Statistical Mechanics
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Lecture – 20
Classical Probability Density and Liouville Equation

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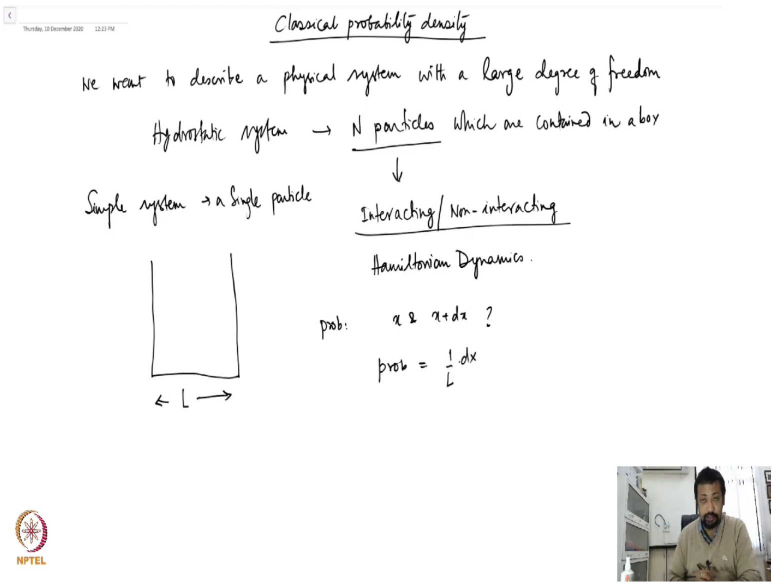

Welcome back. So, today what we are going to talk about is Classical Probability Density. Now, we have seen we have had a very brief outline of probability theory. And we basically reviewed the points we required that things were required to develop statistical mechanics. So, continuing on the same lines, we want to look at classical probability density. So, typically, we want to describe a system a physical system with a large degree of freedom ok.

For example, this can be a hydrostatic system with N particles with N particles which are contained in the box in a box right. Now, these N particles can be interacting as well as or can be non-interacting right, but essentially the dynamics is governed by the Hamiltonian dynamics. So, you have the Newton's equation of motion, and the particles trajectories are updated based on this Newton's equation of motion.

So, before when we want to look at this N particle system, let us look at a very simple system where I have a single particle. And when I have a single particle interaction does not come into the picture, and this particle is contained within a box of length L right. Now, clearly if I now ask you the question that what is the probability of finding the particle, probability of finding the particle between x, and x plus dx. The answer is since the particle does not have any interaction present that probability is 1 by L dx, so that you can immediately read off that the probability density is given by 1 by L.

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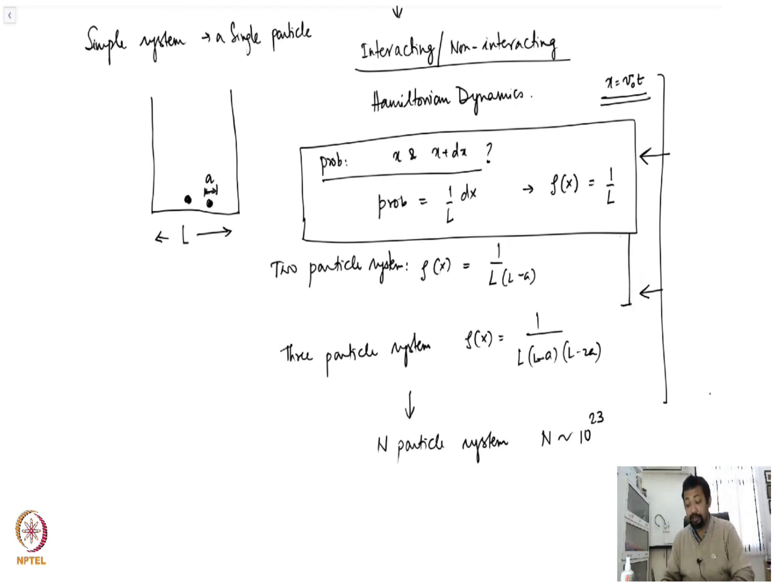

If I now put in, so I have one particle over here, then I put in another particle over here. Each of these particles has a size of let us say a. Then my; for two particle system, this quantity becomes 1 by L, L minus a. In the formal picture, when I had only one single particle of course, talking about probability is meaningless in the sense that I have exactly I can solve Newton's equation of motion, I know that the trajectory is x equal to v naught t right. So, I can find out where the particle is at exactly the same time.

But now when you go to a two particle system see this question becomes slightly more difficult to answer. It is non-trivial to answer. And then I can go to a three particle system right. I can go to a three particle system, where my density probability density is going to be L L minus a L minus 2 a.

And this question becomes even more complicated that if I want to know what is the probability of finding, well, forget about the probability if I know where particle one particle is at a given position given that there is a size of this particle, so that they cannot overlap. There is an excluded volume interaction over here. This question becomes even more complicated.

So, with this thing, if I now go to an N particle system, where N is of the order of 10 to the power 23, the Avogadro number our problem is even more complicated. So, we cannot have the deterministic picture that we had when we started off with one particle. We can make an effort in solving this problem, but three particle becomes even more complicated right.

So, we can make an effort in solving the two particle problem by going to the center of mass frame and figuring it out, but three particle problem becomes even more complicated analytically. And the whole real picture when you have N particles in the system is even more complicated.

So, what do we do? We essentially sacrifice this deterministic we have too much information in our hand, and we essentially sacrifice this deterministic picture that we know from classical mechanics to go into a probabilistic picture.

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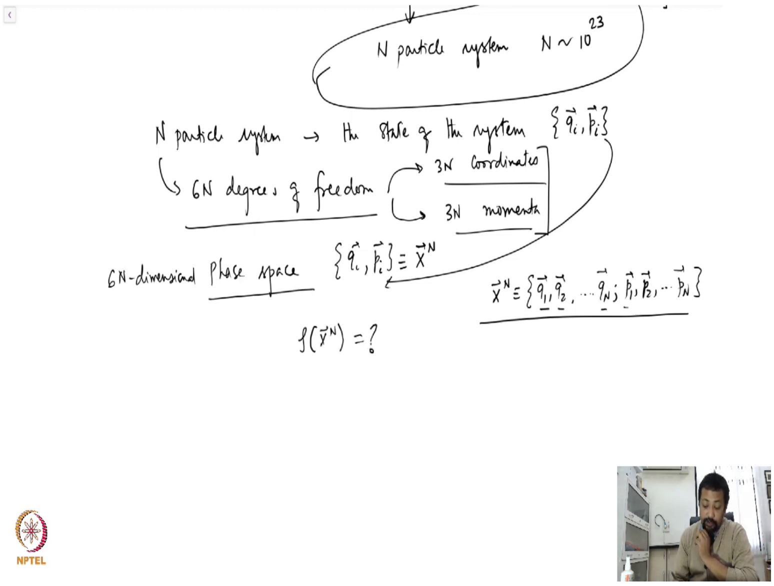

Now, the state for N particle system or for any particles, so N can be 1, 2, 3 anything, the state of the system is characterized by the coordinates and the momenta right. So, for this there are 6 N degrees of freedom. So, you have 3 N translational degrees, well, sorry let us write coordinates and you have 3 N momenta. We are ignoring the internal degrees of freedom over here. So, there are 6 N degrees of freedom altogether.

Since we have 6 N degrees of freedom, 3 N coordinates and momenta, one can visualize try to visualize the phase space of this system. It is complicated to visualize, one can think about the phase space of the system.

A 6 N dimensional phase space where this particular quantity the state q i comma p i is represented by a point right. So, therefore, in the phase space, there is a point, this is a point we shall denote it by this vector X capital N, where X capital N is equivalent to q 1, q 2, all the way up to q N, and then p 1, p 2, all the way up to p N right.

So, given in the phase space, there is this at any instant of time if you had the knowledge or if you had the tools to know all the coordinates and all the momenta of this particle of the system, then essentially you can plot it in the 6 N dimensional phase space, and this will just be a point. But then over you can measure, if you are able to measure, then you can track this way states of the system, you can track the coordinates and the momenta for later times also.

Therefore, you see that in the phase space the time evolution, so the movement of the particles within this box essentially is going to give you the trajectory in the phase space. However, one has to realize that since this contains so much of information that this deterministic picture of keeping track of all the coordinates and the momenta starting from the initial conditions at all later times is just an impossible task.

So, what we say? We rather say that look we are going to sacrifice this and we are going to talk about a probabilistic description of this evolution of the system, time evolution of the system. So, what we say? We say that in the phase space, the state of the we can only know with certain probability the state of the system. We cannot exactly for sure know with certainty the state of the system.

We could have known that. If we could have solved the Newton's equation of motion, written down the equations of motion used the initial conditions and solved it. But this is just an impossible task for an N particle system, where N is of the order of 20, 10 to the power 23 right. So, therefore, one can think about the phase space as filled with the probability fluid. And our task is to figure out what this probability density is going to be or how the evolution of this probability density is going to be right.

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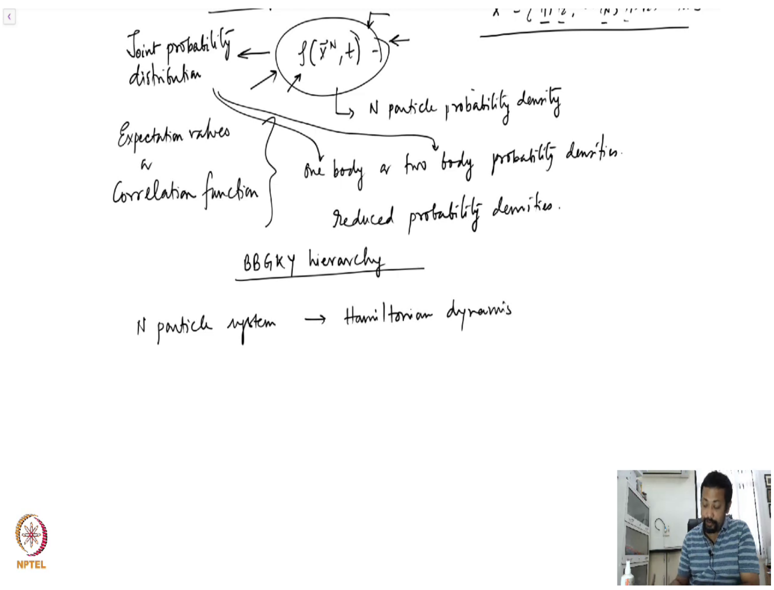

So, how the rho of X N comma t is going to evolve? What is the dynamical equation that governs the evolution of this probability density? Note that this probability density rho of X N comma t is essentially an N particle probability density right. It depends on all the coordinate and the momenta of all the particles. However, in reality, in practice, we do not, so this contains too much of information that we need, but we do not need so many so much of information.

The main purpose of this density is typically to calculate expectation values or correlation functions which are typically measured in the experiments. And therefore, so we at most need generally one body or two body, one body or two body probability densities right.

If you recall, then this is what is called the in terms of probability in the probability theory, this is what is called the joint probability distribution. And from this joint probability distribution, we can construct one body or two body probability densities which are reduced probability densities.

Now, typically, let us just write this typically this rho of X N comma t is an extremely complicated quantity, and it is not trivial to evaluate this. So, essentially one breaks down this problem into one body or two body probability densities. So, there are hierarchy of probability densities that you have one particle density, two particle density, three particle densities so on and so forth.

So, you take this equation, dynamical equation for rho of X N comma t, and then you essentially break it down into several dynamical equations that involve one particle, two particle, three particle such reduced probability densities. And then these probability densities are essentially they form a equation which is called BBGK hierarchy right. Bogoliubov, Born, Green, Kirkwood and Yvon hierarchy.

So, in systems depending on the system you are looking at sometimes it is possible to close this hierarchy and to estimate this one particle and two particle densities exactly. But typically it is not possible for in evaluating this quantity exactly in a classical system right. So, now, what we want to try to do is we want to figure out, how to measure how to write a dynamical equation for this.

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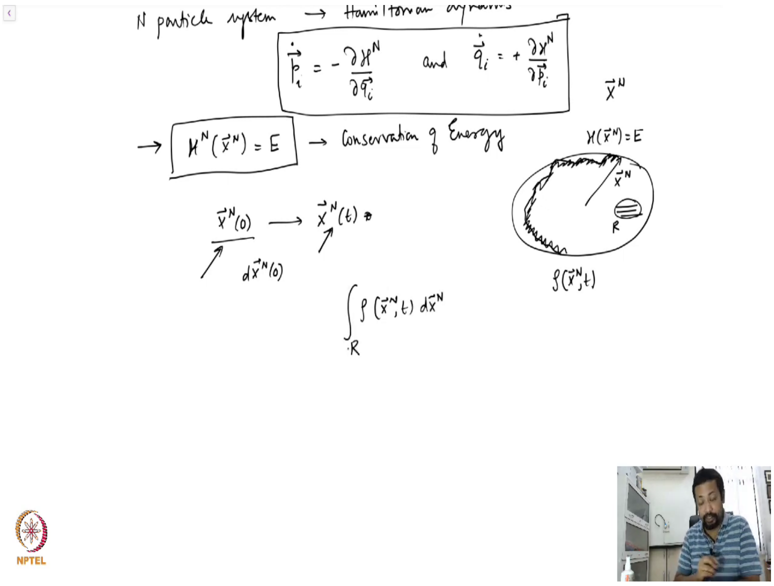

Since I have an N particle system that obeys Hamiltonian dynamics that means, that p i dot is minus del H N del q i, and q i dot is plus del H N del p i. Further I also have the Hamiltonian of the system as a constant. This is the, this follows from the conservation of energy. So, from it is from this particular equation, it is clear that in the phase space, if I construct this vector X N, then this vector X N is going to trace out.

So, this is just a schematic interpretation in the 6 N dimensional phase space. If I construct this vector X N, then the tip of this vector essentially traces out the surface which is given by H of X N is equal to E right.

If I had the capability of solving this N particle system, look solving these equations of motion exactly for all the particles, then I know that I will trace out a trajectory in the phase space right. But this and this trajectory by its property is not going to intersect with itself, but this uniqueness is lost because of my inability to keep track of so much of information.

So, for example, if I have this N particle system, I can start of the initial conditions might not be known exactly for us. So, if I start off with X N 0 precisely with X N 0, and then I track X N as a function of t solving the Hamilton's equation of motion, then I then this is the picture that I expect I expect that a trajectory is going to form in the phase which is not going to intersect with each other. But it can happen, it will very will happen that I may not know the initial condition of all the particles.

So, there is an uncertainty which is associated with this initial condition. And therefore, there is also an uncertainty which is associated with the subsequent trajectories right. So, essentially you get a bunch of a spread in the phase space right.

So, if you wait long enough, if you wait long enough, then this phase space will be completely filled by these trajectories. It will come back to this point this is one of the pillars of statistical mechanics what we call Ergodic theorem.

However, right now, so there what we want to look, what we want to emphasize as we have done earlier is that we want to imagine or think of this phase space to be filled with a continuum of state points. And since I have a continuum of state points like a fluid, I will we will define this rho of X N, t. So, that the probability if you want to say that what is the probability of finding the system within a region R, then that probability is rho of X N comma t dX N integrated over R right.

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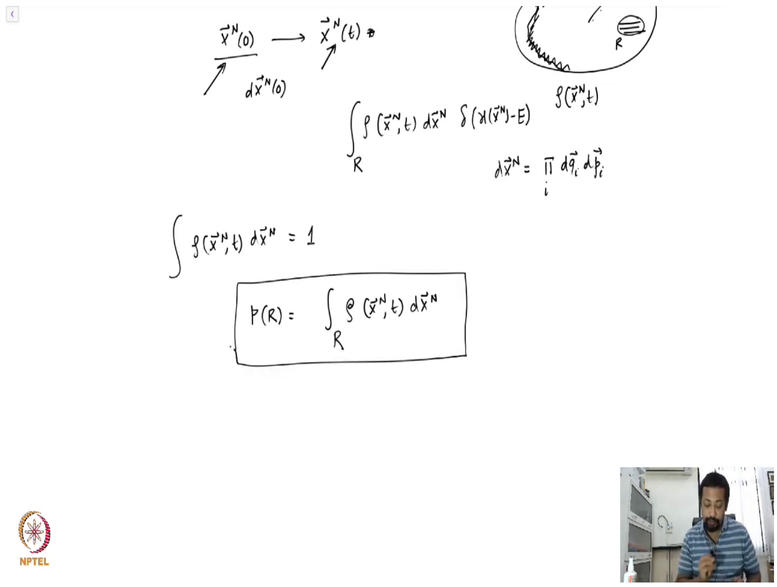

Where dX N the measure is d q i d p i on the surface. So, you also need to include delta of H of X N minus E right nevertheless. So, we will see that we can circumvent this delta function only in the thermodynamic limits, but that we will do it later on.

So, of course, rho of X N comma t dX N, if you allow all values of energy that starts from 0 less than equal to E, then this is going to be normalized this is going to be 1. And as we said that the probability of finding the system in a region is rho of X N comma t d of X N. So, now I want to evaluate the flow of probability from this region R.

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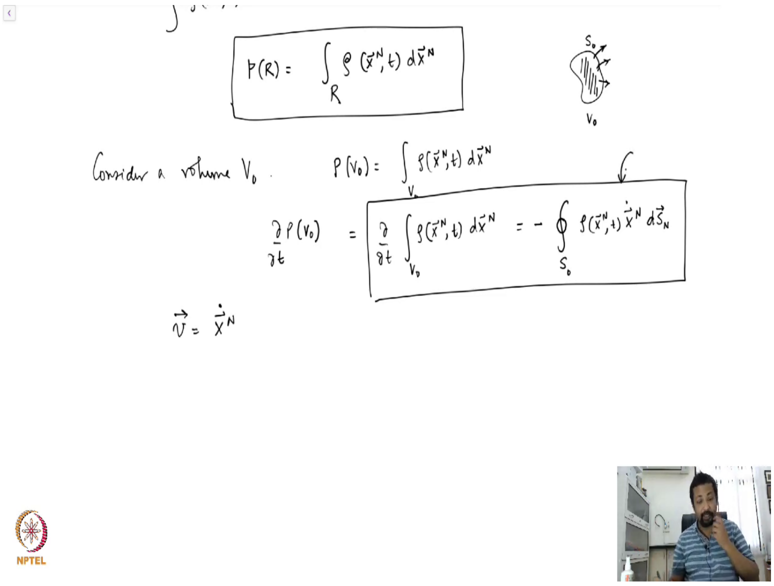

Consider a volume V naught right. Then the probability of finding the system within this volume is P of V naught is equal to integration over V naught rho of X N comma t d of X N right. Now, if I have this region V naught, so let us not make it a sphere, let us make it slightly arbitrary, so that. So, if I have this volume V naught, this will enclose a surface S naught.

So, the loss the time derivative of this probability if I want to write down del del t of P of V naught is going to be del del t of rho X N comma t d of X N V naught. This change rate of change of probability will be is entirely due to the probability which is flowing out right.

If you denote v capital, this v which is essentially X N dot as the velocity of the state points, then just as you have probably done in fluid mechanics. If you have not done them, this is how you do it. Then this is integral over surface rho X N comma t we will save X N dot over here right. So, this is how you write down.

This equation that you see over here is essentially a; it is one of the form so, it is the continuity equation. So, the change in the density in the probability density within this region V naught is entirely due to the probability which is flowing out of the region through the surface that is enclosed by V naught and that is the left hand side right.

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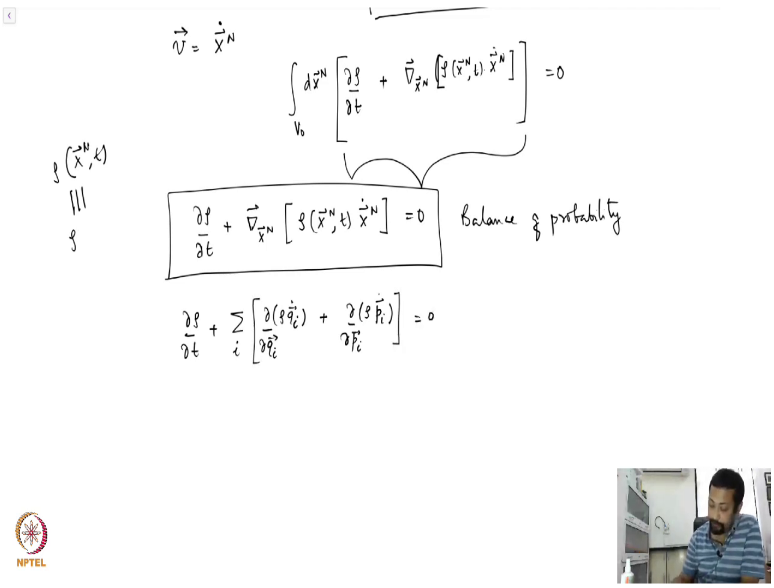

So, it follows, therefore, integral d of X N del rho del t plus if I use the divergence thing convert this surface integral into a divergent into using into a volume integral using the divergence, then this becomes divergence of X N rho of X N comma t times X N dot is equal to 0.

Since this is valid for any arbitrary volume V naught, this means that the bracketed quantity that you see over here must be 0, so that we have a dynamical equation for evolution of the probability density which we write down as X dot N is equal to 0. This is just a balance of probability. It is the continuity equation that you are writing down for the probability density rho of X N right.

Let us write down this equation explicitly. What does this mean? This means that I will write expand this divergence term, I will write del rho del del q i rho q i dot plus del del p i rho p i dot. I have suppressed rho X N, this means rho in this equation right. So, there is a sum over this.

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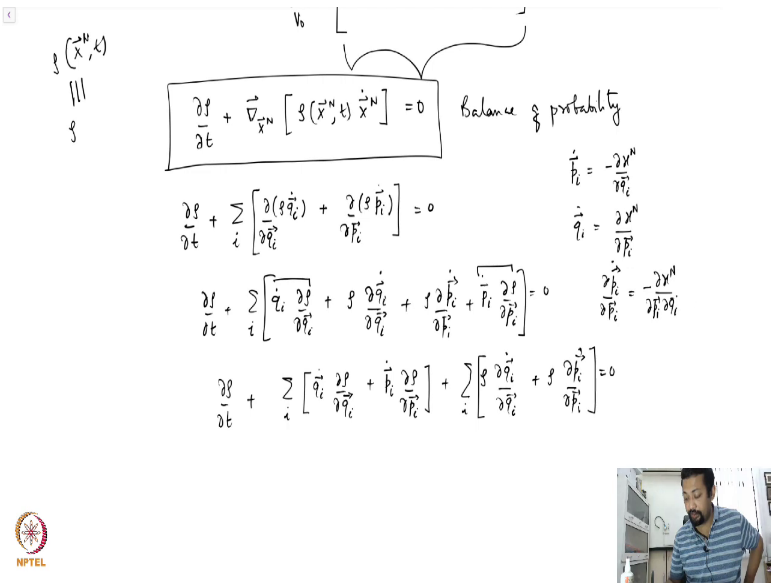

Let us see, let us do this sum over i q i dot del rho del q i plus rho del q i dot del q i plus rho del p i dot del p i plus p i dot del rho del p i must be 0. Let us collect the terms together sum over i I want to put this term and this term together. So, I have q i dot you will see in a moment, why I want to do that. So, this is del q i plus p i dot del rho del p i plus sum over i rho del q i del q i del q i dot del q i plus rho del p i dot del p i is equal to 0.

Now, recall your Hamiltonian, Hamilton's equation of motion which says that p i dot was minus del H N del q i. And therefore, let us write down the second equation q i dot was del H N del p i. So, this means that del p i dot del p i is equal to minus del of H N del p i, it gives you a mixed derivative.

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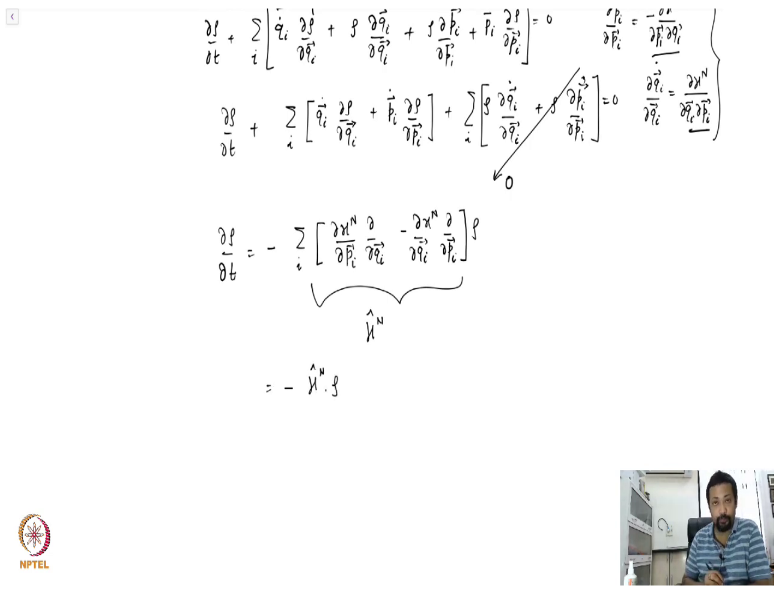

And similarly del q i dot del q i is going to give you del of H N del q i del p i. Since H N is essentially analytic, therefore, it follows that these two mixed derivatives have the opposite sign. They are equal the mixed state sorry I mean to say that the mixed derivatives are equal.

Therefore, these two terms del p i dot del p i, and del q i dot del q i will have opposite sign. So, that this term vanishes.

And therefore, you have an equation which is del rho del t, I will take it to the other side sum over i. Let us replace this del H N del p i del del q i plus sorry it has to be minus del del q i H N q i del del p i times rho. We call this as an operator now which is N. The superscript N essentially denotes that it is an N particle operator. So, this equation becomes H N times rho.

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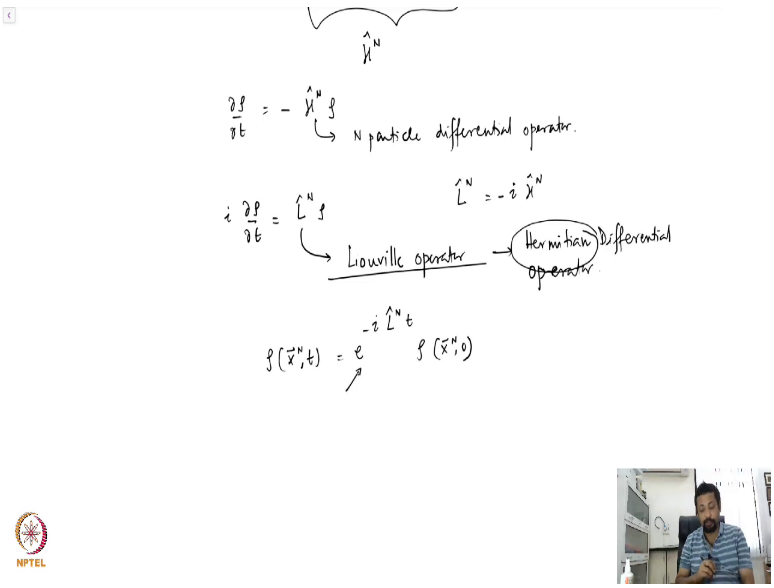

So, I have del rho del t is equal to minus of H N rho this is an N particle differential operator. Typically, this equation is recast and written as L hat N times rho, where L hat N is minus i H hat N and this operator is called Liouville operator right. So, this if you look at it carefully, you can easily do it that this is a Hermitian differential operator.

I leave it to you as an exercise to prove that this is indeed a Hermitian operator. It is not very difficult to do. The solution to this operator is del sorry I want to write down the solution to this differential equation, so that rho of X N t is e to the power minus I L hat N t rho of X N comma 0.

So, given the initial probability density, I can know the probability density at later times, by operating this differential operator this quantity e to the power minus i L hat N on the initial probability density.

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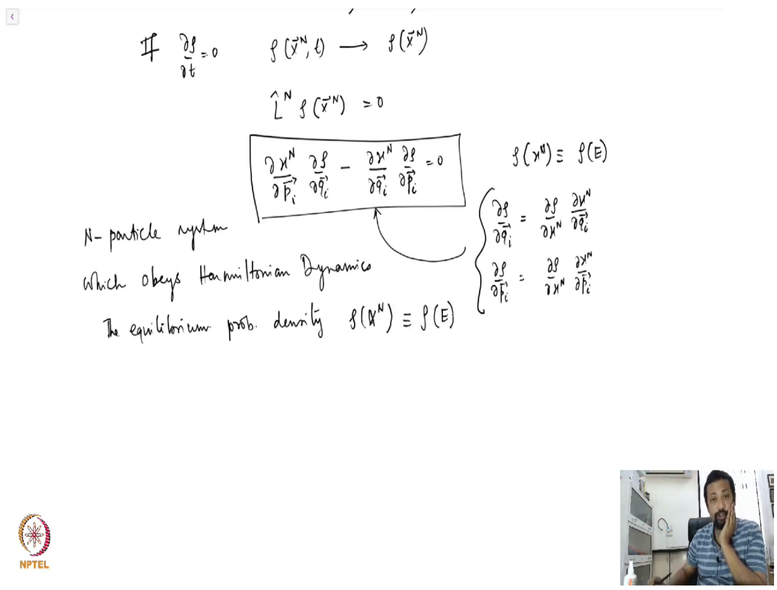

If let us say del rho del t is equal to 0 right which means that you have actually no longer have you have this density probability density rho of X N of t becomes just a function of the phase space variables, and no longer is a function of time. Typically that is what happens when you are in equilibrium.

Then essentially, that means, that L N of rho X N is equal to 0 which is means that del H N del p i, del rho del q i minus del H N del q i del rho del p i is equal to 0. This can only happen when rho is a function of H N which is equivalently like saying that rho is a function of the density.

If that is the case then you can see that del rho del q i is del rho del H N del H N del q i and del rho del p i is del rho del H N del H N del p i right. And when you substitute this over here, you will see that this is going to give you 0. So, very important thing that for a N-particle system which obeys Hamiltonian dynamics the equilibrium probability density rho of e of X N must be a function of the energy right.