Statistical Mechanics

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Lecture – 02
Laws of Thermodynamics

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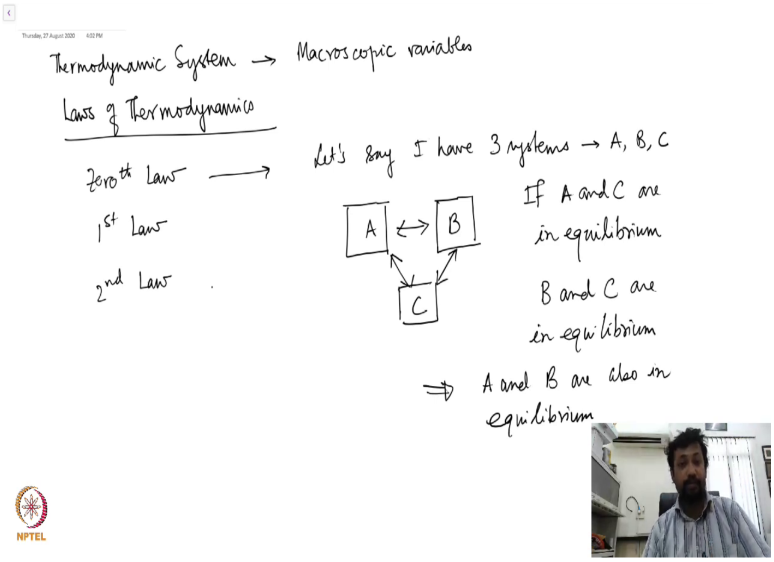

Now, in the last class, we had seen what thermodynamics is all about that given a thermodynamic system, how do I describe the, given a thermodynamic system that we describe the system using a macro set of macroscopic variables. Today our starting point of the discussion is with the Laws of Thermodynamics.

Now, these laws are essentially, they originate from the from a common experience. And we know that there are three laws; the zeroth law, the 1st law, and the 2nd law. Now, the zeroth law is very very simple; what it says is the following, let us say I have 3 thermodynamic, 3 systems, I have 3. So, I have 3 systems; I will call them as A, B and C. So, I have these systems which is A, I have this system which is B and then I have this system which is C.

The law of statement of the law is the following. If A and B are in equilibrium, let us do it the other way around, so that it is easier to; well you can do it, anyway you want to do it. If A and C are in equilibrium and if B and C are also in equilibrium; then it follows A and B are in joint equilibrium.

So, essentially the statement of the law says that, if A and C are in equilibrium, B and C are in equilibrium; then it necessarily means that A and B are also in equilibrium. When I will say equilibrium, this essentially means, that there is a joint equilibrium between these two.

We will wrap later on, we will essentially clarify what we mean by an equilibrium; for thermodynamic system you understand that there are so many microscopic variable, equilibrium would necessarily mean that there is a mechanical equilibrium, there is a thermal equilibrium as well as there is a chemical equilibrium.

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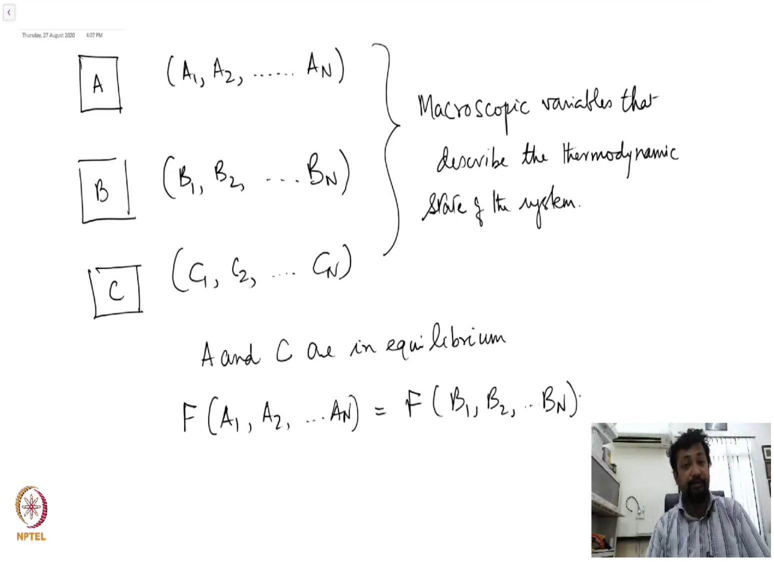

Now, clearly let us say the system A that I have is characterized by a set of macroscopic variables, which are A 1, A 2 all the way up to let us say N. Similarly system B is also characterized by B 1, B 2; I can have different N, but let us keep it the same way and then system C is characterized by C 1, C 2 all the way C N.

So, these are my macroscopic variables which we discussed in the last class, which describes the thermodynamic state of the system; that describe the thermodynamic state of the system.

Now, when I say that A and C are in equilibrium that necessarily means that, I can have a relation of this form, a functional form between the macroscopic variables that describe this thermodynamic state of A and the macroscopic variables of the thermodynamic state B. The function F can be different for both of them; but for ease of this discussion, we will assume them that is true.

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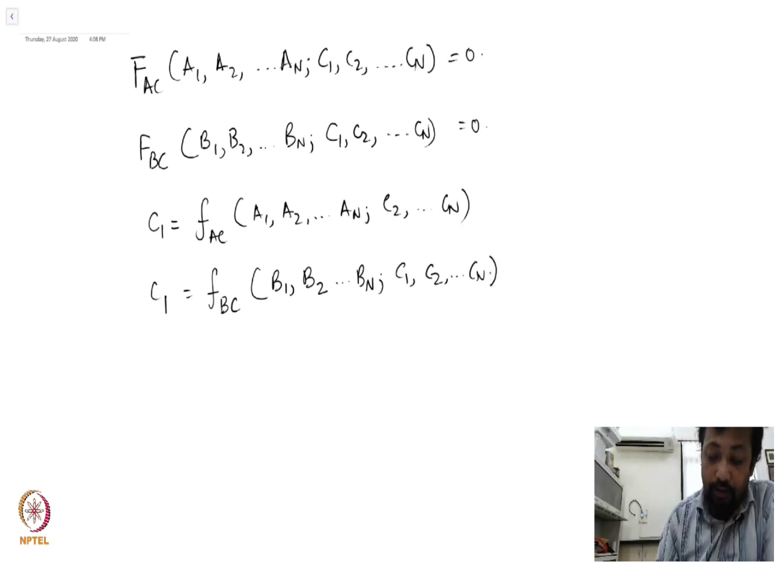

So, therefore, if A and C are in equilibrium, it follows that I can recast my equation in the following way. I can have A 1, A 2, A N; C 1, C 2 all the way up to C N is equal to 0. Similarly, if B and C are in equilibrium, then it follows that I can have B 1, B 2, B N and C 1, C 2 all the way up to C N to be 0, right.

Now, from this above relations it is obvious, I can write down C 1 as some function of A 1, A 2 all the way up to this; but then I will write it down like this way. And similarly from the second equation it will follow that, I have; I can make C 1 or take the C 1 on the right hand side and write it down and I will have, I am sorry this is.

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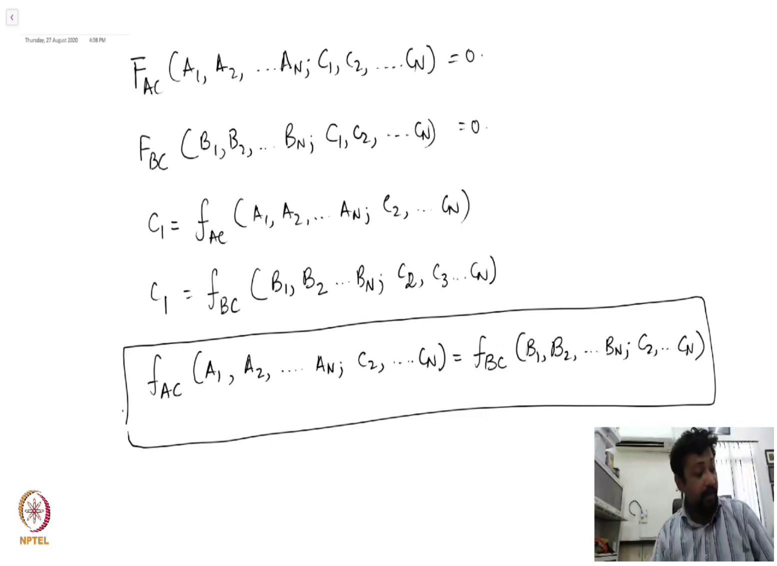

So, B N and then I am going to have C 1, C 2 all the way sorry, no longer C 1; because I have already made C 1 as my subject C 2, C 3, C N. So, I can have these two functional relations. So, since the left hand side is the same therefore, it follows f of A C A 1, A 2 all the way up to A N; C 2, C N is equal to right.

So, this is one of the equation that I have, everything is fine with this. But now comes the zeroth law. Zeroth law also says that if A and C are in equilibrium, if B and C are equilibrium.

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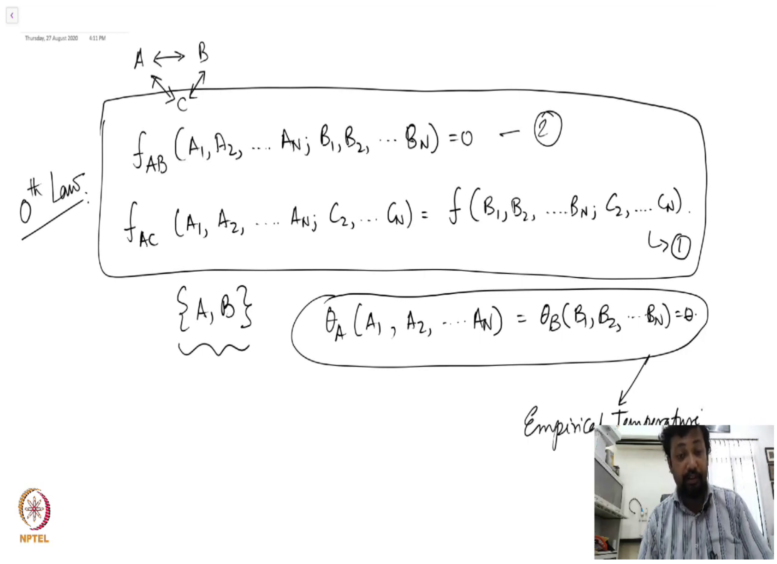

So, we will write it down like this way; if A and C are in equilibrium and if B and C are in equilibrium that necessarily means A and B are also in equilibrium. So, it follows therefore, I should have an equation that tells you that f of AB that describes the joint equilibrium always. Together with this equation, of course I have f of A 1, A 2, A N; C 2, C N is equal to f of B 1, B 2, B N then C 2 all the way up to C N. So, this essentially forms the crooks of the 0th law of thermodynamics.

So, this looks very simple, there is nothing complicated in this particular thing, right. But now, if I look at the second equation; then I can choose any set of parameters in A, B right, I can choose any set of parameters if I look at this equation on the top equation, I can say choose any set of parameters A, B and substitute this in 1, right.

So, let us call this equation 2, well it is the other way round; but this one we had earlier, therefore we will call this 1. So, I can choose any set of parameters in A 1 and A 2. So, if I increase one of the parameters in A; then the corresponding parameter should and B should also decrease. So, that this constraint equation into is satisfied.

So, I can choose any of this parameter without changing C, without changing any parameter in C; that is because this resulting equality, so if I change let us say A 1, then maybe there is a change compensation in B 1, right. But you see there is no change in C right, there is absolutely no change in C.

So, therefore, it follows that any variation of these parameters that moves along the manifold which is defined by this; any variation in A, B which you do, as you move along this manifold which is defined by 2, equation 1 must remain valid. Hence you conclude that the equilibrium the zeroth law must, these two equations together must tell you that something let me; it tells you that there must be an equation.

So, the constraint, the variable C 2, C N in equation 1 on the both sides must drop out; because we have already seen that if I make any change in A 1 and A 2 that lies on this manifold which is defined by the equation 2, the equality is still valid without changing anything in C.

Therefore, I must have this; this one essentially means that, there is a state function which is a function of the thermodynamic variables that describes the equilibrium state of the system that remains constant and we call this the empirical temperature. This is the first concept of temperature that enters thermodynamics and that enters through the zeroth law.

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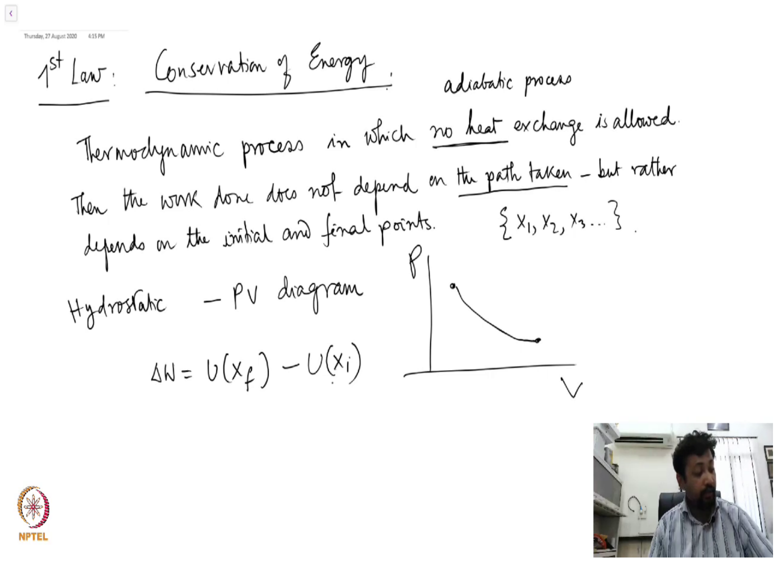

What about the 1st law? The 1st law is very simple; it is essentially a statement of the conservation of energy. And the statement is a following. Suppose that I have a thermodynamic process in which no heat exchange is allowed. As you will go on further and further, you will realize that no heat essentially means an adiabatic process; we will slowly give you the terminology as we go ahead.

So, in which no heat exchange is allowed, then the work done depends only on the initial and the final points or in a different way, the work done does not depend on; the work done does not depend on the path taken, but rather depends on the initial and the final points.

Now, you are clearly you want to ask, what do you mean by a path taken, right? The path taken is in the space of your macroscopic variables, which we shall call X or let us put a vector sign right now; the path taken in this space.

For example, for a hydrostatic system, for a hydrostatic system, the P V diagram, in the P V diagram, if I take the system from one point to another let us say like this way and if it is an adiabatic process that which means there is no heat that is allowed to be exchanged with the environment, then it follows the work done delta W does not depend on the path that you have taken, but it only depends on the initial and the final point.

Now, this is very very similar to what we do in mechanics. In mechanics we see that, whenever I have a conservative force field; I know that the work done depends only on the initial and the final points. And from this analogy, you essentially from this definition, you essentially bring in the concept of the potential energy.

In thermodynamics, so this adiabatic process is synonymous to a conservative force field in mechanics. So, here also I can see that the work done does not depend on the path; therefore clearly if I just draw the analogy between mechanics, then I can write down this work done as a difference between this.

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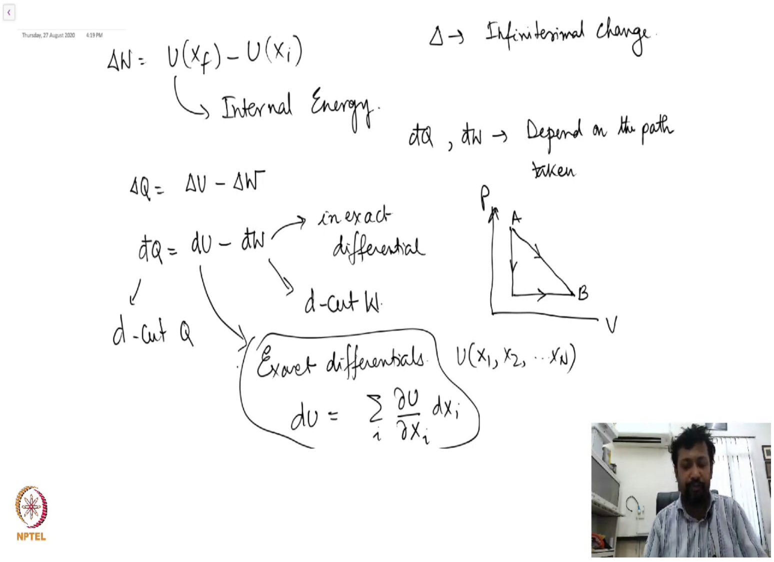

So, delta W is U of X f minus U of X I, where U is now and we called it as an internal energy. So, the work done depends only on the internal energy of the system on the change in the infinite energy of the system. If I remove the constraint of adiabatic process; which means that the system is allowed to exchange in heat during going from the state A to B, then the general rule is delta Q is delta U minus delta W.

Now, remember delta is always infinitesimal change; if I want to change it, I can write down this in this particular form. But I have to be careful that, I put a cut on the two derivatives over Q n. So, this is d cut Q and this is d cut W. The reason I have put it, I have written it like this way; because here d cut sorry d cut Q and d cut W will depend on the path that is taken.

So, for if it is not an adiabatic process, if there is a change exchange of heat that is allowed which means if I go back to my P V diagram, if I go back to my P V diagram. So, if I go from here to here, I can either go like this way or I can go like this way, right. And if it is not an adiabatic process, this is a pressure volume diagram; the system either goes from A to B via the straight line or it goes from this, the work done would be different in the two cases.

So, therefore, the cut essentially tells you that, these are path dependent quantities and the quantities which are path dependent are essentially what is called in exact differentials. Quantities which are not path dependent, such as the internal energy are called exact differentials.

Which essentially means that, if U was a function of X 1, X 2 all the way up to X N; then I can write down the infinitesimal change d U as sum over i del U del i del X i d X I, this is for a exact differential. So, we shall do it very briefly, how do you differentiate between inexact differential and an exact differentiation.

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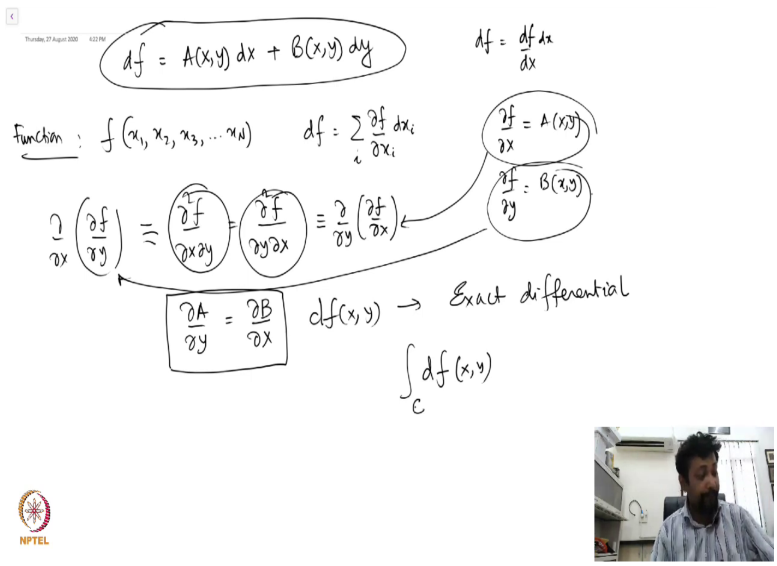

And in exact sorry, let us just do it over here. And in exact differential for example, if I have a function d f which is I can write down this as d x plus B of x, y d y, right. This is the in change in this function. Now, remember when for a single, if you have done calculus of a single variable; then I know that d f is d f d x times d x right, but now this is calculus of many variables.

So, there are more than one variable more. So, if there is a function which is dependent on x 1, x 2, x 3, x N; I have a function which depends on x 1, x 2, x 3, x N, then the change in the function, the total change in the function is del f del x i d x i with a sum of i and this is exactly what has been written over here.

So, if I have a function which is like this, if I draw the analogy with this; then it immediately follows that del f del x is A of x, y and del f del y is B of x, y. But since it is an analytic function it follows that, the mixed derivatives must be the same and del 2 f del y del x.

So, therefore, it follows del A del y, which is essentially del l; if you look at this, this is equivalent to del del y of del f del x. And if you look at this, this is equivalent to del f del y del del x of this. If I now put it over here and put this one over here; then it follows that del f del y, del A del y must be del B del x. If this is the condition that is satisfied, then the function f of or rather d of f x, y is an exact differential.

If it is not, then the function is an inexact differential. And if it is an inexact differential, then the value of the integral d of f x, y over a contour C will depend on the contour that you have chosen. If it is an exact differential, then this value is only dependent on the initial point and the final point, right.

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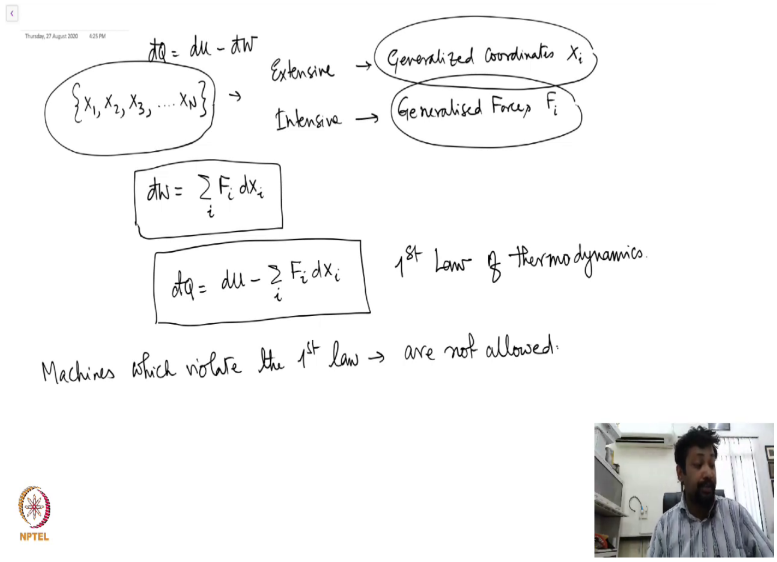

So, therefore, the 1st law essentially tells you d cut Q is d U minus d cut W. Now, remember in the last class, we have we have seen that of all these generalized of this microscopic variables, the thermodynamic variables that describes the system; some of them are extensive and some of them are intensive. And the intensive ones are what are we call them as generalized forces and we will change their notations from X to F i.

On the other hand, the extensive variables are generalized coordinates and they depend on the system size and we will keep them as X i. So, that the work done and here also again I am drawing the analogy from mechanics is sum over i F i d X i. So, the whole game in thermodynamics is to identify this macroscopic variables and then choose find out from which of these are the, your generalized forces and which of these are the generalized coordinates.

Once you have identified them, then you can write down the work done like this way and it follows; therefore that your 1st law takes the form sum over i F i d X i, 1st law of thermodynamics, right.

Interestingly you cannot design a machine which violates the conservation of energy. So, machines which violate the 1st law are not allowed. So, these are machines which are called perpetual machines of the first kind; you cannot have perpetuous machines of the first kind, because you are violating the conservation of energy.