Statistical Mechanics
Prof. Dipanjan Chakraborty
Department of Physical Sciences
Indian Institute of Science Education and Research, Mohali

Lecture – 01
Introduction to Thermodynamics

Course on Statistical Mechanics. This course is designed particularly for undergrads who are pursuing their bachelors in physics masters students as well as the PhD students and is designed for physics major students. Now the structure of the course is the following that first we are going to review thermodynamics and then we are going to move over to statistical mechanics, but in between these two we are going to review very briefly probability theory.

Now, thermodynamics, why thermodynamics? That is a very natural question. Now thermodynamics deals with behaviour of systems as a collective body in some sense its unique as compared to your classical mechanics and quantum mechanics. It does not give you a new equation way of it does not develop anything new such as a Newton's equation of motion or Schrodinger equation of motion, but rather it uses some of the old tools, some of the tools that is already existing to study such systems.

Now, for example, take the system of a liquid which is contained within a container I am sure you have, the first things that comes to mind that if you are given a bottle of a clear liquid. If I ask you what kind of questions can you ask? Then the first thing that you ask is, what is that liquid? Which means, what is the chemical composition of that?

Well and then the questions that arises in the mind at, what is the temperature of the liquid? What is the pressure of the liquid? What is the density of the liquid? Now, these are very general questions and these questions are essentially within the scope of thermodynamics answering these questions are within the scope of thermodynamics.

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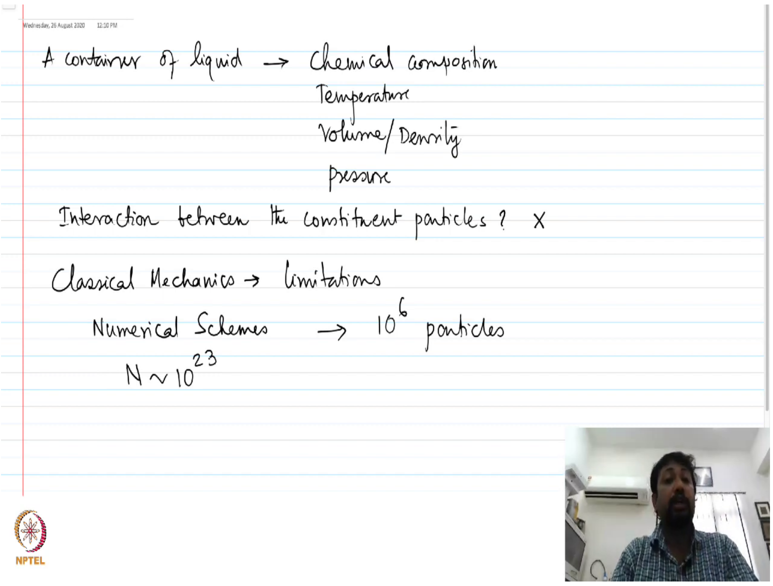

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A container of liquid → Chemical composition
Temperature
Volume/Density
pressure

Interaction between the constituent particles ? X

Classical Mechanics → limitations
Numerical Schemes → 10^6 particles
$N \sim 10^{23}$

So, if I take for example, a container of liquid. So, the typical questions that you can ask of course is chemical composition, the temperature, volume, density, pressure all these are valid questions that you can ask. But you see nowhere you ask, what is the interaction between the particle, the constituent particles of the liquid? So, in some sense this is never asked in thermodynamics; you never ask the microscopic interaction between the particles.

So, the need for thermodynamics arises from the fact that classical mechanics as we know it today has its own limitations. What does it mean? It means that if I give you a one single particle, if I give you one single particle and if you know the force on that particle then you can very clearly find out the trajectory of the particle given the initial conditions, if you do not know initial conditions then of course, you have a family of trajectories.

If you if I give you two particles which you have already done, you can go to the center of mass (Refer Time: 03:48) and analyze their motion exactly, analytically 3 particles it is still durable more particles if you keep on adding more and more particles then the problem that no longer remains analytically attractive.

You have to resort to some kind of a numerical scheme and with the advent of advancement of computational resources at best we can go to 10 to the power 6 particles, at best we can go to 10 to the power 6 particles.

But that also simulating such a system is also very very time consuming. In contrast if you look in nature then you know that a typical avocado number is 10 to the power 23. So, it is just not possible to analytically track such systems as well as to track its computation. So, what we do? We have too much information in our hand and we just do not want to deal with so much information.

So, we sacrifice some of the things and the whole idea in this respect is to rather not to go into microscopic details, but to look at the system as a whole and for that you see a thermodynamic system is always characterized by a set of variables which are macroscopic in nature.

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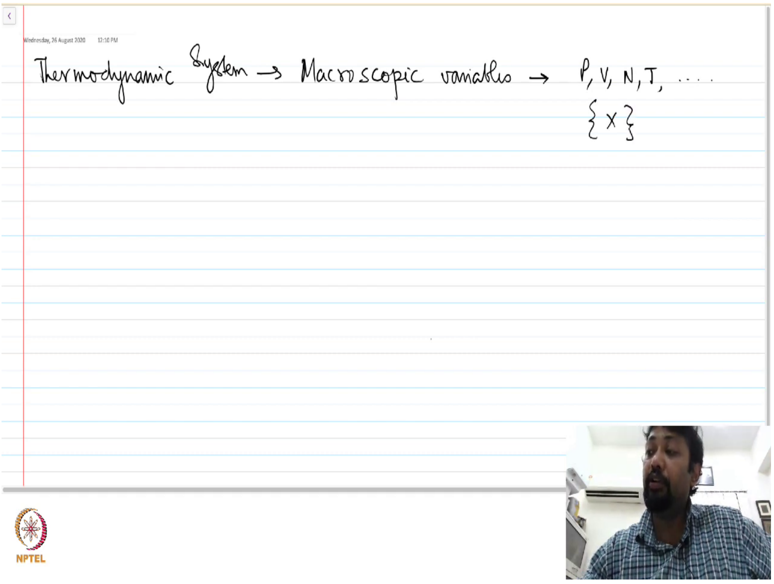

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Thermodynamic System → Macroscopic variables → $P, V, N, T, \ldots$

$\{X\}$

So, a thermodynamic system; a thermodynamic system is always characterized by macroscopic variables. And, we just saw what these variables are for a hydrostatic system. A hydrostatic system is a system which is typically a fluid or a gas, I mean the general term is the fluid its either a liquid or a gas.

A hydrostatic system such as pressure, volume, particle number, temperature so on and so forth. I mean it can be a different system, but you always describe it with a set of microscopic variables with a set of set of microscopic variables you shall call this. Let me let us not introduce the notation right now. So, there is a set of microscopic variables. What are these characteristics of this microscopic variable? You please remember one thing that any system that you consider any system that you consider.

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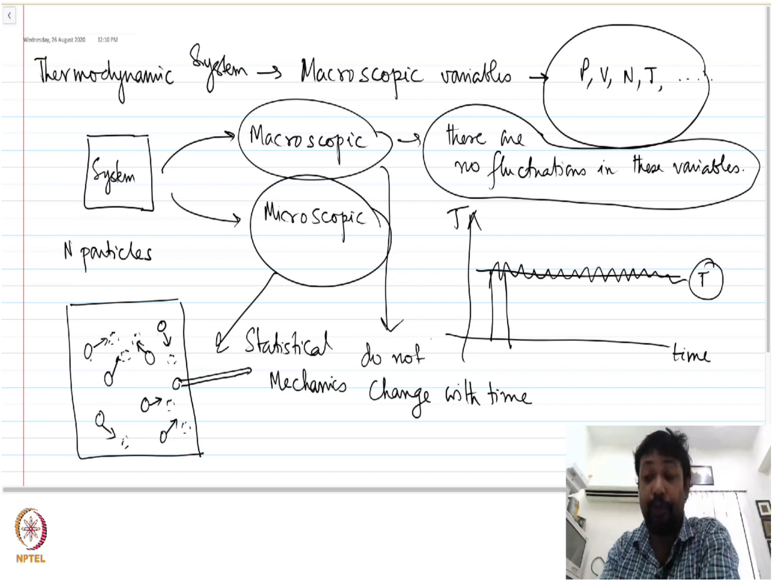

If this is your system, I have 2 perspectives of looking element, one is the microscopic perspective, which we just described the other is the microscopic perspective. A macroscopic perspective as we just defined is essentially looking at the system as a whole, but not zooming into the system. Now all these macroscopic variables that we have written down over here has a very interesting characteristic.

In the sense that there are no fluctuations in the system, in this parameters or in these variables, this is not really true, but thermodynamics chooses to ignore these fluctuations and therefore, kind of questions and answers you can get from thermodynamics is also limited we will get to get the (Refer Time: 07:29).

So, there are no fluctuations in these variables, clearly if I for example, measure temperature as a function of time. Then thermodynamics tells me that this temperature is a constant number there are no fluctuations in reality of course, if you measure there is no fluctuation above this average.

And this average temperature is the one, which is described which describes this system within thermodynamics, it is also true for pressure right. And if it is an open system, which means it can exchange particles with the environment then of course, your particle number (Refer Time: 08:04), but we will come back to the essence of this.

But in reality this does not happen in reality for example, if your system consists of N particles which are moving around. So, if I have a container which has gas particles then I know that these gas particles are all moving around randomly right. This is what you have learned in kinetic theory.

So, clearly this picture is different than this picture, in this picture you can easily see that I am looking into a more microscopic. I am looking at the system more microscopically, what does it mean? That if I want to measure temperature at this instant and if I want to measure at this distance.

So, if you have a thermometer let us say if I attach a thermometer to this system and if I want to measure the temperature of this system then clearly that measurement equipment also has a certain time scale. But within that time scale I can see that this particle probably has moved to over here, this particle has moved to over here, this one has moved over here, this one has moved over here so on and so forth.

So, there is a rearrangement of this particle position within the time scale of my measurement, but yet these thermodynamic variables do not change with time. So, this is a very very crucial thing for a macroscopic variable that they do not change with time.

In contrast microscopic variables if I really look into the system the microscopic variables are fluctuating which you can; obviously, see and which you can intuitively understand. That if I want to try to measure something then it is very clear that within the measurement my particle positions have changed so alright.

So, here if I want to measure the, here I have shown you for the temperature I can do it also for the pressure, but if I want to take two pressure measurements within which will have a certain time lag between these two. Then it is clear that within that time this microscopic these positions of the particles have changed.

So, you see this is within the purview of statistical mechanics. Here if you want to know the position of the particles then of course, you have to know the inter particle interaction. Thermodynamics does not care about that. So, this is one of the very interesting characteristics of thermodynamics. That it describes the system within using a set of variables which we shall call microscopic variables and or thermodynamic variables, which has no time variation right.

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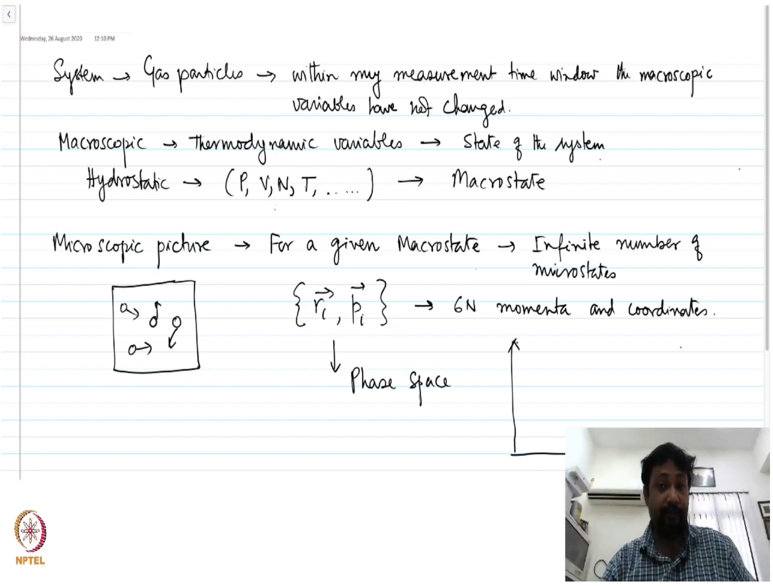

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System → Gas particles → within my measurement time window the macroscopic variables have not changed.

Macroscopic → Thermodynamic variables → State of the system

Hydrostatic → $(P, V, N, T, \ldots\ldots) \rightarrow$ Macrostate

Microscopic picture → For a given Macrostate → Infinite number of microstates

$\{\vec{r}_i, \vec{p}_i\} \rightarrow 6N$ momenta and coordinates.

↓ Phase Space

So, let us remove all of this from this. Now let us take a specific example where I want to talk about, well we just saw the I mean one of the system that we considered was gas particles. And here I can see that within my measurement window time window, the microscopic variables have not changed.

So, when you when the question comes in, if I want to look at a system microscopically. For a system with a macroscopic picture the thermodynamic variables in the macroscopic picture the thermodynamic variables, describes the state of the system this is very important. It describes the state of the system. So, we follow this particular system of gas particles; N gas particles which is contained within a container.

If I want to change the temperature then it goes to a new thermodynamic state. If I change the pressure it goes to a new thermodynamic state. So, for a gas particles or we shall write generally as a hydrostatic system where it is described by P, V, N, T, U looking at this and for a hydrostatic system, I do know right now. Let us just write it down in the following way that I have this thermodynamic variables and the state of the system is clearly defined.

The thermodynamic state of the system is very clearly defined by these thermodynamic variables by this microscopic universe. So, if you change any of this for example, if you change the pressure, if you change the temperature, if you change particle number, which means you also change the density. Then it goes to a different thermodynamic state.

What about the microscopic picture? But ok, so this is what is called the macrostate of the system. What about the microscopic picture? Now the microscopic picture I know here, but for this particular system that all of this given macro state, for a given macro state, for a given macrostate which means that, for a given value of pressure volume particle number and temperature they corresponds to infinite number of microstates; number of microstates, why?

Because I know that, if the pressure of the if the pressure of the thermodynamic pressure of the system is fixed even though it is fixed the particles within the system constantly undergo motion right. So, they change their position and momentum. Therefore, a microstate of this system is characterized by the position and the momentum for a hydrostatic system. Remember this we are going to use this later on.

Whereas are 6 N momenta and coordinates. Now you know that such a space which is made by the position and the momentum is what is called the phase space. We have studied this in classical mechanics. In the phase space if I have the possibility.

So, this is a 6 N dimensional space, but if I can visualize it or something at any instant of time your macro state is fixed, you have not changed any of these variables. But your microstates, which is comprised of the position of the momenta form a point in your phase space, if this is your phase space then this is a point in the phase space.

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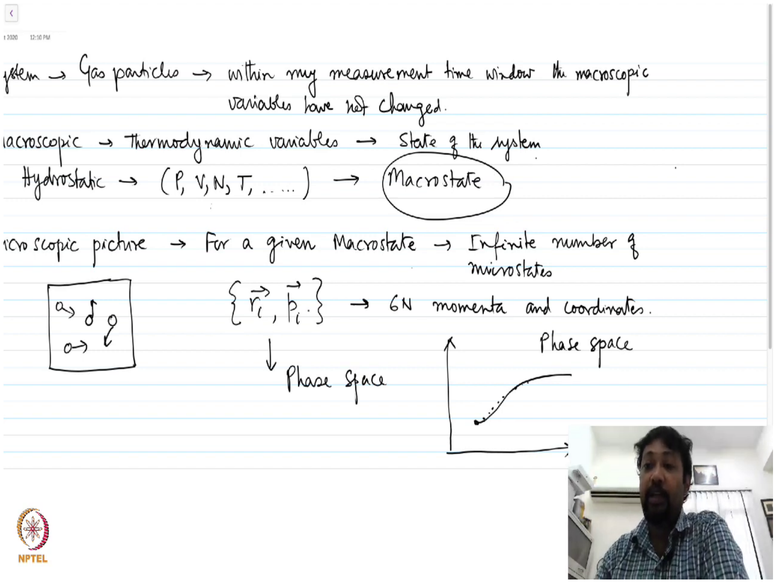

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↓ Phase space

Clearly if you can devise a way to measure the microscopic position and the coordinates of all the particles, then you see you can track this; then the you can this corresponds to a line or a trajectory in the phase space. Let us not call it a line a trajectory in the phase space all of these points which lie on this trajectory corresponds to the same macro state which you have prescribed. We have not changed the microstate.

Therefore, for a given macrostate for a given macrostate it is always that it corresponds to an infinite number of microstate. Now this is a particular example where your degree of freedom can take continuous values or your macrostates can take continuous values, because r i and p i can take continuous values on the pl line.

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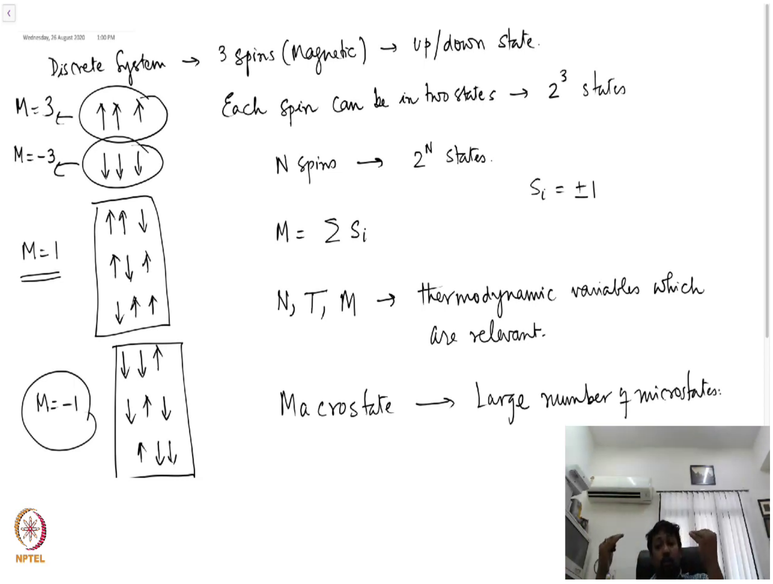

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Discrete System $\rightarrow$ 3 spins (Magnetic) $\rightarrow$ up/down state.

Each spin can be in two states $\rightarrow$ 2^3 states

N spins $\longrightarrow$ 2^N states.

$S_i = \pm 1$

$M = \sum S_i$

N, T, M $\rightarrow$ thermodynamic variables which are relevant.

Macrostate $\longrightarrow$ Large number of microstates.

We can even consider a discrete system. And if for this I will take let us say not N spins, but 3 spins which are magnetic in nature. Now I am asked, so what are the and they can be in a up or down state. If this is the case then what are the possible configurations I can have? I can have up all the spins up, I can have all the spins down, I can have 2 spins up and I there should be one more which is this, and I can have 2 spins down.

Since each of this can be in 2 state each spin can be in two states. I have 2 to the power 3 states, the generalization of this if there are N spins then there are 2 to the power N states, but then the question is does all these states let does all these states belong to the same macrostate. If you look at it carefully that this corresponds lets define first the magnetization which is sum over the spin values.

Now S i can be plus minus 1 just for our computational ease we will take a value of plus minus 1. So, this corresponds to a magnetization, this corresponds to a magnetization of M equal to 3, this corresponds to a magnetization of M equal to minus 3 and you see that all these states corresponds to a magnetization of M equal to 1 and this corresponds to a magnetization of M equal to minus 1.

So, for our case if I want to describe the system particle number N, microscopically I want to describe which means within the scope of thermodynamics I am describe this particle number N, temperature and magnetization are the thermodynamic variables, which are relevant.

Not all these microstates belong to the same macrostate. These 3 microstates belong to the macrostate, which has a magn etization of 1 and these 3 microstates belong to the macrostate where the magnetization is minus 1.

Therefore with these 2 system with these 2 examples is very clear that for a given this is of course, the case when I have 3 spins you can see that if I have 2 to the power N spins or the number of microstates for a given magnetization will also increase. We will do it when later on, when we do statistical mechanics we learn how to count such microstates.

Now, so therefore, the whole idea is a macrostate always corresponds to infinite. Well, let us not let us modify this thing a little bit for this case it corresponds to a large number of microstates. In principle it corresponds to an infinite number of microstates because whenever you study these systems you always say that N is very very large and we have seen that the typical value of N is 10 to the power 23.

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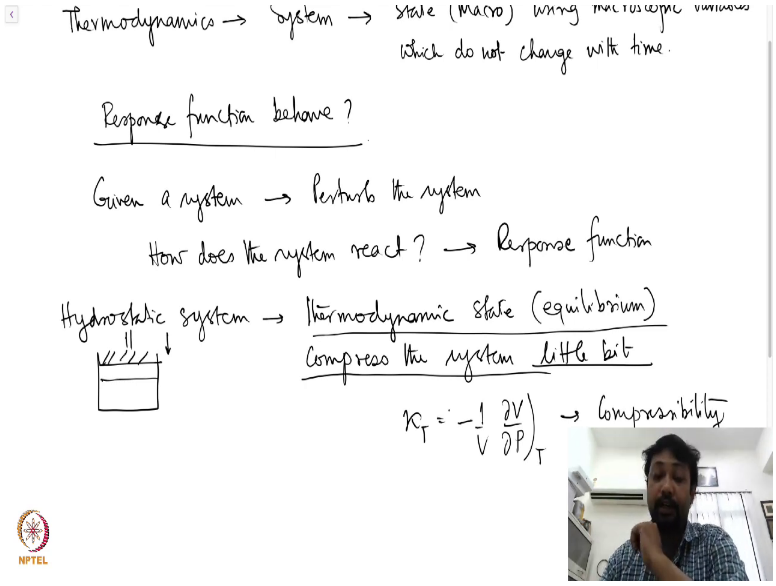

Thermodynamics → System → State (Macro) using macroscopic variables
which do not change with time.

Response function behave ?

Given a system → Perturb the system

How does the system react ? → Response function

Hydrostatic system → Thermodynamic state (equilibrium)

Compress the system little bit

$\kappa_T = -\frac{1}{V}\frac{\partial V}{\partial P}\Big)_T$ → Compressibility

So, therefore, we have the following idea on thermodynamics, the it when given a system if I want to describe it even using thermodynamics, using the framework thermodynamics.

I will define the state of a system which is a macrostate using microscopic variables which do not change with time. Again I repeat that this is a very important property in statistical mechanics, what we shall see is that fluctuations in this physical variables are very very important and we shall use these fluctuations.

Now, what kind of question we can ask? The most. So, you see this in some sense that thermodynamics is limited. And therefore, the kind of question and answers that you can get using thermodynamics is also limited. So, one of the most important thing that you can ask is, how does the response function behave? What is a response function?

Response function is very very simple. So, given a system; given a system I can perturb the system which means I can add apply a field to the system. How does the system behave? How does the system react? That is given by the response function. Take the example of a hydrostatic system, for a hydrostatic system which is in a thermodynamic state and is in equilibrium we shall always deal with these systems within in thermodynamics we shall always deal with systems which are in equilibrium.

In principle we will come to this later on. So, the thermodynamic state which is an equilibrium right so it is characterized by pressure volume temperature and particle number. Now, you compress the system little bit, the little bit is important because what the reason it is important is because we are not you are staying in the linear response.

So, these things you will learn slowly. So, anyway the idea is that we compress the system which means that, if I have this particular system one part of the system is a piston and I compress the piston right. So, that the gas is compressed that is what you observe that the gas the volume decreases, how do you know that?

That effect is given by the quantity del P del V let its the other way around. So, its given by the quantity 1 by V del V del P temperature constant with a minus sign. I am holding the temperature of the system constant that is why I have given the temperature constant. This is called the compressibility of the system right.

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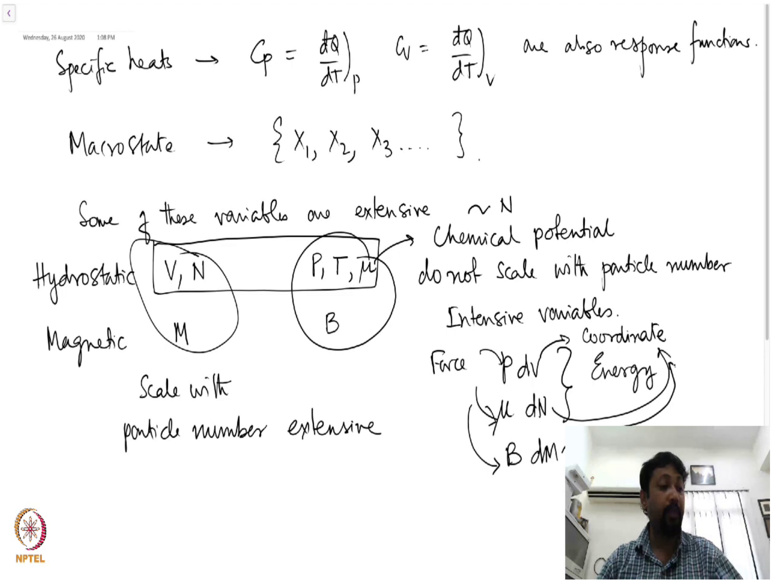

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Specific heats → $C_p = \left.\frac{dQ}{dT}\right)_p$ $C_v = \left.\frac{dQ}{dT}\right)_v$ are also response functions.

Macrostate → $\{ X_1, X_2, X_3 \dots \}$.

Some of these variables are extensive $\sim N$

→ Chemical potential

do not scale with particle number

Intensive variables.

Scale with particle number extensive

Force → P dV, μ dN, B dM → Coordinate; Energy

Specific heats are also examples of response function specific heats for example, C p which is d cut Q d cut T at constant pressure and Cv is d cut Q d cut T at constant volume are also response functions. So, thermodynamics is well equipped to answer these questions right for a magnetic system you know that the magnetic susceptibility is there.

Interesting to note over here is that there are two kinds of specific heats I have defined. One is at a constant pressure and the other one is at a constant volume. We are going to come back to these definitions the more general definitions of this right. So, now given a macro state which is characterized by a set of variables X 1 X 2, X 3 so on and so forth. Right now, we will write it down in this particular way. You see some of these variables are extensive in nature.

What does extensive mean? That means, they scale as particle number N. So, if you add more number of particles you will see that particular physical variable also changes. For example you can see that volume N for a hydrostatic system volume and N, for a magnetic system magnetization all of these are extensive variables.

So, if you have a system which has N particles, if you double up the particle number then N also doubles right. On the other hand if you look at this for pressure and temperature and in this case the magnetic field, they do not scale with particle. So, an extends these are essentially they do not scale with particle number or the other way of seeing is with system size, these are called intensive variables.

And these which scale with particle number are called extensive variables. We want to make one more classification here, it is understood here that using these quantities. Now just look at for a let us start with the hydrostatic system which is this one. Here of course, there is yet another quantity which is called the chemical potential of the system which probably you have encountered when you do did chemical kinetics.

Now, here for example, if you look at this thermodynamic variables that I given to you two of these which are essentially extensive variables volume and particle number, the other two which are other three which are intensive variables not scalable. You see P d V mu d N if I want to look at these two they have the dimension of energy.

Similarly, for a magnetic system B d M has the dimension of energy right. And it is interesting and this is what the analogy with mechanics come. This is a force and this is a coordinate a generalized force and a generalized coordinate. This, these are all forces and these are all coordinates which you can.

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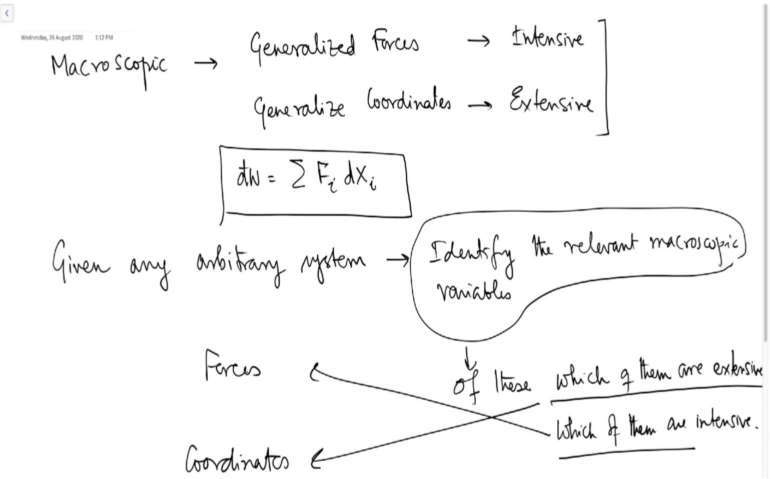

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Macroscopic → Generalized Forces → Intensive

Generalize Coordinates → Extensive

$\boxed{dW = \sum F_i \, dX_i}$

Given any arbitrary system → Identify the relevant macroscopic variables

of these which of them are extensive

Which of them are intensive.

Forces

Coordinates

Therefore, for a macroscopic variables I can classify them in 2 categories. I have a set of generalized forces and I have a set of generalized coordinates. These are extensive in nature and these are intensive in nature. I can combine them to write down the work done as sum over F i dX i right.

So, given any arbitrary system, the first task is to identify the relevant macroscopic variables and once you have identified this relevant macroscopic variables you can easily figure out of these which of them are extensive and which of them are intensive? Right.

Moment you have identified which of them are extensive and which of them are intensive you immediately they understand; you immediately also take the next step in saying that, these are my coordinates and these are my moment sorry my mistake these are my forces right.

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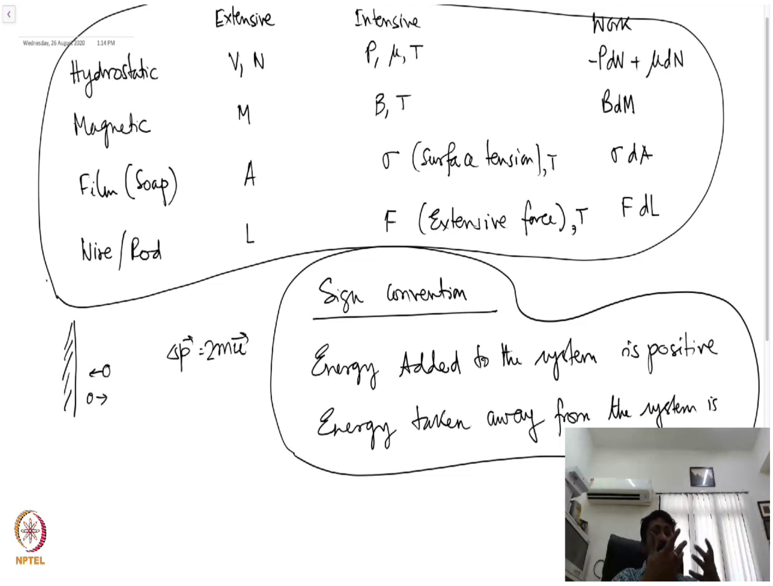

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	Extensive	Intensive	Work
Hydrostatic	V, N	P, μ, T	$-PdV + \mu dN$
Magnetic	M	B, T	BdM
Film (Soap)	A	σ (Surface tension), T	σdA
Wire/Rod	L	F (Extensive force), T	F dL

$\Delta \vec{p} = 2m\vec{u}$

Sign convention

Energy Added to the system is positive

Energy taken away from the system is

Let us take some examples I know that for a hydrostatic system pressure sorry; for a hydrostatic system my coordinate thermodynamic coordinates which are extensive are volume and particle number. So, we will write extensive on top and intensive on top, pressure chemical potential and temperature are the intensive variables. For a magnetic system I have only the magnetization and therefore, the magnetic field and the temperature of the intensive variable.

For a let us say film for example, a soap film right. You see the area is the extensive variable area of a film is the extensive variable and the surface tension is the intensive variable. For a wire, metal wire or a rod the length of this is the extensive variable. So, if you keep on adding more and more rod the length is also going to change is going to scale with particle number and the force the extensive force is the intensive variable.

So, it is always important to note that given any arbitrary system, I can describe that system thermodynamically by identifying the relevant microscopic variables. And once I have identified the relevant macroscopic variable all I am left to do is to identify, which of these are extensive and which of these are intensive variable?

Once I have identified that then I know that the work time is P d V plus mu d M. Here I want to; I want to write down as minus P because the pressure that we measure for a hydrostatic system is the (Refer Time: 33:02) the way we calculate it essentially. We calculate it by calculating the change in the momentum of particles which are hitting the wall.

So, when you calculate the pressure this is the wall of the container the particles come they get reflected back like this way and you calculate delta p the change in momentum is twice m u right. We do it this way by Newton's third law the wall also exerts the equal amount of force which is negative in sign.

Therefore by our sign convention the pressure is negative here. For a magnetic system I have B d M, for a soap film I have sigma d A. The temperature is also here the temperature is also here and I have F d L. Throughout this course the sign convention for the energy is the following energy added to the system is positive, energy taken away from the system is negative.

Please understand that I mean you can follow any sign convention that is ok. For me right now for all the set of lectures that we are going to give the energy added to the system is positive, the energy taken away from the system is negative. We shall use this later on when we start to write second law first law right.

So, this is what we have right this is fine. So, now that we have understood that how to write down how to identify the relevant thermodynamic variables given in any arbitrary system, but then where do we go from here.

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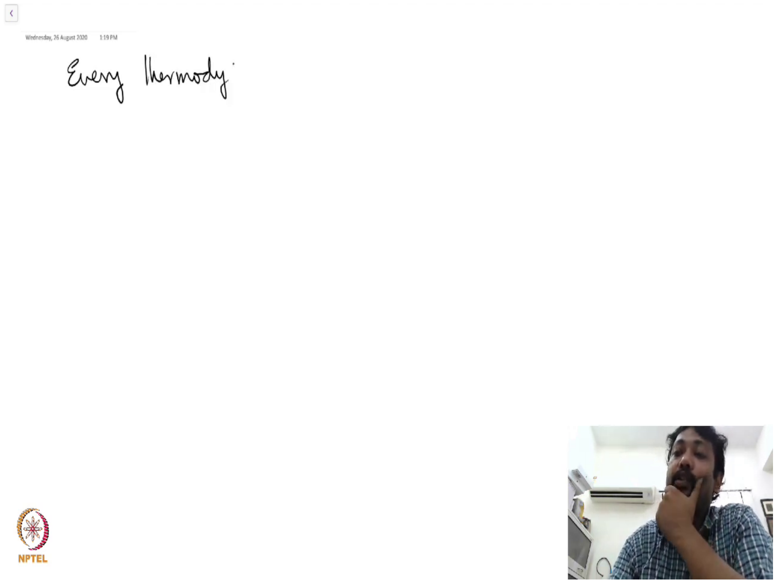
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Every thermody

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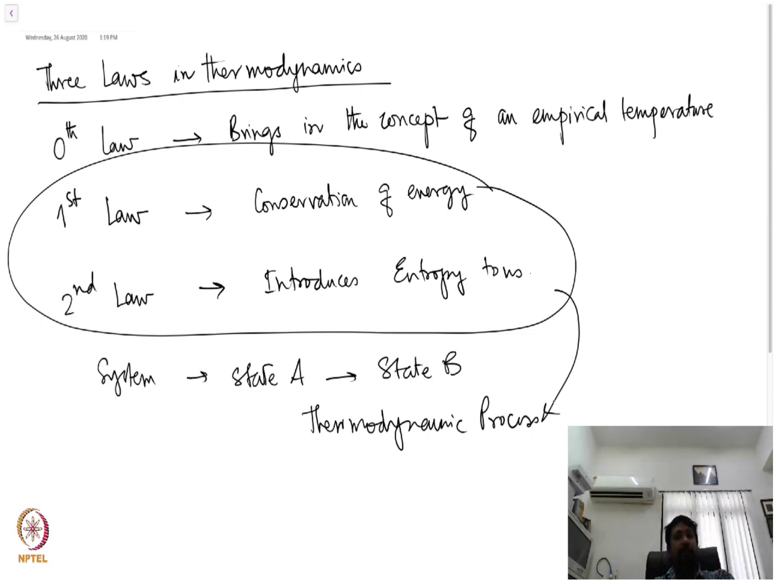

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Three Laws in thermodynamics

0^{th} Law → Brings in the concept of an empirical temperature

1^{st} Law → Conservation of energy

2^{nd} Law → Introduces Entropy to us.

System → state A → State B

Thermodynamic Process

Every thermodynamic so let us not write down like this way let us say that there are three sacred laws, well actually there are 4 of them. There are three laws in thermodynamics right, which you have done the 0th law, the 1st law and the 2nd law right. This is the guiding principle of thermodynamics.

The 0th law is very very interesting even though apparently it is very intuitive or very you can I mean, how do you say it? So, it is very intuitive I mean it is very clear obvious it brings in a very important. It brings in the concept of an empirical temperature.

The first law you know it is just the conservation of energy and the second law essentially introduces entropy to us right. So, we shall revise it all these words. So, any thermodynamic process must obey this 1st, 0th law, 1st law and 2nd law. The 0th law is extremely significant in the sense that what we understand as temperature is introduced by the 0th law.

Now, given a thermodynamic system of course, the system is never going to remain in its state. I mean you have to at some point of time it is very natural that you take that system to a different thermodynamic state. Therefore, essentially if you take a system from state A to state B you have done a thermodynamic process. And thermodynamic processes are usually guided by the 1st law and the 2nd law, this must dictate what kind of processes they are.

In thermodynamics, not only that we say that A and B are equilibrium states then only I can apply the concepts of thermodynamics. We also say that processes are typically irreversible sorry the processes are typically reversible or quasi static. The main consequence of this statement that these processes are reversible and or they are quasi static is essentially at every point. While it undergoes or available the system goes from state A to state B thermodynamic variables are well defined.