Chemical Principles II
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Module 07
Lecture 38
Statistical Formulations of the Second Law

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Ok, so welcome to the next topic of Chemical Principles 2. And in this particular part we are going to talk about Statistical Formulations of the Second Law.

So we have seen from the classical descriptions of the Second Law and classical descriptions or evaluations of entropy rather formulations of the entropy formula from Carnot Cycle and all, there we have learnt that entropy increase will be favorable.

However, we did not understand from that, that why entropy increase will be favorable. So we have learnt that reversible heat change at a given temperature is entropy. And therefore essentially entropy is some, similar, there is a similarity of entropy with heat energy because it is reversible heat.

Then the common notions that entropy is associated with chaos or disorder or randomness is somehow does not come from that particular description unless we say that heat energy is nothing but random motions of molecules.

We know that heat is proportional to temperature. And that is how we actually we derived in the earlier part the heat expression or from relations of heat gain from the earlier part

And we have seen that temperature in principle is nothing but the kinetic energy of the particle and kinetic energy we know that it is proportional to velocity square.

So in a way, we are talking about when we are talking about heat, we are talking about random motions of molecules having set of particular velocities.

And you can really associate that with the entropy. So it means that if the motions are more vigorous, more random, the velocities are somehow higher, we can associate roughly to an increase in entropy.

But it does not give us a certain feeling that why that will be something that will keep on increasing with time. How we get the time arrow? How do we know that certain events like, you know falling of an egg and breaking it when hits the floor is an entropical increasing process.

We have discussed that when something falls, it hits the ground and that energy which was initially potential energy converted into kinetic energy and that energy get dissipated among the molecules of the floor and therefore we do not get ever back.

That means for a reverse process to happen all the energy that got dissipated in the atoms of the floor has to do exactly same reverse motion in order to push that egg back. And that is unlikely. And unlikely even according to our own understanding and feeling.

However to get more concrete idea we have to talk about Second Law that in a context of the fact that the entropy of the universe is increasing is true only on average. That means the Second Law is true only on average.

So it is, and when you talk about an average, we talk about statistical outcome of certain occurrences. The fact that this cannot happen, the reverse process that all the particles on the floor cannot come back and push the broken pieces of egg and all other things together and pushes it back to our hand is because the Second Law is a statistical law.

So the fact that entropy of the universe is increasing is true only on an average. It is a statistical outcome of certain occurrences.

However where is the statistics in the breaking of an egg? If the egg falls and breaks we do not get to see the reverse process and where do we understand, from where we understand that there is some statistical outcome associated with that.

So in order to do that we have to delve deep into the constituents of a microscopic system. By that what I mean is that we have to see that every macroscopic system like cricket ball or an egg or a glass of water is made of tiniest smallest particles like atoms and molecules.

So while it is required that only smallest number of variables like in V and T describe equilibrium properties of a macroscopic system; by that again I will remind that if you want a glass, a bottle of water from a shop you say that I want a 1 liter bottle.

At room temperature or thanda, so you say thanda which means 4 degree Centigrade, if you want room temperature then you get around 27 degree Centigrade. And you specify the volume and you do not have to specify the pressure but that is already specified.

So by saying these 3 variables you are specifying entirely the macroscopic system. However actually what it requires is specifications of 10 to the power 23 variables, not only 10 to the power 23

So there as you know that in 1 mole, So 1 liter of water has 55 point 5 mole which means we have 55 point 5 multiplied by 6 point 0 2 3 multiplied by 10 to the power 23 number of molecules multiplied by 3 will be the number of atoms.

And every atom has 3 positions and 3 momentum coordinates, so multiplied by 6 will be the number of variables. That are required in order to specify the state the a particular system.

Only one difference though, for macroscopic systems you can only specify the equilibrium properties with n, V and T, smallest number of variables.

However for microscopic systems we can specify any, any state of the system by specifying all the variables, especially classical, we are talking about classical system. Here we are not going into quantum system so we are actually, on top of these coordinates you also have to specify the, you know other things like electrons.

We do not have to consider about electrons at this, in classical expressions, we only consider atoms and molecules.

So coming back, so once we know the position and momentum of all the particles we can then obtain any property we like and that is the subject that is known as statistical thermodynamics or molecular thermodynamics.

So this subject will help you to calculate entropy as a statistical outcome of things. Remember again we will use the configurations of these atoms and molecules to predict what will be an observable thermodynamic property.

For example if I talk about pressure or volume, we will be able to calculate from the motions of atoms and molecules. The pressure that you observe is actually an average pressure. It always fluctuates around the average.

When we say 1 atmospheric pressure it is just on an average it is 1 atmosphere. When we talk about volume, on an average is, you know 1 liter, if I specify 55 point 5 moles water volume is only on, at room temperature, only on an average it is 1 liter. It will be always fluctuating.

So macroscopic properties are, we will show that it is nothing but the average properties obtained from statistical distributions of these atoms and molecules. However it is not possible to precisely state this humongous number of variables and conditions

As I said 55 point 5 multiplied by 6 point 0 2 3 into 10 to power 23 into 3 into 6, it is not possible. Therefore probabilistic approaches are used in approaching the properties of thermodynamics using atoms and molecules description.

So these probabilistic approaches will not give us individual detail. However it will give the property according to the average outcome.

For example, we will give an example. So in quantum mechanics also we had seen that given a wave function we can calculate the average expectation, expectation of the, expectation of certain property which are nothing but averages over all possibilities

So we do not have to know that how an electron moves. Still we can get the average property right. Although not quite similar but in these classical expressions also, once we know the entire distributions of systems we will be able to calculate the average property.

So connection between thermodynamics and statistical thermodynamics is probability which will provide us an average expected outcome as I said. Now let us see some examples of how probability helps us to obtain a good understanding of the outcome.

For example if you ask will it rain tomorrow, and if we know all the conditions of, like how the, you know rain happens and measure all the properties like humidity, air pressure you know, in a given range of, you know certain kilometers

If we calculate the grid wise pressure and humidity and use some Navier-Stokes equations and solve that, probably, almost deterministically, unless the condition is not turbulent and all that, we will be able to predict whether it will rain tomorrow or not. It requires huge computations and actually meteorological department will do that.

However we can resort to a probabilistic description. Will it rain tomorrow? And we need some information. For example in the month of November, what is the probability of having rain? So has it rained in last 20 years in the month of November? Or has it been raining for last few days?

So these are things that will help us calculate the probabilities whether it will happen or not. Of course probability always means that it is not certainty but it means that if we do many, many, many observations then we will get that as an average. So with some confidence you will be able to say that whether it will rain tomorrow or not.

So another important thing about the statistics is that, as I have said it is more accurate when there are more sample points, that means observations. It will give us better average.

So therefore statistics in chemistry especially works because when you talk about observations we have huge number of observations in terms of Avogadro number of molecules.

So our sample points is huge because we are doing the statistics on 10 particles or 20 particles. We are doing that on 10 to the power 23 number of particles. So I will give an example that how the large number of observations help in the probability.

So many of us know that, you know the casinos where the gambling takes place, there are like slot machines where you put some small amount of money and you can get benefit or you know, let us say you put 25 cents and you may get like 2 dollar or more in the slot machine.

But the slot machines are designed in such a way that it is slightly in the favor of the casino, let us say 2 percent.

So 52 percent the probability is that the casino will win is point 5 2 and probability that everybody else will win is point 4 8. So which means that if you play once or twice and you may get lucky, however if you keep on playing, keep on playing then eventually you will lose.

Because it is, the slot machine is designed to have probability in favor of the casino. So now if you play, you do not have to play so much. We will give some examples. If you play 1000 times, the probability already will be in favor of casinos.

Now imagine if you play 10 to the power 23 times what will happen. It will be almost exact to the value that casinos will actually win.

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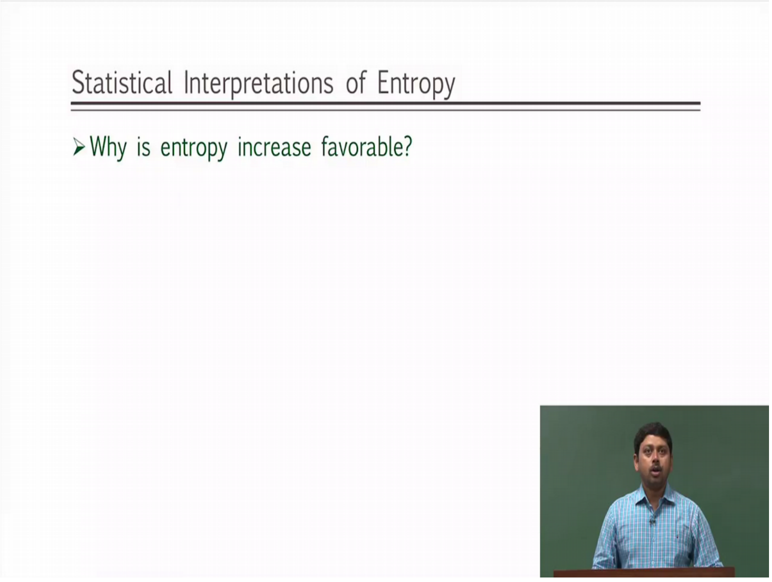

So now coming back, why entropy increase is favorable? We do not understand that so well from classical descriptions.

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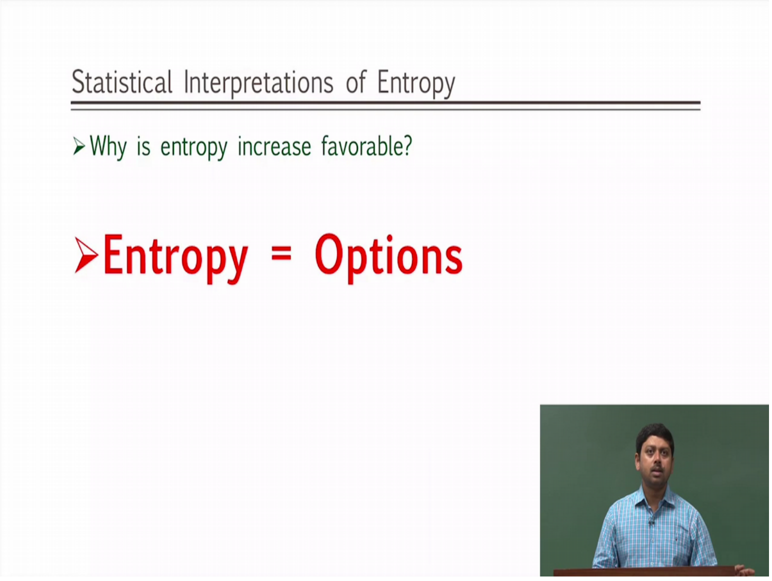

However statistically we can say that entropy is nothing but options. What I mean by that is that exactly like what is written. More entropy is more options.

So for example if I have an option to be anywhere in the campus, I will be found anywhere in the campus. If I constrain to be in the room, I will be, so my options are limited to only the room. So which entropy is higher, when I am all over the campus or when I am only inside the room?

So intuitively we can feel that of course entropy, when I can be anywhere in the campus will be higher because there are more options. I can be found, you know in the mess, in the hostel, in the field anywhere.

So obviously more choices, more options are there when I am free anywhere in the campus. Within the campus, let us say (()) (15:43). Similarly these options will always play a role whenever you can think about entropy.

So what is, what is the possibility when something falls and hits the ground that the energy will be distributed, let us say if there is no option to be distributed, it cannot.

But if there are particles in the floor that can absorb those energy, more particles are there there will be more options for the energy to be dissipated.

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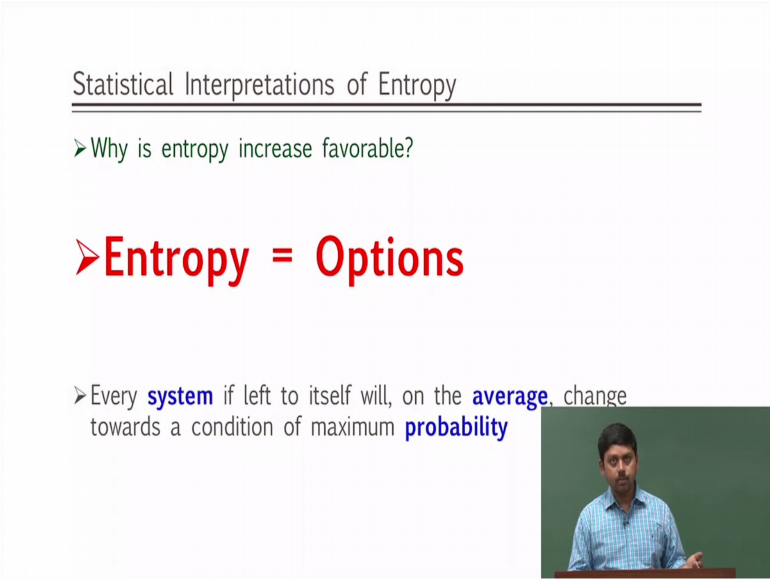

So the statement of the Second Law from the statistical point of view is that every system, if left to itself will, on the average change towards the condition of maximum probability. So we have to know about the system.

Left to itself means we do not put any constraint, on the average which means since it is a statistical law it is not deterministic. We will see that entropy will not always increase. There may be decrease also.

And it will change to the condition of maximum probability. Which means that wherever it will find a most probable situation, it will go there. So we will talk about probability then because it is going towards maximum probability.

So we will talk about that in a moment. We will give an example that what we mean by most probable situation and yeah, we will come back to that.

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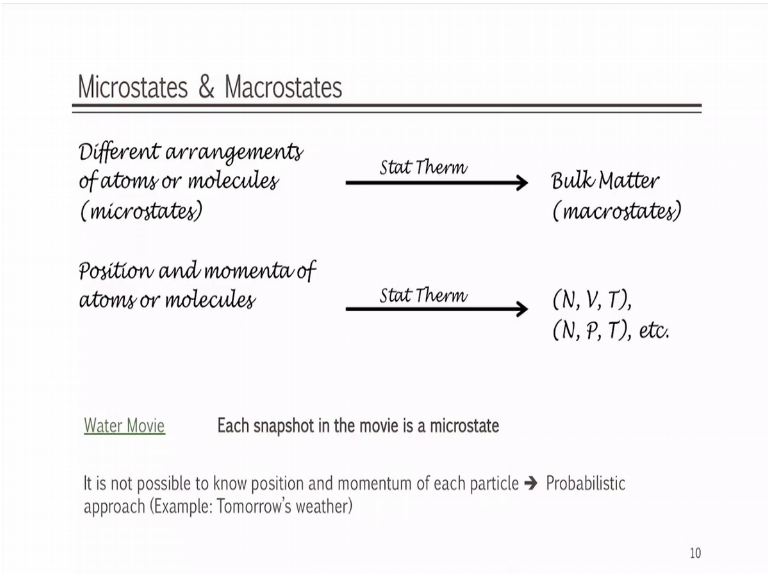

So in a nutshell different arrangements of atoms and molecules is called microstate. So every arrangement of atoms and molecules is microstate.

Statistical thermodynamics is a theory that connects those microstates or those arrangements to something called bulk matter meaning a glass of water, a cylinder of gas.

So a cylinder of gas or a glass of water is a macrostate where we do not care about atoms and molecules.

We only care about the state defined by some number of particles. It can be anything, their configuration, their momentum, their positions do not matter. We need to know only volume and temperature.

These are all called macroscopic variables whereas these are microscopic variables, position and momentum, microscopic variables. And in short form we write that by r N.

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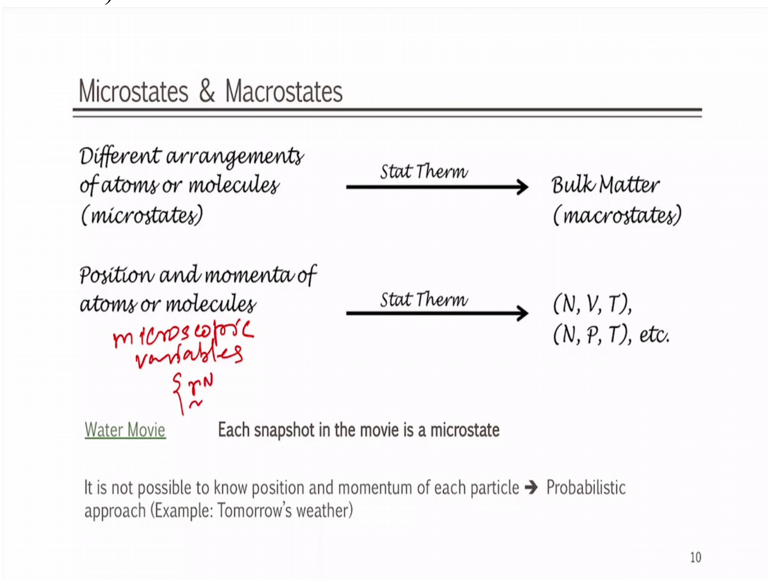

So there are N particles, r is a vector x y z to the power N means there are N number of vectors, which means 3 N number of positions. And p N,

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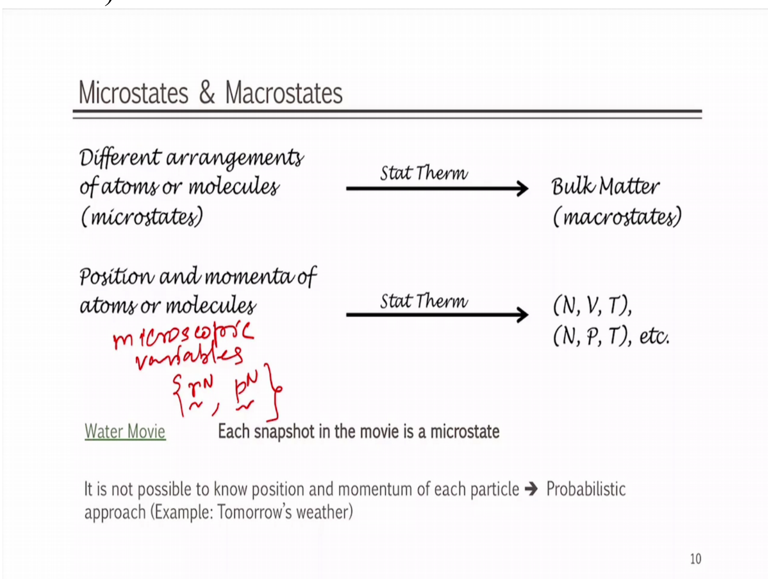

p N is momentum. So this defines a system. Our system is defined by this.

Whereas in the macroscopic system, a glass of water let us say

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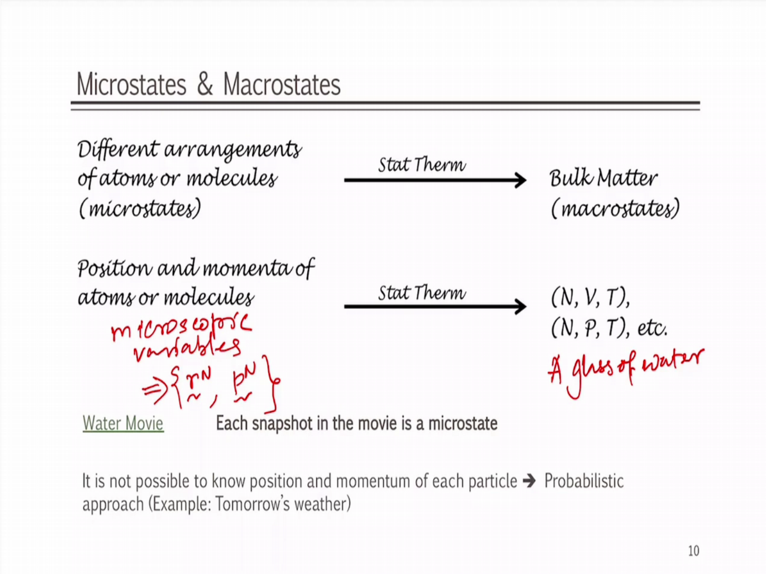

250 m l glass, so I know that N, I know the P, I know the temperature, temperature, let us say room temperature.

So 250 m l means that is one fourth of a liter, right. So 55 point 5 by, 55 point 5 by 4, into 6 point 0 2 3 into 10 to the power 23 number of, into 3, because we are talking about water so atoms will be into 3 and then pressure is 1 atmosphere. And temperature is 27 degree Centigrade.

So these are the variables that

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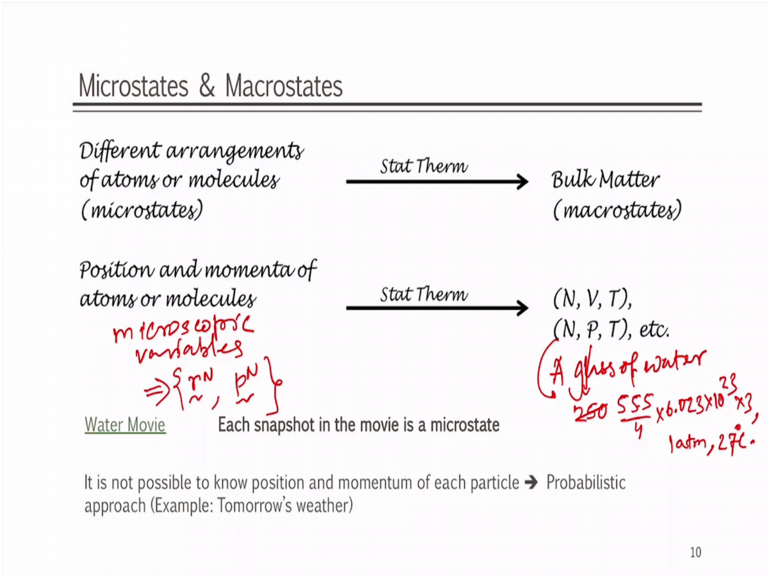

I use for defining a macroscopic system. And these are the variables that I use for defining a microscopic system. And these microscopic systems, this motions, these position and momentum, as you can understand that they are not going to be always same.

See this is going to be same. When the system is in equilibrium then our N, V and T is not changing. Let us say, Ok if the, what is the water molecules is evaporating. No, we are not talking about condition because that is an open system.

We are talking about the condition, let us say in this particular case n P T is closed system where energy can change. However the number of molecules are not changing.

So if, we are talking of closed system where number of particles remaining same, pressure remaining same and temperature is also same. So that is precisely, this bottle of water.

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Now this bottle of water I have defined by N P T, but believe it or not there are all these 6 point 0 2 3 10 to the power 23 into 55 point 5 by 4 number of molecules continuously changing their positions and momentum.

And each snapshot of that, that means if any of the positions or any of the momentum of any of the particle is changing then it is creating a new state. And each of that is a microstate. That is why we call it a microstate.

So microstate is string of numbers mentioning positions and momentum of each particle. In that string if any element is changing, is creating a new microstate.

So now let us say like if I could take a picture of, a frame of this at every instant of time, that would be a microstate. And all those microstates will give us an estimate to calculate the statistics from that. And of course that will give us the thermodynamics property.

So we will show you, we really cannot do, cannot take a femto second camera and see the positions and momentum of this but you can do that in computer. So in computer what we do is we run molecular thermodynamics simulations.

So if you are not aware of that what it does is that we consider each atom as some ball, a particle and we calculate the force that is acting on each of the ball from some potential energy that is already defined and then we propagate, the propagate meaning we change the positions of the particle with time.

Exactly what is expected of things happening in this bottle of water? So try to simulate the same system in computer and since we do that femto second time scale we can actually capture the microstates in femto seconds.

So I am going to show you an example of such microstates from our own simulations.

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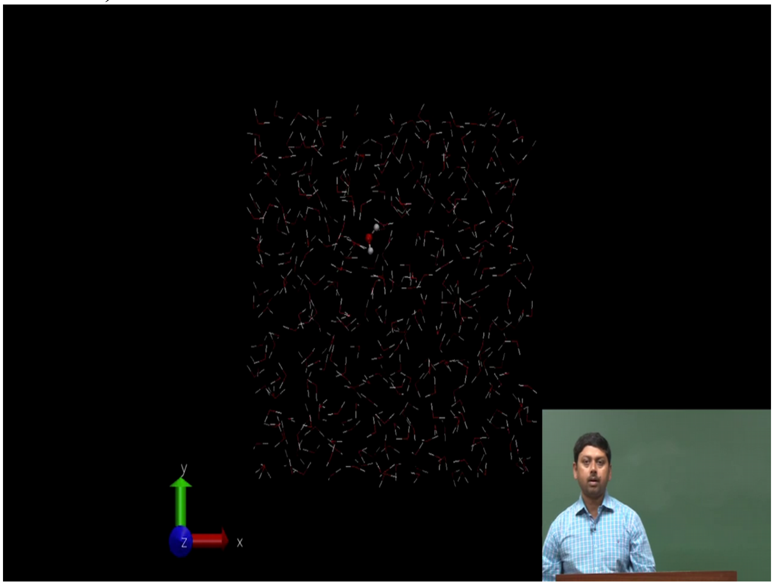

So as you can see that I am showing you a system of some 1000 water molecules. And this blue, red and green coordinate showing x, y, z frame.

And this is the software called V M D that we use to show the trajectories obtained from simulations of these water molecules. One of the water molecule is represented in something called C P K model just to show you that. But each of them can be represented.

We are just showing one of them just to show you how the water molecules is moving, I mean just to tag, it called tagging a particular molecule and just to show that they are moving.

Now you are able to run the simulations and you can observe them. For example

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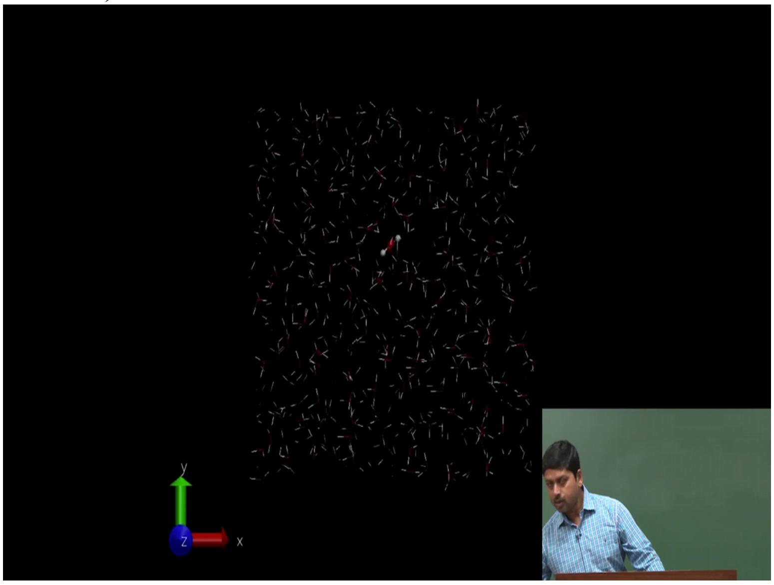

we are running it now. As you can see every atom is wiggling and ziggling.

All of them and the special water molecule that we are tagging, we can see that it is rotating, it is vibrating and it is translating, all sorts of things happening. Now if I

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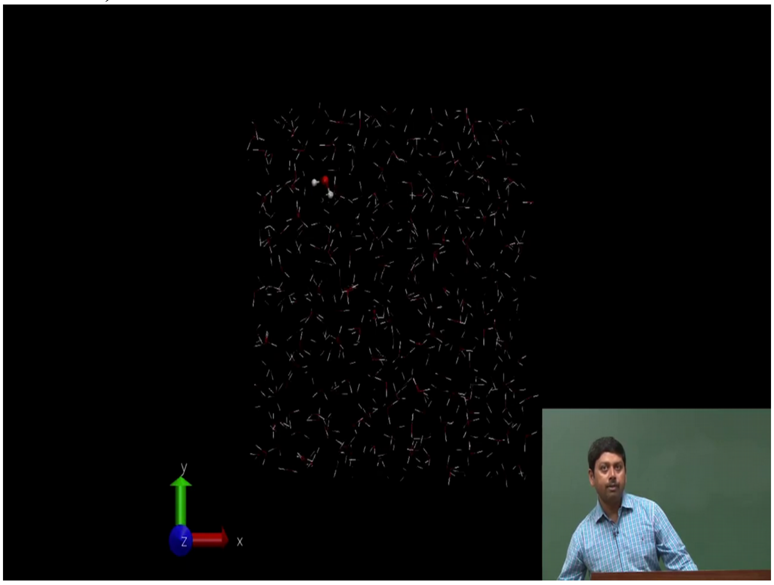

stop it at any moment this is one microstate you can think of.

Because at this state it had all the particles at some fixed positions and fixed momentum. I run it and I stop it.

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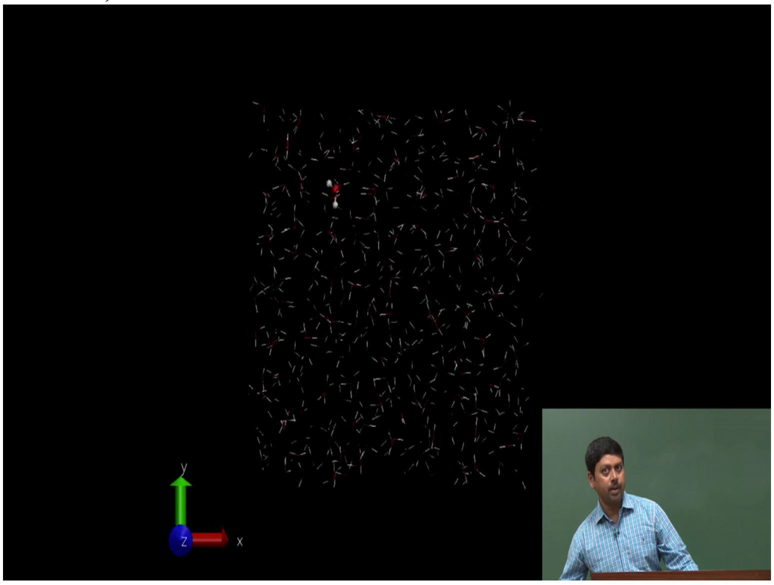

Another microstate, run it.

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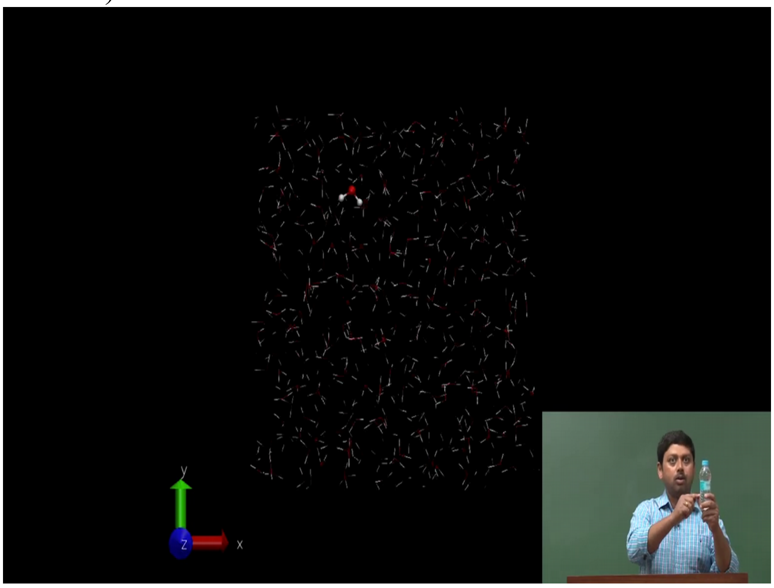

Stop it. Another microstate. So every instant of time gives me a new microstate.

And we can use all those microstate, all those microstate represent this particular system. We are not talking about any other system which means that this bottle of water has all those microstates representing the same bottle of water.

So once we do that we get an idea that, once we have all those microstates we are going to then estimate our properties based on those microstates, right. But then is it possible to do that? If not we will have to use some other approaches in order to understand

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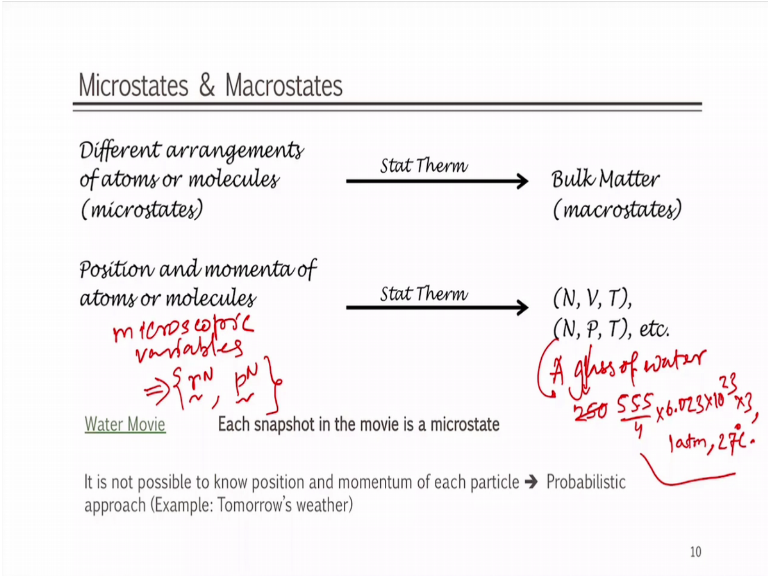

the desired calculations.

So that is why we say that it is not possible to know the position or momentum of each particle and therefore we use probabilistic approach similar to tomorrow's weather and all.

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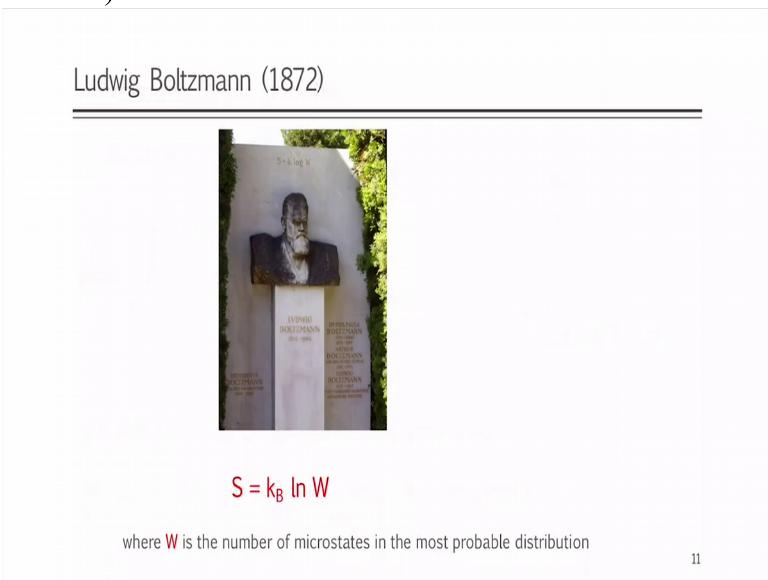

Now if we could, if we could actually estimate all the properties, all the microstates and represent that number by W then Boltzmann defined this formula for entropy where entropy will be equal to k B l n W where W is the number of microstates.

So if we could, if we could count the number of microstates, different possible microstates by the way it is not the same microstate, we do not count.

Let us say we calculate the numeric all possible different arrangements of positions and momentum of that glass of water we could say that is equal to k B l n W where W is those states.

Now what Boltzmann said, so this is 1870, remember that we talked about Second Classical, Second Law of Thermodynamics exactly around 1850s, Boltzmann worked parallely and that was the time that even electrons were not discovered, because electron was discovered in 1894.

So the, and the concepts of atoms, like something was that you know that was the smallest thing and all. Quantum mechanics did not get discovered by then because that came later, much later in 1925.

So imagine the power of mind where, you know without almost any information he could come up with such a remarkable, remarkable equation in which we get an idea from, you know, definitive formula for calculating such a quantity as entropy.

So his idea is simple that, S is proportional to the number of microstate.

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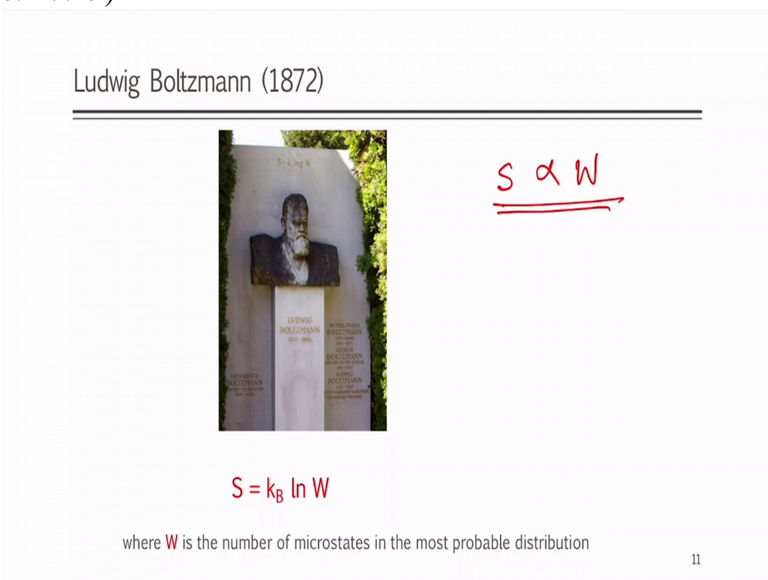

It is just proportional to. That means more microstates, more options, more entropy. That is it.

Now let us take, I take one system W, one system I take which has a W. I repeat the same system. That also will have W, right.

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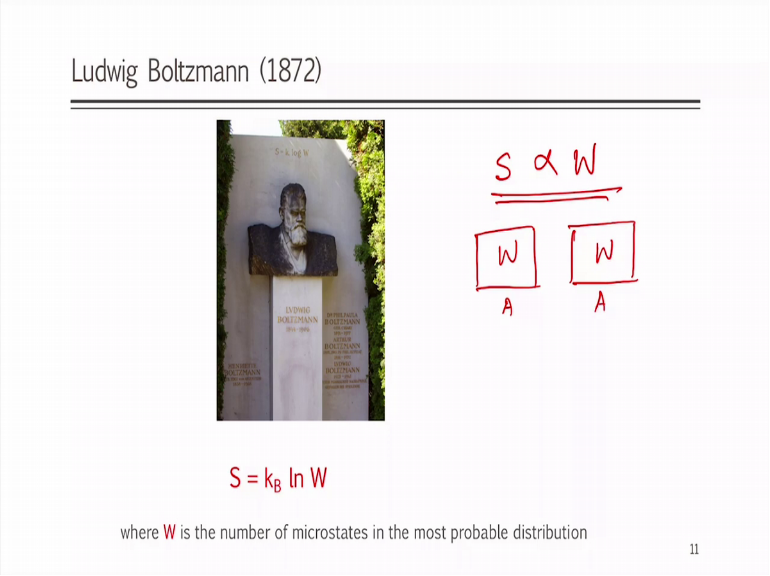

Now if I calculate the microstate of the combined system, when I combine them together you will see that, that will be nothing but W square,

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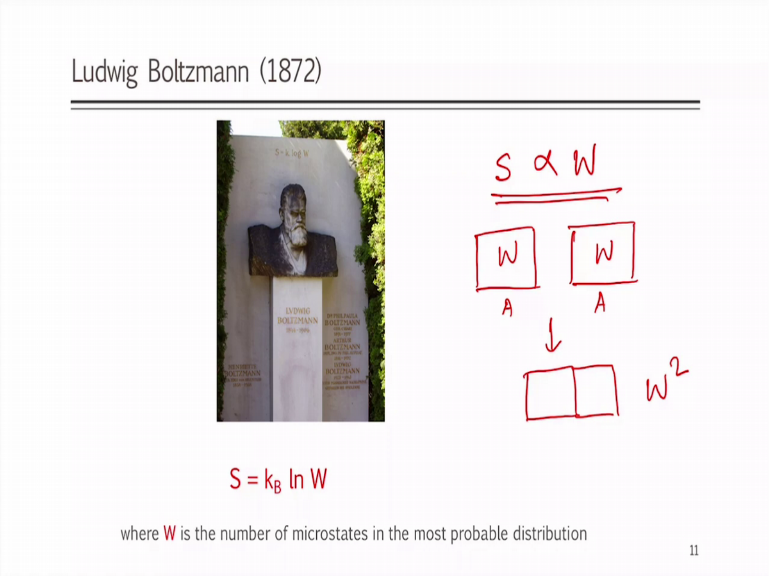

Ok.

We have to talk about what is microstate. In a moment we will do that. So it is, so W is the number of possibilities that A can have.

So then when you say that for all possibilities of this system what are the possibilities of this system, or for a given possibility of this system what are the possibility of that system to be W, in that case it would be W into W as W square.

However if we calculate associate entropy of this system as S A, this also will be S A

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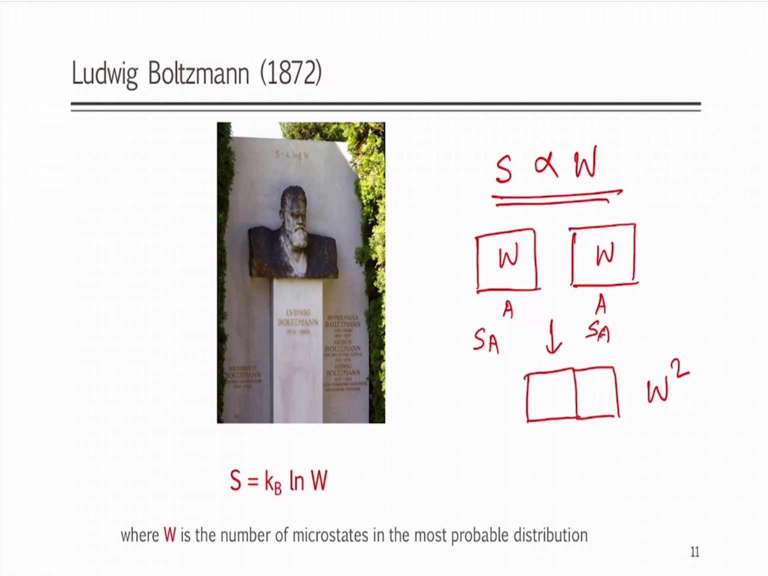

and we know that entropy is an additive quantity so the combined system the entropy will be 2 S A,

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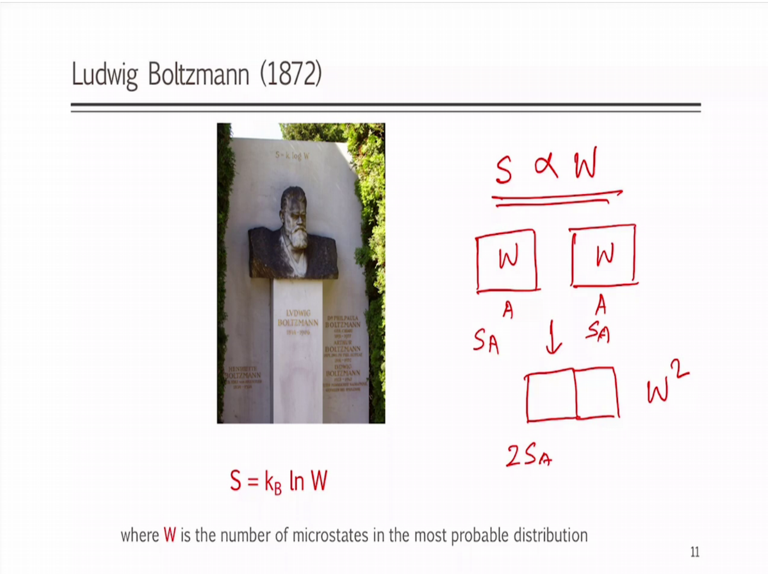

right. So in one case it will be 2 S A, and another case you have W square. That is only possible if I use an l n function.

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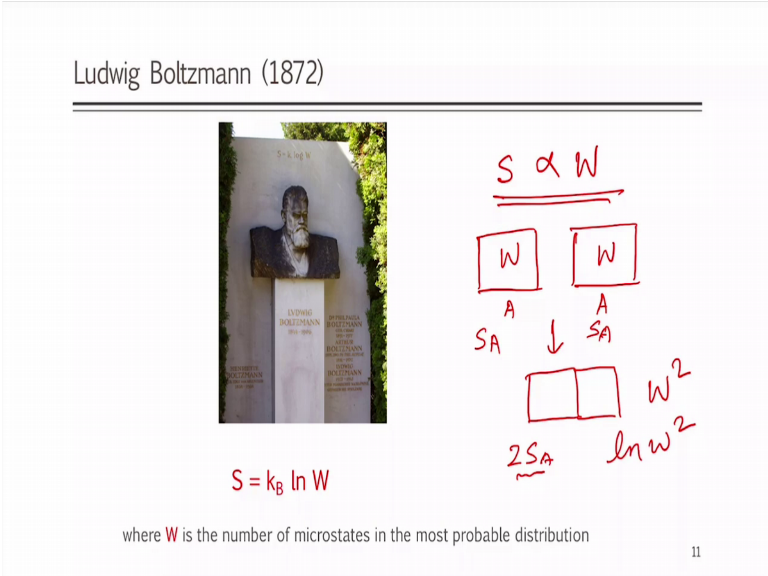

Because l n of W square is nothing but 2 l n W.

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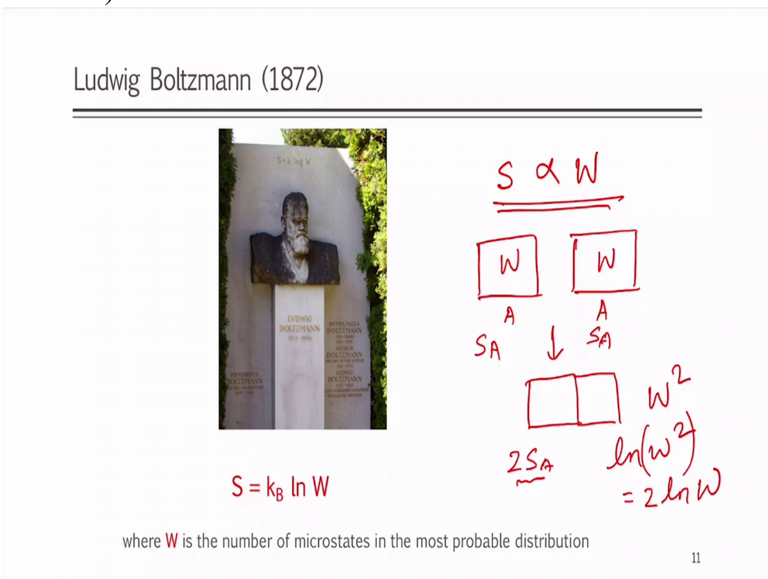

Now if l n W is S A, so 2 S A will be 2 l n W. So you see because the microstates of combined systems get multiplied you need the l n function

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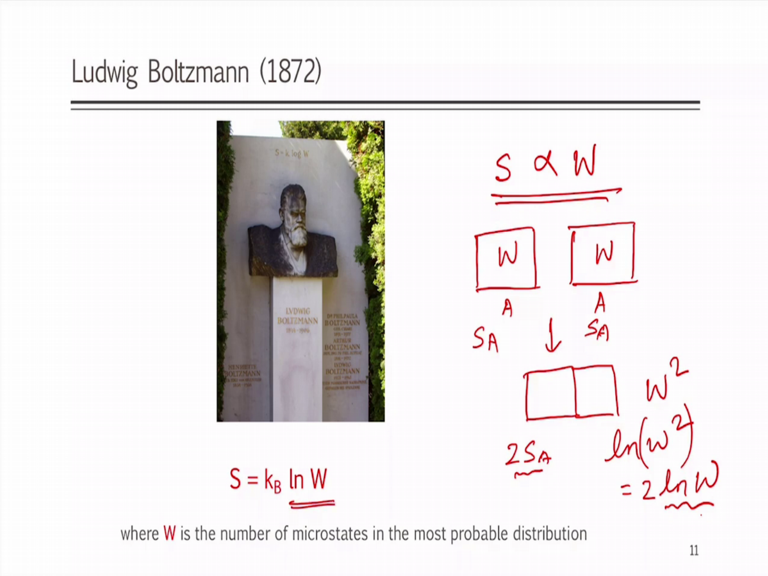

and k B is nothing but

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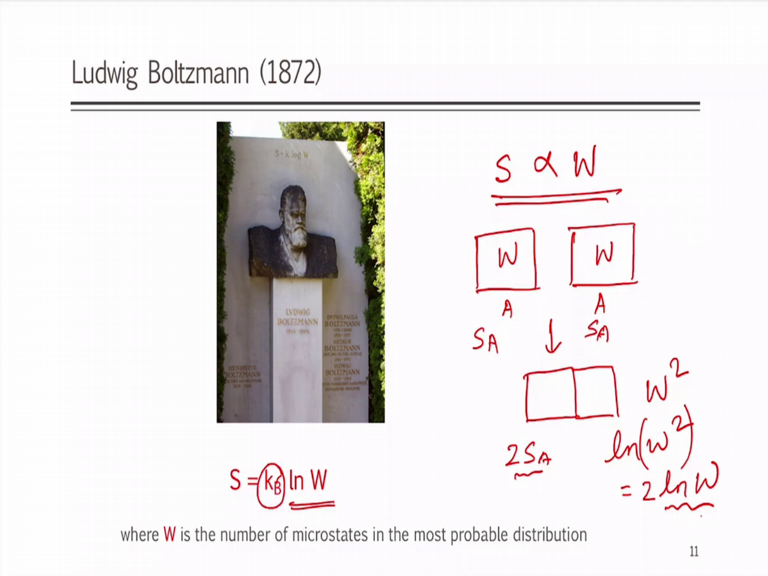

a proportionality constant called Boltzmann constant.

Note that this equation is a postulate just like Newton's equations of motion

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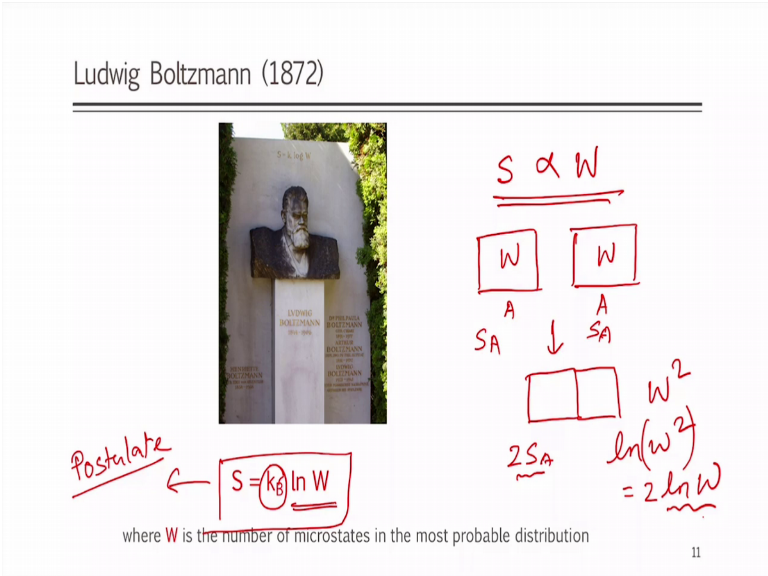

which does not have any origin. It is a postulate from which classical mechanics comes. This is the equation from which statistical mechanics start. We do not, cannot go back from this. We cannot ask that, Oh where do we get that?

We get that from phenomenonal logic. Second Law, First Law of Thermodynamics, they are also phenomenonal logical equations. We have no so-called fundamental proof that heat cannot go from low temperature to high temperature spontaneously. It is an observation.

And therefore postulate that, and that is the Claussius statement which then got connected to Kelvin statement which then got connected to all the other things and then entropy derivations came and then we said that the entropy of the universe is increasing.

So there was a starting point, the starting point was the phenomenonal logic observation. Similarly here also the starting point of definition of entropy is that it is number, it is proportional to number of microstates.

If it is that then lesser the things you will see, they will unfold just from this equation and we will be able to explain certain things the way we understand them. So only logic that we tried to give here is that while entropy is additive, microstates are multiplicative and therefore the need for l n is there.