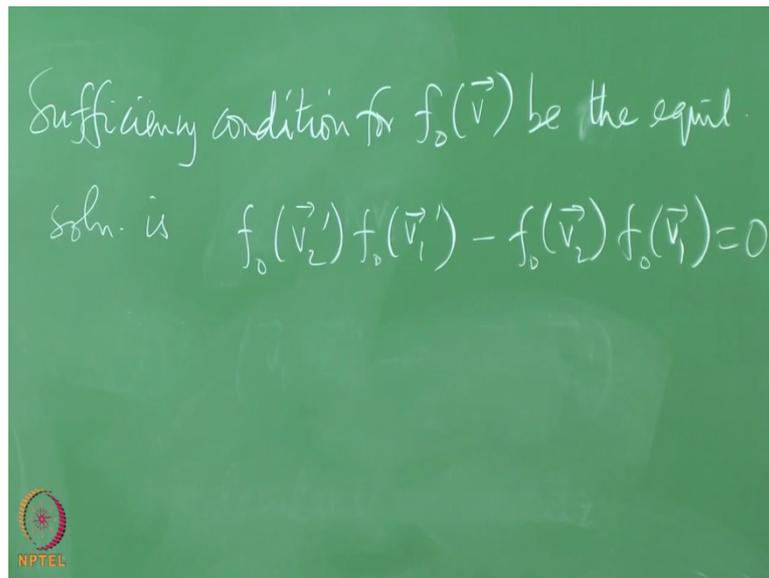
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$f_0(v_1)$ must satisfy

$$0 = \int d^3 v_2 \int d\Omega (-\Omega) |\vec{v}_1 - \vec{v}_2| \left[f_0(\vec{v}_2) f_0(\vec{v}_1) - f_0(\vec{v}_2) f_0(\vec{v}_1) \right]$$

So this will imply that that is f_0 satisfies this term equal to 0, the collision term to be equal to 0. So it must satisfy integral $d^3 v_2$, so f_0 of v_1 must satisfy integral $d^3 v_2$, integral $d^3 \Omega$ of $\Omega \sin \theta |\vec{v}_1 - \vec{v}_2|$ times and let us write this out explicitly. So this is f_0 of v_2 prime, f_0 of v_1 prime - f_0 of v_2 , f_0 of v_1 equal to 0, because that is δf_0 of v_1 over δt and that is 0. So for every v_1 , this function must satisfy this equation here. Okay, whatever be the scattering, whatever be the scattering. Now of course we can write one solution down by inspection and that is to say if this quantity is 0, this bracket is 0, where v_1 , v_2 , v_1 prime, v_2 , v_1 prime, v_2 prime are related by scattering events, nonzero cross-section, which are nonzero cross-section, otherwise this term will vanish.

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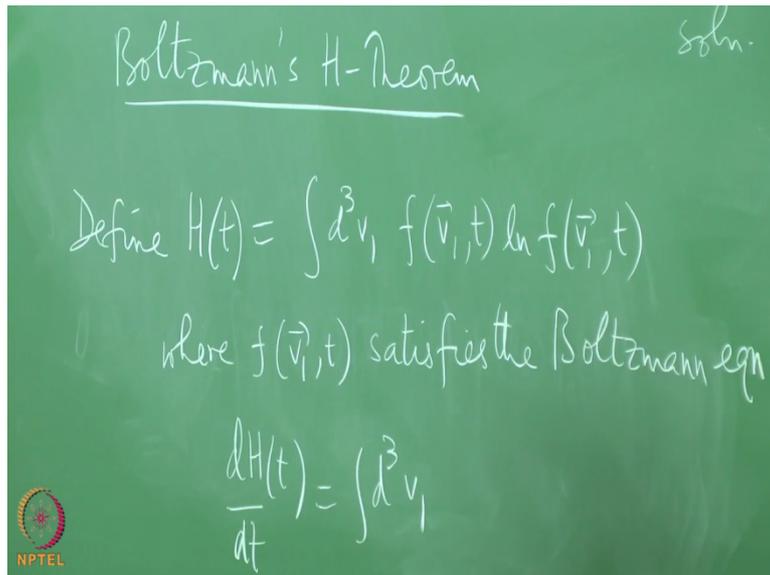
So there is genuine scattering, if the cross-section is nonzero, that is really collision and some scattering, then if this bracket vanishes, then that is a solution and then we should offer that examined to see what sort of solution it possibly is. So let us write that down, so sufficiency condition for f_0 of v to be with equilibrium solution is the following. f_0 of v_2 prime, f_0 of v_1 prime - f_0 of v_2 , f_0 of v_1 equal to 0, where v_1 , v_2 , v_1 prime, v_2 prime are related by a scattering, nonzero scattering cross-section. Okay. So that is always at the back of our minds, so we will draw that picture where these fellows are in this fashion.

And then we have to follow this up and they come okay if this is so, what are the consequences, can we guess what the function or can we solve for the functional form of this S , given all this information about scattering, that is one possibility, okay. But notice the

interesting thing, if this is so, if this is so, there is no reference to the actual details of the scattering. It only says the scattering cross-section should not be 0, so we do not care what sort of scattering cross-section it is but you would still get that to be so. So this of course is a very important consequence that whatever be this equilibrium distribution, it cannot depend on the details of the actual scattering.

So that is the reason why different gases with different molecular interactions have exactly the same Maxwell indistribution, we know that already by hindsight. The reason for it is very clear here that this thing is independent of the scattering some actual details of the scattering, okay, as long as the scattering is nonzero, that is all that is required. So that is one important lesson but it does not give us, that is very far unless we find out if this is also necessary condition. We proved it is sufficient that by Inspection, if this is so, the integral vanishes, then Δf over Δt is automatically is 0, that is the end of it.

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The image shows a green chalkboard with handwritten text in white. At the top, it says 'Boltzmann's H-Theorem' with a horizontal line underneath. To the right of this title, the word 'soln.' is written. Below the title, the text reads 'Define $H(t) = \int d^3v, f(\vec{v}, t) \ln f(\vec{v}, t)$ '. Underneath that, it says 'where $f(\vec{v}, t)$ satisfies the Boltzmann eqn.'. At the bottom, the equation $\frac{dH(t)}{dt} = \int d^3v,$ is written. In the bottom left corner of the chalkboard, there is a small circular logo with a star and the text 'NPTEL' below it.

$$H(t) = \int d^3 v_1 f(\vec{v}_1, t) \ln f(\vec{v}_1, t)$$

where $f(\vec{v}_1, t)$ satisfies the Boltzmann eqn.

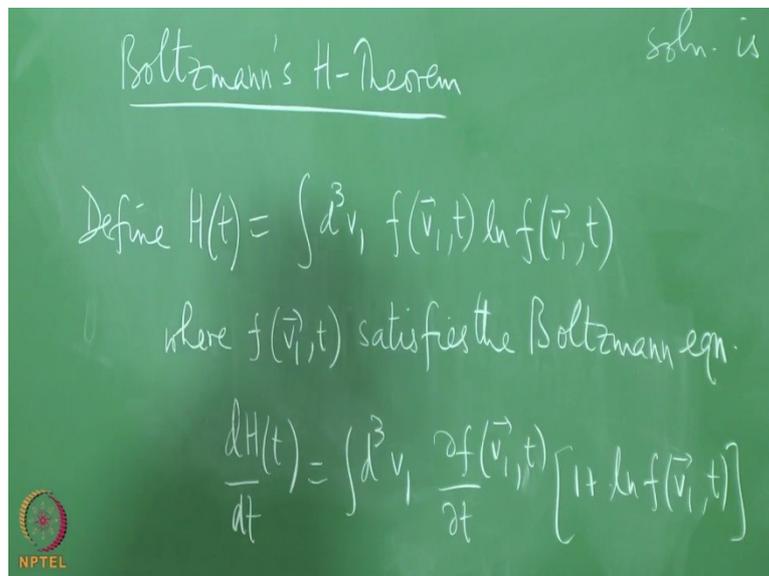
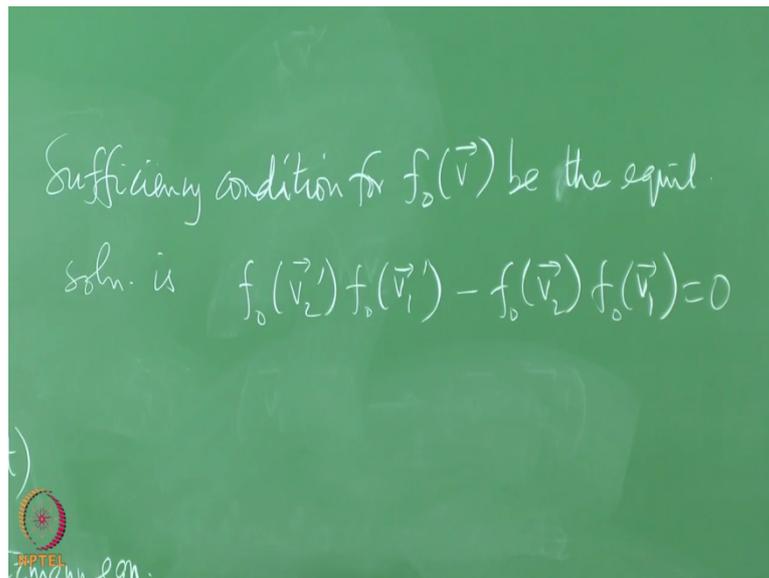
$$\frac{dH(t)}{dt} = \int d^3 v_1 \frac{\partial f(\vec{v}_1, t)}{\partial t} [1 + \ln f(\vec{v}_1, t)]$$

But is it necessary or not, to do that, Boltzmann used a very clever trick, okay. And this leads us to the Boltzmann H theorem, so let me write that. So we define a quantity each of t to be integral $d^3 v_1, f$ of $v_1, t, \log f$ of v_1, t where (19:44) the Boltzmann equation. So define this where f of v_1, t satisfies. And look at dh over dt , it integral $d^3 v_1$ with derivative of this quantity here. But that is a function of v and t , so derivative will be $\frac{\partial}{\partial t} + \vec{v} \cdot \text{grad}$. But this is independent of r , this thing here does not have any r dependence, okay. So therefore the $\vec{v} \cdot \text{grad}$, the convective derivative part is 0 and we just have $\frac{\partial f}{\partial t}$ inside.

So $\frac{\partial f}{\partial t}$ of v_1 and t , that is this term, there is a log there, the next term has 1 over f times $\frac{\partial f}{\partial t}$, it cancels this. So you have this multiplied by $1 + f \log$. Okay. So that is dh over dt , the next step that we took was to show that this dh over dt is not positive, it cannot be positive, it is less than equal to 0, okay. But that proceeds in several steps to show this. The 1st step is to note that if this fellow is 0, if this is an equilibrium distribution and this one vanishes because that in equilibrium distribution, then this is of course 0.

So it is necessary that this be 0 in order that $\frac{\partial f}{\partial t}$ be 0, it is a necessary condition. Okay. If $\frac{\partial f}{\partial t}$ is 0, identically, it means that it cannot have explicit time dependence and is therefore an equilibrium distribution. The statement is if this is 0, it implies dh over dt is 0, right, so you cannot have this to be 0 without having dh by dt to be 0. Therefore it is a necessary condition that dh by dt is 0 in order for this to be 0, okay. So what I am trying to do now is to show sufficiency condition, I am trying to show that this condition is sufficient for f to be an equilibrium distribution.

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We know it is, I am sorry, we are trying to show it is necessary, we already shown that it is sufficient by Inspection, okay. So you have to appreciate the subtlety of this argument. You want to show that f_0 of v is an equilibrium distribution if and only if this quantity is 0, okay. So that is necessary and sufficient, the sufficiency is by Inspection. We saw that the equation for Δf over Δt , Δf_0 over Δt was a big integral, the collision integral, and if the integrand and this vanishes identically, then of course the left-hand side is 0. So that was the sufficient condition, now we are trying to show that it is necessary.

And that proceeds by saying that define an H of t in this fashion, this time-dependent by the way out here, where this fellow satisfies Boltzmann equation with the collision integral. Now

the statement is the time derivative of this is this quantity here. And the observation is that you cannot have this to be 0 without having this to be 0, it is necessary.

How is it (0)(24:30).

Because there is no way this can vanish without this being 0. If this is 0, then this vanishes.

Converse if (0)(24:41).

Yes but there is no, it is necessary, without this being 0 how can that be 0? Suppose this is not 0, there is no way this can be identically 0.

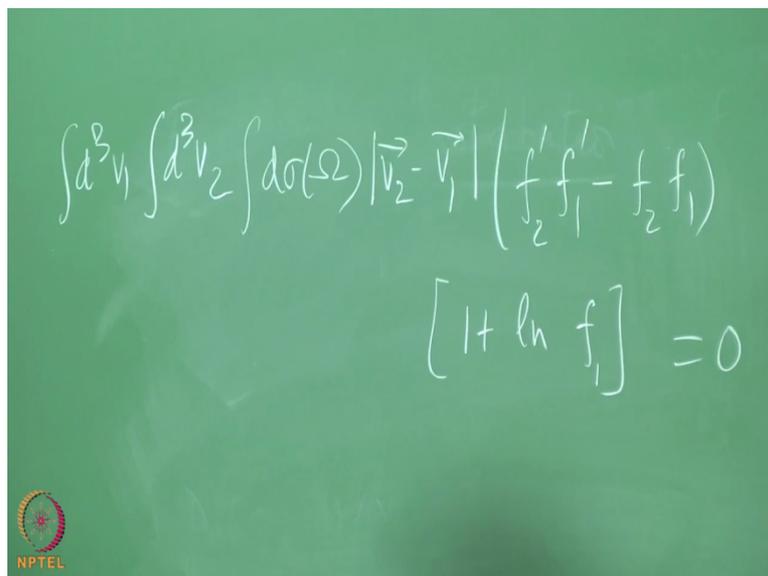
Yes but the converse dh by dt is 0, it does not mean df by dt is 0.

Why not?

That is a solution but I could have things like (0)(25:07).

It is necessary for this to be 0, for this to be 0, it is necessary that dh by dt be 0, necessarily. I had the same problem, everytime you look at the theorem, one has this little thing. But it is exactly, I mean look at the contrary. Suppose this is nonzero, there is no way this can be identically 0, right. It has got to be 0 in order for this to be identically 0. It is necessary, right. We have still not established that that condition is a necessary condition. We have only established that dh by dt must be 0 is a necessary condition for this to vanish. Because if it is nonzero, there is no way this can be identically 0. Okay.

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$$\int d^3v_1 \int d^3v_2 \int d\Omega(\Omega) |\vec{v}_2 - \vec{v}_1| \left(f_2' f_1' - f_2 f_1 \right)$$
$$\left[1 + \ln f_1 \right] = 0$$


$$\frac{1}{2} \int d^3v_1 \int d^3v_2 \int d\Omega(\Omega) |\vec{v}_2 - \vec{v}_1| \left(f_2' f_1' - f_2 f_1 \right)$$

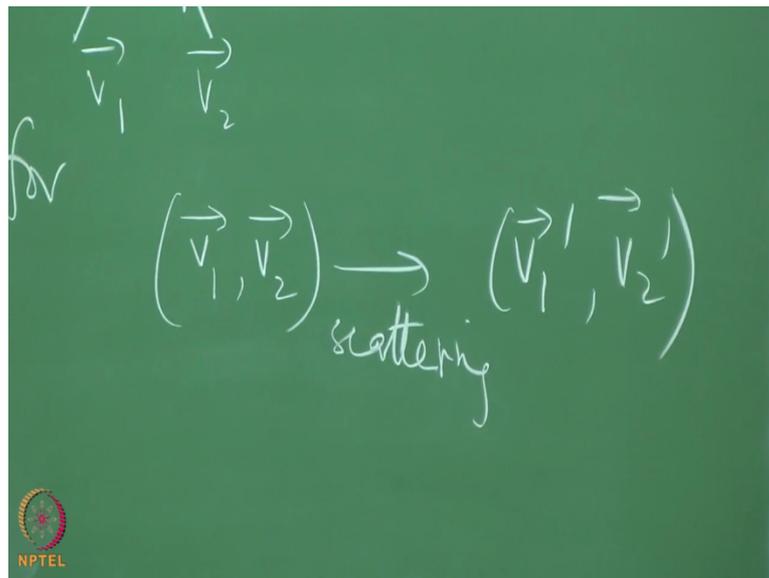
$$\left[2 + \ln(f_1 f_2) \right] = 0$$

Now let us see what that implies. We have already said that f of v_1 satisfies the Boltzmann equation. So I am going to put that in here in this. So this means, let us write it out. This means that for Δf by Δt I am going to put in the collision integral. Right. So it says the integral d^3v_1 , integral d^3v_2 , this is already there, this integral, the definition of dh over dt times Δf over Δt and that is equal to integral $d\Omega$ of $|\vec{v}_2 - \vec{v}_1|$ times $f_2' f_1' - f_2 f_1$, actually it is little, sorry no prime, f_2, f_1 , little bit of a messed up notation.

You see once you put a 0 here, there is nothing to do with 1 and 2, the velocities, so you are stuck for notation. These are all f_0 s, I really right f superscript equilibrium or something like that. Okay, I am too lazy to do that. So this quantity, that was this portion, I hope we have not left out anything in it, times $1 + \log f$, this is v_1 , so this is f_1 equal to 0. This is now a necessary condition. Because this equal to 0 was a necessary condition, I substitute from the Boltzmann equation for this quantity and this whole this double integral being equal to 0 is a necessary condition for this thing to be an equilibrium distribution with argument v_1 , okay.

It is the same function everywhere, only the argument changes. But now in any scattering event, you can interchange v_1 and v_2 and no physics changes, because what appears here is $v_2 - v_1$ modulus and the scattering event does not change, does the event v_1, v_2 the same scattering cross-section appears. So I do the same thing with an interchange of 1 and 2, v_1 and v_2 . This remains the same, this remains the same, this remains the same because you have got an integral over both, right. Therefore this condition can be rewritten with v_1 and v_2 interchanged and it would look exactly the same, except out here, this will become f_2 , right. So I add the 2 and take the average.

(Refer Slide Time: 30:24)



$$\frac{1}{2} \int d^3 v_1 \int d^3 v_2 \int d\Omega' |\vec{v}_2' - \vec{v}_1'| (f_2 f_1 - f_2' f_1')$$

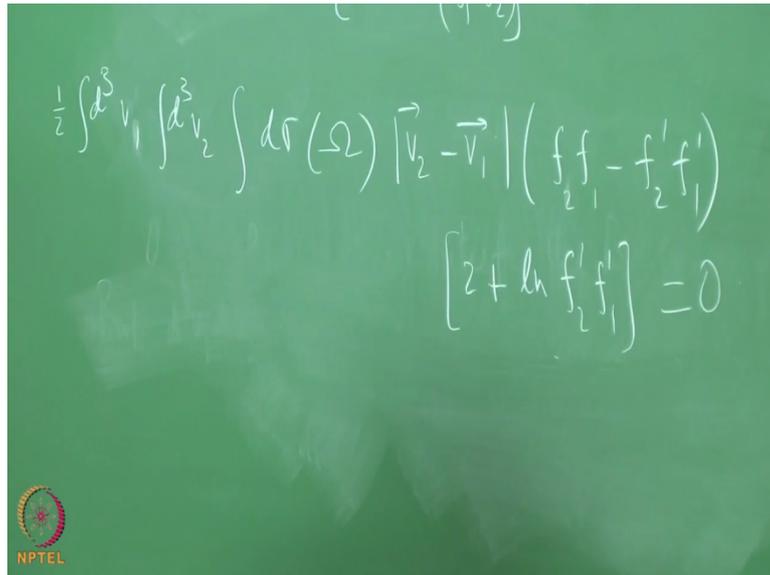
$$\text{But } d^3 v_1 d^3 v_2 = d^3 v_1' d^3 v_2' \quad [2 + \ln f_2' f_1'] = 0$$

So it says one half and this becomes $2 + \log f_1, f_2$ equal to 0, right. $1 + \log f_1 + 1 + \log f_2$, that is $2 + \log f_1 f_2$. Now let us interchange v_1, v_2 with v_1 prime, v_2 prime. Because of scattering process, so you have v_1, v_2 under scattering went to v_1 prime, v_2 prime. But you know because this whole thing is time reversible, you can interchange the final with the initial and you would get exactly the same scattering cross-section. We saw that, we asserted that the last time. Now what happens when you do that, when you interchange the initial and final states? This becomes one half integral $d^3 v_2$ prime, v_1 prime, v_2 prime, integral $d\Omega$ prime of ω , that is the reverse process.

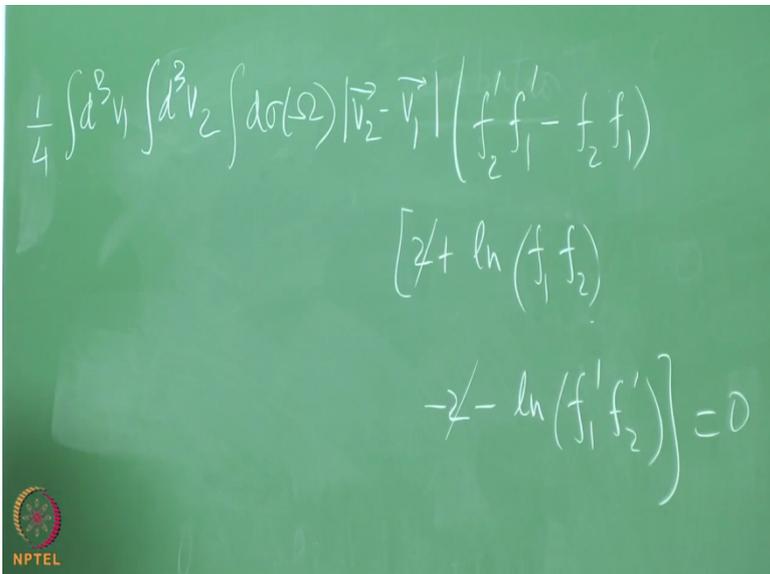
And then v_2 prime - v_1 prime, what goes on here is now $f_2 f_1 - f_2$ prime f_1 prime. Because this is the final state now and that is the initial state. Okay, times $2 + \log f_2$ prime f_1 prime

and this must be equal to 0. But then we already saw that under the scattering process $d^3 v_1 d^3 v_2$ equal to $d^3 v_1 \text{ prime } d^3 v_2 \text{ prime}$. If you go to centre of mass coordinates, then this becomes $d^3 \text{ capital D, } d^3 \text{ little U}$ and that is the same as the $d^3 \text{ capital V prime}$ which is the same as capital V times $d^3 \text{ U prime}$ which in turn is equal to this. So I can actually erase this and write it in this fashion, it has the same measure.

(Refer Slide Time: 33:02)



$$\frac{1}{2} \int d^3 v_1 \int d^3 v_2 \int d\Omega(-\Omega) |\vec{v}_2 - \vec{v}_1| \left(f_2 f_1 - f_2' f_1' \right) \left[2 + \ln \left(\frac{f_2' f_1'}{f_2 f_1} \right) \right] = 0$$



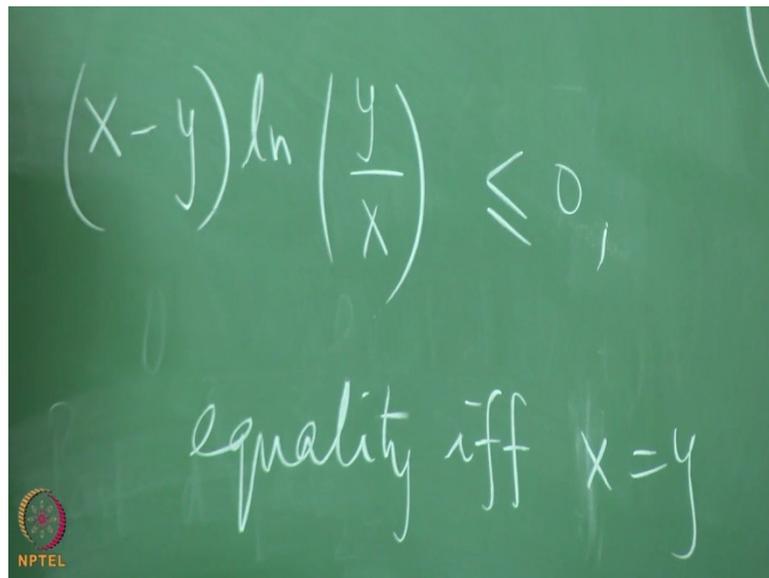
$$\frac{1}{4} \int d^3 v_1 \int d^3 v_2 \int d\Omega(-\Omega) |\vec{v}_2 - \vec{v}_1| \left(\frac{f_2' f_1'}{f_2 f_1} - \frac{f_2 f_1}{f_2' f_1'} \right) \left[2 + \ln \left(\frac{f_2 f_1}{f_2' f_1'} \right) - 2 - \ln \left(\frac{f_2' f_1'}{f_2 f_1} \right) \right] = 0$$

$$\frac{1}{4} \int d^3v_1 \int d^3v_2 \int d\sigma(\Omega) |\vec{v}_2 - \vec{v}_1| \left(\frac{f'_2 f'_1}{f_2 f_1} - \frac{f_2 f_1}{f'_2 f'_1} \right) \cdot \ln \left(\frac{f_2 f_1}{f'_2 f'_1} \right) = 0$$


And the scattering is the same, exactly the same scattering cross-section. So Sigma prime is the same as Sigma. We also know that the relative velocity does not change, we know that, v_1 , we know that $v_2 - v_1$ equal to U , v_2 prime - v_1 prime equal to U prime and we know that $\text{mod } U$ prime equal to $\text{mod } U$ prime. All that happens is that it is rotated by the scattering angle, okay. So these 2 you can remove, the prime. So now this is 0, that is 0, we have done all the manipulations we need, so the average of the 2 must be 0. Right. So that says it is one quarter, there is a - sign here, there is a - sign, so I can get rid of that - sign by making this f_2 prime, f_1 prime, $f_1 f_2$ and then subtracting instead of adding.

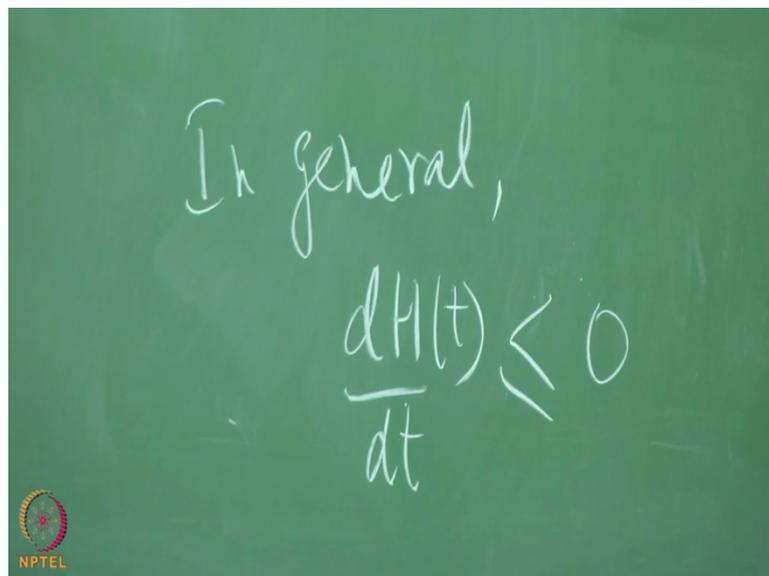
So let me write it as this. So what goes on inside here is $f_1 f_2 - 2 - \log f_1 \text{ prime } f_2 \text{ prime}$ equal to 0. So I kept the + side but I subtracted this bracket and 2 cancels out. And I can rewrite this as, right, I can rewrite this as $\log f_1 f_2$ divided by $f_1 \text{ prime } f_2 \text{ prime}$. So if you permit, I write this as $\log f_2 f_1$ over $f_2 \text{ prime } f_1 \text{ prime}$ and this is equal to 0, one fourth is relevant. This is nonnegative, this is nonnegative, the only way this thing can be 0 is for the integral to vanish. Now call this part, we call it X, we call this Y, then you were to term which is $X - Y \log Y$ over X, that is this integral equation.

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$$(x-y) \ln \left(\frac{y}{x} \right) \leq 0,$$

equality iff $x=y$

The image shows a green chalkboard with white chalk writing. The equation $(x-y) \ln \left(\frac{y}{x} \right) \leq 0,$ is written in the upper half. Below it, the text "equality iff $x=y$ " is written. In the bottom left corner, there is a small circular logo with the text "NPTEL" below it.



In general,

$$\frac{dH(t)}{dt} \leq 0$$

The image shows a green chalkboard with white chalk writing. The text "In general," is written in the upper half. Below it, the equation $\frac{dH(t)}{dt} \leq 0$ is written. In the bottom left corner, there is a small circular logo with the text "NPTEL" below it.

That quantity cannot be positive, where X and Y are real, this quantity cannot be positive, because if X is bigger than Y, this is positive but there is log of a number less than 1, then that negative. If X is smaller than Y, this fellow is negative, that is a number bigger than 1, that is positive. But in any case this quantity cannot be negative, it cannot be positive, cannot be positive, it is less than equal to 0, equality if and only if X equal to Y, there is no other way. Okay.

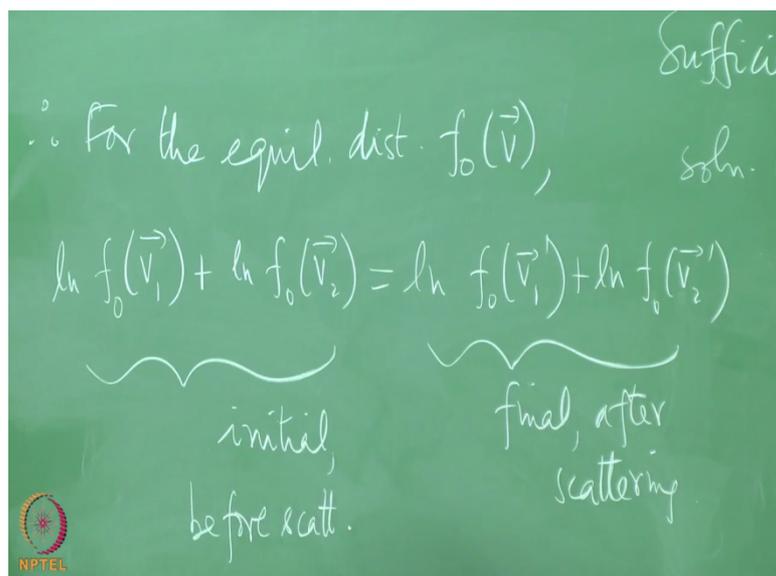
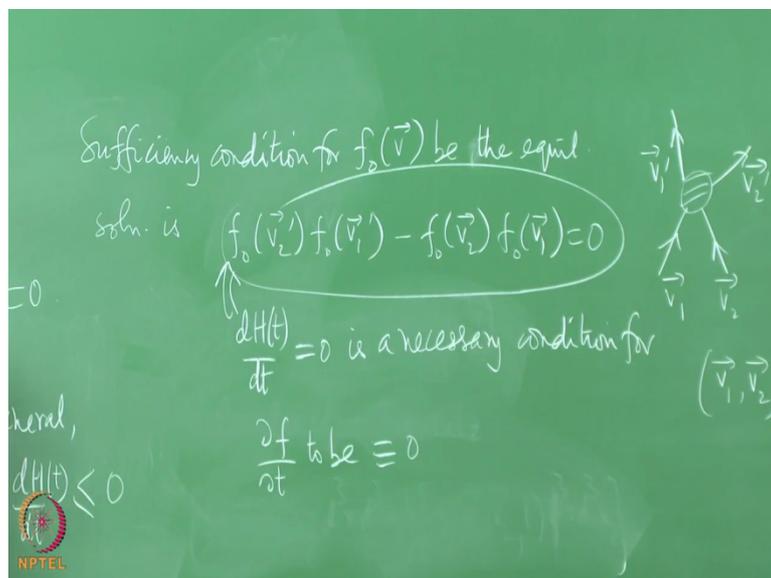
This is very important right, which says dh by dt is we have proved (0)(36:52).

We have proved more than what we need. We have actually shown that in general it is less than equal to 0. And we will see what the less than implies, we will see what it does. Because when you are out of equilibrium, that is going to play crucial role. Yah.

(0)(37:27).

Yah, it is a convexity property, definitely, I do not know what you call it, it is called Jensen's inequality or something, what is the inequality called, there is some name for it somewhere. Yes, it is a general property and this is yes and there is more than one place where this inequality appears. Okay. But whatever it is, in our context, it says this fellow must be equal to that, X must be equal to Y, that is the only way this integral can vanish, because everything else is positive, this quantity, this quantity, etc. So it is a necessary condition, this is this thing or this quantity, this equal to 0 implies this equal to 0, we have shown that, okay.

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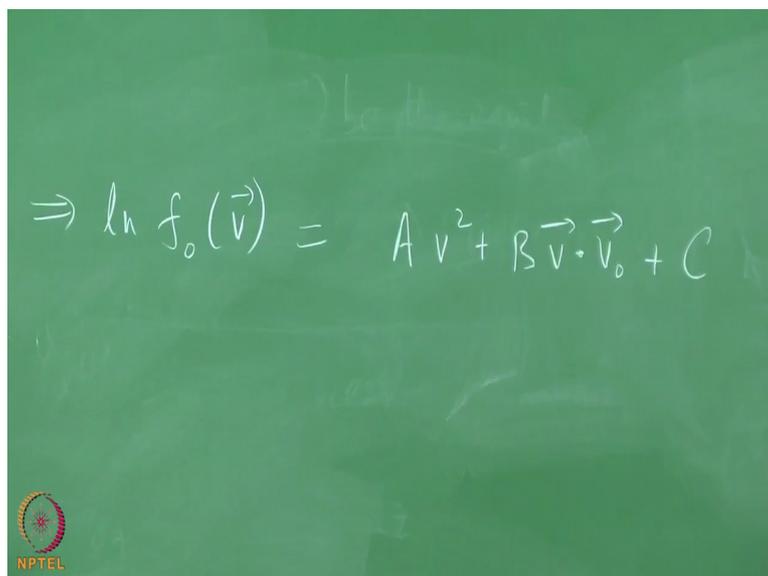
We already saw that is a sufficient condition but now we are saying it is a necessary condition for equilibrium. Therefore equilibrium density is given by this equation or rather equilibrium

density is such that if and only if this condition is satisfied do you have equilibrium. Yah, very much so, very much so, exactly, exactly. H is like an entropy function, $f \log f$ kind of structure. Okay. But we are completely out of equilibrium in this situation because in general you define h of t , it is a time-dependent quantity. Okay. The only assumption be made is that there is no dependence on the position, that was important, now we got to put that back, we got to put that back.

But as long as f is a function of v alone, any equilibrium density has to satisfy this. So once we have that in place, let us examine what this implies. So this condition is needed for an equilibrium distribution here. Which means that \log therefore for the equilibrium distribution f_0 of v , you must have $f_0, \log f_0$ of $v_1 + \log f_0$ of v_2 must be equal to $\log f_0$ of v_1 prime + $\log f_0$ of v_2 prime, where v_1, v_2, v_1 prime, v_2 prime are related by scattering event. But these 2 things here are the initial states before scattering and this is final after the scattering, but this is before scattering.

So it says in the scattering process, arbitrary scattering process with velocity v_1, v_2 initially and v_1 prime, v_2 prime initially, f_0 which happens to be the equilibrium distribution is such a function that the \log of this f_0 is conserved, this four-part velocity is conserved. Therefore $\log f_0$ of v must be some constant of the motion which is conserved, it depends on some quantity which is conserved, what are the only quantities that are conserved, momentum is conserved and energy is conserved. So therefore this $\log f_0$ of v can at best be a quadratic function of v . Right, so it immediately implies, we are not home yet, we are getting there.

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$$\Rightarrow \ln f_0(\vec{v}) = A v^2 + B \vec{v} \cdot \vec{v}_0 + C$$

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$$\int d^3v f(\vec{v}, t) = \frac{N}{v} = n$$

So it implies $\log f_0$ of v and now let us forget all the subscripts must be equal something of the form $A v^2 + B v$ possibly + constant, but it cannot be anything like v , it is clear that this is not a scalar.

(42:21) quadratic function.

Because energy is the only constant of the motion.

Energy square (42:26) or sum of the energies?

Yes, sum of the energies, sum of the energies is constant, kinetic energy is added. So no other functions are possible, okay. It cannot stick out like this because this is a vector. So you can actually say that this must depend on some arbitrary initial velocity. So $Bv \cdot v_0 + C$, where capital A , B and C are constants independent of v . It depends on the mass of the molecules, it depends on whatever, we do not know yet. Now this of course with little effort one can show, this will imply that the whole gas is moving with the velocity v_0 , there is no other interpretation you can give to this v_0 .

So this part of it I am slurring over but if you look at the elementary treatments on statistical mechanics and kinetic theory, it will tell you that. So this B goes away and you are left with this $+ C$. Now of course f_0 is the exponential of this guy, so this C becomes multiplicative. It is your overall normalisation constant. And you can fix it by remembering that we needed this to start, we needed $\int d^3r f(r, v, t)$ to be equal to, we wanted $\int d^3r \int d^3v f(r, v, t)$ to be equal to the total number of particles and in the case where it did not depend on r , you can do the r integration, get the volume and therefore this is equal to N/v equal to the

number density n . So you have a normalisation which depends on the number density. Pardon me?

Yes, this is very important, you want this to be normalised able, right. So if you do this, this will imply, it goes like E to the $A v$ squared and if A is positive, it cannot be normalised, this will not be a finite integral. In case it is a Gaussian, so if you try to normalise it, you will get 1 over square root of whatever it is and that is only valid if A is positive. Okay. Now you need 2 pieces of information, you need to convey...

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A is negative, so A has got to be negative. So there are 2 pieces of, because you want to use finally the fact that E to the $- A v$ square integral, this is going to exist, etc. And this is going to be some square root of π over A or something. A . Now there are 2 cases of information that you need to fix these constants and here is where the physics has to come in. We have to say something about the average energy, if you prescribe that for each particle, then I find the moment of this thing multiplied by v square, that will be 1 and then normalisation which is the density which would be the other. So with these 2 fellows you get precisely the Maxwellian distribution. Okay.

But we have to put in 2 pieces of information, okay. After all we are doing kinetic theory and you have no other piece of information, except that what you know from thermodynamics. So it is an ideal gas, I know the equation of state, I know the internal energy, it is two thirds of the internal energy densities the pressure. And I know P is equal to rt , Pv equal to rt . So I put that in, if I put that piece of information in, then purely from kinetic theory to get the Maxwellian distribution as the equilibrium distribution. Okay. So it was a long route but H theorem is the crucial one on the way. Now you could ask what happens if I put an external...

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$$\begin{aligned} &\text{If } f(\vec{v}, t) \text{ satisfies the Boltz. eqn,} \\ &\& H(t) \stackrel{\text{defn.}}{=} \int d^3v f \ln f, \\ &\text{then } \frac{dH(t)}{dt} \leq 0 \quad (\text{H-Theorem}) \end{aligned}$$


$$\begin{aligned} &\text{Ext. force } \vec{F}(\vec{r}) = -\nabla \phi(\vec{r}) \\ &f_0(\vec{r}, \vec{v}) = f_0(\vec{v}) e^{\frac{-\phi(\vec{r})}{k_B T}} \\ &\frac{\partial f}{\partial t} + \left(\vec{v} \cdot \nabla_{\vec{r}} + \frac{\vec{F}}{m} \cdot \nabla_{\vec{v}} \right) f_0(\vec{r}, \vec{v}) = \end{aligned}$$


$$\text{Ext. force } \vec{F}(\vec{r}) = -\nabla \phi(\vec{r})$$

$$f_0(\vec{r}, \vec{v}) = e^{-\frac{1}{2} \frac{m v^2}{k_B T}} e^{-\frac{\phi(\vec{r})}{k_B T}}$$

$$\sim e^{-\beta H}$$

Statement of the H theorem is if f , f of v , t satisfies the Boltzmann equation and you construct d^3v , f of v , t , $\log f$ of v , t , you call that H of t , then dh over dt is less than equal to 0, that is the statement of the theorem. So, this is the H theorem. Now finally what happens if you put in the external force on the system? Well the claim is the following. Not surprisingly and we can see this by verification. The claim is in that case f_0 of r , v , if you put in an external force f of r , so external force equal to - gradient of some potential, I do not want to use v because I use it for the relative velocity, so for the total velocity, so let us say this derived from the scalar potential. It is important that it should be, this thing should be independent of the velocity, this is crucial for reasons which you will see in a minute.

This force should not depend on the velocity, there is no velocity dependent force. Then this quantity equal to f_0 of v , when f_0 of v the distribution we have just been talking about. E to the - ϕ of r over K Boltzmann t is the equilibrium distribution. Okay. How we are going to check this out? Because we want to have δf over $\delta t + v$ dot gradient with respect to r f , let us write the f outside + f over M dot gradient with respect to v f of r , v , f_0 , this is equal to whatever the collision integral is and we went through this argument by saying that if it is an equilibrium distribution, this guy is 0 and you have the collision integral on the right-hand side.

Now in that integral if instead of f_0 of v you put in this fellow here, then I assert that you can pull this factor out, all the way out of the integral. Because there is no factor that that depends on the position, so it comes right out. And it is going to sit there and that Collision part of it was 0 with f_0 of v was 0. So that means this portion alone must be 0, otherwise it is now going to, this ansatz is not going to satisfy, right. What I am saying is that when you have a

force which is depend, derived from a potential, scalar potential of this kind, the equilibrium density distribution is just the original one which we found without the external force is multiplied by this factor.

There are some normalisation, suitable $d^3 r$ of this should be equal to 1, okay. Now the way to argue is, well if I put that in and this is equilibrium, this term is 0. I put this whole business into this collision integral, this factor comes right out of all the integral because it does not, scattering cross-section does not depend on it, etc., etc. And whatever is left is already been shown to be 0 because f_0 of v satisfies that equation, therefore this must be true, we have to check this now with this solution. But that is a trivial matter because if you pull this delta gradient with respect to r , you are going to keep the same exponential but bring grad Φ downstairs, that is going to be $v \cdot f$ and this is going to act on the Gaussian in v .

So if this fellow acts on it, we are going to get v downstairs.

- v .

- v or whatever. And this f is grad Φ , so this term will cancel that term, okay. And therefore this is really an equilibrium density, suitably normalised. Check this piece of, check this algebra of it.

(())(52:05) M.

No, f is fine as it stands it is okay.

Because of the left-hand side there will be no (())(52:11).

It is okay. But there is always this confusion about what this Φ is, okay. It is the potential energy per unit mass, okay. We are so used to saying it is potential energy, potential energy per unit mass. Okay, this is a force per unit mass. So you have to put some M factor somewhere, so putting in this 2π factor or whatever. So I leave it to you to figure this out. I mean the whole physics of, the essential point is to see how this is going to cancel out at all. This is going to pull out, gradient is going to pull out grad Φ times an exponential what that is f is already sitting here. And this is going to act on v square and pull out v , $v \cdot f$ when they cancel out.

We already know, I mean we know this is consistent, after all this fellow here was of the form, this is of the form E to the $-1/2$ Mv square over k_B , so this whole thing is of the form E to the $-\beta$ times the Hamiltonian. Yah.

Is this something that guarantees the uniqueness of f_0 (53:45).

Yes because we said this is the necessary and sufficient condition that this vanish. Now once that vanishes, it says this f_0 of v , $\log f_0$ we can only depend on whatever is conserved in the collision process. And that is it. Okay. So of course once you put in correlations, then the matter becomes very different altogether. So this is the 1st elementary consequence that this equilibrium density turns out to be what we know from the canonical example.

But this of course now derived purely without making the fundamental postulate of statistical mechanics but in some sense it has been put in by saying that there is a molecular chaos, it is ansatz. But that is a different kind of statement altogether. It is not immediately obvious these 2 are the same. It is a purely kinetic theory argument here. This was Boltzmann's big contribution. So we can stop here today.