Statistical Mechanics
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Lecture – 14
Stability of Thermodynamic Potentials

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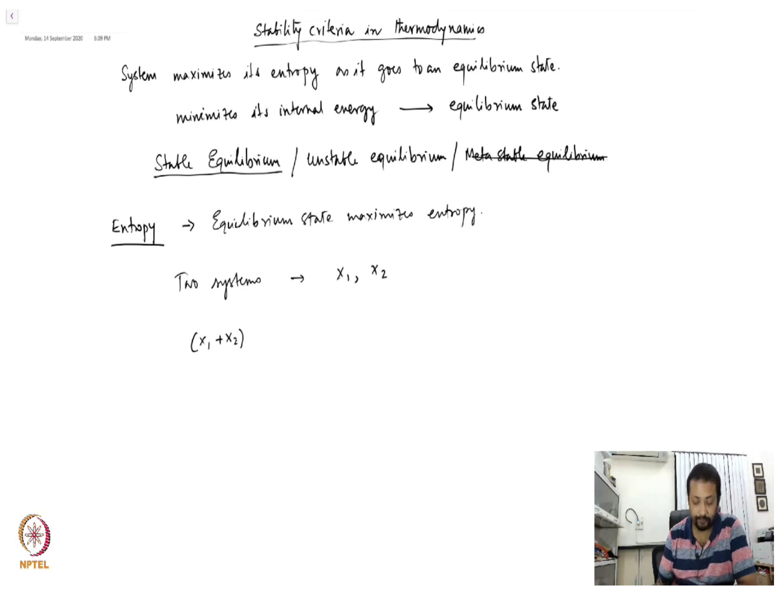

Welcome back. Today, we are going to look at stability criteria in thermodynamics. Now, in our earlier classes what essentially we have done is that we have shown that a system maximizes its entropy as it goes to an equilibrium state, right. Now, alternative alternatively the statement can be recast or said in terms of the energy that it minimizes internal energy, its internal energy as it goes to an equilibrium state.

Now, in mechanics we have learned about different kinds of equilibrium. A stable equilibrium and unstable equilibrium that is it one more kind of equilibrium which we are not going to talk about in this lecture or in this course, but which is very relevant particularly for people who do who study classes system that is essentially what is called the meta stable equilibrium, but we are not going to talk about this.

Our idea now concerns is the following that given a system in its equilibrium state, in its stable equilibrium state what does this stability criteria mean? So, we will first look at the entropy. So, we will look at entropy first and as stated before the equilibrium state maximizes my entropy or the entropy of the system right.

So, now consider that we have suppose or consider that we have two systems and for each of these systems there are very its described by variables X 1 and X 2 right. So, then let us bring these two systems together so that the combined variables, the combined system can be described by the variable X 1 plus X 2, correct.

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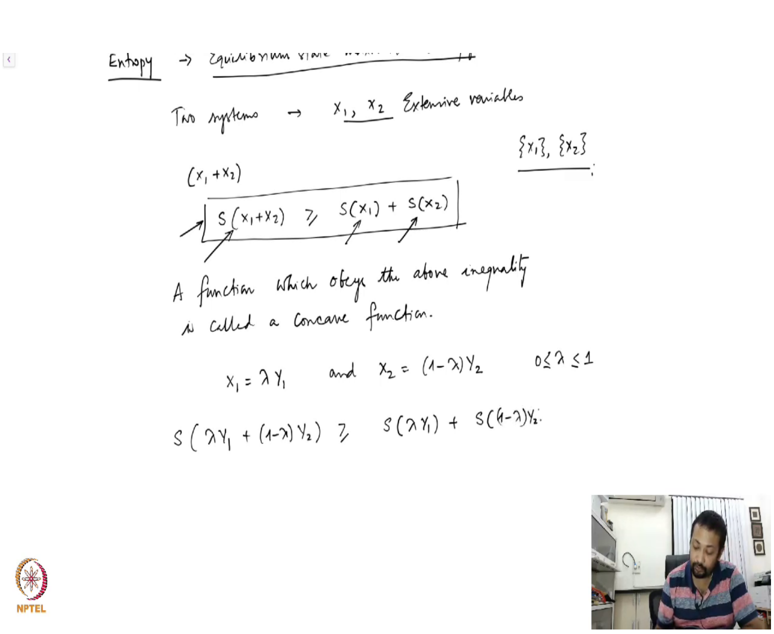

In which case if you were to write down the entropy particularly the maximization of the entropy then this would mean that S of X 1plus X 2 must be greater than equal to S of X 1 plus S of X 2. So, following is experiment that you are doing that you have two systems and each of this system dresses the first system is described by a set of variables X 1, the second system is described by a set of variables which are X 2. Now, let us bring these two systems together so that these two systems come into a joint equilibrium.

Now, in this process of coming to a joint equilibrium it maximizes its entropy and once you have that then you write down this maximization relation like this, because your joint system is now described by the set of variables X 1 plus X 2 and therefore, the entropy is going to be of the joint system is going to be a function of X 1 plus X 2 and the maximization would mean that the entropy in the final state is more than the entropy that you started off with right.

Think about it, now that you have a single system and suppose you can partition these two systems the extensive variables, which are these X 1 and X 2. So, these are your extensive variables that you have, that can describe the systems and this extensive you can partition this single system into two subsystems which are denoted as X 1 and X 2.

Such that the above inequality is violated then what is going to happen? Then the system as a whole would be unstable. If this inequality was not violated then the system would be in a stable equilibrium, but if this inequality is violated then the system is in an unstable equilibrium and it would immediately separate out into two separate systems right.

It will break; it will break into to the smaller systems each variable's X 1 and X 2. So, this is exactly the idea behind the stability criteria. Now, a function with such a property, with this particular property that we have written down is what is called a, let us write down completely a function which obeys the above inequality is called a concave function. But, what does this concave function mean?

Exactly, for this what we want to write down if I want to jump, if we want to understand the geometrical property of this inequality let us write down X 1 as lambda times Y 1 and X 2 as

1 minus lambda times Y 2 right where we put the condition that lambda is greater than equal to 0 less than equal to 1. Then, it follows that S of lambda Y 1 plus 1 minus lambda Y 2 is greater than equal to S of lambda Y 1 plus S of lambda X 2 is 1 minus Y 2. So, we will write it down as 1 minus lambda Y 2.

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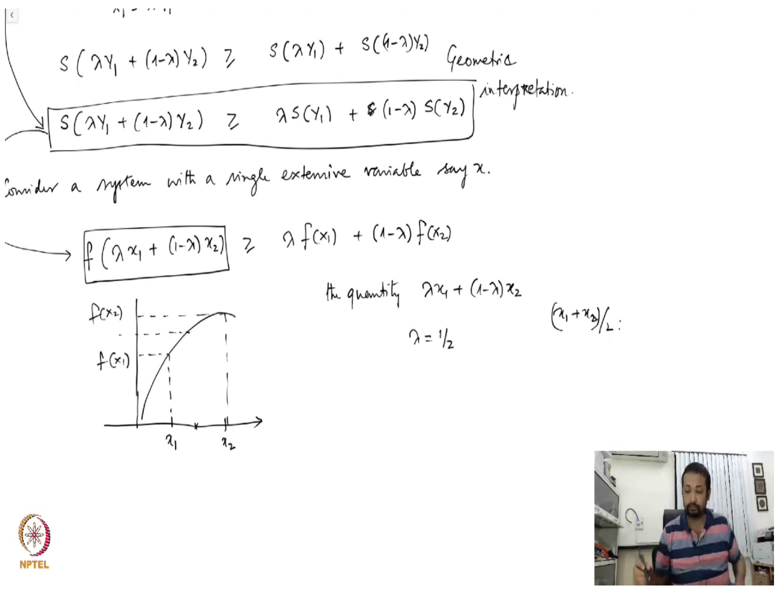

And now, we use the homogeneity property of the entropy to write down S of lambda Y 1, 1 minus S of lambda Y 2 is greater than equal to lambda S of Y 1 plus S 1 minus lambda S of Y 2. So, we have come down from this above inequality we have written, re-written this inequality in a particularly different form. Now, to understand this equation further, we will consider a system where we have a our single extensive variable let us say x 1 or sorry let us say x, x would be the general.

So, we consider a system with a single extensive variable say x. Now, if you want to do the mapping which we with the earlier lectures that we had recall that our fundamental relation always had the form for a hydrostatic system S of U, V and N. Similarly, U was as a function of S, V and N. So, we can consider a system when we have a single extensive variable where we do not allow any fluctuations in V and N.

So, they are held fixed or it could be we do not allow any fluctuations in U and N and V being held fixed something like this way we are thinking along this line. Then, this follows that if I have the function more generally for such a function; I would have f of lambda plus x 1, 1 minus lambda x 2 is greater than lambda of f X 1 plus 1 minus lambda f X 2.

So, the idea is that I want to have a geometric interpretation, a geometric interpretation of this inequality and to make our life simple we consider essentially system with a single extensive variable x 1 sorry, x and that essentially is like looking at a function of one variable.

So, therefore, I have just written down this inequality in terms of a function of one variable. Now, if I want to look at the plot so, here is x 1 and here is x 2 and I have something like this. Now, clearly if I look at this value, then this value is f of X 1 and this value is f of X 2.

The quantity lambda x 1 plus 1 minus lambda x 2 is any value, which is in between x 1 and x 2 therefore, the left hand side that you see here corresponds to the value of the function at an intermediate point lying between x 1 and x 2 right. So, this is it can be anywhere over here. So, if you choose lambda is equal to half, if you choose lambda is equal to half then you see that you have come up with x 1 plus x 2 divided by 2.

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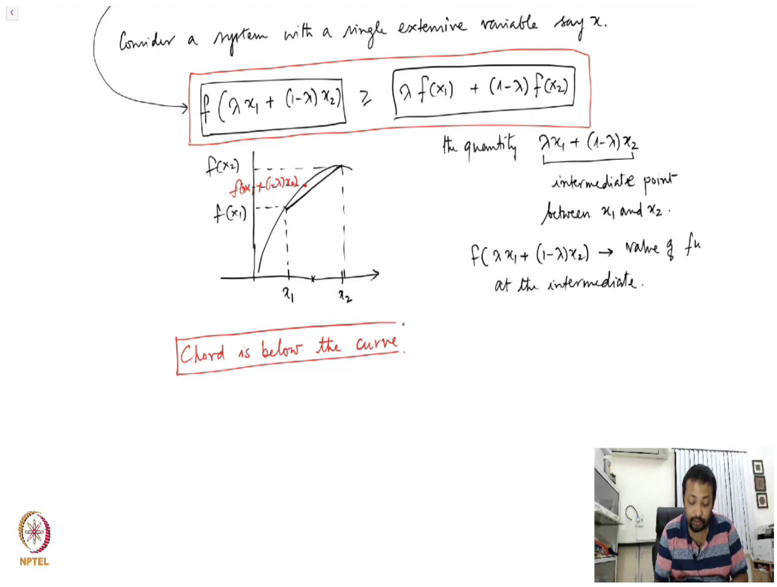

So, it corresponds to an intermediate point this particular, an intermediate point between x 1 and x 2. And therefore, f of lambda x 1 plus 1 minus lambda x 2 is essentially the value of f the function; there is something wrong with the surface at the intermediate point.

Look at the right hand side. The right hand side says that essentially what I have as lambda f of X 1 plus 1 minus lambda f of X 2 that is essentially belongs to the line joined by f X 1 and f X 2.

So, this inequality, if you carefully look at this inequality, this effectively means that the chord is below the curve. There is nothing essential I mean there is extreme this is idea is extremely simple. If I just look at the inequality, the left hand side essentially corresponds to any value f of X lambda X 1 plus 1 minus lambda x 2 and this is the value of the function and that must be above the chord.

So, essentially this inequality tells you that its a concave function is essentially one where the chord is always below the curve. However, the point problem with this thing is this inequality essentially, does not talk about this geometrical interpretation that we have developed, does not talk about anything about the differentiability of the curve.

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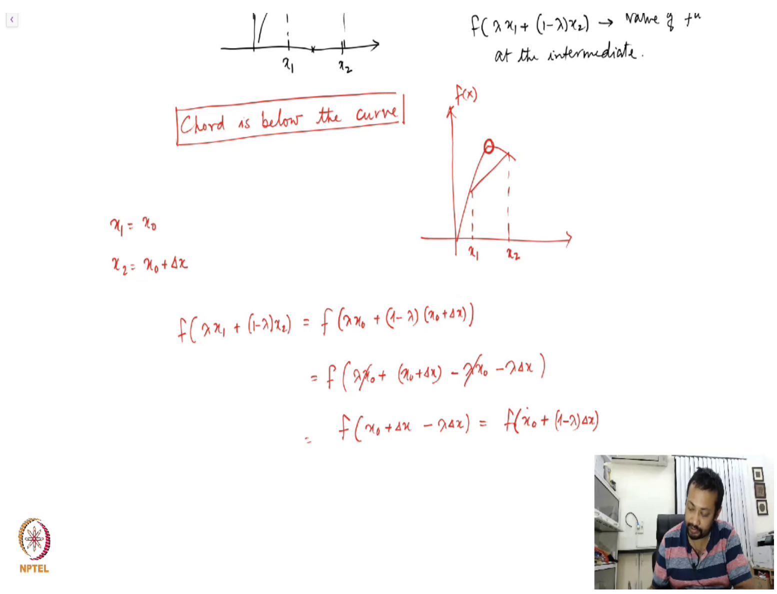

For example: I can, what I can do here is I can draw a straight line. Again, its not very straight, but let us try it again to draw a decent enough straight line and you see I can have the curve like this way. You see it is still the chord I can choose x 1 and x 2 like this way and essentially what I will have is, I will have this inequality satisfied for this particular function, but yet the problem with differentiability will come at this point.

So, here is what I want to do? I want to see if I can modify this to take into account the differentiability of the curve. Now, for that purpose let us write down x 1 as x naught and x 2 as x naught plus delta x if this is the case, then f of lambda x 1 plus 1 minus lambda x 2 is equal to f of lambda x naught plus 1 minus lambda x naught plus delta x. one can expand this now, right.

So, if you expand this becomes lambda x naught, x naught plus delta x minus lambda x naught minus lambda delta x. This, this, gets cancelled out. So, essentially you will have x naught plus delta x. So, you have x naught plus del essentially, you have x naught plus delta x minus lambda delta x, which you simply recast as f of x naught plus 1 minus lambda delta x.

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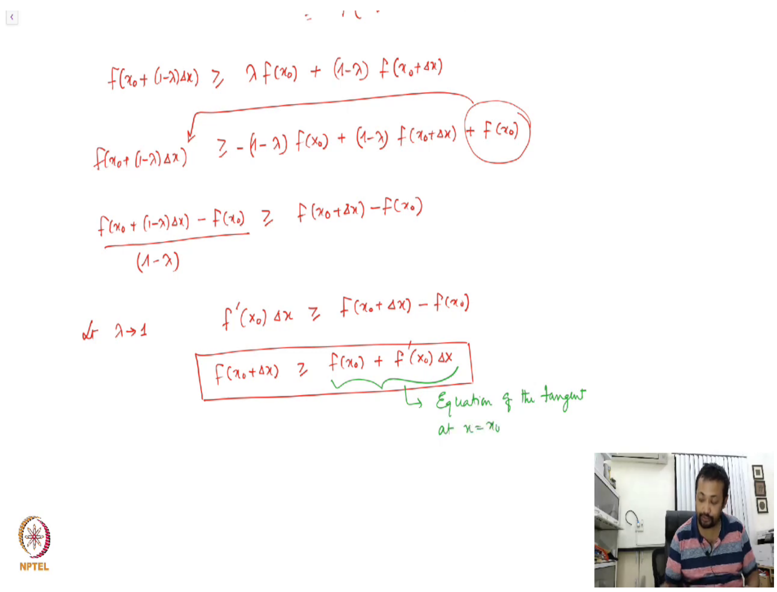

The right hand side the inequality now takes the form f of x naught plus 1 minus lambda delta x is greater than equal to lambda f of x naught plus 1 minus lambda f of x naught plus delta x good, let us see. So, I have a 1 minus lambda in the right hand side. So, let us write down this as 1 minus lambda f x naught put a minus sign in front plus 1 minus lambda f of x naught plus delta x.

And since I have put a minus I have added a minus f x naught I need to add an f x naught over here to keep the right hand side as same as the above 1 and here of course, I have f x naught plus 1 minus lambda delta x. Let us bring this part to the right hand side, which would mean that f of x naught plus 1 minus lambda delta x minus f of x naught is greater than equal to f of x naught plus delta x minus f of x naught.

There is 1 minus lambda which is there and which I am going to bring over here right. Not very complicated, it is very very simple algebra that we are doing over here. Now, let us take the limit of lambda to 1, if I take the limit of lambda to 1 essentially the left hand side I have is f dash x naught delta x must be greater than f of x naught plus delta x minus f of x naught.

I am going to recast this equation again and I am going to write f of x naught plus delta x must be greater than f of x naught plus f dash x naught delta x and this is the equation that we have come down to.

If you look at this equation very very carefully then you will realize that the right hand side the one that we have over here is the equation of the tangent at x equal to x naught right. This is simply the value of the function at x naught plus delta x and therefore, this inequality means that the tangent is above the curve sorry, there has been a slight error with a sign change.

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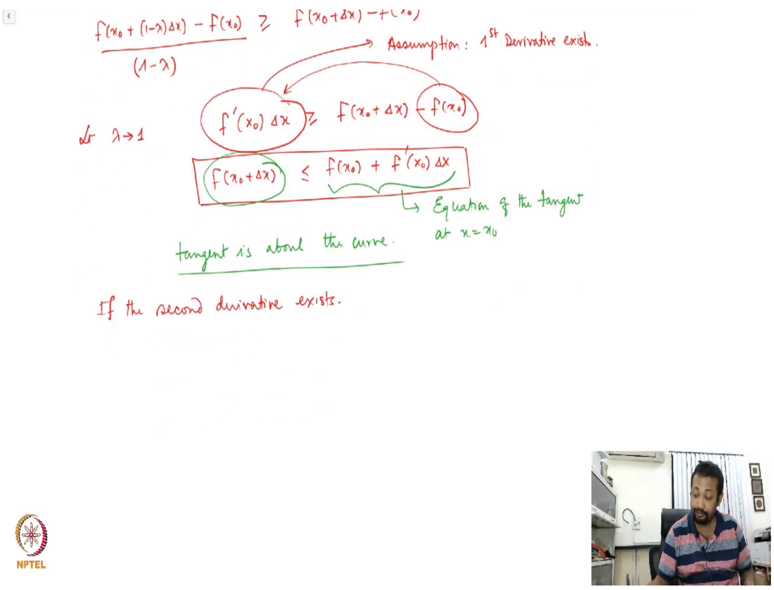

This if I just follow it from over here, I am bringing this term to the right hand side therefore, this must be less than equal to and therefore, this equation essentially tells you that the tangent is always above the curve.

So, what we started off with is essentially we started off with the fact that the chord is above below the curve and one can bring x 2 closure to x 1 and x 1, so that you will see that the tangent comes up above the curve. Now, if this is the case, if the second derivative exists. So here of course, when I have written down this particular term in the left hand side, I have assumed that the first derivative the assumption here, 1st derivative exist.

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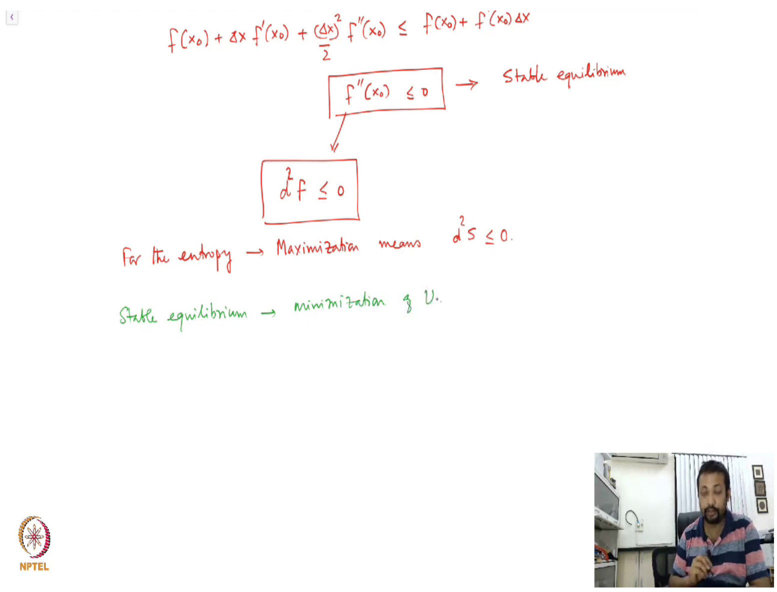

Further, if I now assume that the second derivative exist, then essentially I will expand the left hand side to write down as delta X f dash X naught plus delta X whole square over 2 f double dash X naught must be less than equal to f X naught plus f dash X naught delta X, right. One can of course, why am I not considering the third derivative?

Well, because essentially you have done extra calculus and therefore, you know the principle of extrema how to determine extrema and it is a sign of the second derivative, which determines everything therefore, it suffices to keep the second derivative is essentially, the rate at which the tangent is turning.

And you immediately see that f double dash X naught is less than equal to 0. And this would imply that this is a stable equilibrium, but we had started off with a function of a single variable. If I now want to generalize to a function of more than a one variable then this would mean that this equation translates to d 2 f is less than equal to 0.

I invite you to work out this relation. Hence, for the entropy a maximization, a maximization means that d 2 S is less than equal to 0. What about the internal energy? Well, for internal energy, I know the system goes to a stable equilibrium minimization of U.

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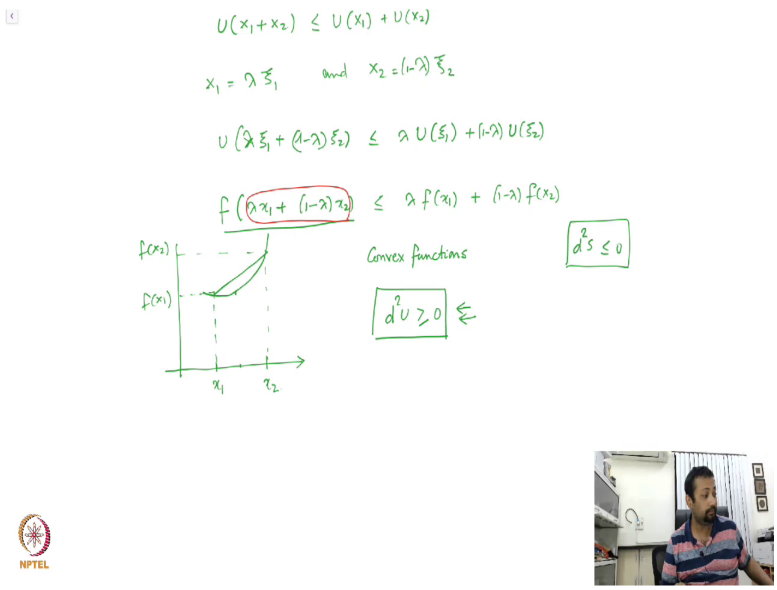

And therefore, one can immediately see that if the same line of argument that X 1 plus X 2 the composite system the internal energy of the composite system must be less than U of X 1 plus u of X 2 right and now, therefore, one writes down X 1 as let us say lambda times xi 1 and X 2 as lambda times 1 minus lambda times xi 2 and therefore, use the homogeneity principle of the internal energy as we have used it for the case of the entropy.

It follows lambda xi 1 plus 1 minus lambda xi 2 is less than equal to lambda U of xi 1 plus 1 minus lambda U of xi 2, which of course, means that again, if we consider a function of one variable that translates to lambda x 1 plus 1 minus lambda x 2 is less than equal to lambda of f of x 1 plus 1 minus lambda f of x 2 right. Now, we attempted to draw the function.

So, we took look at x 1 we look at x 2 clearly, let us say the function has some value f of X 1 and at this point it has some value f of X 2 and this essentially means the value. So, x 1 plus x 2 if you take any midpoint over here any intermediate point between x 1 and x 2, which is represented by lambda x 1 plus 1 minus lambda x 2 and the function value of this must be less than the chord.

So, essentially you have a function which is something like this, right. Such functions are called convex functions, right. Now, what does again this definition, this the way we have written it down, it does not take into account the differentiability of the curve and if we have to look at the differentiability of the curve we have to do the same thing that we have done over here, we have to follow the same route that we have done.

And you will see that this would come out to be d 2 U is greater than equal to 0. Therefore, for thermodynamic; as far as thermodynamics is concerned as a system goes to an equilibrium it maximizes the entropy which would mean that d 2 S is less than equal to 0 or it minimizes the entropy which would mean that d 2 U is greater than equal to 0.

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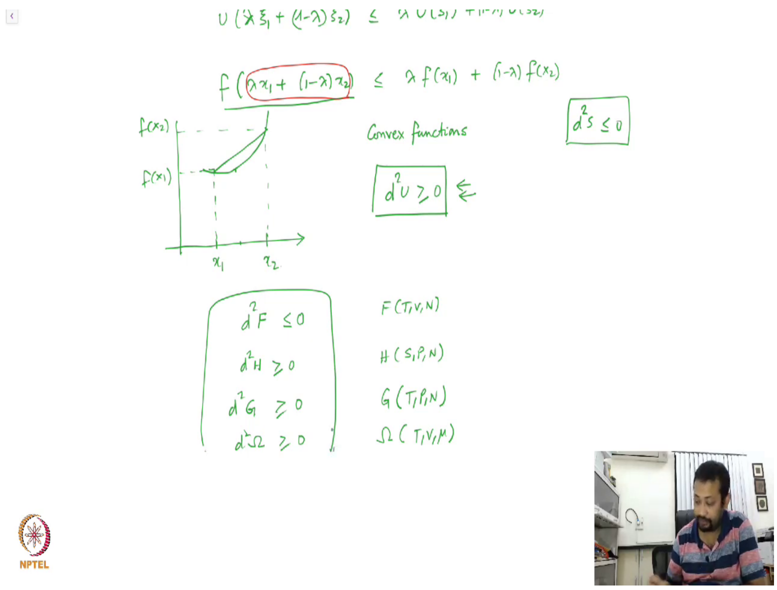

Similarly, for the other thermodynamic function one can show that for the Helmholtz free energy d 2 F is less than 0 F is a function of T, V and N, d 2 H is greater than 0, d 2 G is again greater than 0 and d 2 omega is again greater than 0. H is a function of S, P, N, if you recall your Lagrange transformations sorry, legendary transformation not Lagrange transformation.

If you may recall your legendary transformation G is a function of T, P and N and omega is a function of T, V and mu. So, this forms the stability criteria for a thermodynamic system.