Statistical Mechanics
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Lecture - 06
Exact and Inexact differentials, Legendre Transformation

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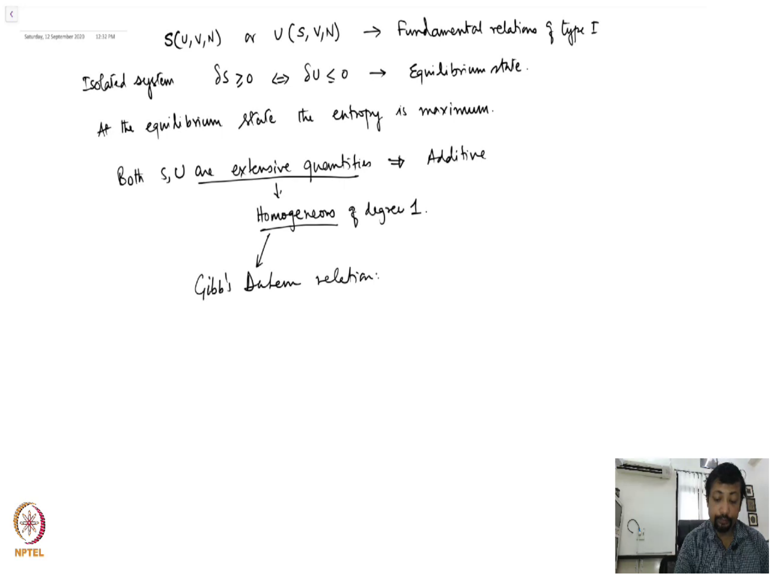

In our earlier lectures what we saw was that, entropy as a function of U, V, N or U internal energy as a function of S, V, N are the fundamental relations of type I, relations of type I. And we also saw that, for an isolated system for an isolated system, which is not allowed to exchange energy with the environment. The maximization of the entropy is equivalent to the minimization of the energy and that takes the system to an equilibrium system, to an equilibrium state.

At the equilibrium state, the entropy is maximum. Further we also studied that, both s and u are extensive quantities; which means, which implies that they are additives. And the consequence of this extensivity is that, they are homogeneous of degree 1. And since they are homogeneous of degree 1, they must satisfy the Euler relation. And the consequence of the Euler relation, this homogeneous property, homogeneity property of the internal energy and the entropy leads to the Gibbs Duhem relation.

So, today what we are going to do is, we are going to slowly very quickly and briefly review partial derivatives and then we are going to move on to something else.

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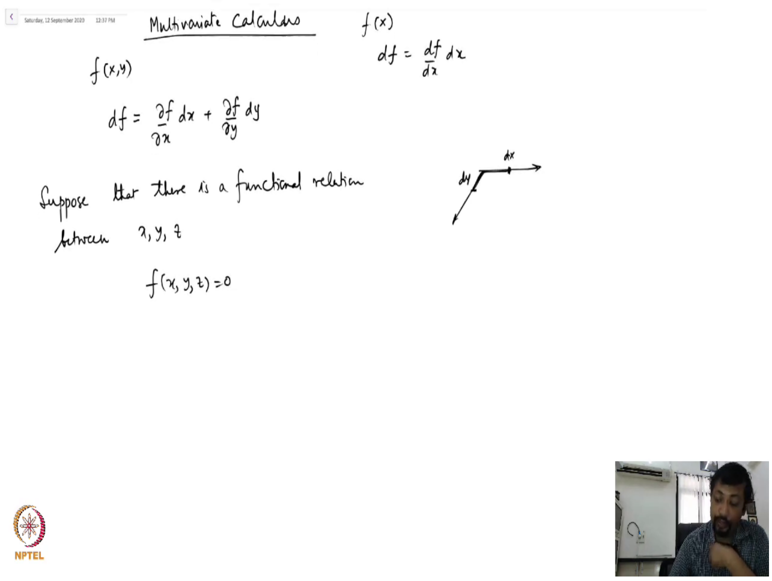

Now, partial derivatives, particularly is a area of a multivariate calculus. So, if I have a function of x and y; earlier for one variable calculus, I know that if I have a function of f x, then d f I can write down as d f d x.

But now I have a function of two variables and therefore, I want to find out the total change in the function d f; which mean this essentially means that, I have to go a distance d x along the y direction and a distance d y along the y direction. So, I go a distance d x along the x direction and distance d y along the y direction and I want to calculate the change that, in a very simplified motion notation is d del f del x del f del y d y, right.

Now, suppose that, there are there is a functional relation between three variables x, y, z. So, that we can write down f of x, y and z is equal to 0.

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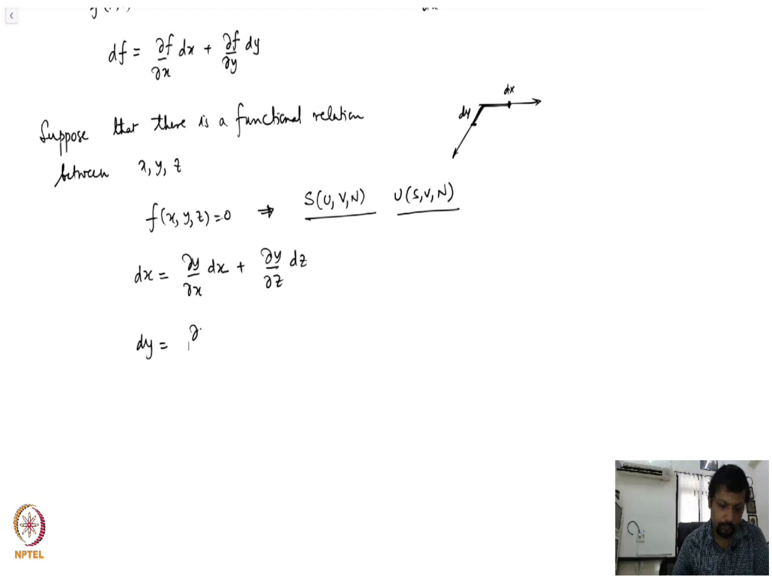

This is if you can imagine the example being S of U, V, N or U of S, V, N. So, this describes a manifold as is given over here. Then if such is a relation, then I can write down d x; x can be a function of y and z as del y del x d x plus del y del z d z. I can do the same exercise and write down d y as; I am sorry, this relation is wrong. So, then I can write down.

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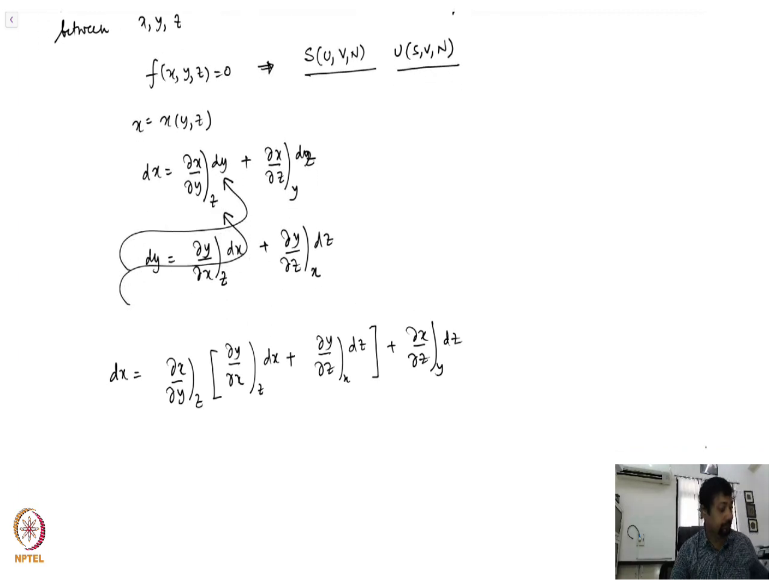

If x is a function of y and z, then d x is del x del y d y plus del x del z d z; here y is held constant, here z is held constant. And I can do the similar exercise in writing for d y, where I will have del y del x d x plus del y del z d z, here x is held constant and here z held has z is held constant.

So, if I now substitute d y over here, then this becomes del x del y, z constant times del y del x, z constant d x plus del y del z x constant d x plus del x del z, y constant d z.

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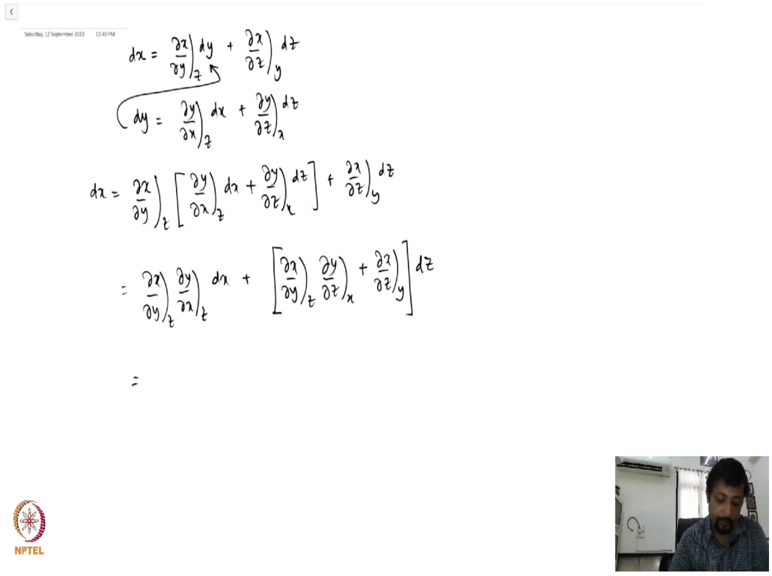

So, d x is equal to. So, we have del x del y d y z constant plus del x del z y constant d z and d y was del y del x d x, z constant plus del y del z it is constant d z and we substitute it for del x, we substitute d y over here. That essentially means, I have del y del x set constant d x plus del y del z x constant d z plus del x del z, y constant d z.

Open the brackets, del x del y z constant, del y del x z constant, d x plus del x del y z constant del y del z x constant plus del x del z y constant times d of z.

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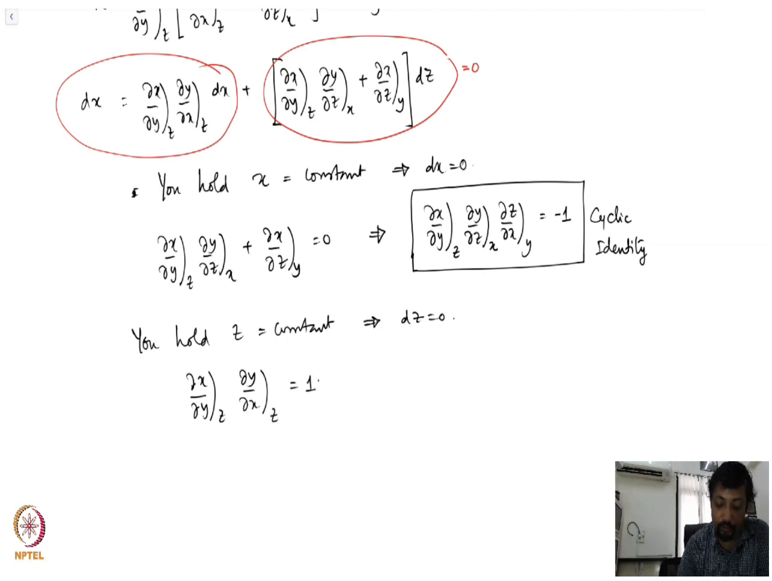

Now, imagine you hold x is equal to constant; this implies that, d x is equal to 0, in which case the coefficient of d z must vanish, because this equation then this just becomes this is equal to 0. And if it is valid for all values of z, then it must be that the coefficient must finish.

Therefore, you have d x d y del x sorry del x del y z constant del y del z x constant plus del x del z y constant is equal to 0; which means you come up with a very nice identity del y del z x constant and del z del x y constant is equal to minus 1, this is what is called a cyclic identity. You now, you hold z is equal to constant. So, you fix the z and this implies that d z equal to 0 and therefore, you see the left hand side and the right hand side which is this and this is an identity.

So, this means that, del x del y z constant del y del x z constant must be equal to 1, which gives you the reciprocal relation that del x del y z constant is equal to 1 over del y del x z constant right.

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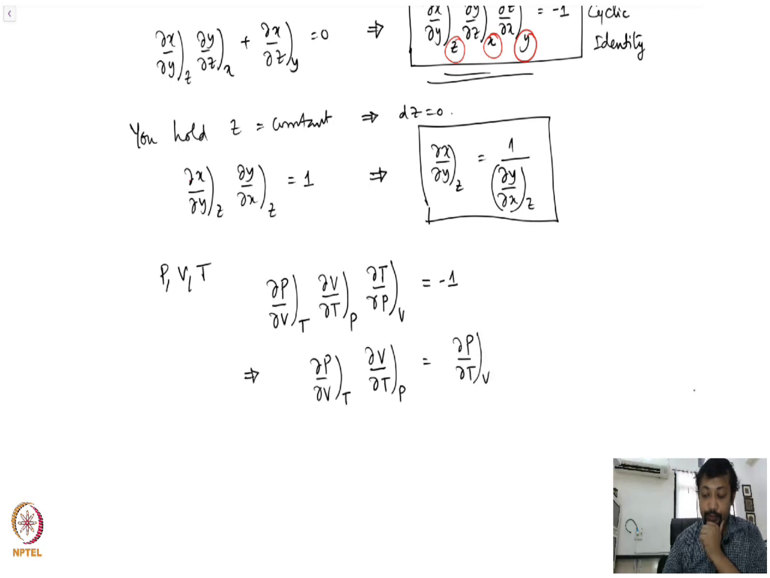

So, you must pay attention to the quantities which are being held fixed in the partial derivatives, right if I now want to apply this to our hydrostatic system, we will take this relation, the cyclic relation and we will consider P, V and T.

If I apply this to P, V, T; then it means that del P del V temperature constant. Then I have del V del T pressure constant and I have del T del P volume constant must be equal to minus 1. So, this implies that del P, del V temperature constant del V del T pressure constant is del P del T volume constant with a minus sign in front of it. But the compressibility, which is the isothermal compressibility of the solvent is defined as minus 1 by V del V del P temperature constant, right.

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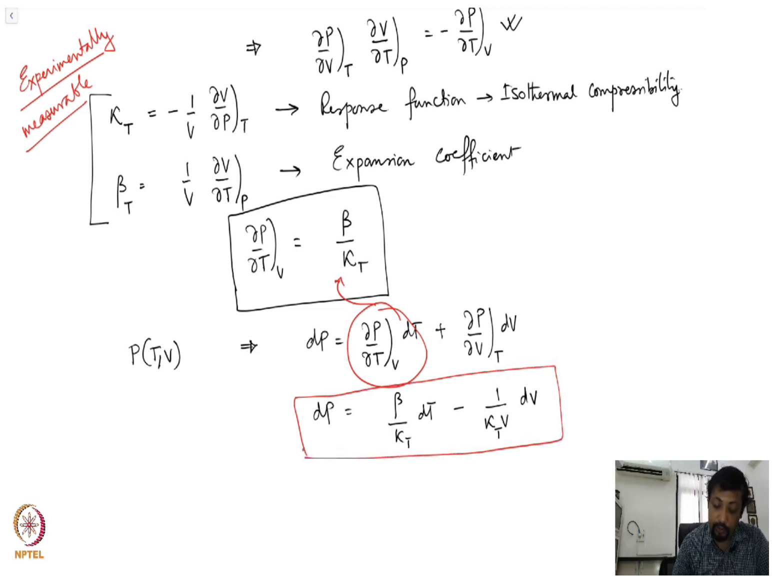

So, this term is a response function and is called the isothermal compressibility; the other one which will call beta T or just beta is 1 by V del V del T pressure constant and this you know is the expansion coefficient.

In the formal case, that isothermal compressibility or the compressibility in general; determines how your system is going to react, if you apply an additional pressure, compress or remove the increase or decrease the pressure. In the second case, it determines how the system is going to react, if you supply heat to the chain system; which means, you if you increase the temperature of the system.

So, once I know so, these are my thermal, this is my response function and the advantage of this response function are that, these are experimentally measurable. So, I can know their dependence on pressure temperature and all these things. So, if I have this, then I quickly look at the equation that we have written down over here and then I have del P del T volume constant is beta over capital T.

We will use this later on in several on several equations, but the simplest application is; if I want to for any hydrostatic system, which is a fluid, if I want to write down P as a function of T and V, then this implies that d P is del P del T volume constant d T plus del P del V temperature constant d V.

And this one I have already calculated just now; the first term is the one which I have calculated just now which is this. So, therefore, it follows that, this is beta over kappa T d T minus 1 over kappa V d V.

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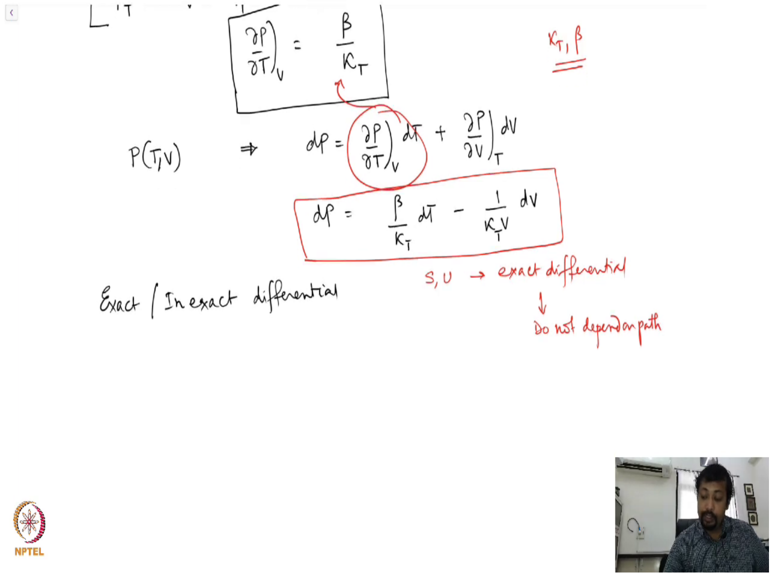

So, you see, now you have a very nice equation; you do not even have to know the equation of state, if you can measure this quantities experimentally, if you can measure kappa T and beta experimentally, you can find out how the system is going to behave, right. So, if you say that well; I will change both T and V, then I know what is going to happen to this system, correct.

Finally, we come to what is called an exact and inexact differential; this we have already done. And the consequences that the example is first that, the entropy and the energy are exact differentials. Why are they exact differentials? Because they do not depend on path. And once they are, they did not depend on path; therefore I can write down the following way, but before you, before we do that what we want to say. So, what exactly do we mean by exactly and inexact differential?

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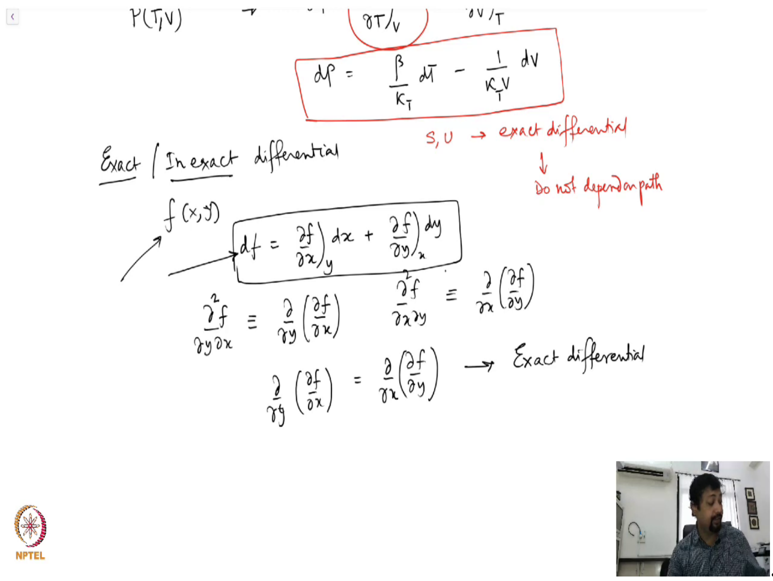

As we had shown before that, if f is a function of x and y; then d f is equal to del f del x y constant d x plus del f del y x constant d y. But the function f is analytic, therefore if you take the second derivative of this function; which means del x f which is equivalent to you are taking the derivative del del y of del f del x. And here you are taking a derivatives, which is del del x of del f del y they must be equal, right.

So, therefore, I have del del y of del f del x must be equal to del del x of del f del y and this is the condition for f to be an exact differential. So, if you can write down the function in this particular form; given this f if you can write down d f in this particular form, then you know that it is an exact differential.

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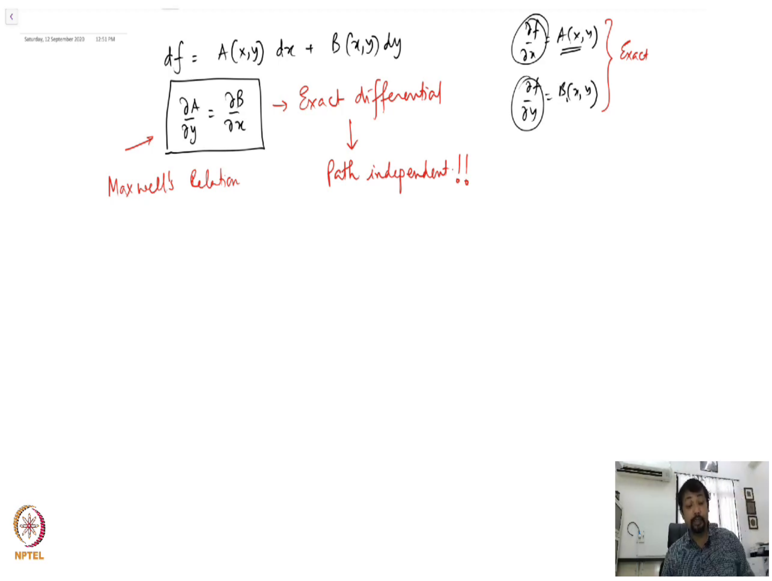

Which means that for any quantity, now I have changed it the notation plus B x, y d y; what does this mean? This means that, I have replaced del f del x is equal to A x, y and del f del y as B x, y; but with the understanding that this can be any, this may not be del f del x, this may not be del f del y. So, this can be any functional form. So, if I am given any an arbitrary differential of this particular form; if it was an exact differential, then I would have this equality.

For an exact differential, I would have this equality satisfying; but in principle I can have any function times d x, any function time d y. And if I want to find out whether B, whether this function f is an exact differential; I will simply do del A del y must be equal to del B del x. And if this is satisfied, then I know that the function; this is an exact differential, which means it is path independent, right. So, now you know how to determine exact and inexact differentials.

So, this we shall use this is the criteria of an exact differential; we shall use later to find out determine what are called Maxwell's relations, but not right now. So, right now it suffices to say that, if this relation is valid for a differential; then that different that then the function that you are considering is an exact differential or the differential is an exact differential and the functioning in the is a state function, in the sense that it does not depend on the path that you have taken.

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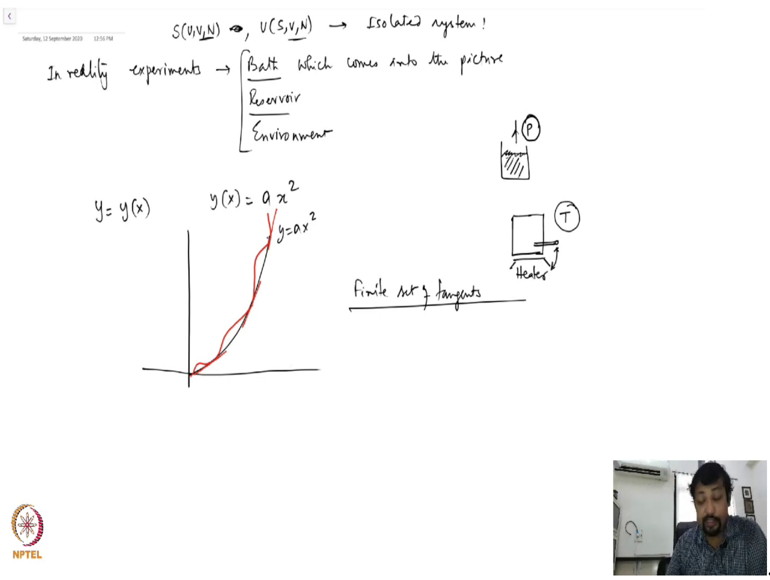

What we want to do right now is, move to some something else. Now, whatever we have been discussing so far as we summarized in the first part of the lecture S and U as a function of S, V, N; these are my fundamental relations of type I and these are valid for an isolated system. But isolated systems are very very difficult to find. In reality, reality whenever you do an experiments; there is something what is called the bath, which comes into the picture.

And the bath essentially it has several way of people calling it, it is a reservoir, it is an environment; whatever it is, but they play a very significant role. For example, if you are doing it in an experiment, sorry you are doing an experiment in a beaker with a liquid; then you know that this is the part of the surface is exposed to the atmosphere, right. So, and it maintains a constant pressure.

If you are doing it with a closed beaker, but fixing the temperature; which means that you have applied a thermostat to the system, which is either you have put it on a heater or which is connected to a thermostat that maintains the temperature of a system. So, here temperature is constant. So, all of these in an experiment realizable situations, these become very very important.

So, the question is then; you would like to deal not directly with the code the coordinates that you have over here, but essentially you want to bring in these forces, because they are being held fixed. And therefore, the differentials are also going to be easy to manipulate. So, the question is, how to do that? Now, to answer this we shall look in some different area.

So, let us consider now y as a function of x, right. Now, typically what happens is, if I want to plot this function; if I know the functional form, for example, I can take y x is equal to a times x square and all of you know how the plot is going to look. Let us make the plot like this. So, this is y is equal to a x square.

But now if you know the function, you can definitely plot it; you can find out the derivatives to calculate the extrema of the function and the asymptotic behaviors as well as the behavior in a 0 to plot the. Or you can use a plotting software that is even more easier nowadays; but now alternatively you see what I can do here is, I can specify the tangents.

Let us say I specify the tangents. So, this is my tangent at this point, this is a tangent at this point, this is a tangent at this point. The question is, can I reconstruct the function from this tangent? Clearly if there are only three tangents; then you can say no how can I do that. For example, I can have a curve which goes like this and then like this; this is a different curve.

But you see the tangents are the same; therefore if I just give you only a finite set of tangents, if there is only finite set of tangents, then you may not do it. Then you cannot extract the same information or you can do not encode the same information. But in principle, since if I can specify the tangents at three points; of course I can specify the tangents at all points.

So, that would mean that, I have specified the tangent here, here, here, here, here all along the curve and then you see no longer there is an any ambiguity. Then the curve has to, I can reconstruct the curve from the tangent itself.

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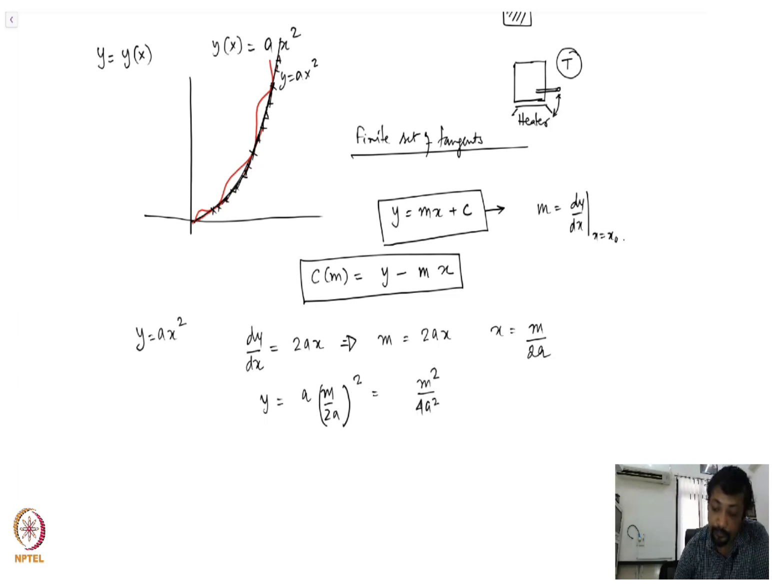

But the tangent, equation of a tangent is m x plus c, right. And that is a very very simple equation; it is an equation of a straight line. So, now, if I specify the tangents only at these three places; then of course you can see that it is not possible to reconstruct that function, because the red and the black curve have identical tangents at this points.

But if I can specify it at three points, I can specify it continuously at all points on the curve and then you see, there is no ambiguity in this; I can reconstruct that the whole function. So, the idea is very nice and I know that here the equation is very very simple; the equation of a tangent is y is m x plus c, where m is the slope and is d y d x at the point x equal to x naught and c is the intercept.

So, therefore, I have to define a function c of m which is y minus m times x; the moment I define the c as a function of m. If m varies along the curve, so does the intercept; therefore I have encoded all the information that is required to reconstruct that the curve.

Let us see. So, y is equal to a x square that is the function that we started off with and then it follows that d y d x is twice a x; which means m, which implies that m is equal to twice a x and x is equal to m by twice a, correct. Y is a m by twice a whole square, which is m square over 4 a square.

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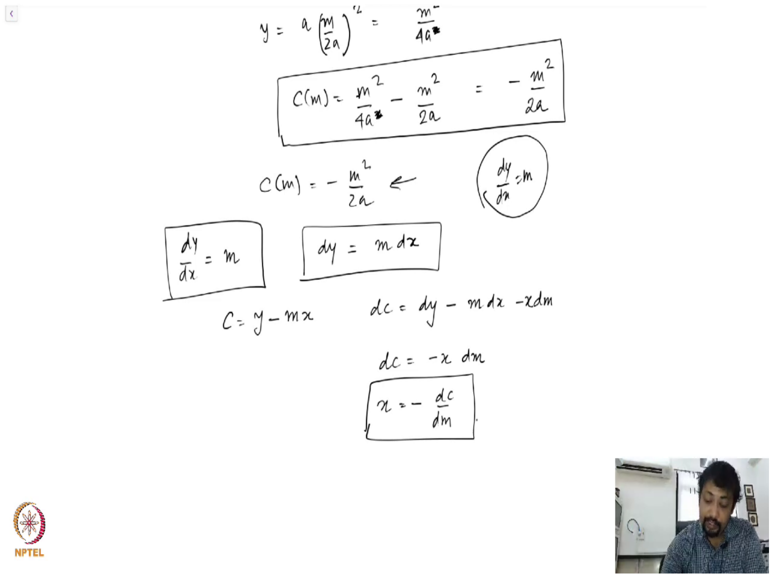

And therefore, c of m is m square over 4 a square minus m square over twice a, sorry this has to cancel out, this has to a be a.

So, this is minus m square over twice a. And this is the function that I am looking for, c of m is minus m square over twice a. But then you can ask me, given this c of m; how do I construct that the function? That is a valid question. So, let us start off. So, I know d y d x is equal to m, therefore d y is m times d x. Now, c is equal to y minus m x.

So, that d c is d y minus m d x minus d x d m; but d y is m times d x, this is what we have got from the definition of the slope. And therefore, it follows d c is minus x d m or x is minus d c d m. This is the answer that we are looking for. Just at we had just as we had d y d x is equal to m; when we went from the x y to c n, this is the answer that we need if we want to reconstruct that the function.

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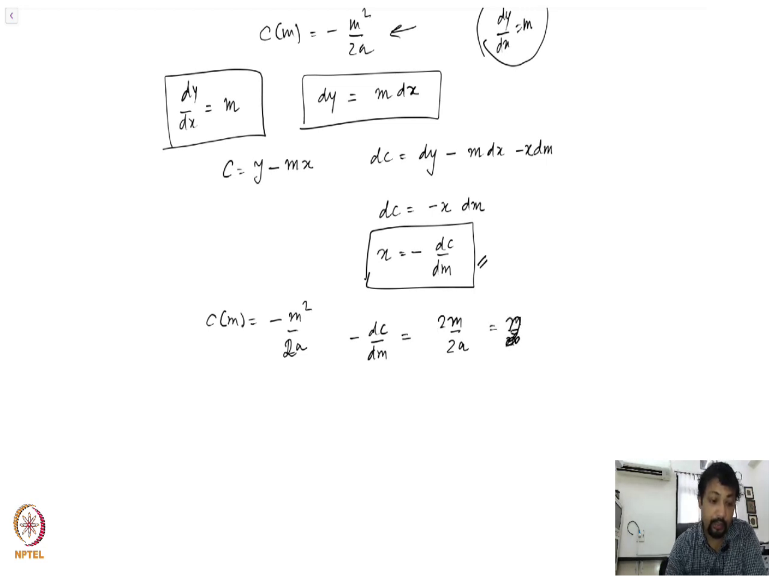

So, if c of m is minus m square over twice a, then d c d m is m over twice a and minus d c d m is m over twice; am I right, no. So, it is twice m over twice a, which is m over a; let us just rub this out right; which implies that this is equal.

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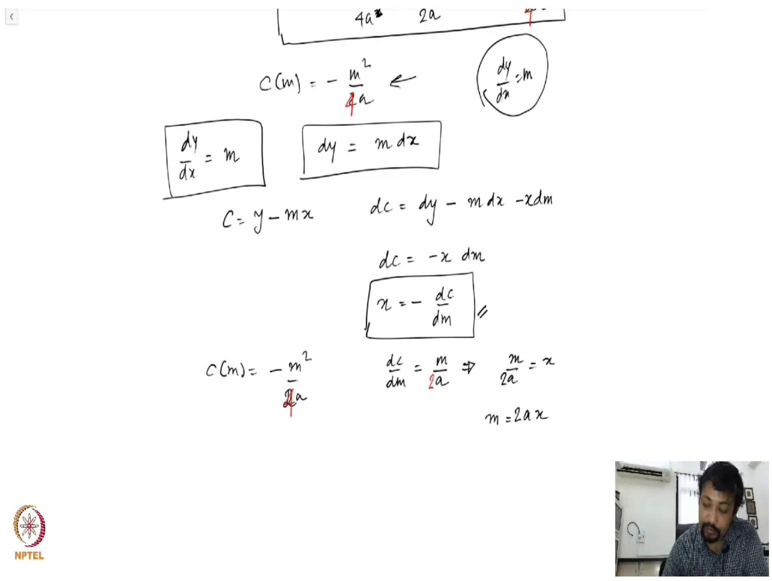

So, m over a is equal to x or m is a x. So, there is a problem somewhere; yeah the problem is over here. You see this is m square by 4 a, this is this is minus m square by 4 a.

And if this is minus m square by 4 a; then this has to be 2, this is the error that we did. So, if this is 2, then this is twice a x, right. So, now, we have m.

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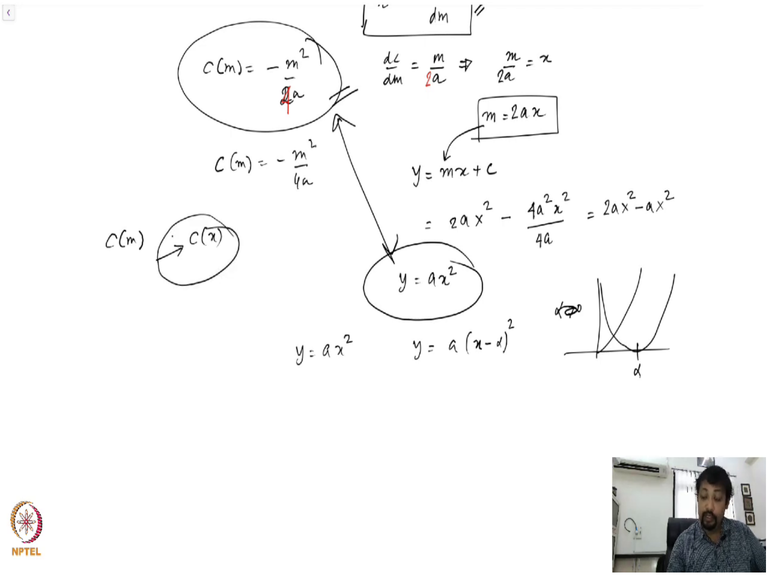

So, c of m is minus m square over 4 a, m is twice a x; now y is m x plus c. If y is m x plus c, then you see that this is twice a x square; if you substitute for m over here plus c is minus m square by 4 a. So, let us do it carefully now. So, that we do not make any mistakes; this is minus of 4 a square x square divided by 4 a, which is twice a x square minus a x square and the answer is y is equal to a x square.

So, you see whatever you have encoded over here, that completely contains the information about this function y equal to a x square. So, though both the descriptions are equivalent and equally valid. You could have argued that, look I have specified c as a function of m; why not specify c as a function of x?

See this will not encode the same function; because if you see y is equal to a x square and y is equal to a x minus let us say alpha whole square, where alpha is a positive, well alpha is a shift essentially. So, essentially y is equal to a x square is this and y is equal to; this is your alpha will have the same value of c of x. So, then this information contained is not the same and from this definition that if you just have c as a function of x; you cannot reconstruct back the function completely.

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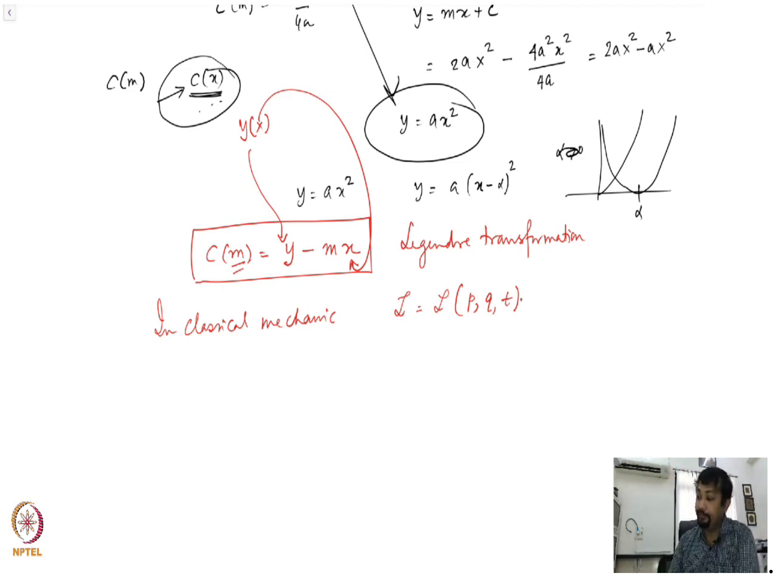

So, the bottom line is that, I can equally define this c of m as y minus m x and this procedure is what is called a Legendre transformation. We probably have done Legendre transformation in different way, but this is what the legendary transformation mean. What does it mean?

Look at it very very carefully, you were given a function y of x; you have taken that function as your input and you have replaced x to get a new function, which is now a function of m. So, this is the prescription if you want to replace a variable. In classical mechanics, the

Lagrangian is a function of p, q and t right or in some. So, p does not enter over here, you write it down as q, q dot and t.

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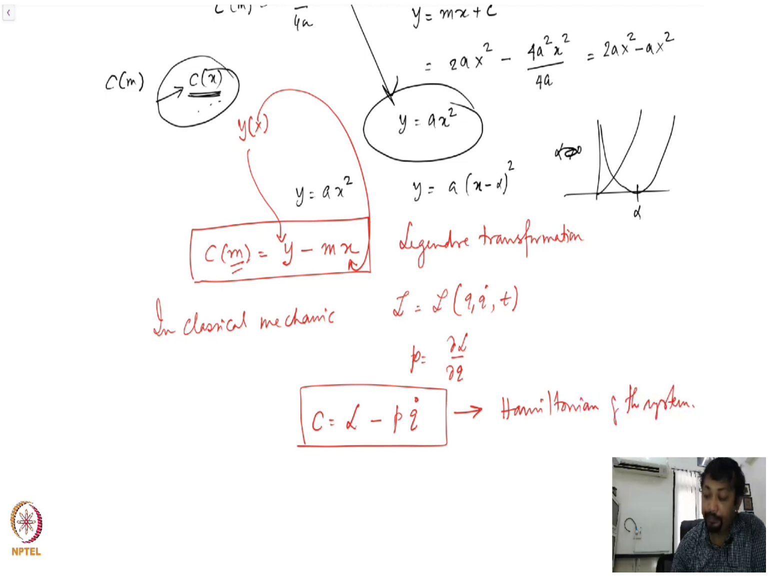

Then the momentum it is, the momentum is del L del q. And you can eliminate q dot by writing down in terms of this momentum. And this is what is called the Hamiltonian of the system.