Chemical Principles II
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Thermodynamics Systems and Variables

So today we are going to talk about zeroth law of thermodynamics. So before we do that, we have to first make the basis clear and we will start with thermodynamic systems and variables.

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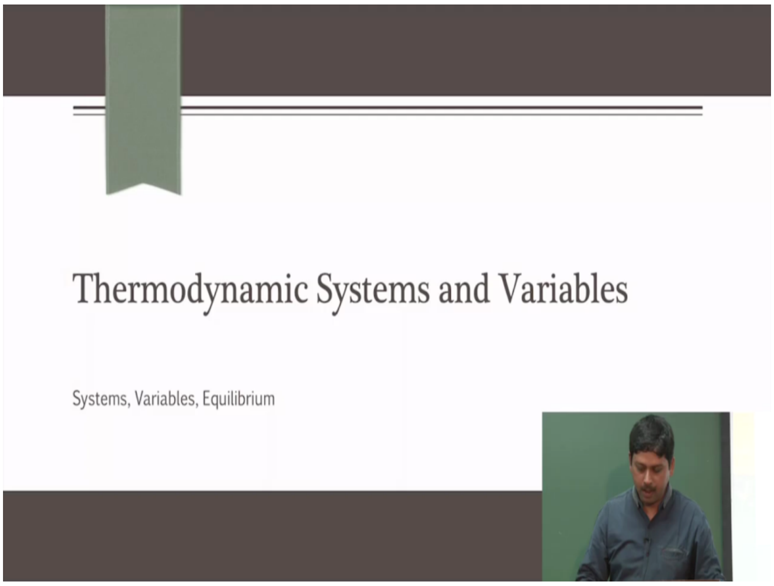

So what I mean by that thermodynamic systems and variables is, that in order to understand the properties of thermodynamics first we have to define the system and the surrounding.

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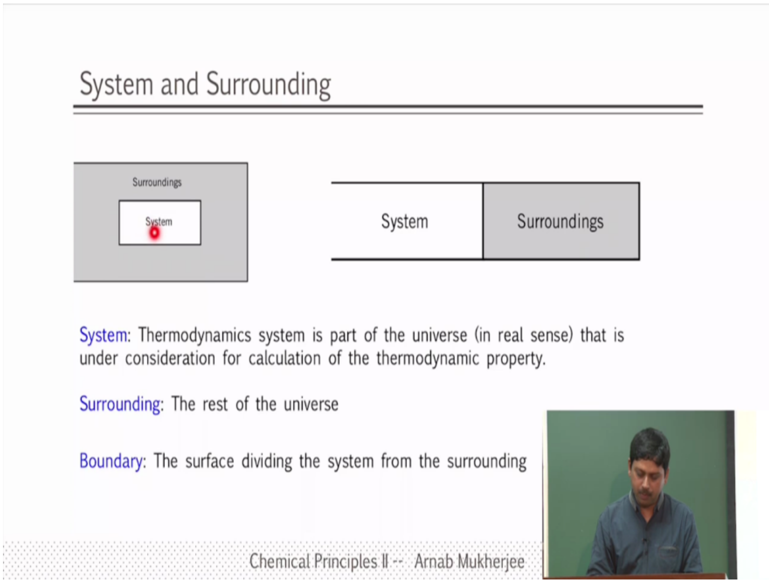

So here you can see that system is you know in a closed region of space, around that everything else can be called the surroundings, right now we have drawn that using some rectangular something it will be clear later on what they mean. System can be of other type where in you know one side is open and the surrounding can be a closed one, so it entirely depends on the Observer who is going to measure thermodynamic properties of a particular object to define its own system and the surrounding.

So system is defined as thermodynamic system is a part of the universe by universe I mean physical universe. The universe in which we live in, in real sense that's what is meant here that is under consideration for calculation of the thermodynamic property. So we can say that a glass of water is a system and everything else apart from that glass of water is the surrounding.

As I said surrounding is the rest of the universe and boundary which separates the system from the surrounding, the surface. So here you know you can say that this part is the boundary. Here you know this part this part is a boundary.

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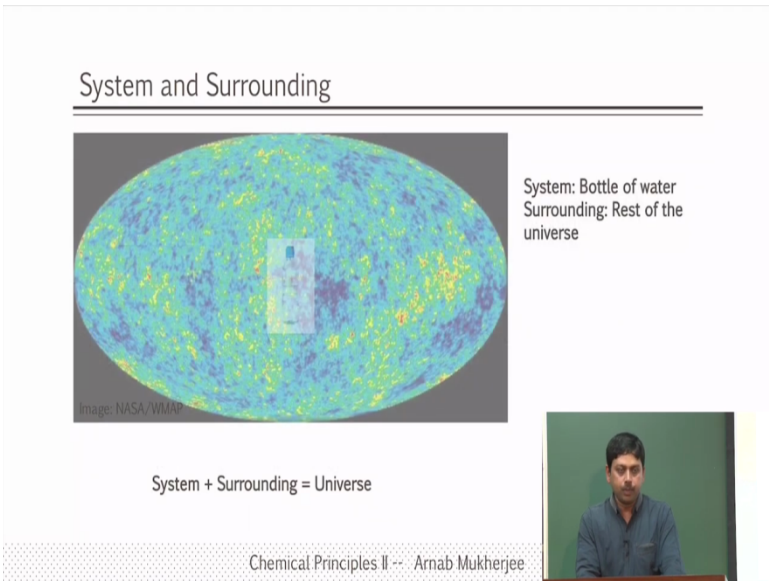

So to give you a better idea of the system and surroundings is that we have taken a picture from NASA's website, the early universe picture. So this is what universe used to look like, one of the earliest pictures of the universe and in which we have put a bottle, so it is not up to scale, okay. The picture is not up to scale you can see that. So let's say the bottle is the system everything else apart from the bottle in the whole universe is the surrounding.

And system plus surrounding as you can see is the universe, so this universe when you mean universe is actually in real sense it is a physical universe in which we live in and you will see that it becomes very clear when we decide that as universe and do the calculation, physical universe I mean.

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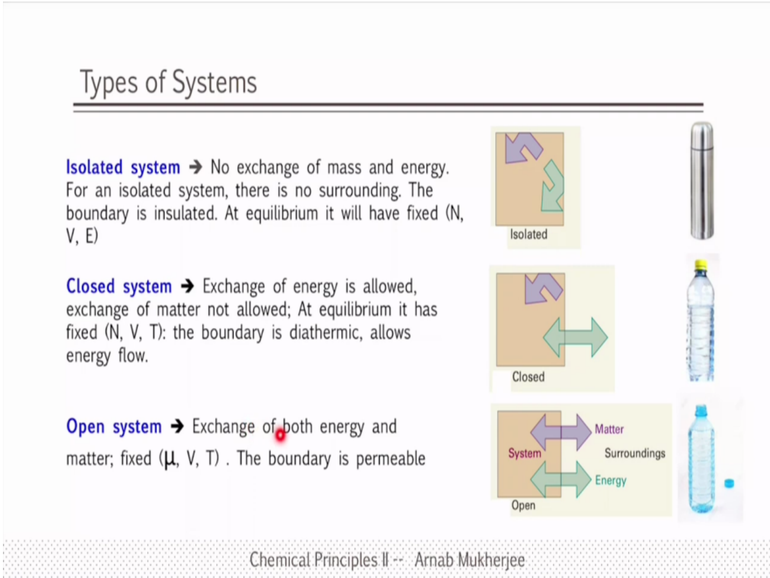

So now let us discuss little bit of type of systems which will be useful or which we need to use in order to calculate certain properties. One is called isolated system in which no exchange of mass or energy will take place and it is depicted in this kind of picture that the mass and the energy is conserved within this particular system and then example of that is a Thermo flask.

Although it is not totally an isolated system but it is somewhat closed to an isolated system possible, we have a thermostat here, you know thermal flask here.

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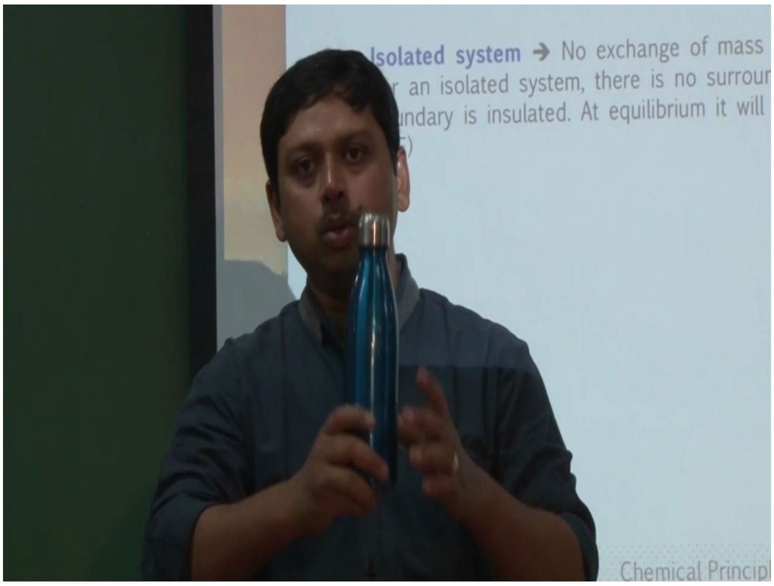

So you know that a Thermo flask is meant to keep hot water hot and cold water cold to some extent, so here we have some hot water kept inside and outside it feels the normal temperature however the temperature of the water inside it is actually high.

So it will result this particular hotness of water for some more time we can say that it is a prototype of an isolated system. So then isolated system is in which there is no transfer of energy or mass and then there is something called closed system which might be little bit confusing when you hear for the first time.

Closed, it is closed means it is only closed for mast to transfer, so it is not closed for energy to transfer, so exchange of energy is allowed in this particular system but exchange of matter is not allowed, so add equilibrium this particular system has a fixed number of molecules, fix volume and fix temperature and in the isolated system at equilibrium will have fixed number of molecules, volume and energy.

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So an example of a closed system we can say, we can take for example this particular bottle which will allow the exchange of energy although you can see that the bottle is pretty closed and what we mean by close is that no mass will be transferred outside of this, so if we have 1 Liter of water in the beginning it will remain 1 liter after sometime also. However right now I feel that the water is hot but after sometime it will cool down.

So there will be transfer of energy from the bottle to the surrounding, so this is an example of a closed system. So it is closed however the energy transferred is allowed.

And then the 3rd system is called open system in which both mass and energy or matter and energy transfers are allowed. So exchange of both mass and energy allowed and typically add equilibrium this kind of systems will have a fixed chemical potential, volume and temperature. So right now we are not defining this quantity as chemical potential volume temperature but soon it will become clear.

Only thing you can actually right now take is that certain properties of the system will remain fixed in all this 3 different kinds of systems.

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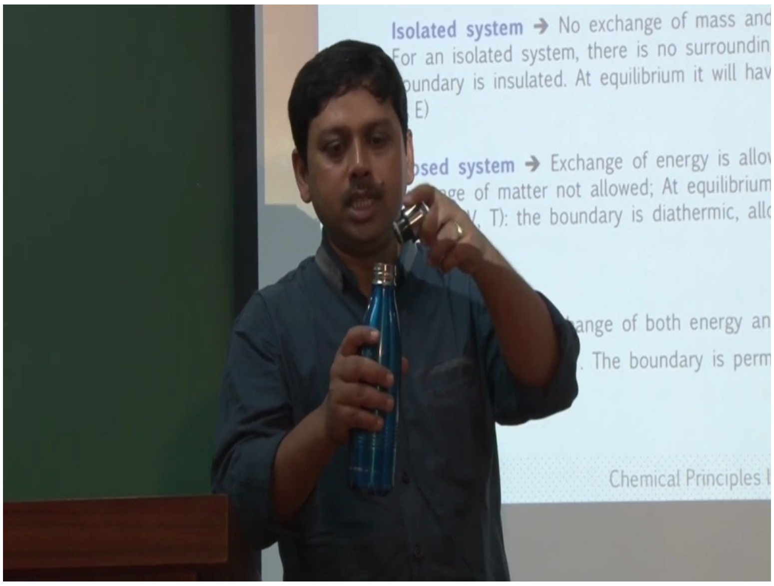

So for an open system we can easily take an example of this particular water and you know I open that and I can you know it's hard, so I cannot drink from this. However as you can see that there are water vapors going out from that, so therefore the mass content of this water is actually changing with time and therefore energy is also changing, when the mass can transfer between the system and the surrounding energy also will transfer along with that. So literally an open system is an open bottle and that is given in this medical example here.

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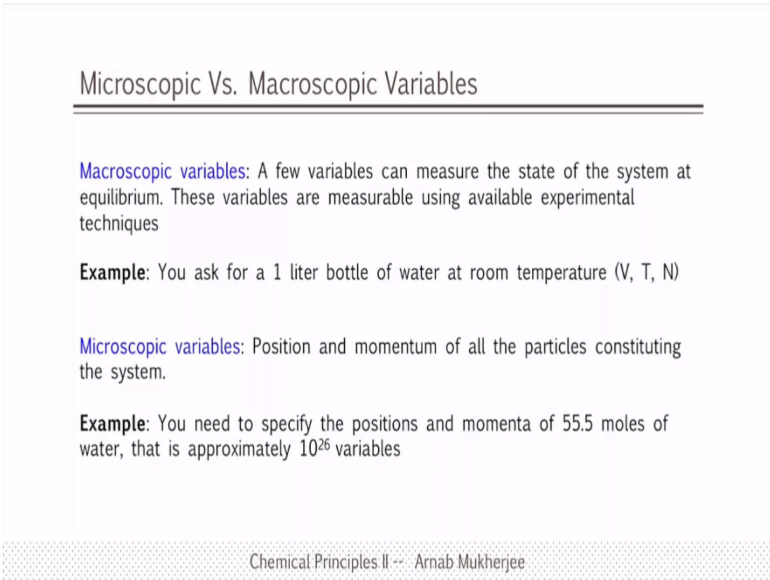

Now let us define variables, so if we have said define systems now we will define variables. Variables are of 2 different types, one is called microscopic variable another is macroscopic variable, what we mean by that? You know become clear in a moment, so macroscopic variables are that, so there are only you know very few number of variables required to define the state of the system in equilibrium.

These variables are measured using available experimental techniques, so for example volume is a macroscopic variable, temperature will be a macroscopic variable, pressure will be a macroscopic variable, they are all macroscopic variable for measuring properties of a system at equilibrium, so let's say if I go and ask in a shop that give me 1 L of water at room temperature.

So what we are specifying there? We are specifying the volume, we are specifying the room temperature which is temperature and we don't have to specify but it is quite quite understood that we are also specifying the atmospheric pressure, so we are already specifying 3 different macroscopic variables. What we are not specifying is enormous number of microscopic variables that are hidden within this fixed value of macroscopic variable.

What do I mean by that? So is that microscopic variables are basically positions and momentum of all particles constituting the system. So when I talk about a bottle of water at room temperature if I want it I microscopic description of the same then I would have to specify the positions and momentum of all the atoms of that particular bottle of water and in fact they will be all the time changing.

So let's say if I talk about 1 Liter of water than 1 Liter of water then 1 Liter of water at room temperature and pressure typically has 55.5 moles of water, right? And we know that one will contain 6.023 in 10 to power 23 numbers of molecules. And then in water you have 3 atoms and then you have to specify positions XYZ and momentum PX, PY PZ, so therefore 6 different variables.

So typically 4n atom system we have to specify 6n number of variables, so that means that for 1 liter of water when I have to specify I have to specify 10 to the power almost 26 number of variables in the microscopic size. So microscopic variables again mean that positions is momentum and you will see later on that given that information of opposition and momentum of all the particles of the given system we will be able to calculate every thermodynamic quantity of that particular system.

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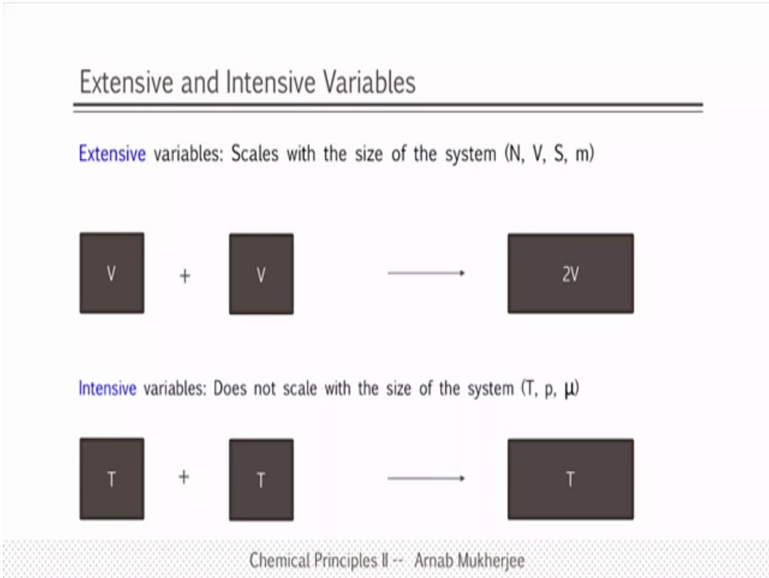

We will discuss more about that later on. Variables also can be of 2 different kinds one is extensive variable another is intensive variable. Extensive variables are something which scales with the size of the system for example number of molecules if I did 1 liter and take another liter bottle of water and then when I add them together it will become 2 liters.

So that means volume is an extensive property because it scales with the size of the system, number of molecules also one mole plus one mole will become 2mole. Similarly there is intensive variable which no variables which do not scale with the size of the system for example if I take temperature of one particular bottle of water and then I measure temperature of another particular bottle of water when I mix them together.

If those temperatures were initially same then when I mix them together the temperature will still remain the same. So let's say I take a bottle at 30 degree centigrade, I'll take another bottle at 30 degree centigrade I mix them I get double the volume however temperature remains the same or let's calculate the pressure of this particular room in one corner and another corner and then calculate for the whole room, you still get the same pressure.

So temperature pressure are intensive variable which will not scale with the size of the system, so here T plus T remains T and V plus V will be 2V.

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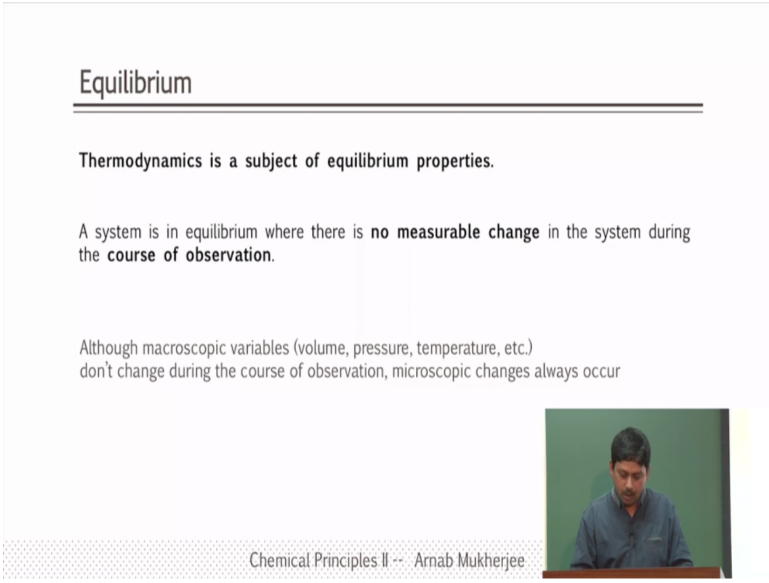

Now we will discuss about the variables description in equilibrium. So when I say that 1 liter of water I mean that 1 liter of water at room temperature at equilibrium.

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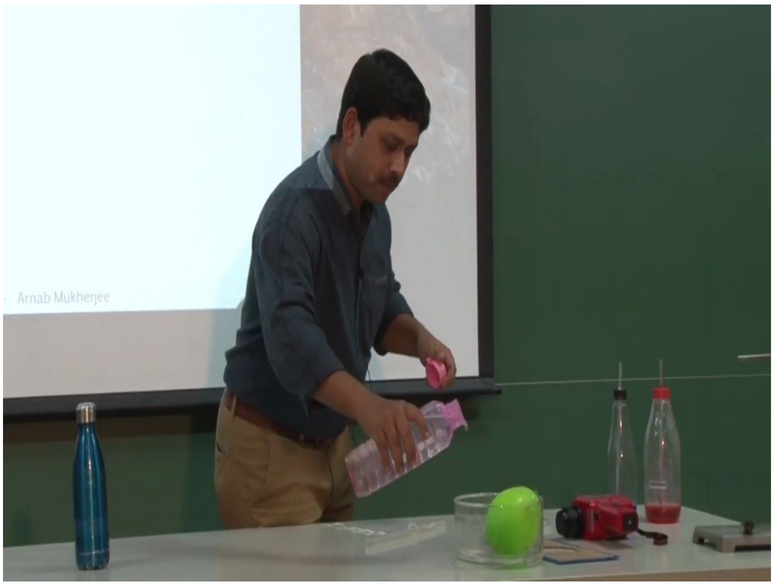

So for example if I take this particular bottle of water and I pour some water here initially when am pouring it while pouring it the system is not in equilibrium, we can see there is bubbles there will be you know small waves in the water and all that after sometime again things will become normal. You throw a stone at a pond initially we will see there will be water waves going on.

After sometime things will become again static stagnant the way it was before, so equilibrium is something in which the observable the one that we are looking at let's say we are looking at height of the water when the observable does not change appreciably we mean that within the error of our own measurement.

So let's say we say that okay if the water level doesn't change more than 1 inches then I will think that water level remains constant. So if the property does not change appreciably within the limit of our observation then we say that the system is in equilibrium. For example the water level if you look at for a month you might find that water level has changed because of rainfall because of extra water from somewhere else and things like that.

So within a span of a month or years that particular thing may not be at equilibrium but within a timescale of let's say one hour you see that it is perfectly static. For example we look at this water in the beaker right now it looks perfectly all right, stable and at equilibrium however if I leave it for a year there water will vaporize and there will may not be any water there.

So therefore in a timescale of an year it is not an equilibrium. So for equilibrium we have to say that a system is in equilibrium where there is no measurable change in the system during the course of our observation. So a glacier typically will change in the timescale of years. When you talk about interstellar systems, so their timescale the even larger.

So always while calculating equilibrium we have to talk about the timescale of observation and the constraints that we have associated with that. So macroscopic variables do not change during the course of observation but microscopic variables change all the time.

So what I mean by that is, this water looks perfectly all right looks like it is in equilibrium because there is no bubbles there is no change appreciably and all that. However the water molecules that are there within that bottle they are constantly changing with time, so they are not static. Although the overall system is in equilibrium each molecule is actually dynamically changing with time.

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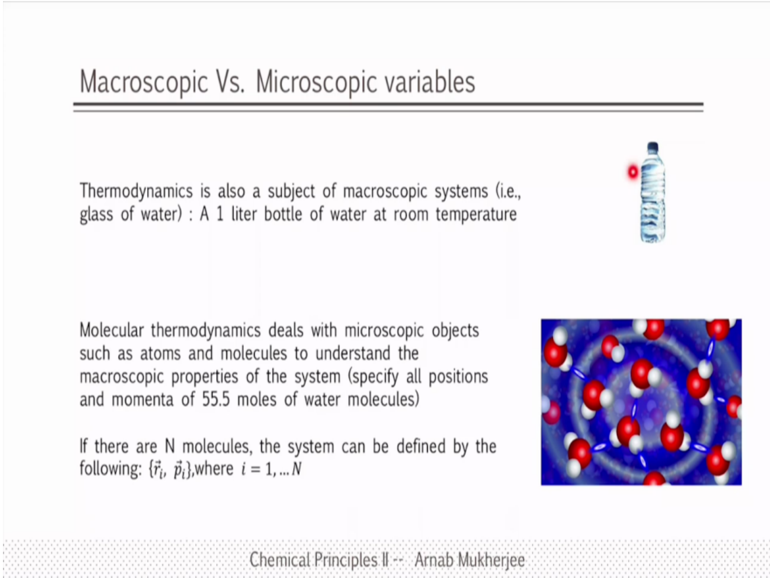

So to give an example of a microscopic variable, I show you this particular picture where you know the water configurations are given and this particular bottle is an example of a macroscopic variable where you don't have to look at the microscopic object. So microscopic means small, macroscopic means big. So when you talk about macroscopic variables we are talking about variables associated with large quantity.

When we talk about microscopic variable we are talking about variables associated with atoms and molecules. So here is an example of looking at the molecular level, here we are looking at the level of macroscopic quantity.