Chemical Principles II
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Module 07
Lecture 42
Two-Level Systems

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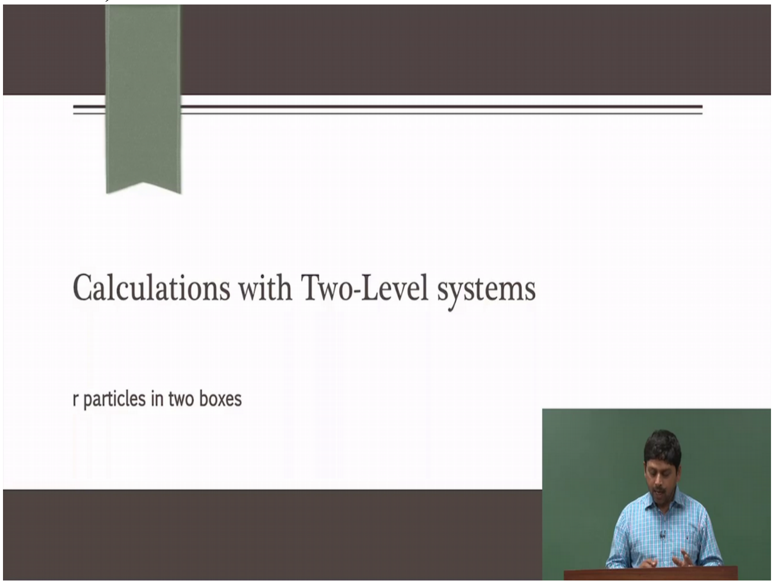

Two-level system you can imagine as putting r ball, r particles or balls in just 2 boxes, 2 level. Two-level means either one level or another level, either level 1 or level 2, which means either box 1 or box 2. You can think of that way also.

So typically when we talk about levels people think about energy levels that keep on increasing. Here we are assuming that the energy levels are not like this. Typically

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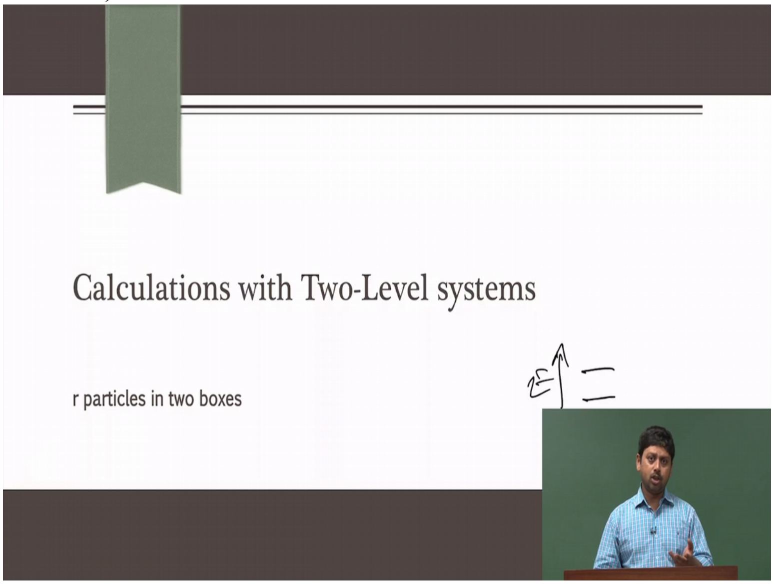

that is the representation of two-level system where energy increases. We will come back to that.

And that is also very, very important and you can, you can look at the Introduction to Molecular Thermodynamics course in NPTEL by Srabani Taraphder who has given several examples using this Two Level systems and the practical applications in a spin systems and other things. It will be, you know, it is elaborate and very clear. So you can look at that.

However here we are just assuming that the energy levels are same. So it does not matter. Energy does not matter right now. Only thing is that the particle has to be, particle can be either of these 2 levels.

And we can either

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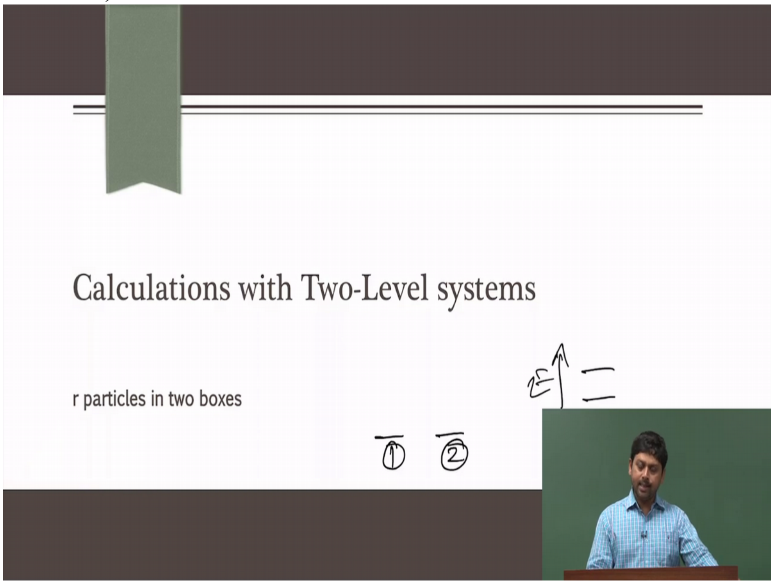

take the boxes to be distinguishable or not. And that will give rise to different statistics but for the time being let us just take them to be distinguishable. So there are 2 boxes 1 and 2, and there are r particles which has to be distributed.

How, what we are going to get out of that? Once you understand that we are going to more complex systems.

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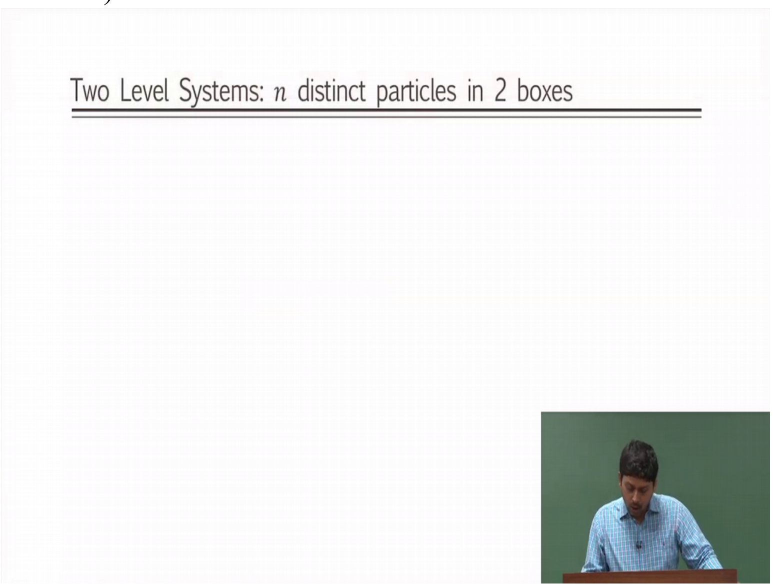

So r, so I have take n fine, so I have taken n distinct particles in 2 boxes.

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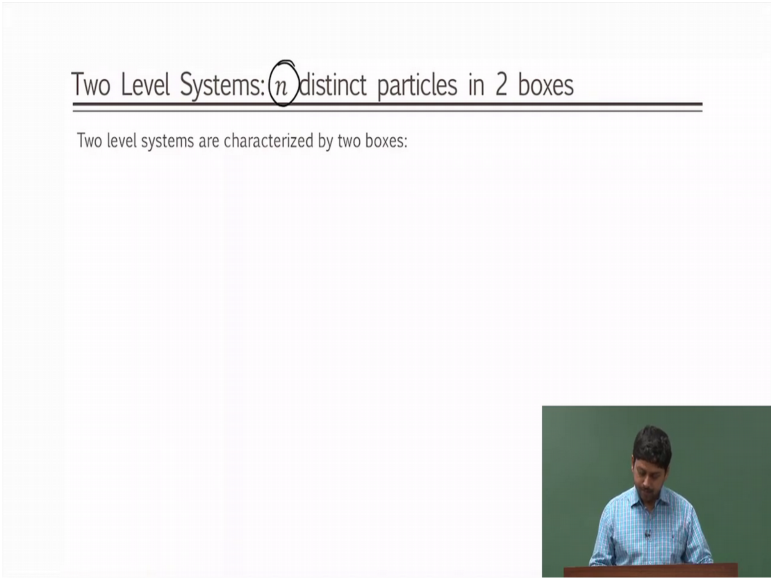

So

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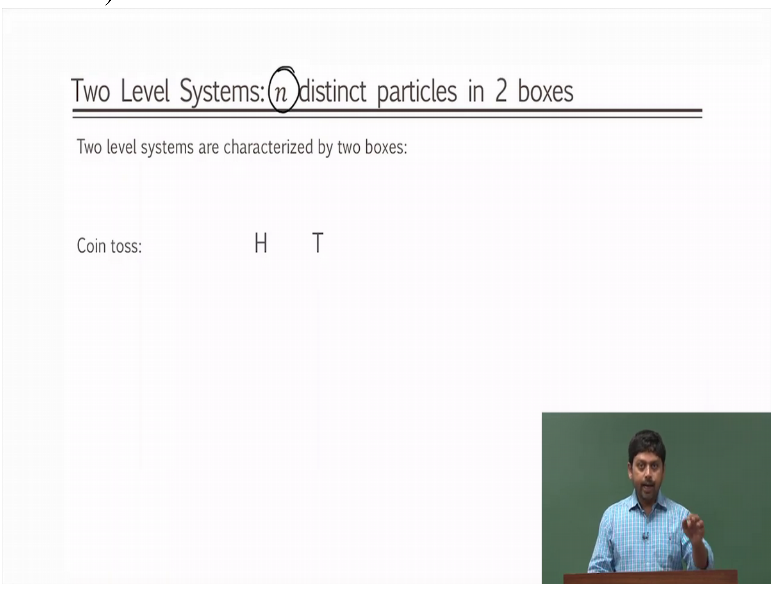

as I said again r balls in n boxes can be also characterized by many different ways so when I am talking about 2 boxes, n equal to 2 essentially what it means is that it has either head or tail, right.

And r particles will mean the number of coin tosses that are (()) (02:18). Or let us say spins,

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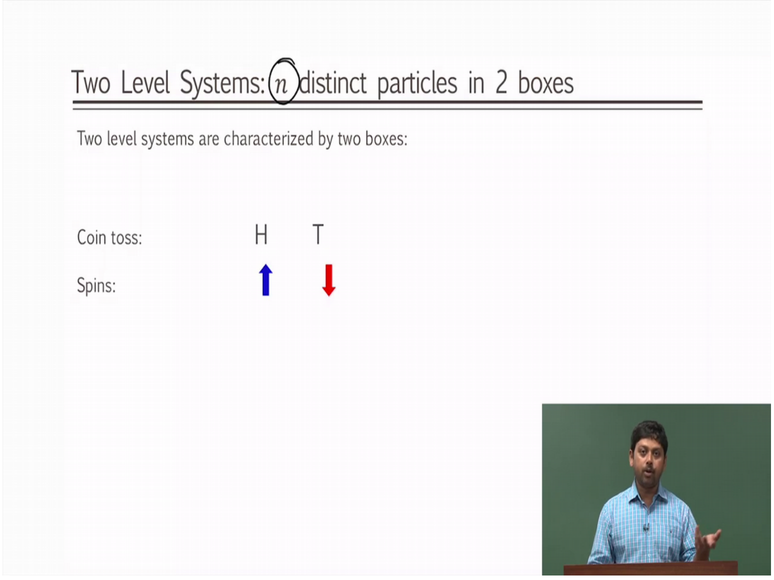

either up or down. I can take one, first spin, it can be up or down. I can take second spin; it can be up or down, third one, up or down.

So that means the number of spins is like number of balls and up and down is like boxes. If it is up, it is box number 1, down, box number 2 as I said before.

Now possible microstates of 6 such particles

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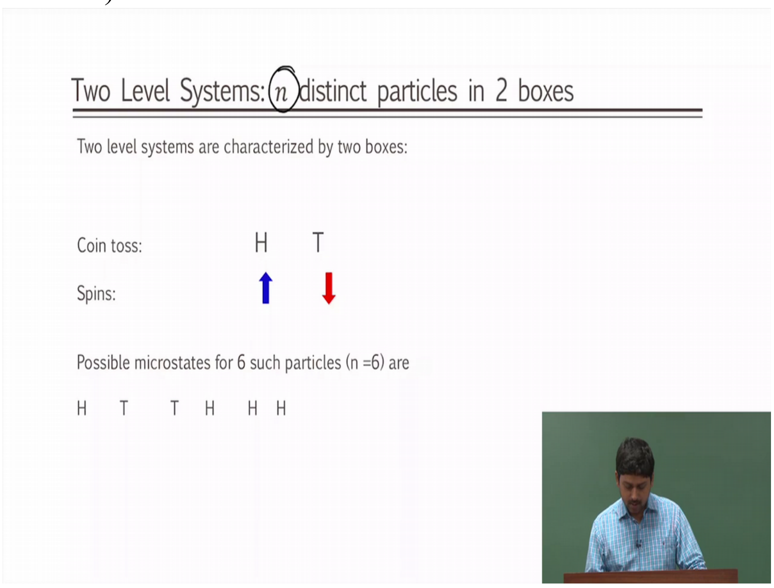

is this configuration H T T H H H, let us say one possible configuration. How many possibilities we will get?

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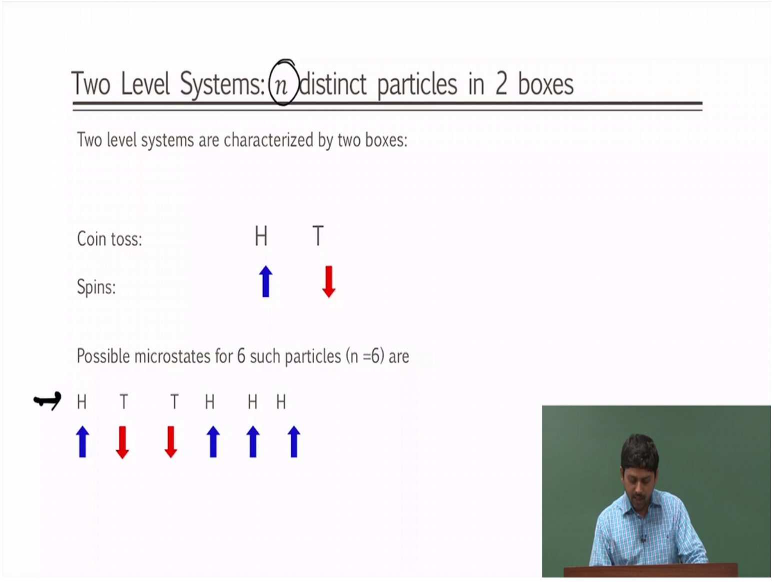

We will get, correspondingly let us say spin is also like up down down up up up. Now let us take a two-level system for n distinguishable particles,

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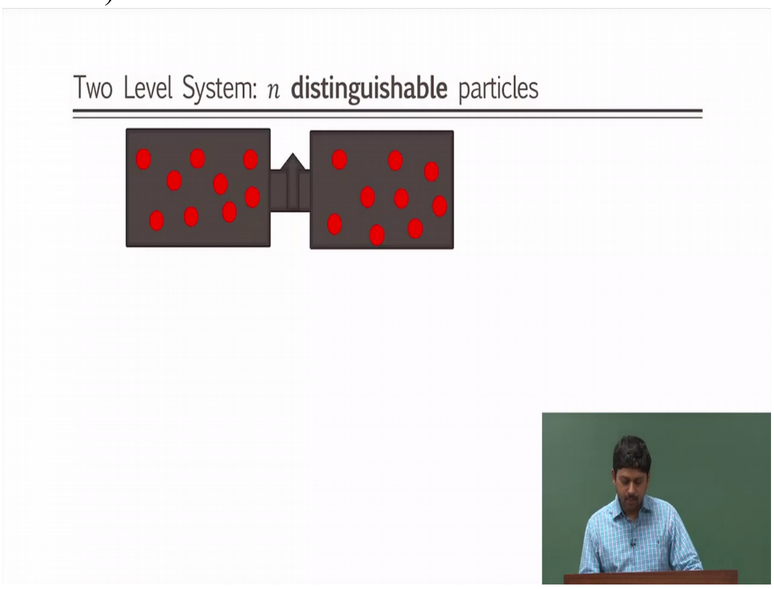

which means essentially that I have 2 boxes, 2 chambers this and this and you know these are the two levels that I talked about.

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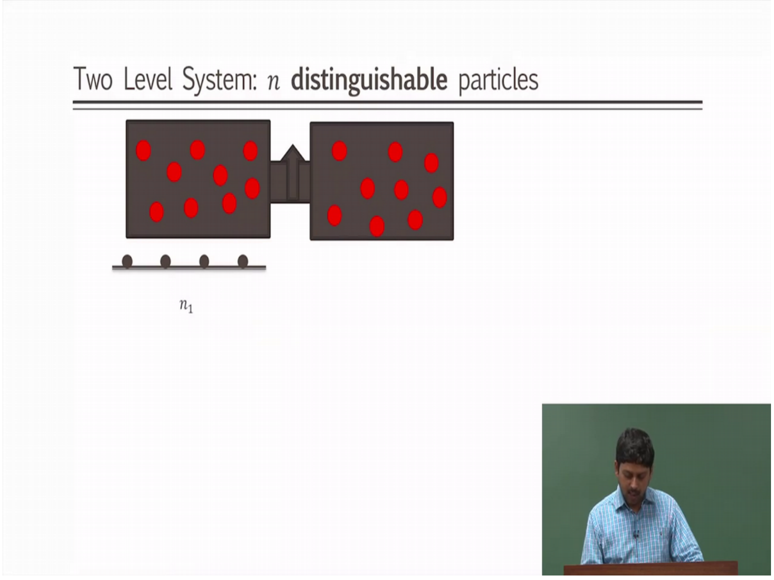

In one level I have n 1 particles. Another level

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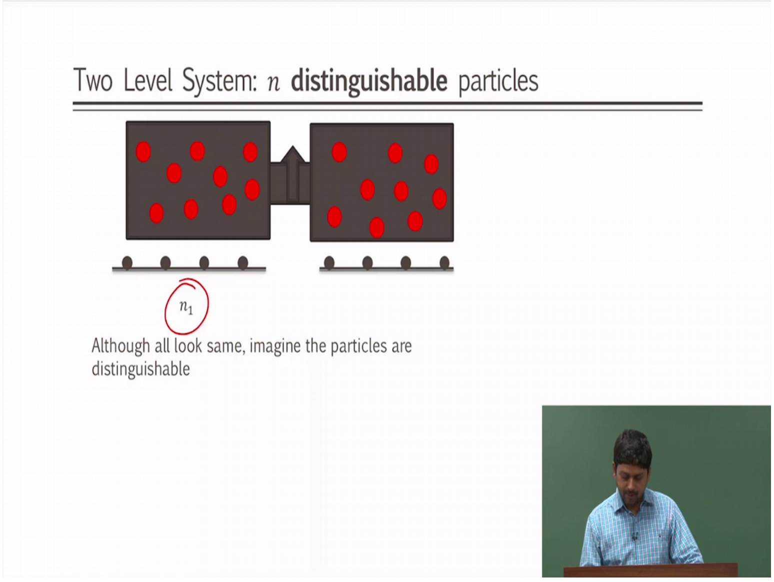

I have n minus n 1 particles.

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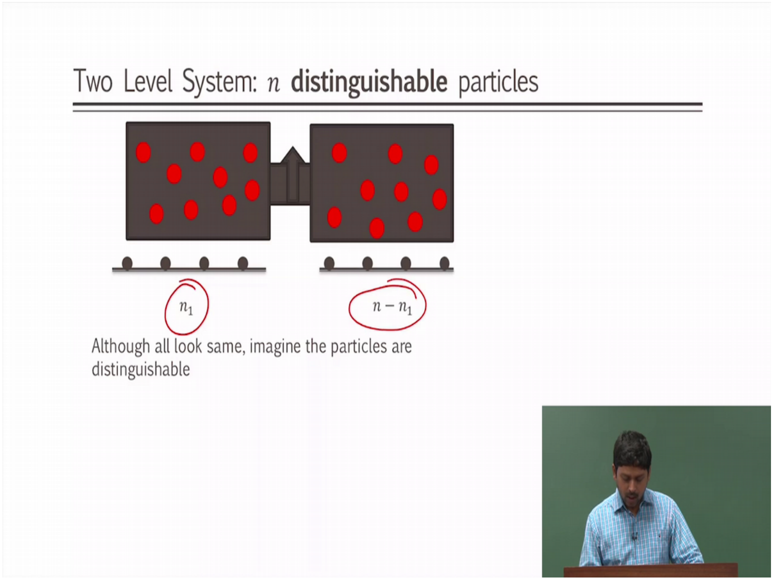

Although all the particles look same, imagine that the particles are distinguishable. Because remember what I said. That it is, it may be our inability to distinguish the particles. However statistics will come according to the distinguishability.

So let us assume that all these particles are distinguishable. And whatever the situation may be, n 1 can be anything, n minus n 1 can be the other thing, right? So whatever may be the situation, let us put some particle in 1 box and some other particle in another box.

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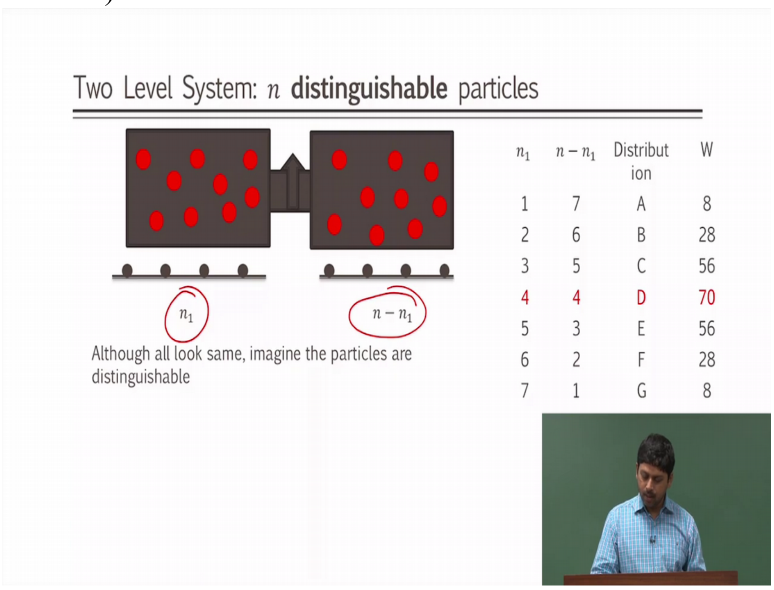

How many possible ways you can do that? I can put 1 particle in box 1; therefore 7 particles will be in box 2. Let us call that distribution A.

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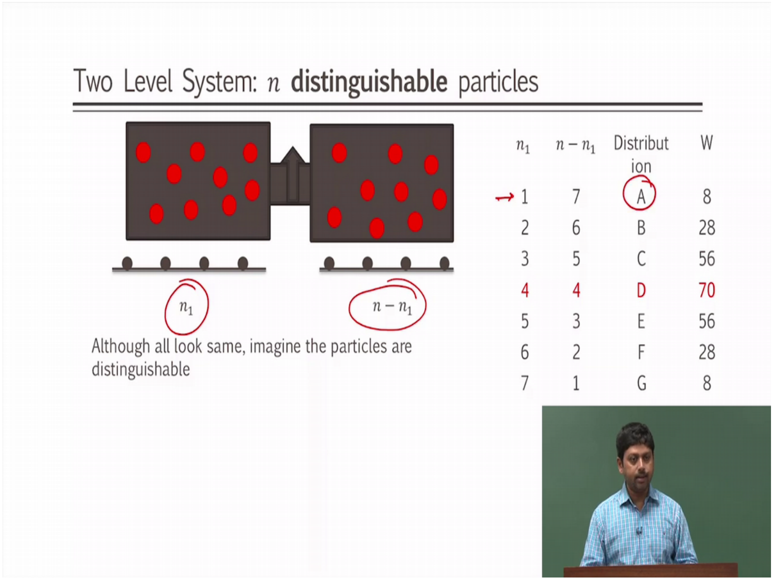

That is one way of distributing n particles.

I can have 2 particles in box 1 and 6 particles in box 2. That is another way

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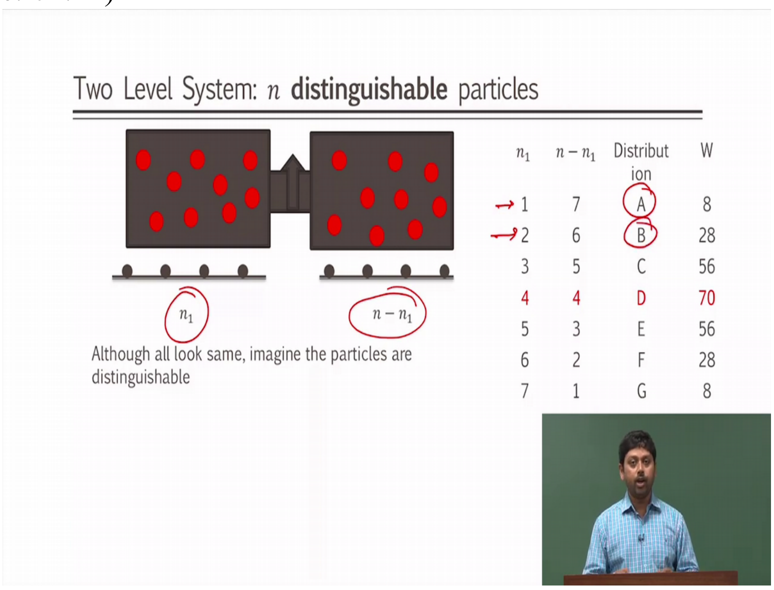

of distributing. Let us call that distribution B. I can have 3 particles in box 1, 5 particles in box 2, distribution

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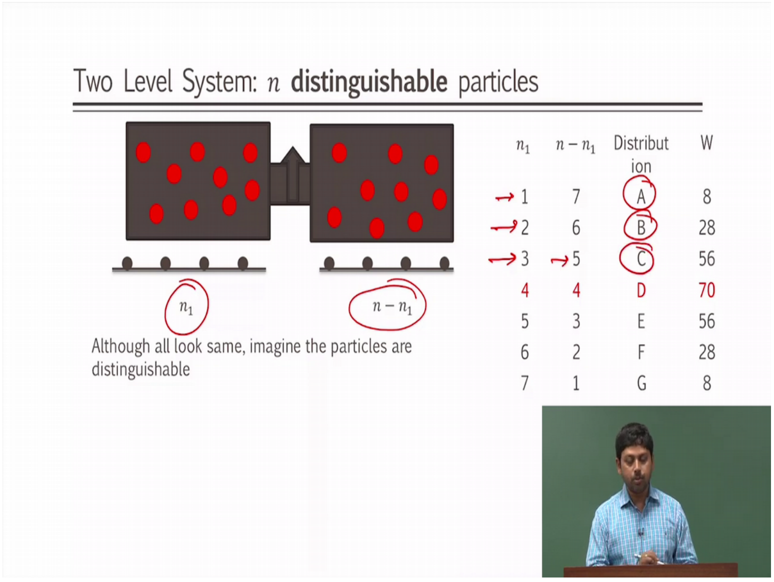

C; 4 particles in box 1, 4 particles in part 2,

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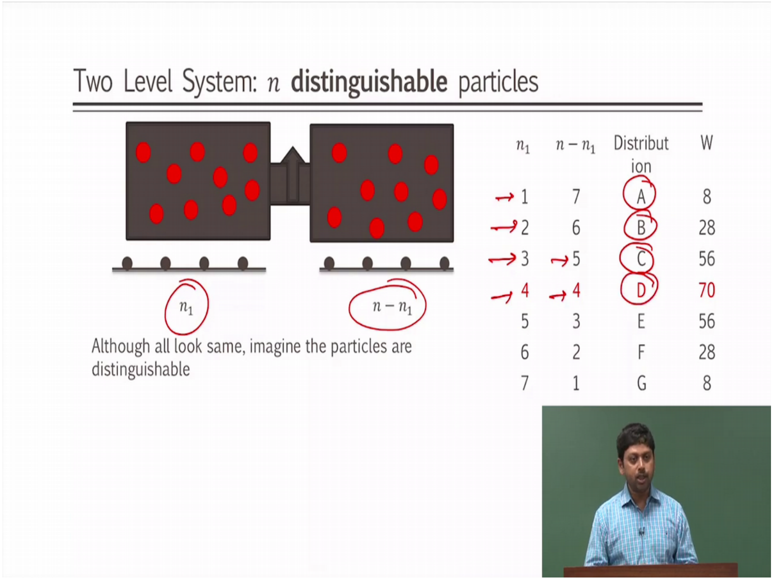

distribution D.

Now if boxes are distinguishable then I can have 5 3 which is same as 3 5 here. 5 3 and 3 5 are same if

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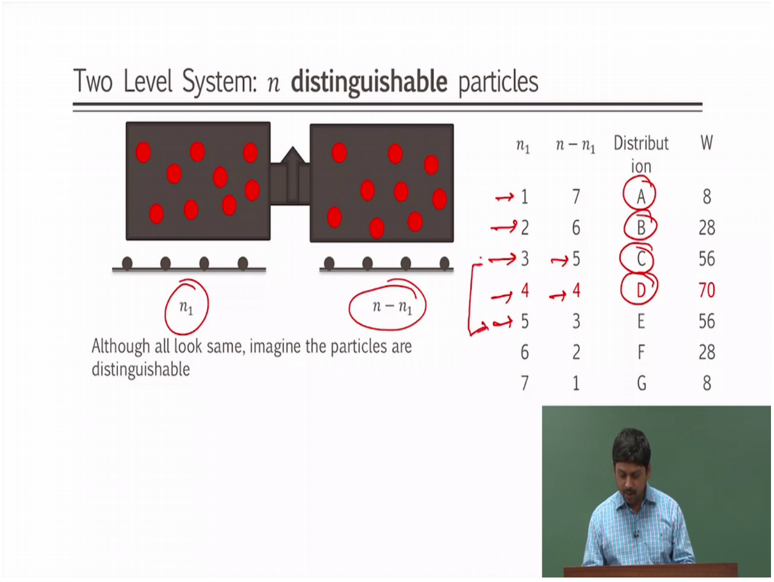

the boxes are indistinguishable but they are different if boxes are distinguishable.

But here let us take boxes distinguishable. So we came back to our initial situation where box and balls both are distinguishable. What statistics do we get? n to the power r.

But when you came to combination and said that no, I am choosing the particles and putting in the box and in that box they are indistinguishable, we got a combination. So it is like I have n distinguishable particles and I am choosing n 1 out of that and putting in one box. Then rest will automatically go to the second box.

So then it becomes n C n 1 kind of a problem.

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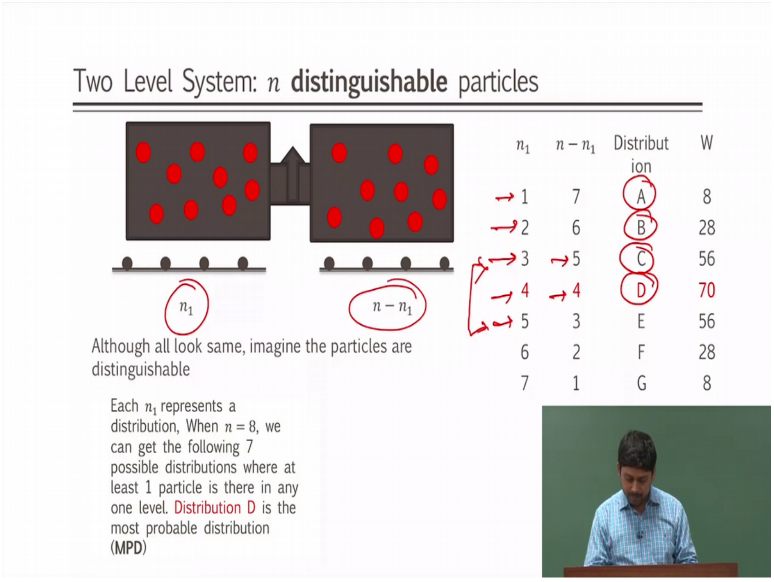

So here each n 1 represents a distribution as I said and when n equal to 8 we can get following 7 possible distributions that I mentioned. Each one is a distribution, meaning just like our cards, these 4 cards we were distributing in 2 hands. Similarly I have 4

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particles. I am distributing in 2 boxes.

Just like that. 4 particles were indistinguishable, sorry 4 particles were distinguishable. But when I distribute them in 1 hand, they are

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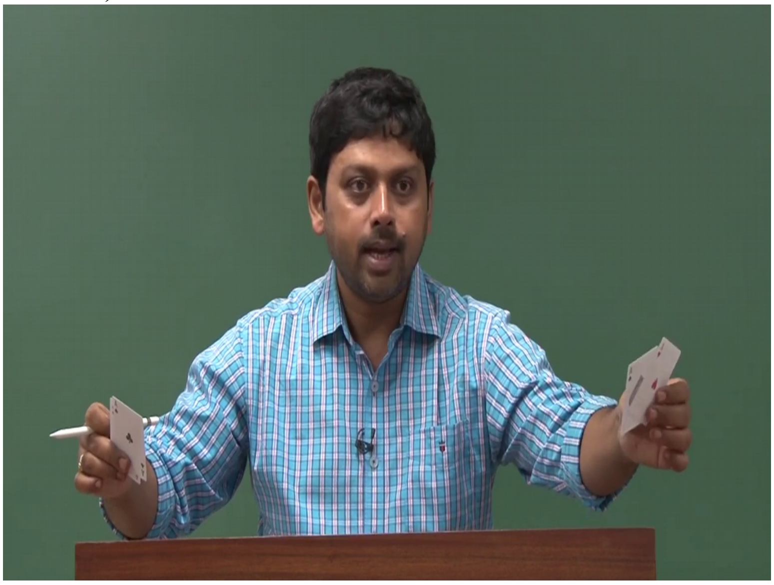

indistinguishable in this hand, this particle.

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So, so it does not matter whether this card came first or this card came first.

Like you know you just look at

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the top part once I put in the box. Once I distribute it you just look the top part. Ok, so in that situation, I have to only choose these 2 out of the 4. So I choose

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just 2 out of the 4. How many ways I can do that? 4 C 2 ways, 4 choose 2.

And that is what is given here. That is my W.

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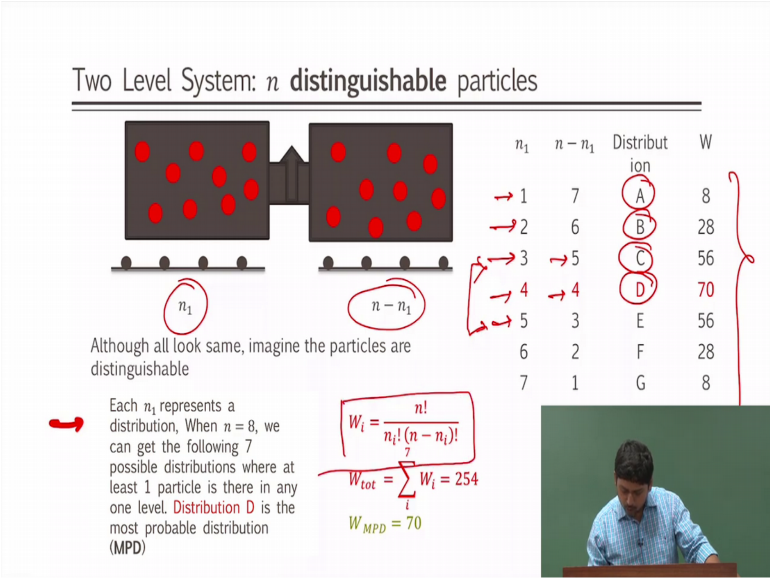

So n C n 1 is nothing but factorial n divided by n 1 factorial into n minus n 1 factorial by the formula

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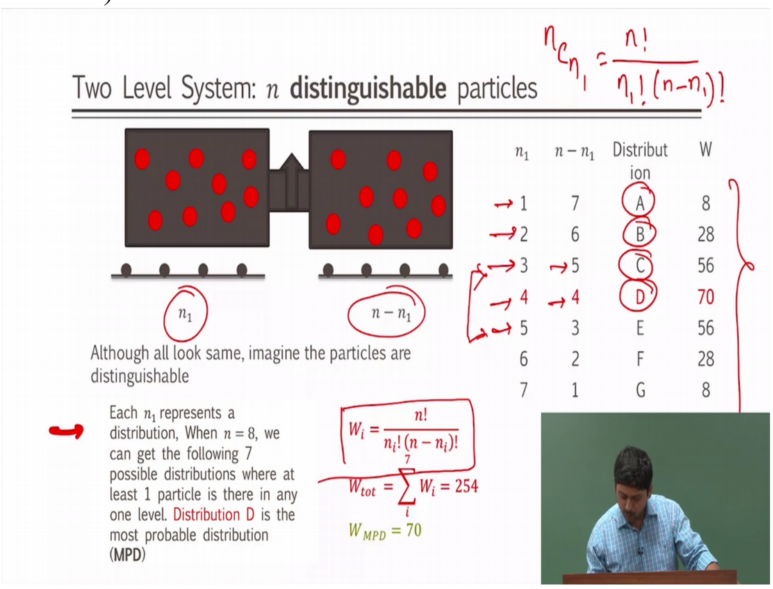

itself. So this is n choose n 1.

In this particular

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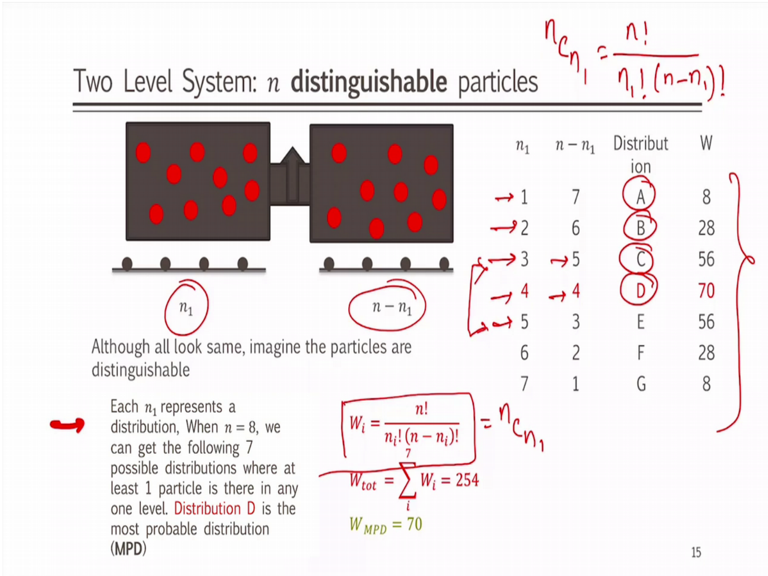

formula it is Ok for any number of particles. n 1 can, you know, be anything as long as it is not more than n. So therefore every distribution, so i denotes the distribution, so every distribution will have a W associated with it. And that W is written here.

So this W corresponds to choosing n 1 equal to 1 and rest of the particles will be the other side. Then this distribution corresponds to choosing 2 particle

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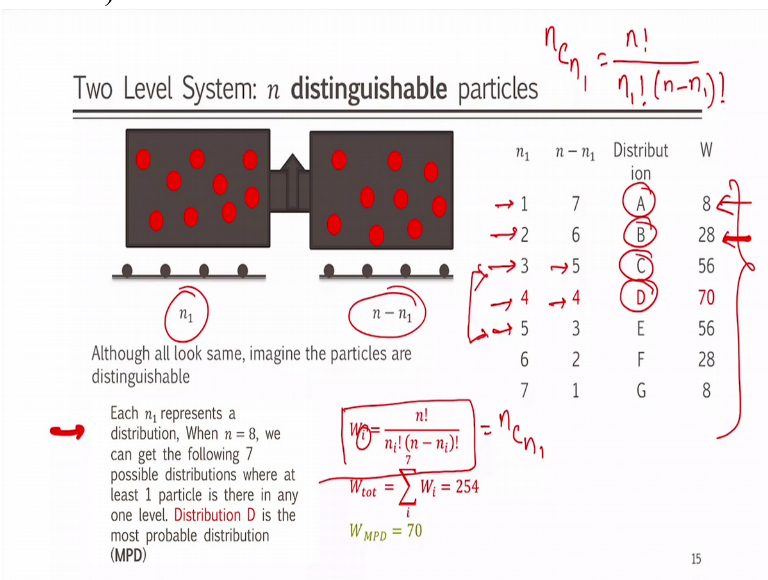

and keeping in 1 box, 6 will go to the other.

This particle, this distribution

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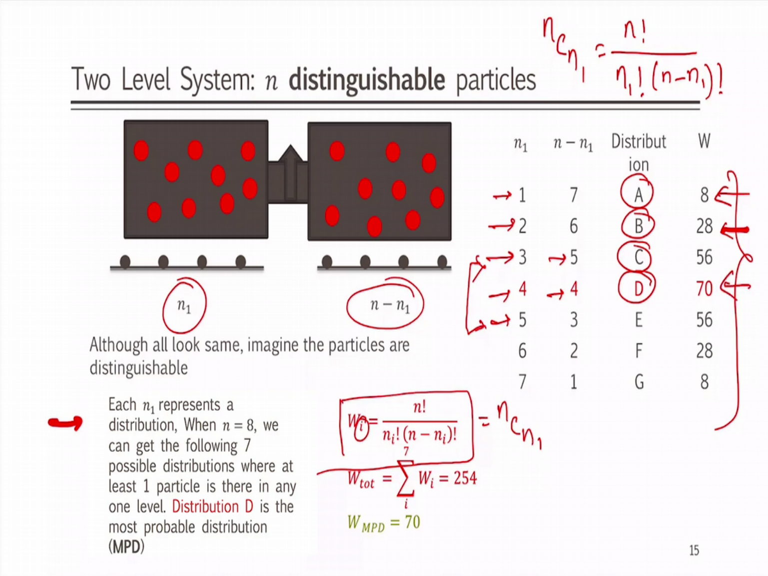

will say that Ok, choose 4 particle, put in a box and the 4 can go to the other box.

And it turns out that if you look at these numbers then distribution D in which you put half the particle, say out of 8 particle, half the particle in one box and half the particle in another box becomes maximum.

So that I can call as the most the most probable distribution. Why it is most probable? Because we can calculate the

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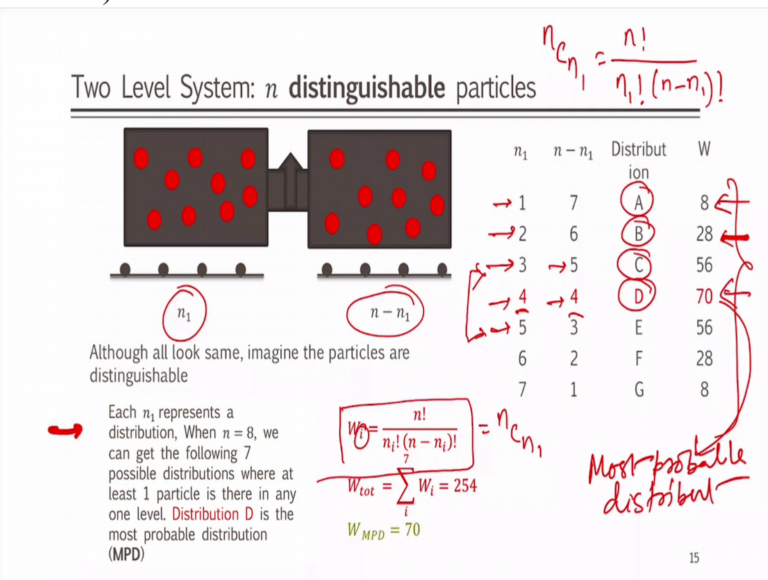

probabilities associated with each distribution.

What will be that probability? That probability will be, let us say I can calculate the probability of D. Probability of D will be 70 divided by the total number. So total number is 254.

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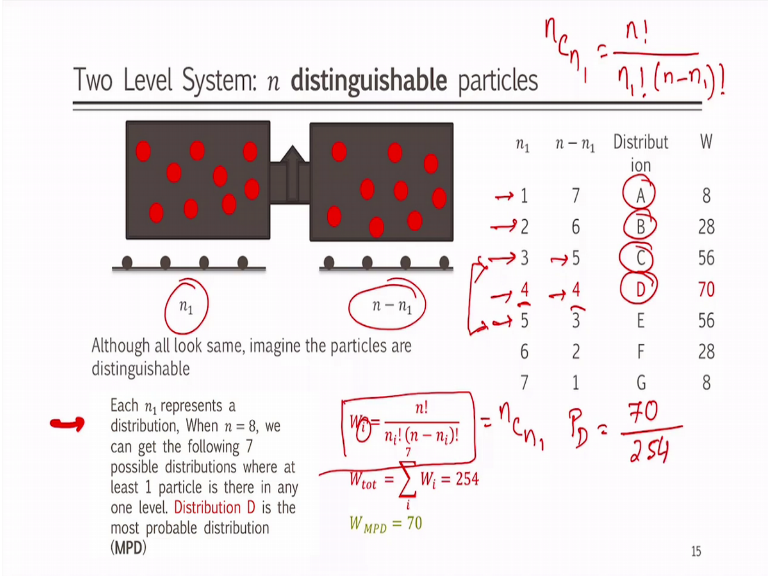

So that is the probability of D. What is the probability of A? It is just 8 by 254.

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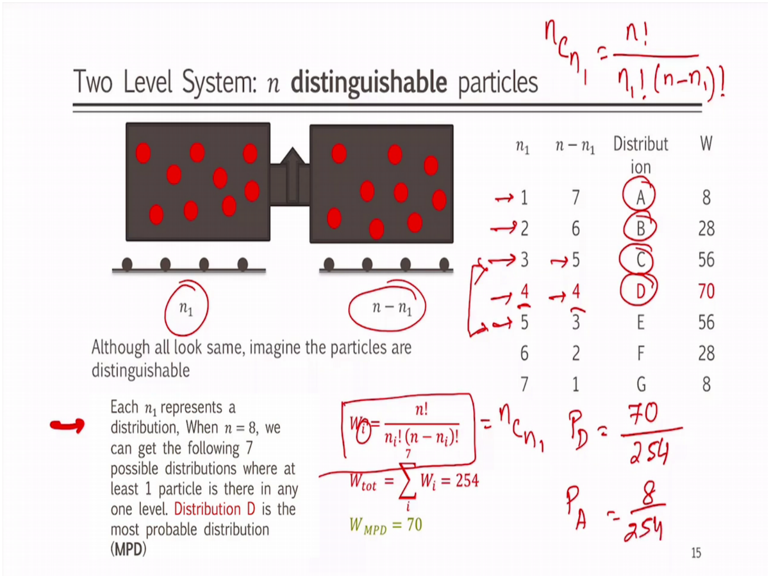

So therefore if you see probability D is most probable, sorry distribution D is most probable. That is why it is called most probable distribution where half the particle in one side, half the particle in the other side.

And you will see that it is so important that immediately it will explain physical phenomena that we observe all the time. And we have no way to explain without using these particular statistics or you know concept of probabilities or concept of microstates.

Again so when I am calculating, when I am talking about W, they are nothing but microstates. So this particular distribution has 70 microstates.

This particular distribution has 8 microstates. And automatically from that you know that entropy of D will be more than entropy of A or any other for that matter.

So such a wonderful thing the statistics is, and immediately can explain to us that why entropy will increase in certain situations. So here, as you can see, if we start with A, 1 particle on one side and 7 particle on other side, it will go towards D, which means that particle will diffuse to the other side.

And that is precisely the reason that when you have the insects in your room in one corner, it goes all over the room, and does not stay in just one corner, because going all over the room is most probable situation rather than staying in one corner. So just doing that will be, you know, enough to understand that.

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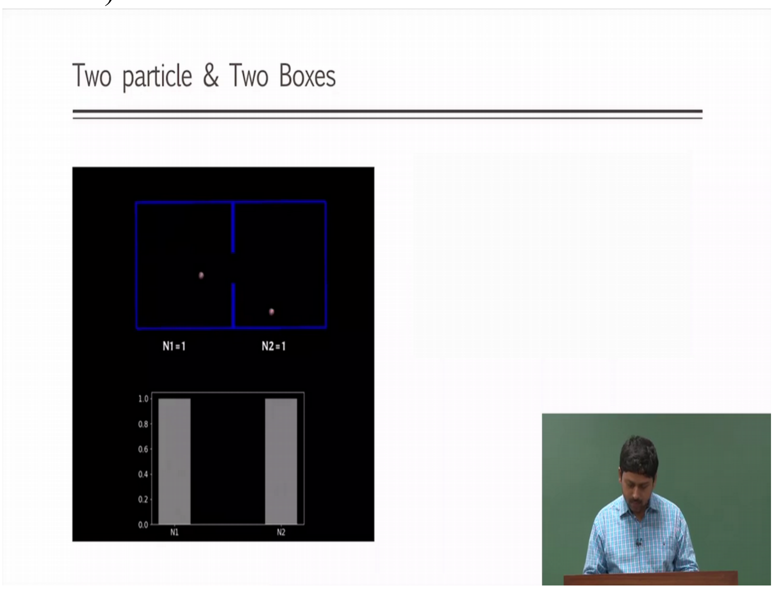

So we are going to show you example, direct example from simulations, computer simulations and show you that

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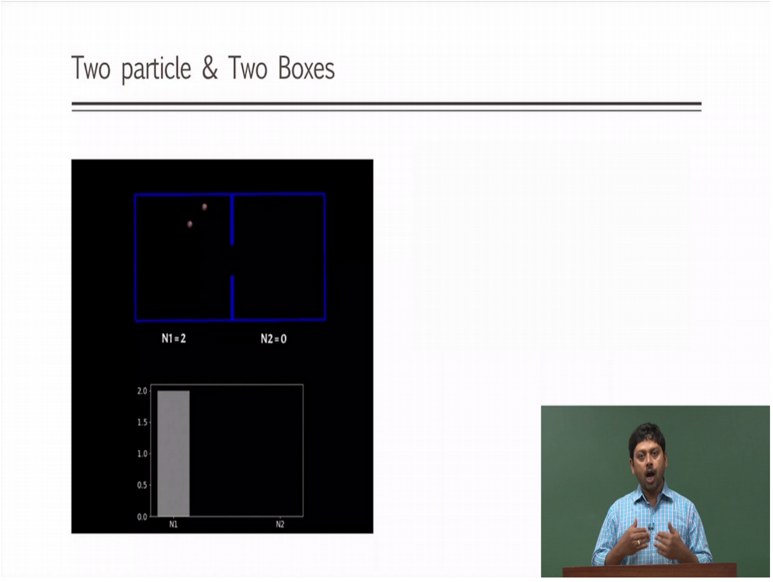

how

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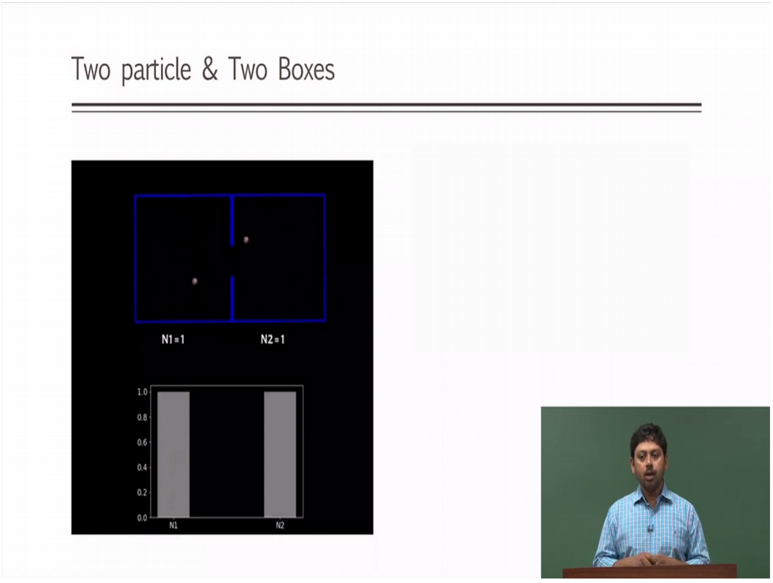

the effect of

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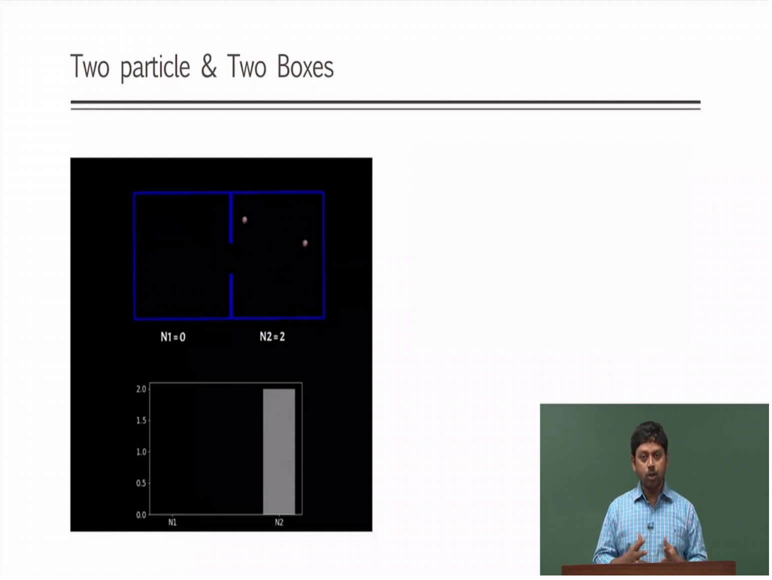

microstates or effect

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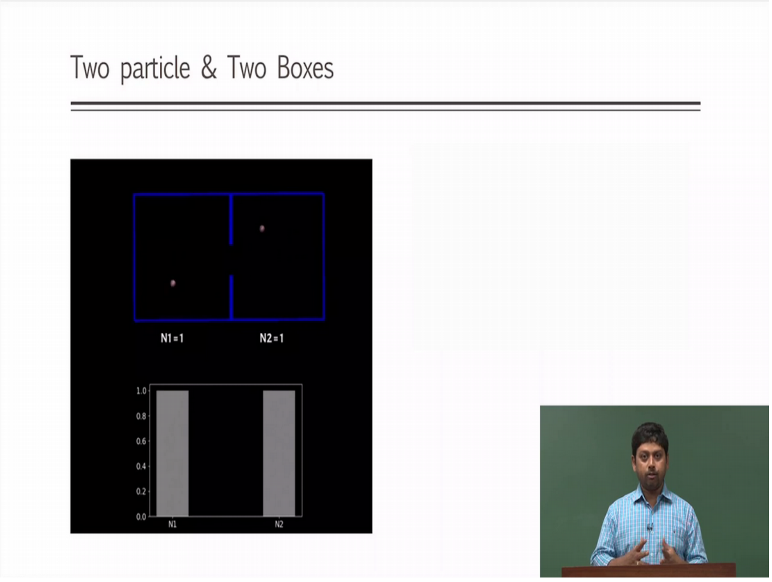

of entropy is, you know driving a change

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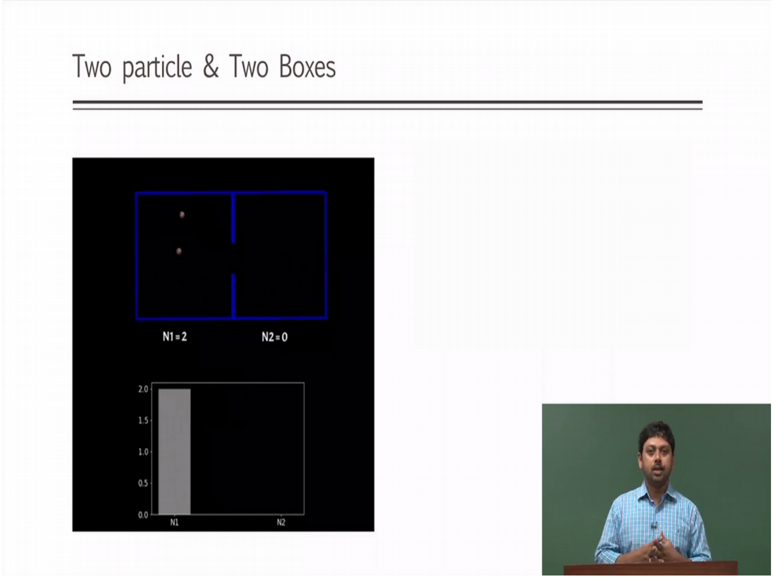

in a system in which a gas molecule expands from one side of the box to the other side.

So before I show you this example, I will just like to point out that this is a simulation. It is done by Raman Kumar Singh.

He is my P h D student and he has used the computer simulation technique to do that with some, some tricks, engineer's tricks to have the cover, the boxes and things like that and then along with my other student Abhijit has taken out the image and put it. So I will show you that.

So this is a zip file. So

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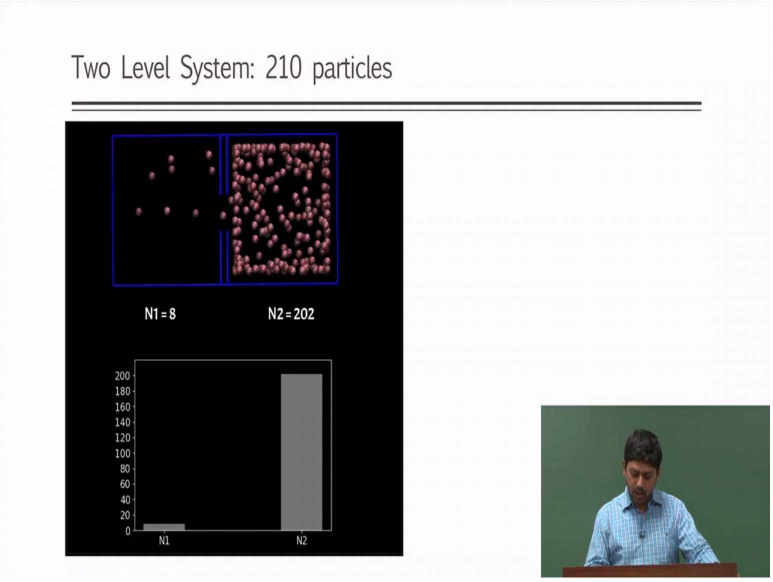

initially you see all the particles, so there are 210 particles. All the particles were on the one side, left hand side denoted by the height of the bar. And you see these particles do not interact with each other.

There is no concept of energy at all. Only thing is that

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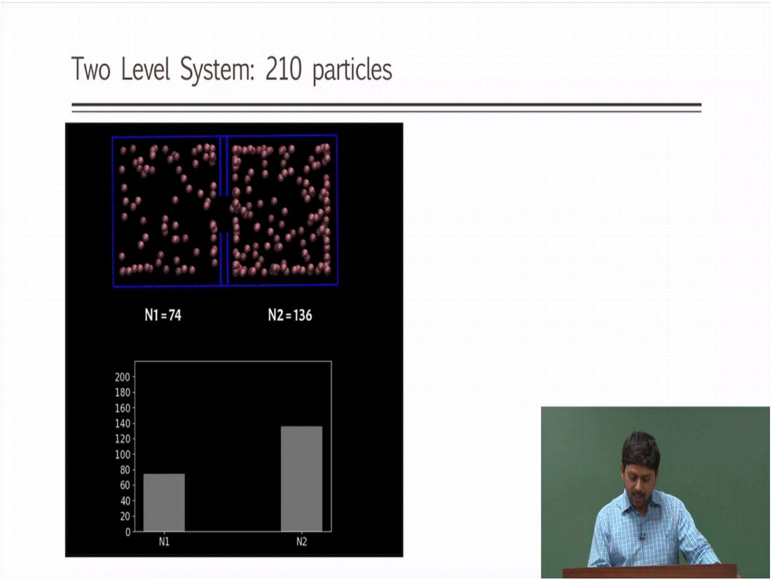

there are these boundaries which is denoted by this blue line. The particle cannot cross that boundary.

And there is a small hole here as you can see, only particle pass through that. So initially all the particles were on one side. The hole was closed and we took out the hole at t equal to 0 and then what happened is that the number of particles started changing. This number, you can see it from here and also it is represented by this bar diagram.

You see now that earlier 210 particles

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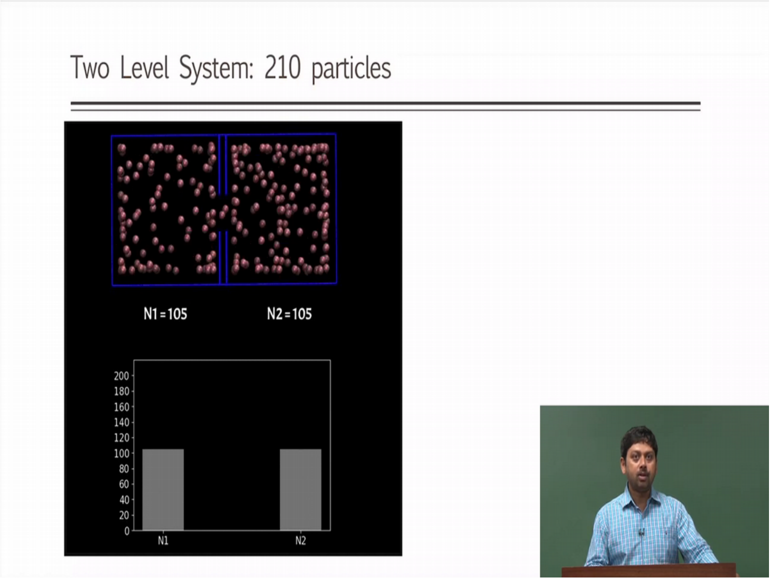

were on one side, there was nothing on the left box. Now these bar heights are almost equal.

You see that this situation is governed only by entropy. Because there is no attraction of this box on these particles at all. If at all there is no...And these particles do not interact with each other.

So there is no reason for this particle other than entropy, increase in entropy to come to this side, so which clearly indicates that when we take N 1 as 105 the entropy or the number of possibilities become more and therefore the entropy is more.

And here you cannot distinguish the particles but these classical trajectories are distinguishable by, by the fact that we can track them from their initial position and momentum.

And that is the reason that they are inherently distinguishable giving rise to the situation. If they were truly indistinguishable then we would not get that statistics that we are getting from this particular simulation. So let us do some

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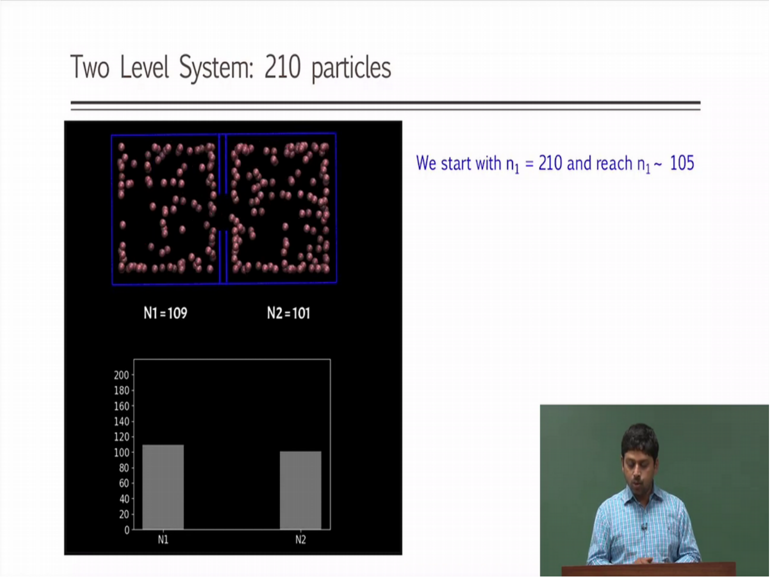

calculation. So here it is n equal to 210 and n 1 is 105.

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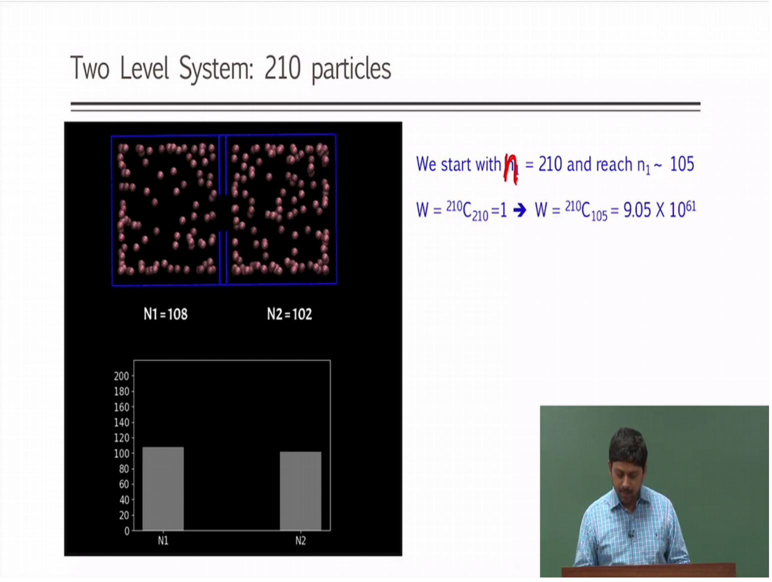

If we do that, all the particles were on side, it is n C n and that is only 1, you can see.

And when half the particle has gone to another side, then n 1 is 105 and that if you do is a big calculation, so W is 210 factorial divided by 105 factorial multiplied by 105 factorial. That is the calculation. And that gives

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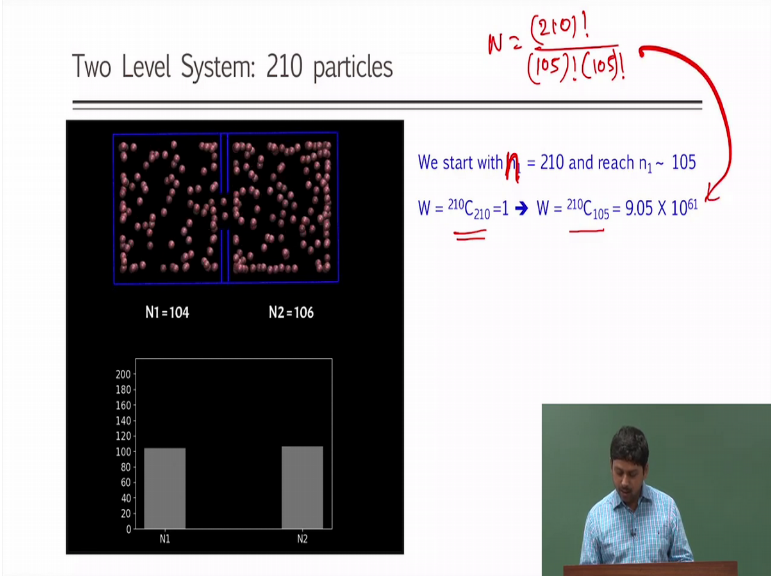

9 point 0 5 into 10 to the power 61, I will show you the calculation here itself.

So 210 C 105,

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you see 9 point 0 5 into 10 to the power 61, what did I write? Yeah. So that many possibilities it is going towards. Does it mean that there will be no systems where 104 particle in one box and 106 particle? Yes, that possibility is also, almost equally Ok.

For example if I do 104,

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that is also 61, If I do hundred and, we do 100 only. That is also

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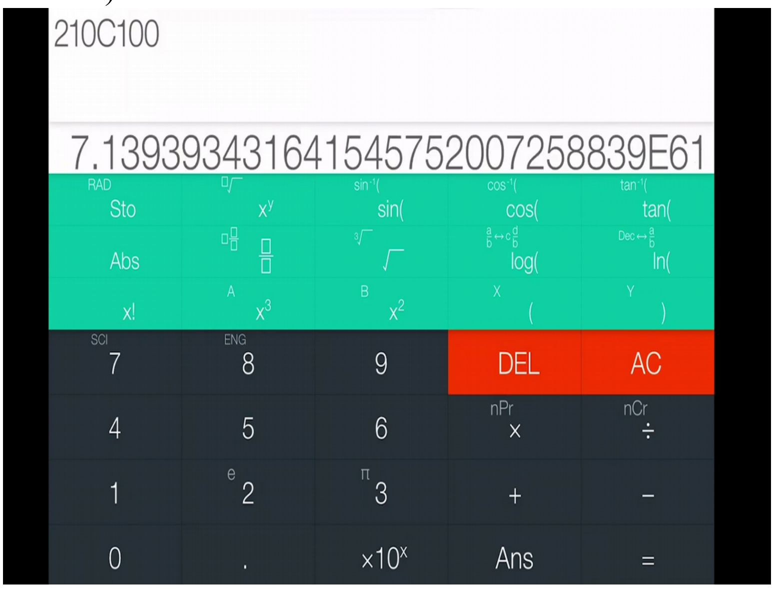

61. So deviation of 5 particles does not matter. Let us do deviation of 10. So let us do 115,

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61.

Let us do 10 percent deviation. So let us say 21.So 21 minus 105 will be, or 21 plus 105, the same thing is 122.

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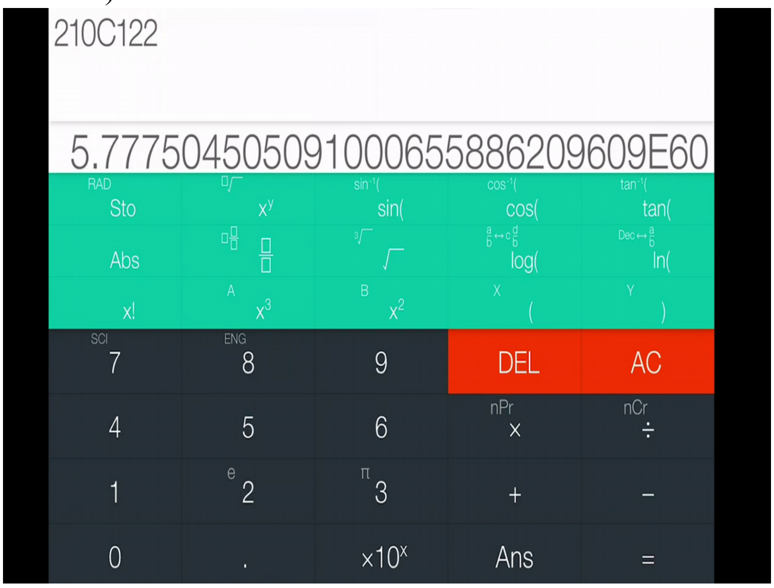

It becomes 60, 1 order less. And with 20 percent deviation let us say, or 25 percent deviation.

So what will be the 25 percent deviation of 105? You see, approximately 25 deviation or 30, so let us call 135. So I am saying that

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135 particle in 1 box and how many it will be, 65 plus 10 is 75, so 75 in the other box. It is 58, so 100 times less than that.

So like that you can see that the probability is that there will be deviations from this 50 50 will be lesser and lesser as, you know more deviation takes place.

Now,

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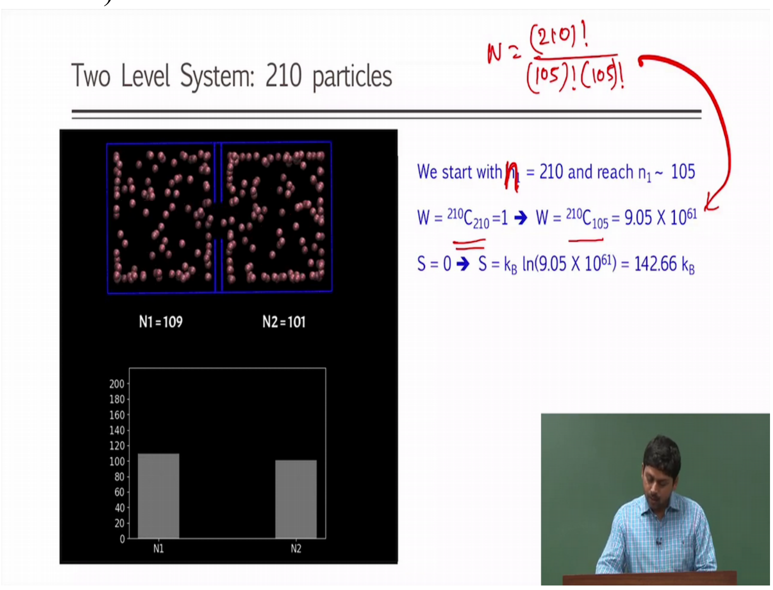

so it only means that initial entropy will be 0, because there is only one possibility, so l n 1 is 1. Because remember S is equal to k B l n W you already said. k B l n W, if W is 1, then S is 0 and then when it goes to the other side then it gives this much k B,

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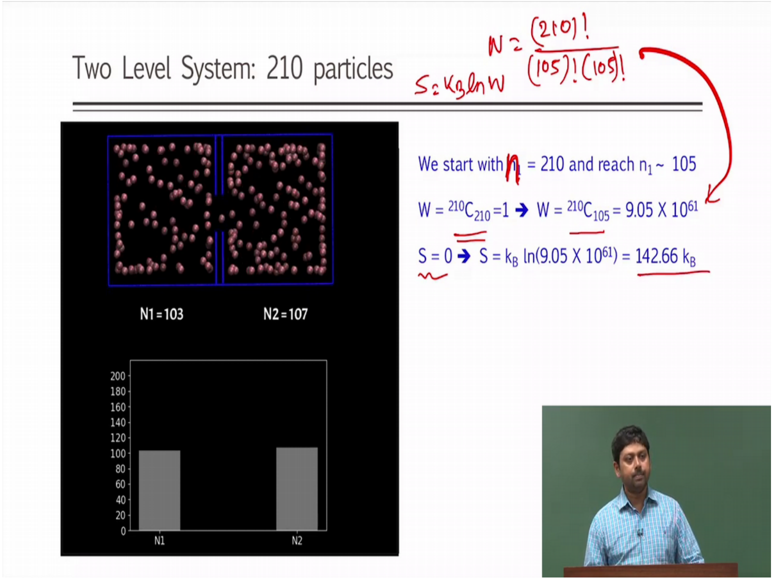

because it is k B l n, this quantity and gives that.

However I would just like to point out that this is not just 105 that will give

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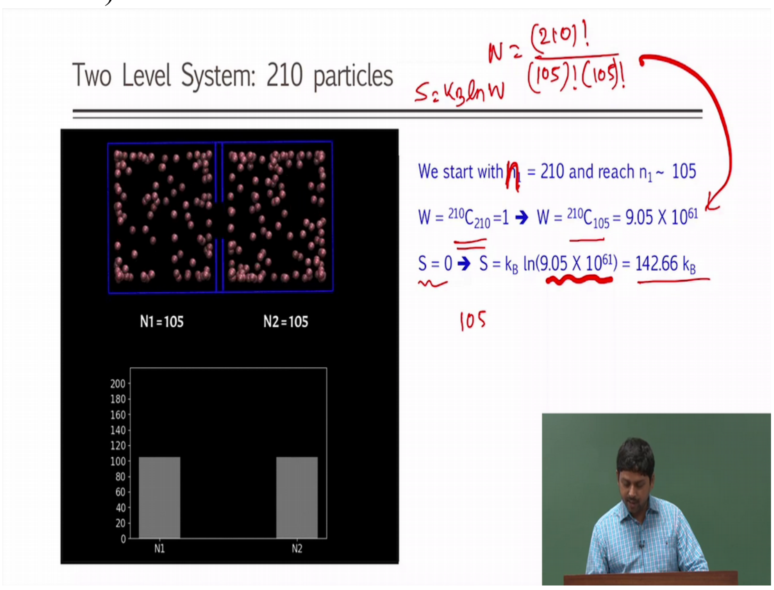

us this entropy. There will be fluctuations around that. And let us say there are 100 other configurations will give us and that will not change much.

Let us say I take 100 such configurations.

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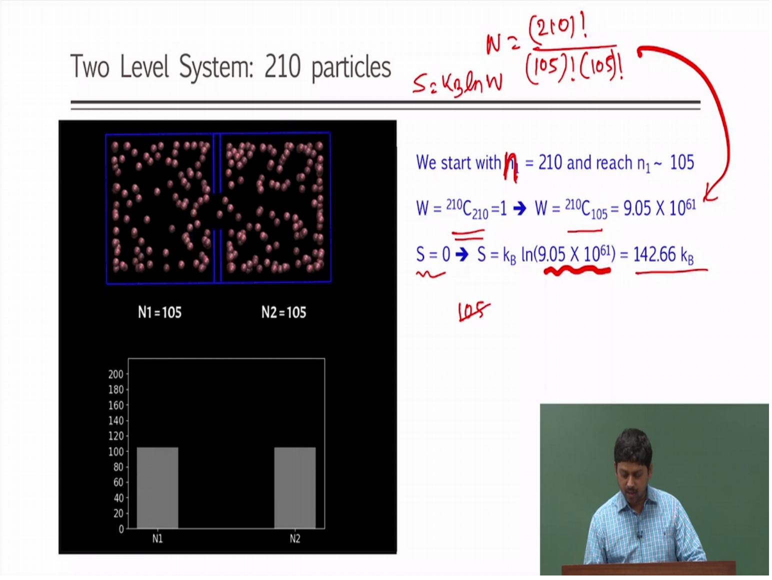

So it will be 100 multiplied by, so in that case it will be, like I consider 100 more configurations. So it will be 100 multiplied by, or m and taking approximately equal of that Ws

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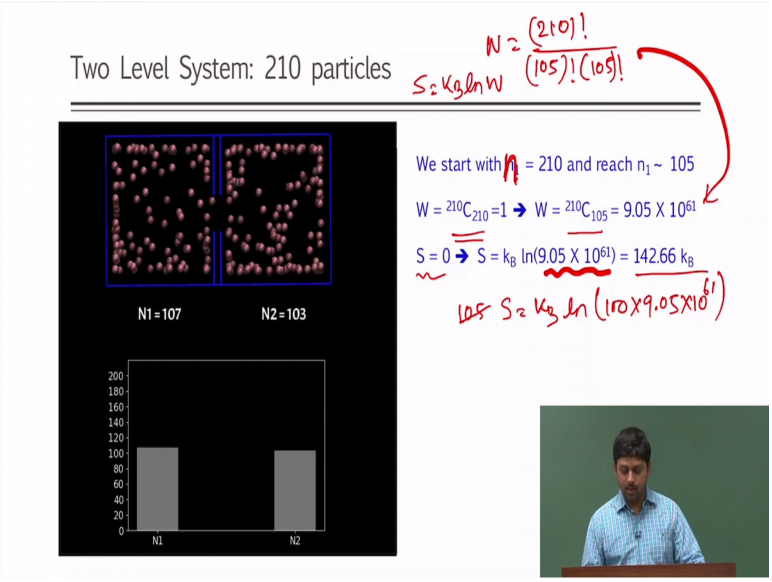

it is not going to change.

Even after we take 100 configurations along the midpoint. So that is the idea that, you know it is not going to really be different. So only one configurations in the middle is good enough.

Now what if we had only 2 particles?

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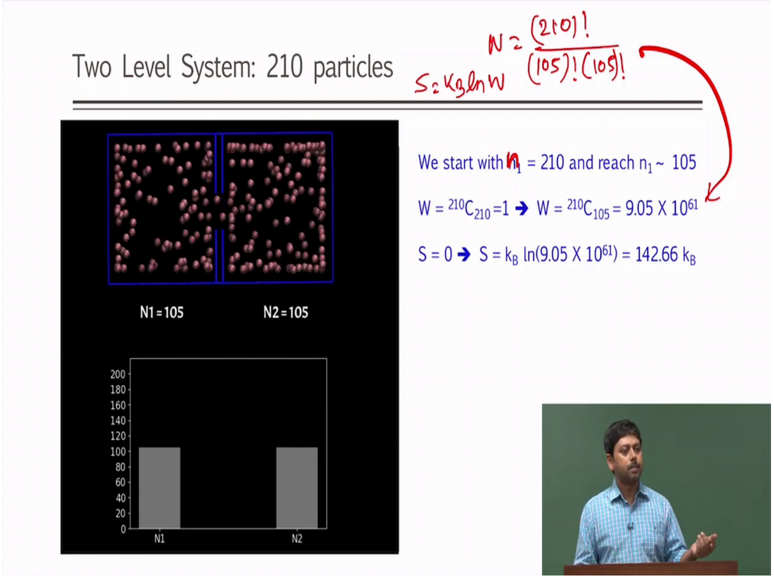

What if I had only 2 particles? Instead of 210 if I had 2 particles, could we see that 2 particles going as 1 and 1? Let us see that.

So here

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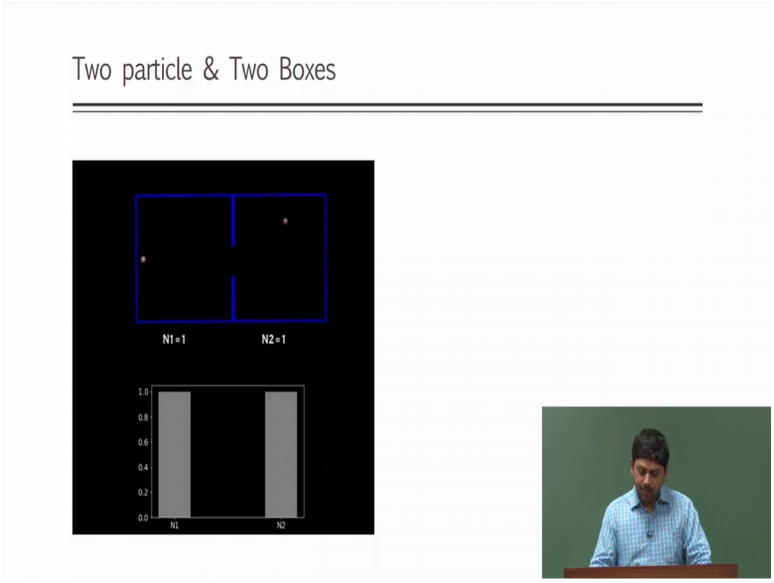

I have 2 particles here on the one side of the box, and as you can see from the bar chart, 1 and 1 is favorable and they are there but in certain cases; when I started with, I had this bar full and

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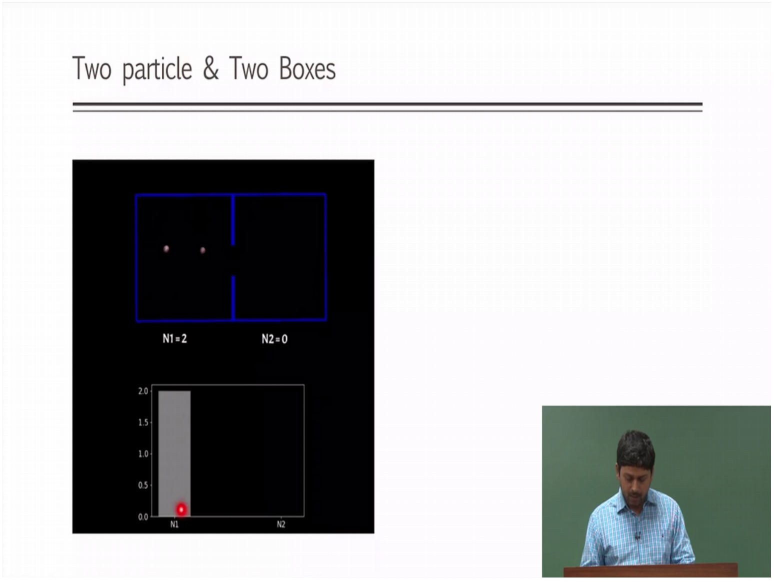

this bar was 0.

Now these 2 particles have come to the one side. So

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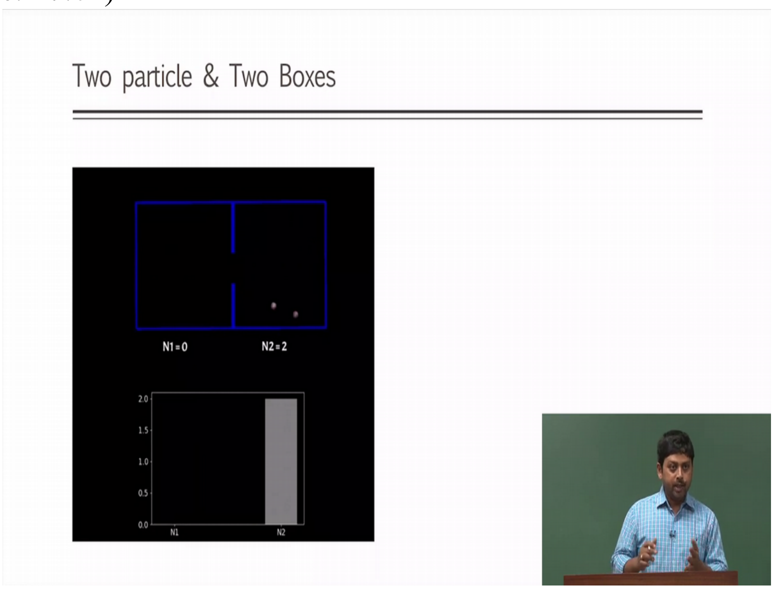

with 2 particles, I often get a situation where 1 box remains empty, another box remains full. With 210 particles I never encountered the situation in which 1 box went totally empty.

It was half half and it was fluctuating around half half. Here I have 2 particles; you can say we have only 2 particles. If the particle goes to the other side then it becomes empty, yes that is right. Also it is right that the probabilities of having 1 1 and probabilities of having 2 on one side, they are not very different with 2 particle.

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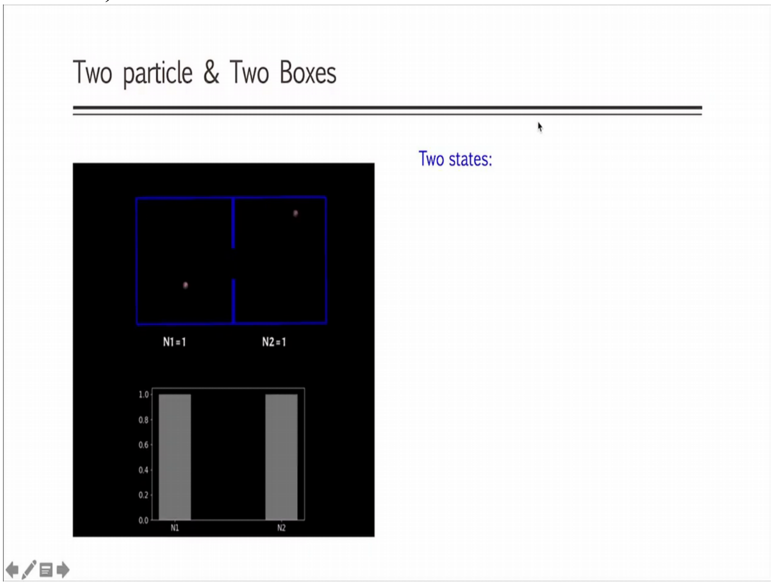

For example let us talk about this two-state system where there are 2 particles in 2 states.

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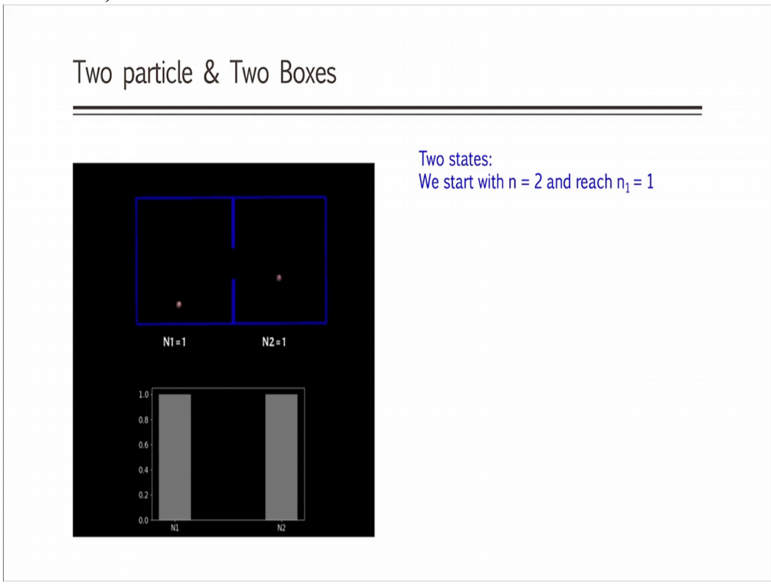

Now we can have 3 different situations where both the particles are on the left hand side of the box and no particle on the right hand side of the box. Or 1 particle in each of the sides of the box, or both the particles on the right hand side of the box.

Now

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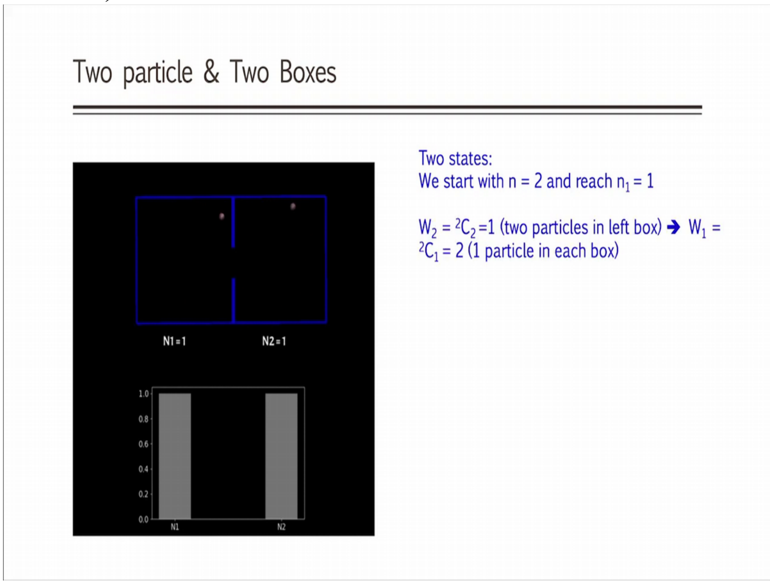

W 2 is the number of microstates when both the particles are on the left hand side of the box and that will be 1. W 1 is when both the particles, one particle in each box that will be the W level 2. And also

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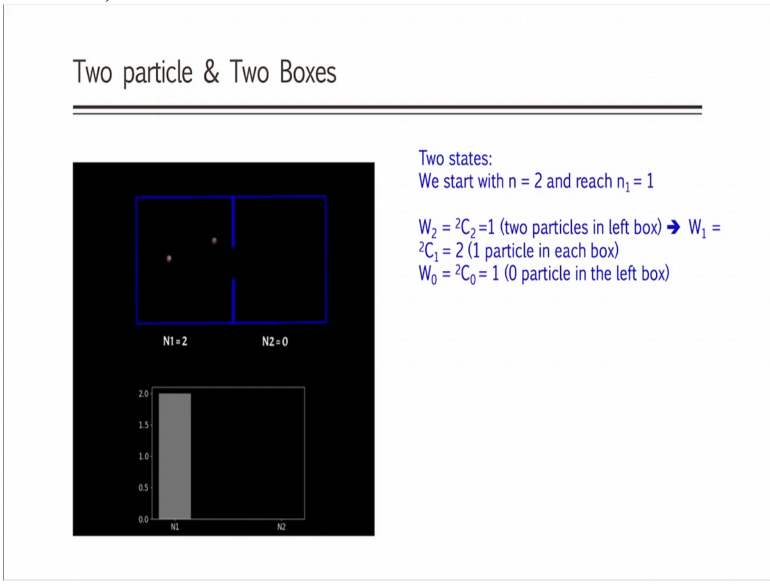

no particle on the left hand side of the box will be a situation where W will be equal to 1.

So if you

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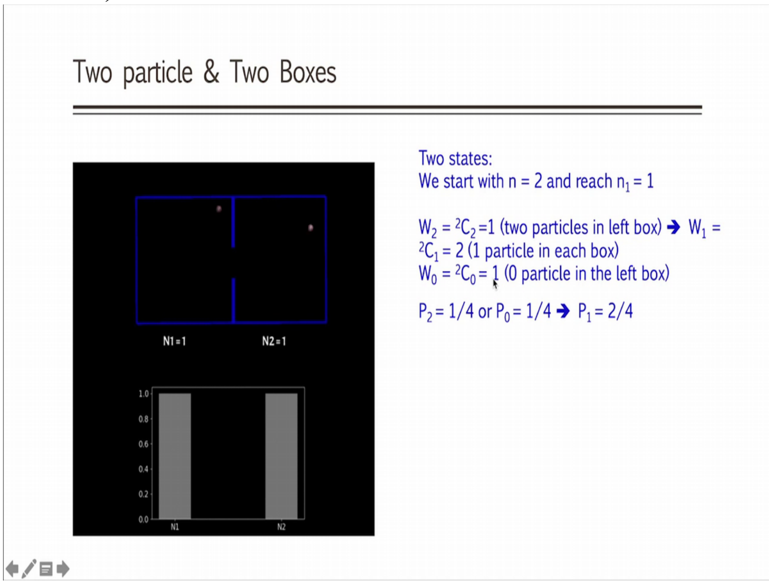

calculate the probability, that probability that both the particles will be on the left hand side of the box will be 1 by 4 and no particle on the left hand side of the box will be 1 by 4 and 1 particle in each side of the box will be 2 by 4 or half.

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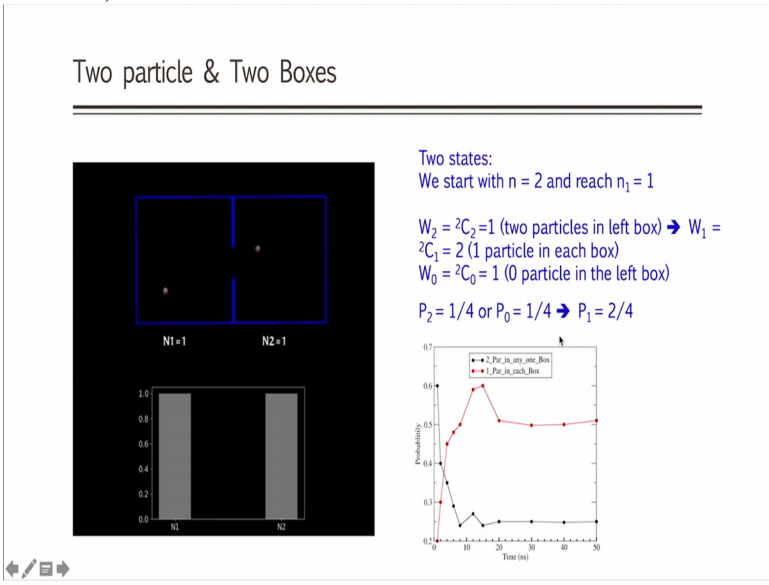

Now here the figure shows that if you put up the simulation long enough then eventually equilibrium or when it will reach the steady state then you will get point 5 or half probability for 1 particle in each box where as point 2 5 is the probability when you will find 2 particles are either on the left hand side or on the right hand side of the box.

Although the probability here is double when the two particles is on the both sides of the box is double than when both the particles are on the same side, however it is not

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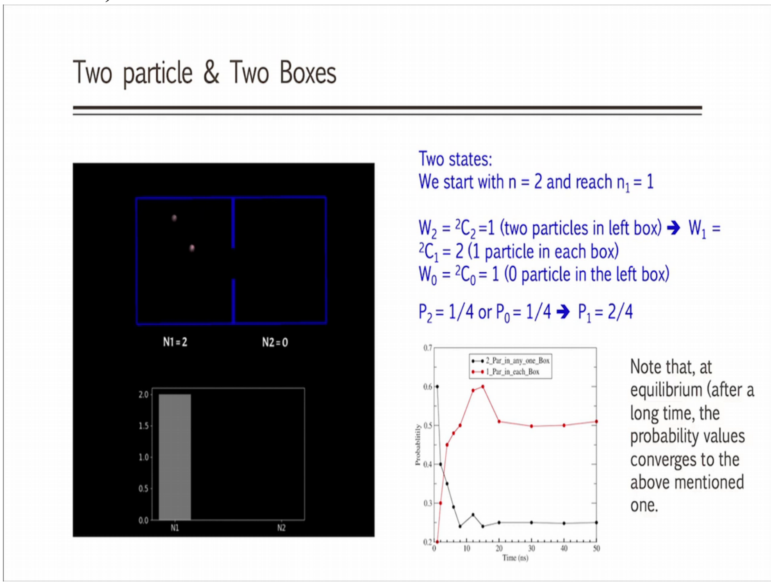

going to be very large compared to the one we see for a large number of system.

The probabilities were extremely large for half half compared to situations where there were nothing on the one side. So therefore as you can see, the number plays a very important role. So I am talking about one, 2 particle and 210 particle.

I have not gone to 10 to the power 23 particles. You imagine what will be the situation there. I will give you a glimpse of that in a moment.

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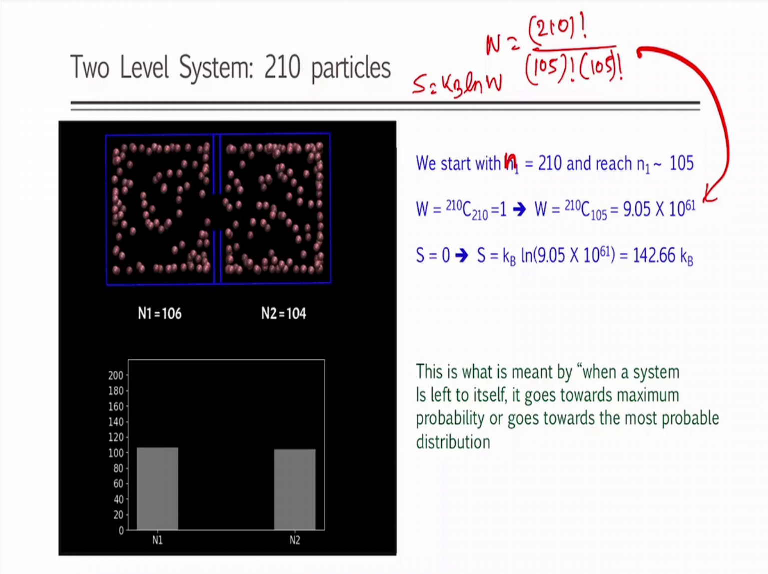

So this is what is meant by, when a system is left to itself it goes towards maximum probability. Or goes towards the most probable distribution. So we left the system with 1 particle in 1 box, it went to a situation where it is most probable.

That means filling both the boxes with more or less equal number. That is the most probable situation. So it went there, and that is what we call entropy.

So entropy then is nothing but just going towards most probable situation. It is as if it is destined to go. It is, the possibility is there and therefore it is going. There is no thoughtful choice is involved.

And that is why you know people say that life is nothing but a chance. Because there is a possibility, that, you know you go and avail that possibility without thinking.

I have possibility to go anywhere over in the campus. So I am just, you know aimlessly roaming around and being found at all the different places; if I did not have, if I had confined in a room the possibilities will be limited only to the room.

So therefore entropy is not just confined to the problems of science or chemistry. It can be associated with anything that you can think of because it is, at the end nothing but the number of possibilities.