Statistical Mechanics
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Lecture - 21
Classical Probability Density, Ergodicity and Microcanonical Ensemble

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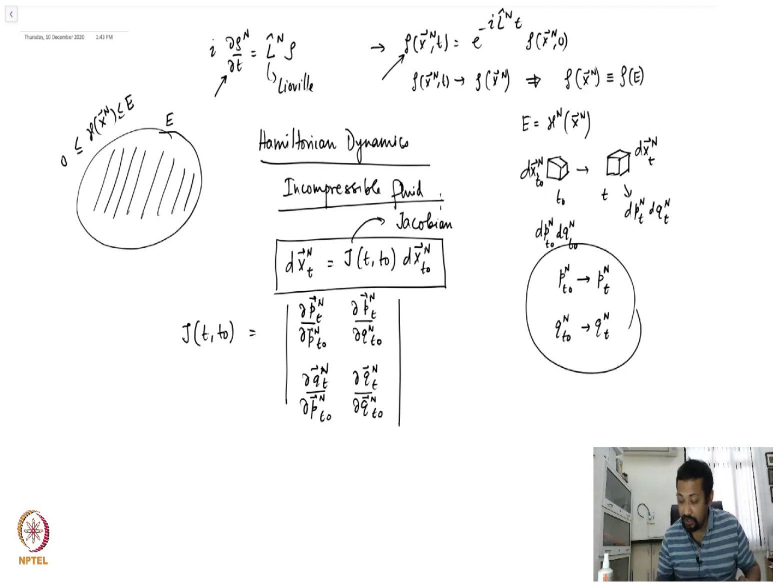

So, we determined the dynamical equation for the Probability Density and we said that this is going to be i del naught; this is the Liouville operator. And the solution to this equation is e to the power minus L hat N times t rho of X N comma 0.

We also saw that if we set the left hand side to 0, so that rho of X N comma t goes to just as a function of the phase space variables. This would essentially imply that, rho of X N must depend only on the energy, where your energy, total energy is given by the Hamiltonian which is a function of X N.

Now, we have been saying that in the phase space, which this inequality let us say. So, when you allow all energies greater than equal to 0 less than equal to E; then E defines a surface and you have a volume contained within this surface, right. And we said that, in this when we develop this picture of probability density, we classical probability density; we said that imagine that this phase space is now filled with continuum fluid of state points.

This fluid is made up of state points and this flow is essentially governed by the Hamiltonian dynamics. And the fluid of continuum fluid of state points that you are visualizing that we are imagining is essentially an incompressible fluid. But how do we see that this is an incompressible fluid? So, the probability flow within this volume is as is similar or is exactly the same as a probability as a flow of an incompressible fluid.

In an incompressible fluid, the volume element does not change, right. So, which means that, let us say if I look at the volume element d of X N at a time t; I have a Jacobian that connects it to the volume element d of X N at t 0, right. So, if you imagine two times snapshots one at t 0, the other one at t and then if you consider a volume element in the phase space, which has denoted by t 0; then this volume element will go to a the volume element d X N at the time t.

So, the question and the relation between these two volume elements are given by this, where J is the Jacobian, which takes you from t naught to t. So, J of t comma t naught; I am sure you have learned Jacobians is p N t 0 q, sorry this has to be. So, note that ok; if you let us take one step backward and we want to. So, the volume element over here is d of p N t 0 d of q N t 0 and the volume element over here is d of p N t d of q N t, correct.

So, essentially there is a transformation that is involved over here; which means that p N t 0 goes to well; we will not say d, we will say p N t 0 goes to p N of t and q N of t 0 goes to q N of t, right. Once, so this is a transformation and therefore, I can write down the transform the Jacobian for this; this is going to be.

And similarly you will have q N of t del p N t 0 del q N t of del q N t 0; it is exactly the same thing that we have defined earlier when we did thermodynamics if you recall. So, this is the, Jacobian is the determinant of this matrix.

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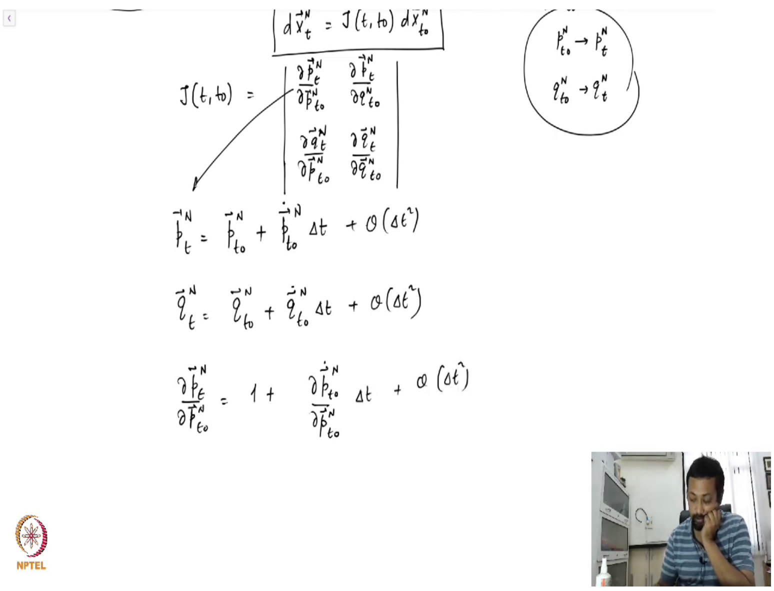

But let us write down the equation for p N t plus right and q N of t is q N of t 0 plus q dot of N t 0 delta t plus of course, you have higher order terms which is delta t square over here, right. Now, let us look at this derivative now, right. If I look at this derivative, then del p N t del of p N t 0 is 1 plus del p dot N t 0 del p N t 0 times delta t plus order delta t square.

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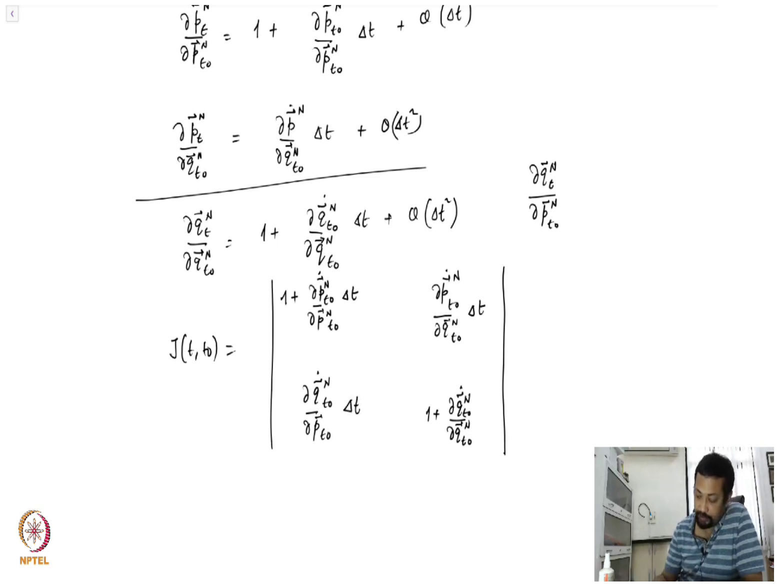

Similarly, N t 0 is del p dot N del q N t 0 delta t plus higher order terms, right. One can do it for the q N t also. So, del q N t del q N t 0 is going to be 1 plus del q N dot t 0 del q N t 0. So, there is no dot here, so one has to be careful; delta t plus order delta t square term. So, once we have this and therefore, one can also write down the corresponding term for del q N t del p N t 0, right.

So, if I now using this form of the Jacobian using the Hamilton's equation of motion; what I should have is del p N t 0 del dot del p N t 0 delta t we will not, we will ignore the higher order terms over here and this one is going to be 1 plus del q N dot del q N both evaluated at t 0. This quantity is going to be del p N dot t 0 del q N t 0 times delta t and this is going to be del q N dot del p N, the N has now come as a subscript t 0 t 0 delta t, correct.

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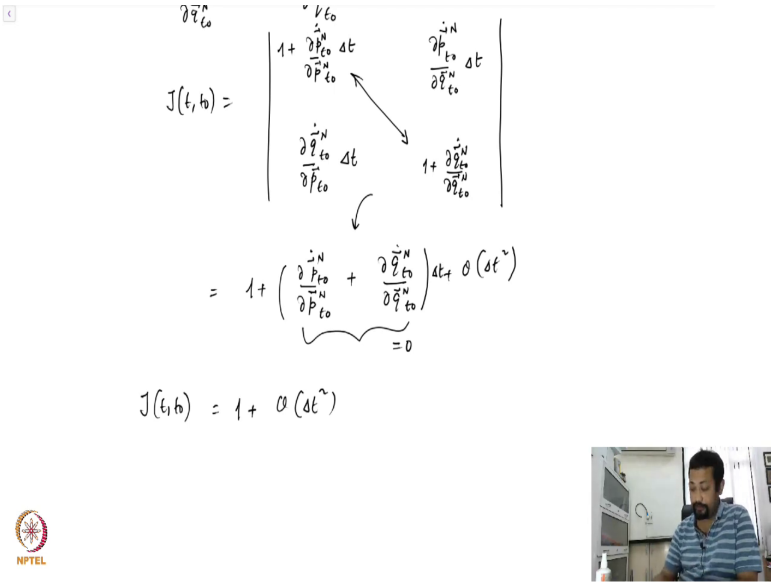

So, 1 plus del q N dot sorry, del p N t 0 del p N t 0 plus del q dot N t 0 del q N t 0; there are higher order terms which we will not consider. So, if we just consider this times this; then this is going to give you this result, right. But we did this, this is equal to 0. So, therefore, J of t comma t 0 is 1 plus order delta t square; there is no delta t term that survives this equation.

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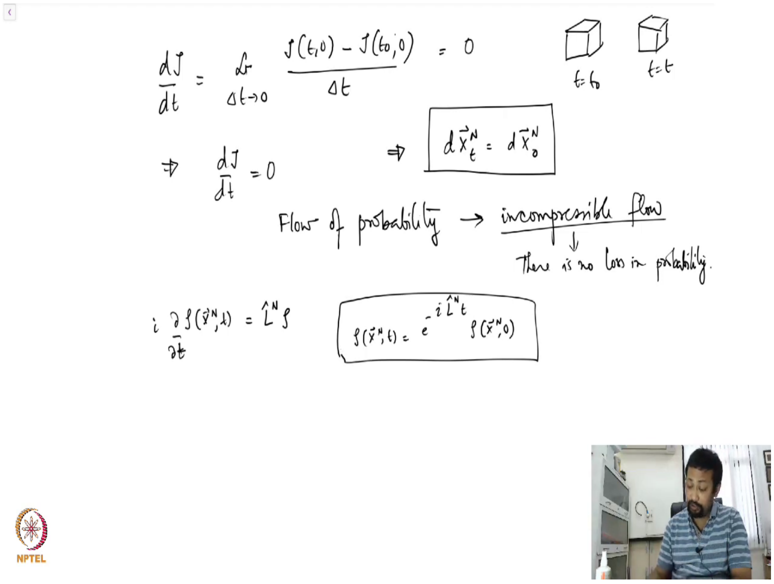

So, one can therefore, write down J of t comma 0 the Jacobian; you start from time 0 to time t is J comma t comma t 0 J comma t 0 comma 0, right. So, this becomes J of t 0 comma 0 1 plus order delta t square. So, d J d t is equal to limit of delta t to 0 J comma minus which is going to be 0, right.

Therefore, it follows that d J d t is equal to sorry, d J d t is going to be 0, which would imply that d of X N comma t is going to be d of X N comma 0. Therefore, the volume at, this volume element that you considered at t equal to t naught and at t equal to t are the same.

So, the volume is preserved. The flow of probability and this essentially is another statement that, this is the conservation of probability; therefore the probability cannot be lost, it does not leak out of the volume. Therefore, this flow of probability is essentially an incompressible flow; which means that, there is no loss in probability.

So, we looked at the probability N particle probability density and we said that, this equation, the dynamical equation for the evolution of this obeys the Liouville equation of motion is essentially the Liouville's equation of motion; the solution to this equation is sorry, there has to be an i here, e to the power i L hat N times t rho X N of 0, right.

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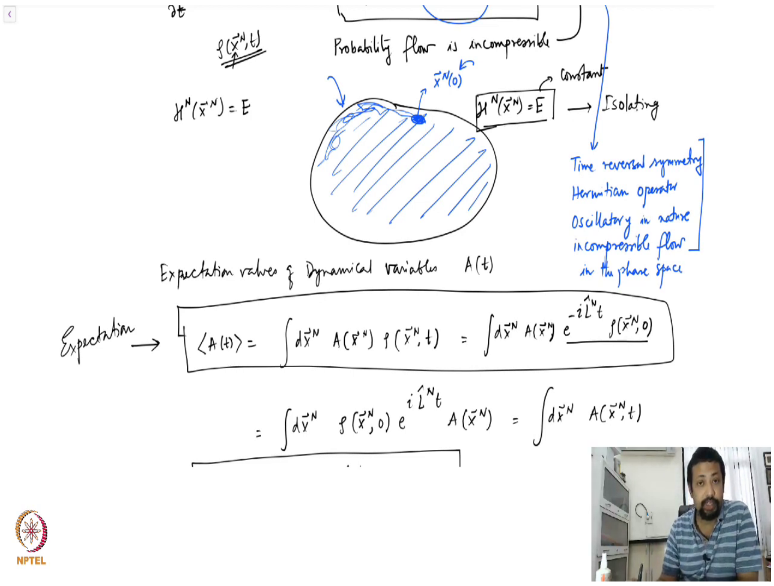

Further we established a little while ago that, the flow, probability flow is incompressible; which essentially means that there is no loss in probability, right. So, how does one visualize this? You can imagine that there is a hyper surface, which is defined by this conservation of energy in the 6 N dimensional phase space. So, I can imagine that there is a hyper surface, which is defined as by this equation with the right hand side E is a constant.

Now, I can consider a small patch, which will denote the initial conditions of all my particles, right. And as the system evolves, this patch slowly and slowly evolves throughout the phase space; because there are several trajectories, this is when if you wait sufficiently long enough, it encompasses the whole of the phase space, it is like spreading of an ink drop in a liquid.

The Liouville equation has several properties; number 1 is this is obeys the time reversal symmetry, because the underlying microscopic dynamics obeys the Hamilton equation of motion which are time reversal, therefore this equation obeys time reversal symmetry, right.

It is a Hermitian, the Liouville operator is a Hermitian operator and if we look at the nature of the solution, particularly this term; this essentially tells you that the solution is always oscillatory in nature. Therefore, one must understand that this equation does not describe the irreversible decay of the system to a unique equilibrium state. So, you one must start off with the equilibrium state from the very beginning itself.

So, as time evolves, in this picture that we have tried to establish that, this is an incompressible flow, incompressible flow in the phase space and therefore, if you start off with a small patch of initial conditions; it is going to evolve as time progresses the trajectories are going to evolve, so that it slowly and slowly covers the whole of this phase space, right.

Now, what does this mean? So, is this always guaranteed right; that is the point that we what, which we want to discuss. Now, before we try to discuss the consequence of what we just described that, if we start off from a small patch of initial conditions, it slowly as the time evolves, if you have sufficiently long enough time; there is a randomness already inbuilt, because in this initial conditions therefore, the whole thing covers the whole of the phase space. And what is the consequence of that before we describe that?

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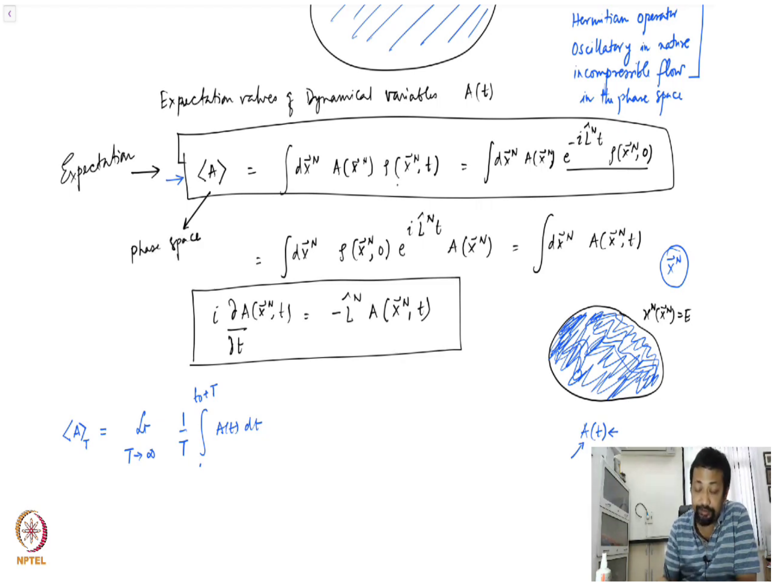

So, we want to, I want to just write down what we are mainly interested in. We are interested in typically our expectation values of dynamical variables, right. And say A of X N right; well not X N, we are typically going to be interested in dynamical variables A of t, right.

Then the average of A of t is defined as d of X N, this is the measure A of X N rho of X N comma t right, which is going to be d of X N A of X N e to the power minus i. So, this is kind of the Schrodinger picture, where the operator does not carry the time evolution; but it is a probability density which carries the time evolution.

We can write down alternatively the same expression for average of this, which is the Heisenberg picture, where I am going to have A of; I am going to take this term, which becomes d of X N A of X N comma t, where now this dynamical variable based an evolution equation which is L hat N sorry, just I am in a little bit clumsy A of X N comma, right.

Anyway this is just as a remark that one should remember; but we are mainly interested in an equation of this form, where I define the expectation of a dynamical variable in terms of the probability density.

Now, coming back to the original question that we posed that, with the picture that we have developed for rho of X N t; we realize that first of all this vector is the tip of this vector is essentially bound to move on the surface which is defined by the conservation of energy, right.

Such surfaces are what are called isolating integrals. So, for an N particle system, this is the only isolating integral that we can have. So, in the phase space, an isolating integral would come would consist of a closed surface; there are other type of integrals which are called non isolating integrals.

So, your conservation, your constants of motion, your conservation of momentum, conservation of angular momentum and your conservation of energy of these, only this one forms the isolating integral. And this is therefore, very very important in what we are going to discuss. Now, clearly let us draw this thing little bit over here; I have this surface which I have again, let us just write down this as this. And as I said that as the system evolves, it slowly and slowly fills up the whole of the phase space, right.

So, what does it mean for us? We cannot observe these quantities right, we cannot observe X of N experimentally; we are rather interested in a limited set of dynamical variables A of t, it can be the total energy, it can be the total momentum whatever that is, we are only limited to observing this.

Now, as we have said that, clearly this is one possible way of defining the expectation value; there is yet an alternative way of defining this expectation value which would say that, if I have the time series of A, which means I measure A as a function of time, then I can define that a different average sorry, with limit of t to capital T to infinity.

So, essentially this means that, you measure this quantity for a large time window and essentially you calculate the average and this is going to be another average which you will write down A of t.

This average, so here it is no longer a function of t, but it is just this. This average is defined in terms of your phase space; why, because you are using the phase space density over here and this is purely a time average, right. Now, the question is, is this equal to the phase space average, right?

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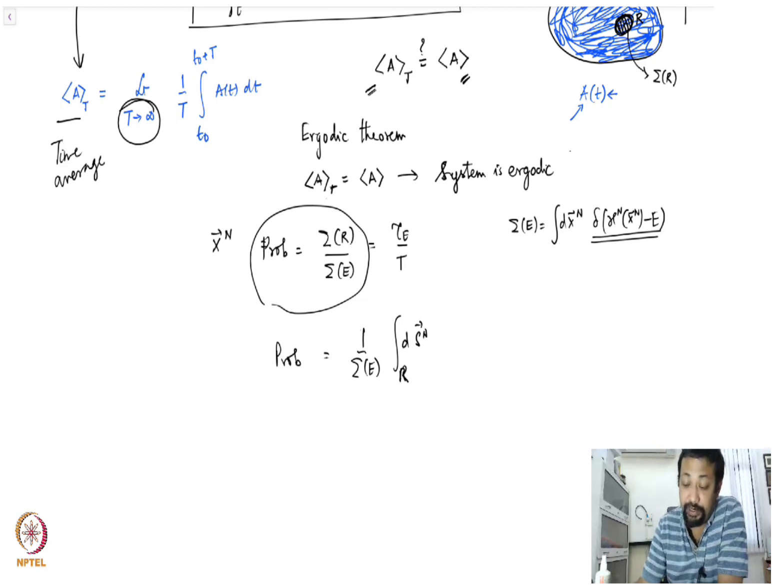

So, now that we have two averages that is defined; one is the time average, average A of t and the other one is the phase space average. The question is whether they are, both of these are equal and when are they equal? And the answer to that, comes from the ergodic theorem; the ergodic theorem essentially tells you that not only that the time average should exist, but if the system is ergodic, then the two averages are equal.

So, this happens when the system is ergodic or alternatively the flow in the phase space is an ergodic flow. There are two kinds of flow generally which is considered in the flex phase space which is an, but we will not worry about that right now. So, our point is that, if the flow is ergodic; then the time average and the phase space average are equal. But what does this mean?

Let us go back to the picture, where we were visualizing the phase space and our phase space trajectories are all covered up the phase space. Now, if you consider a small region R as indicated over here by the black closed surface and you ask that, what is the probability that the state which is denoted by X N is in this region R? Then since the whole of the phase space is completely filled, therefore the answer to that question is essentially that probability.

Let us say is equal to sigma R divided by sigma E, where sigma R is the surface area contained by this black contained within R, and sigma E is the total surface area. Sigma E is formally defined as d of X N delta of H N X N minus E. So, essentially the delta function guarantees that the tip of this vector, this way measure its can only takes account, takes into account the surface area contained within this volume, right.

Now, since the flow is ergodic, the time average is equal to the phase space average; therefore this probability also means that, this is equal to the time that the system spends in this region R to the total observation time. So, when the flow is ergodic, the in equal areas in the phase space, the system will spend equal amount of time.

If there are no isolating integrals for an N particle system; if there are no isolating integrals other than the conservation of energy, then the flow is ergodic. There can be other isolating integrals and find for an any N particle system; there can be other isolating integrals other than the conservation of energy and finding the number of isolating integrals is really really a very difficult job, right.

Now, let us come back to this expression. So, once I have this probability, then you see this probability I can write down as 1 over sigma E integral d X sorry, not d X N; but essentially an integral over the surface area in the region R, right. You can write down in terms of X N; but you have to also include delta H N minus X N and the integral is over the region R, right.

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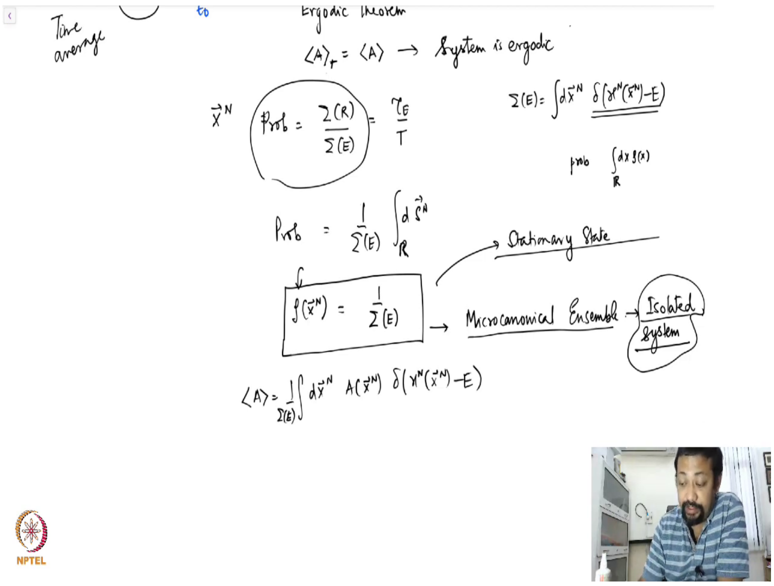

Now, if you recall your, when we discussed continuous random variables and probability densities; we said that the probability of finding a variable x within a range or within an interval R was essentially over the interval d X and rho X, right. And surprisingly if we just look at these two; then this has a similar form and we immediately read off that rho of X N is

1 over sigma E, where sigma E is a surface area and defined by the isolating integral H of X N is equal to E.

This simple looking expression that we have come to, essentially tells you that all the points in the phase space are equally likely to be visited. It is also a point, the point to be noted is that, this expression does not contain time anymore; because we have waited sufficiently long enough for the system to evolve, so that the phase space is completely filled and we have therefore, reached a stationary state, correct.

This equation is what is called a micro canonical ensemble and the average of any dynamical variable is now d X N A X N delta H N X N minus E 1 over sigma E. The delta function once again ensures that it is a surface which is only matters here and not the volume. We shall get rid of this, we shall see later on how to take, how to get around this difficulty, correct.

It is also worth noting that when we visualize this picture over here of the phase space; we said there is no other not we, I mean when we visualize this picture, essentially this also means that there are no other interactions present in the system. So, you do not have; you just have your system, there is nothing else.

So, therefore, this would correspond to an isolated system, what we consider in thermodynamics right. An isolated system in thermodynamics essentially means a micro canonical ensemble in terms of probability or statistics or statistical mechanics for that sake, good.

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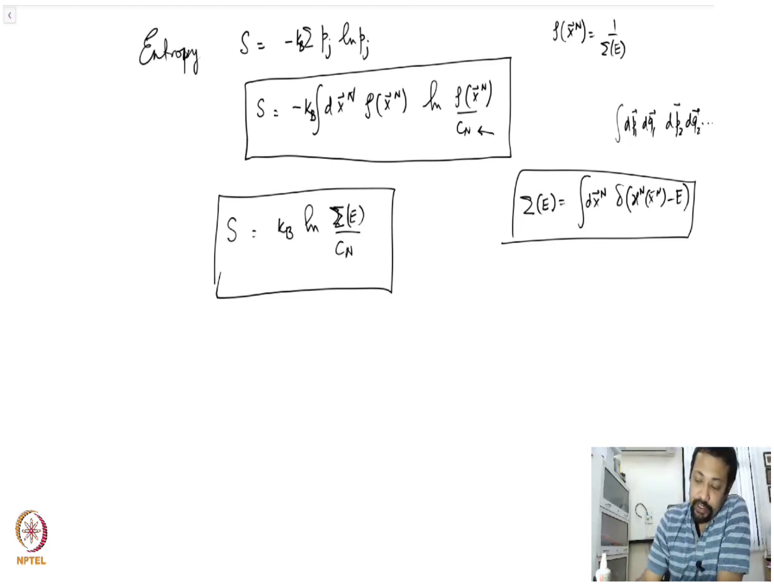

So, now that we have this probability density, what do we want to do? The bridge is given by the statistical entropy or we will just write down entropy S as minus sum over p j l n p j; except now we have minus integral d X N, oops rho X N l n rho of X N divided by C N. But clearly what we are interpreting is entropy, does not have the dimension of entropy. So, what we introduce is a Boltzmann factor S, right.

If I introduce sigma E, rho if we use this expression for rho of X N is equal to 1 over sigma E; then you see your entropy is k B l n sigma E over C N. Note that reason we have introduced the C N factor over here is because this surface area is dimension full; because this surface area has d p 1 d p d q 1, d p 2 d q 2 so on and so forth and we shall later on see what C N is going to be.

Now, coming back to this, this quantity is called the structure function and is defined as d of X N delta of H of N X N minus E. And you can imagine that for a 6 N dimensional space, it is a notoriously difficult quantity to evaluate. So, what do we do?

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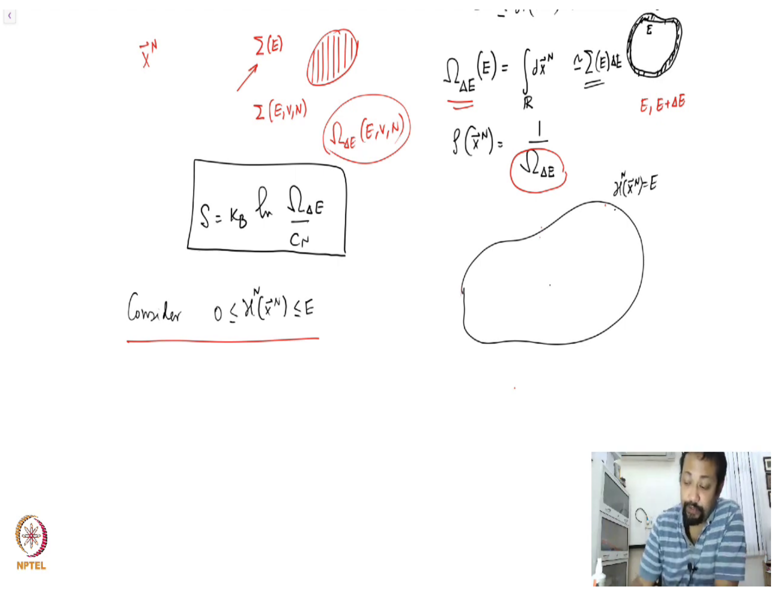

Well we start off by saying that look, instead of considering that the system is strictly at an energy level E; I can also consider a spread in the energy level, so that I replace this by E plus delta E. If that is the case, then you can think then this surface area that we are considering is now replaced by the volume which is contained within this shell defined by E N E plus delta E.

So, that I have now omega of delta E as a function of E as integral d X N over this region and your probability density rho of X N is just going to be omega delta E, so that your entropy is going to be k B l n omega delta E over C N, right. If your delta E is small enough, this can be approximated by sigma E delta E right, not otherwise; we shall also remove this restriction on delta E.

So, now that we have replaced sigma by E by the volume which is contained within this shell of energy E and E plus delta E; even this volume is also very difficult to calculate. Before we go ahead with this argument that, how we can replace this; what we want to say about two points is that, this sigma E that we originally started off with, essentially that represents the surface area of the isolating, it defined by the isolating integral is also a measure of the total number of microstates of the system, right.

What we have been calling is X N as states are essentially the microstates of the system. And in principle, although we have been denoting it with by E; this for a hydrostatic system, for an N particle system which physically occupy a certain volume in space and has certain particle number is more explicitly written as sigma E over N and so, is omega delta E as E, V, N, right.

So, now what we want to look at is, how do I replace this cumbersome calculation of the shell in the hyper surface by something more easier to do. For that again, we consider this inequality, where now my system is allowed to have energies all the way from 0 to E.

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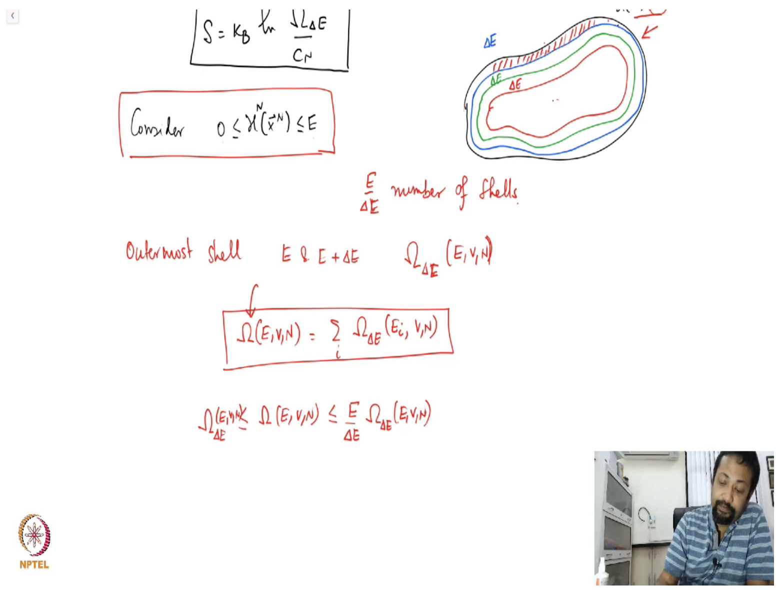

So, essentially you define this hyper surface which is denoted over here. And the surface the bounding surface is defined by the energy E; whereas the system is allowed to have energies from 0 to E. What you now do is essentially, you break up this volume into small small shells of energy of width delta E. So, let me just quickly try to schematically draw them; this is also delta E, again you have an inner. So, you keep on doing it. So, there you have E over delta E number of shells.

The outermost shell which is contained between; so let us write here outermost shell which is contained between E and E plus delta E has the volume omega delta E E, V, N. Why am I suddenly, suddenly interested in this or because this is exactly that quantity we have been dealing with earlier. Therefore, if you look at it carefully; so this is the shaded volume that we are referring to. Now, the total volume omega E, V, N, which is contained by this hyper surface is sum over i omega delta E E i comma V comma N.

But if you look at this expression, it is very very evident; even this pictorial representation is very very evident that, this quantity, the total volume which is contained within this hyper surface is definitely more than the shaded area, right. So, therefore, we can write down this as omega delta E E comma V comma N is less than omega E, V, N; E over delta E number of shells, if I multiply this by delta E E, V, N, then the total volume is less than this volume, right.

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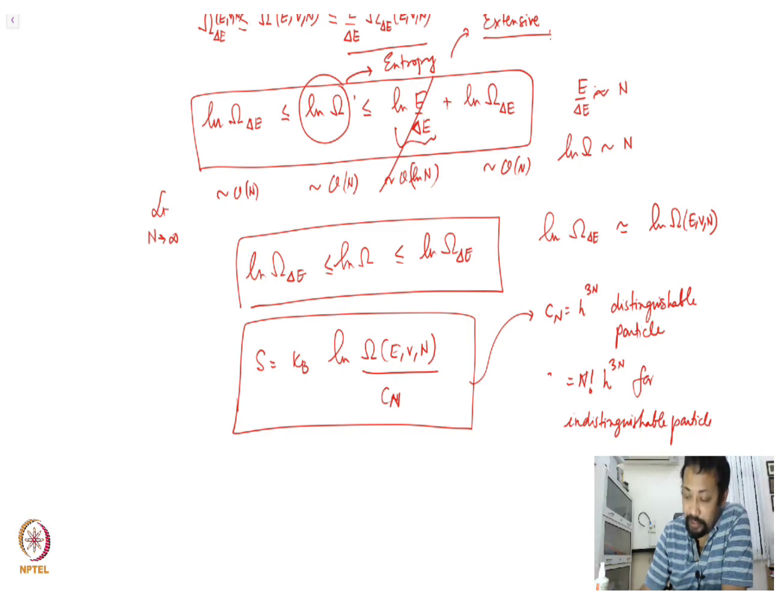

So, now if you take a log omega delta E is less than l n omega, which is less than l n E over delta E plus l n omega delta E. Note that this is the one which enters the entropy, right. On the other hand; so this is a total number of microstates, log of that and is therefore is an extensive quantity. In contrast, E is an extensive quantity and therefore, E over delta E would scale as N; whereas log of omega would scale as N.

So, if you now take the limit, the thermodynamic limit of N to infinity, large number of particles; then you see in this inequality, this term drops out of the computation, because this is only l n of the order of l n N, whereas this term is and this term is N, this term is N. So, not I mean; what I mean to say is, of the order of and this term is of the order of l n N. So, this term drops out from this equation and you have very nicely l n omega delta E is less than l n omega delta E, right.

So, that in the thermodynamic limit, the omega delta E l n omega delta E; what we have been using in place of the entropy is l n omega E, V, N, the total volume contained within the phase space, right. So, we rewrite our equation our expression for entropy as k B l n omega E,V, N divided by C N. We shall come back to C N; but right now it suffices to say that C N is equal to h to the power 3 N for distinguishable particles and is N factorial h to the power 3 N for indistinguishable, for indistinguishable particles.

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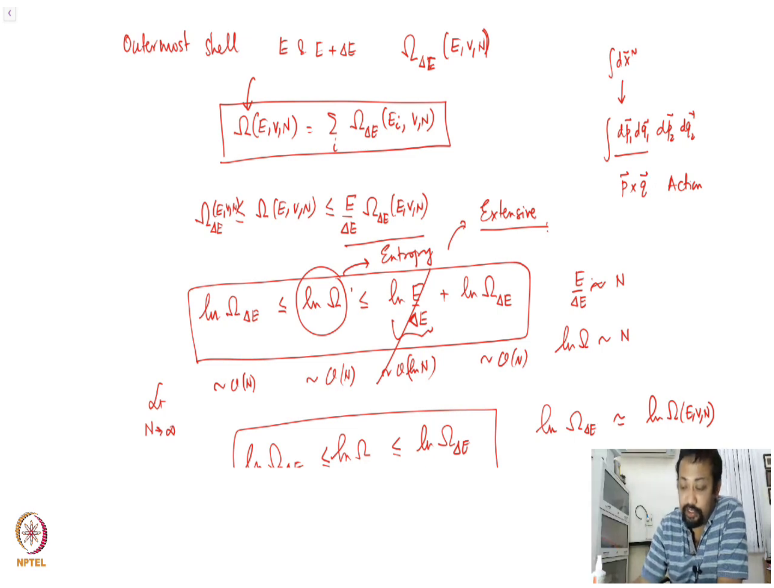

h is the Planck's constant and that is not very surprising to figure out why h comes in; because if you look at the measure in the phase space, it is d of X N. If you expand this, then this is d p 1 d q 1, d p 2 d q 2. So, the product of p times q has a dimension of action, same quantity that as h as the Planck's constant. So, essentially you become, it becomes it non dimensionalize this volume by h to the power 3 N.

The introduction of this h to the power 3 N and the N factorial is clearly something which is done by hand in classical statistical mechanics. We have no way of introducing it very naturally in the theory; we shall see later on how quantum statistical mechanics does it.