Chemical Principles II
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Calculation with Multi-Level systems

We have discussed in the last few classes about the two-level system and distribution of particles in two-level systems. Today we are going to focus on distributions of particles in multilevel systems and later on we will also put some constraints in the total energy of the system as well. So remember till now we did not discuss anything about the energy.

We only discussed about the distribution of particles assuming that all the particles have same energy, so therefore energy was not coming into consideration at all. So we will see that how it comes into consideration.

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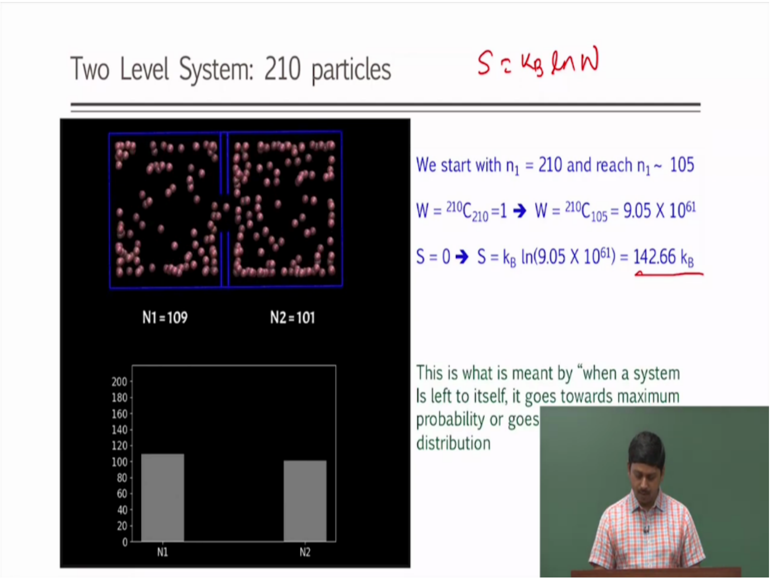

So before we do that I just want to show you again the movies that we have created or rather my student Ramon has created along with the help of Abhijeet another students where you can see that when we actually use, we have seen that, I have shown you that, when we use 2010 particle which is also not like huge not like 10 to the power 23 and all. You can clearly see that starting initially with 200 particles on one box how it actually went and.

So starting with NO 210 particle one box, how it actually went to almost (())(1:35) boxes. You see the reason is here, again that when they are all one side then it is 210C210 equal to 1 but when they are distributed equally then it is 210C105 which gives rise to 9.05 into 10 to the power 61 and when I convert into entropy value, as you know that entropy is kBlnw, so if W is one then ln1 is 0. So therefore it starts with the entropy 0 and then goes to kBln 9.05 into 10 to the power61 which gives rise to 142.66kB.

You know the kB is very small but when you are using (())(2:17) of particles the kB becomes R. So NAkB is nothing but R. So anyways, so this is significantly large number compared to what you get with just 2 particles. Now when you increase the particles more and more of course the entropy dependence will increase more and more and therefore it will be more probable for the particles to be distributed more or less equally rather than being on one side.

In fact being one side is an extreme situation. we have discussed that not being an one-side the deviation from half that means N by 2 N by 2 on both the sides, deviation from half itself significantly reduces when the number of particle increases.

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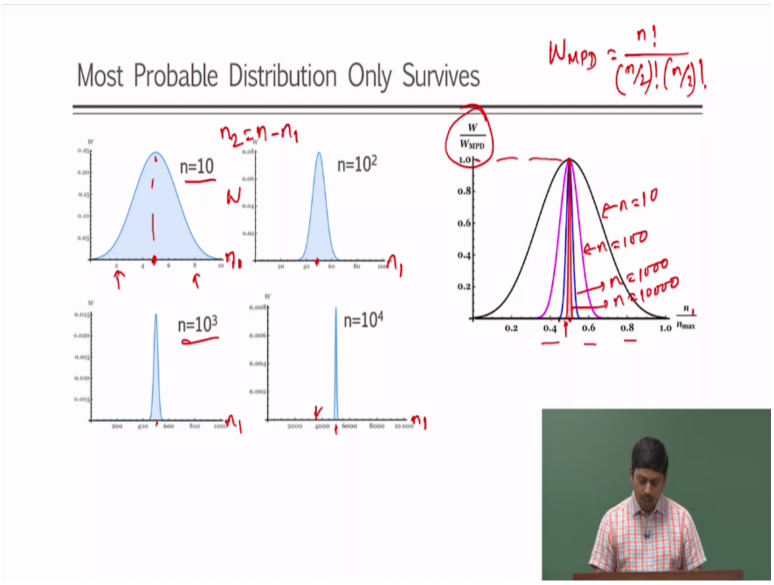

So and that is shown here, so see here that we are using 10 particles and we are plotting here the W and as you can see, as I discuss before that for a real number 5 the value is maximum, value of the W is maximum. However there are some W value is also there for particle number 2 and particle number 8 that means we are talking about the value in 1 box compared to total number.

So 10 is the total number and here what we have plotted is in one, so the value in one of the box. Correspondingly the n2 is already decided because n2 is n minus n1? So if it is 5, n1 is 5 then n2 is also 5 but if n1 is 2 then n2 is 8. If n1 is 8 n2 is 2. So whenever there is a deviation from half which is 5 in this case there is lesser value of W, okay. And you can see that here we have plotted again n1 and W.

And you see that the min the maximum is at n equal to, n1 equal to 50 because the total number is 100 and it falls quickly by 40 itself. So there is a deviation of 10with that it falls. Almost like the deviation of 5 here but we have to think about percentage deviation we will come back to that but you see that fall is faster. Now you go to thousand particle and you see that 500 is the maximum, thousand means n equal to thousand.

So n1 is 500 is maximum and within 400 that is falling off. So 500 to 400 is just hundred, hundred out of 5 and this is 20 percent. Now you see 10 to the power 4 and half is 5 10 to the power 4 is 10,000, so 5000 is where it is maximum and it is falling so it should be falling within just say just 200 itself. So this 4000 is this value, 5000 is this value.

I have one, 2, 3 points in between, so 300 each it is falling even less than 300, it is falling there, so it is a probability distribution or the number of W's that are provable away from the midpoint is decreasing very fast. So it is becoming sharper and sharper. It will be more clearly if we do a percentage deviation or fractional deviation then it will be understood.

So for example, here I am plotting W by W MPD meaning MPDs for the distribution when it is half half, so W MPD most probable distribution is n factorial by n by 2 factorial n by 2 factorial. So this is W MPD I'm dividing by W MPD, so as you can see when it is half or 0.5 n1 equal to half or 0.5 then it should be equal to 1 because W becomes W MPD, so that always is one.

However now I'm talking about fractional deviation. So this is for n equal to 10, this is for n equal to 100, the blue one is for 1000 and the red one is for 10,000. Just what you have seen the left-hand side of the graph. You see by the time it goes to 10,000 the deviation is almost 0.2.

So this is 0.5, and this is dropping towards 0 by this point itself, if this is 0.4 and this is 0.5, this point 4, 5, this point 4, 75, so within 0.48 from 0.5 which is 0.02, within 0.02 it is dropping. So 0.02 is nothing but 2percent, so within 2 percent deviation this is falling off.

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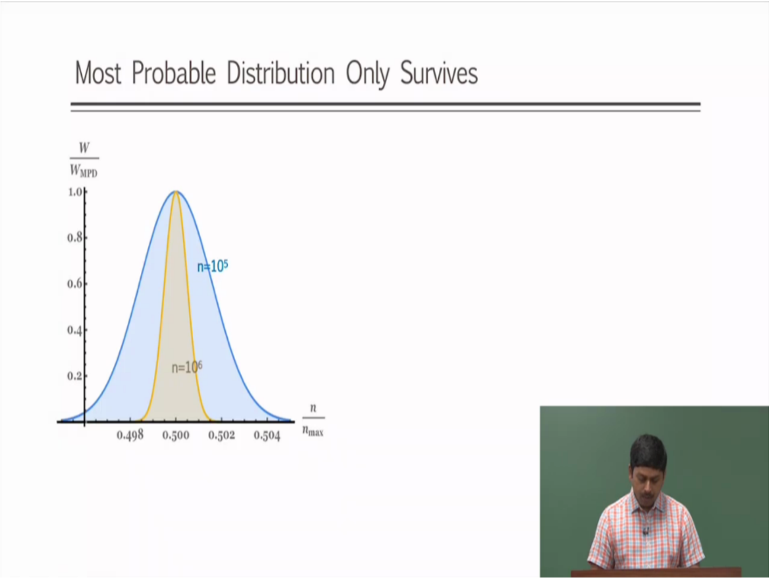

Now I have zoomed in further.

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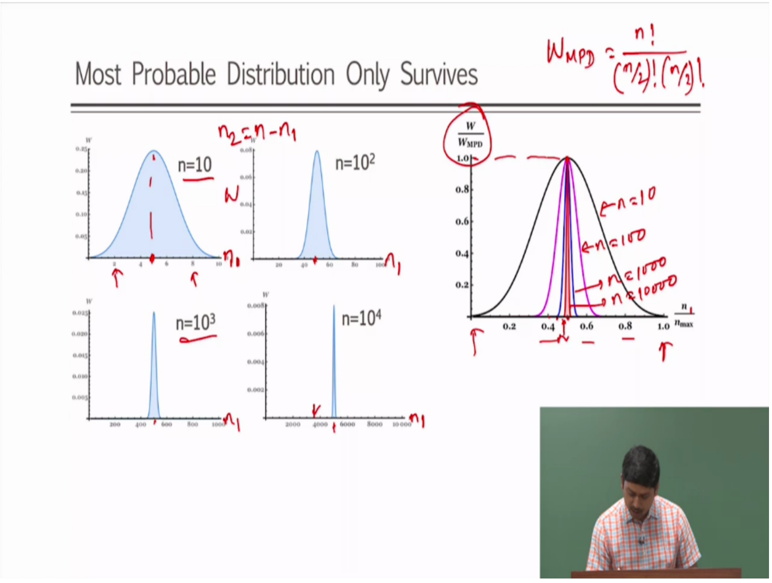

So earlier you see I was plotting from 0 to 1. Now I am plotting only in this region for larger number of particles.

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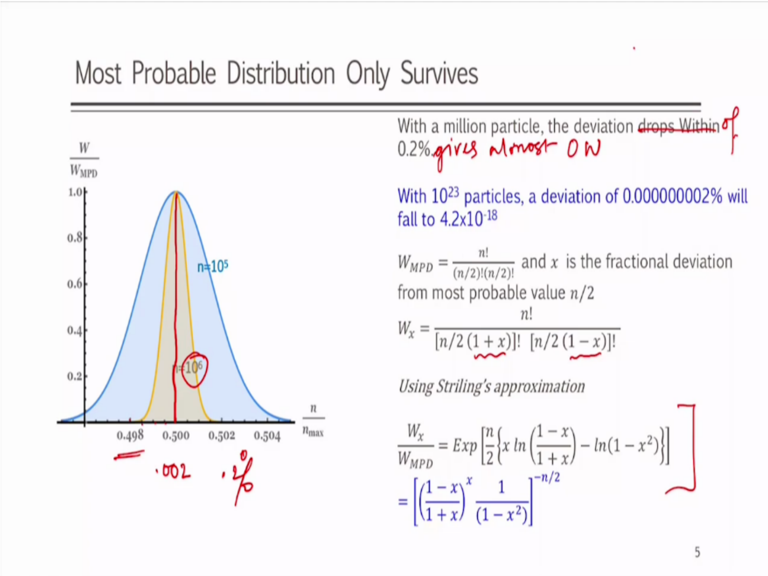

So here I have plotted from let's say this is 0.498 and this is 0.5, so it is 1, 2, 3, 4 it is going 0.002, so I have just plotted 0.49 onwards. And you see when that particle number is 1,000,000 the deviation is 0.002 with 0.002 falling when the number of particles is 1,000,000. So 0.002 is nothing but 0.2 percent, within 0.02 percent deviation it is falling off.

So with million particle the deviation drops to 0 not the deviation with million particle the deviation of 0.2 percent gives almost 0 probability of 0 W. The number of distribution drops to 0 with 0.2 percent deviation. So with million particle the deviation of 0.2 gives almost 0W. However with 10 to the power 23 particles are deviation of 0.000000002 percent will fall to 4.2 into 10 to the power minus 18? So you can see that a percentage deviation of this much is not probable when 10 to the power 23 or one mole of particles will be there.

So that distribution will be just like a Delta function. That means we don't have to consider any other values of n1. We can only consider n1 equal to n by 2. We don't need any other values. We only need W MPD and we don't need any other distributions. With W MPD it will suffice to calculate the entropy of the system and that is the reason most probably distribution is used.

Also I have shown with the derivations that for two-level systems it is exactly same when n is large the total number all possible distributions 2 to the power n is same as nc n by 2 when n is very very large and that is just a pictorial representation and actual calculation also showing you the same thing. It gives you an understanding that how little the deviation will be from the W MPD when a large number of particles are involved.

So it is just that one can do a little bit more mathematical calculation and show that the deviation can be denoted at x and I can use deviation as plus x and minus x using styling approximation, we get this kind of formula. By the way this number I got above is not possible to even calculate using mathematical other software because 10 to the power 26 is so large. So I have used Sterling's approximation which I discussed last time that ln, n factorial is n ln minus n and arrived at this formula where this deviation is represented by these 2 equations.

It is not so important but just to tell you that you can get the number above using a formula like this. This formula if you put it you can get the desired number.

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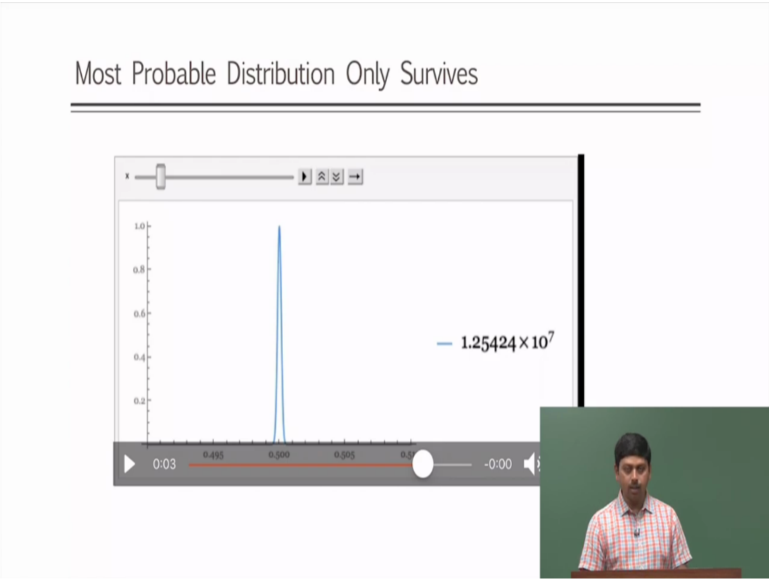

This is a movie showing that with the variation of n it is getting sharper. and this is the n that is showing here, so you can see that with the n it is just getting sharper and sharper. So this is largest value of n is here that much we have considered. The movie is just running back and forth

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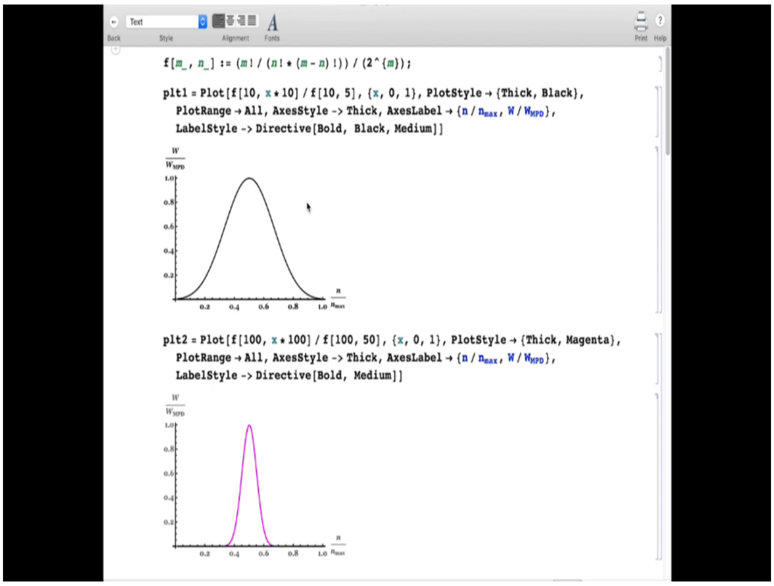

I can show you that same thing in Mathematica. So these are the plots that I have already shown you so this is the function. n factorial editorial by n1 and n2 that I denoted here.

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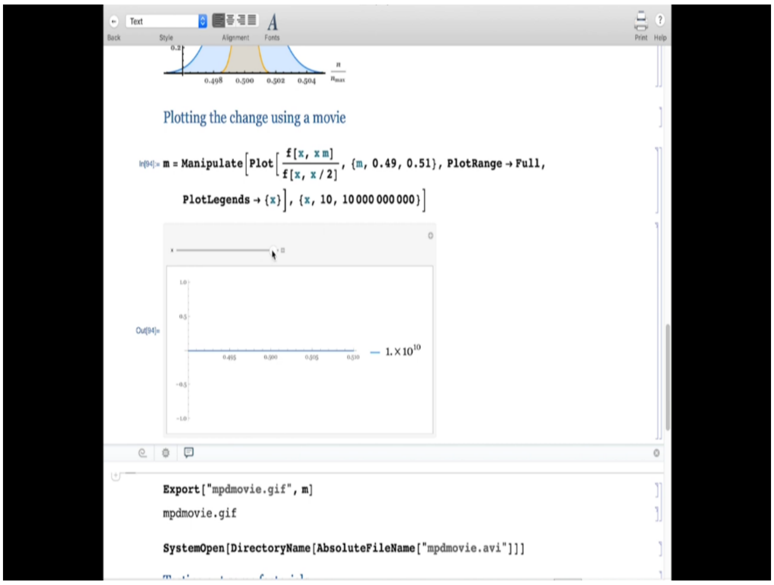

And you can see here I am plotting this W by WMPD and in a fractional matter and then I can get this as this. So you see it is getting sharper and sharper as I am increasing my x.

x is this, the percentage deviation or rather fractional deviation is x and as I am increasing my x that means I am deviating from 0.5 and I am getting a sharper and sharper (())(12:46). I’ve gone up to 10 to the power 7 because it is much difficult to go beyond that. So maybe we can try one more 0 and see how much time it takes. 10 the power 8 did it. Let’s see. Yes, so this is 10 to the power 8.

Let’s do 10 to the power 9. Okay that’s good. Let’s do 10 to the power 10, see what is happening as you can see that your x axis, so beyond that it is just dropping, so there is not enough point to show there is dropping faster that’s what is happening at this region. There is not enough points it is just that dropping sharp enough that you cannot distinguish now that it is dropping, so it is dropping to the next value of it and we don’t have any more points in between, okay.

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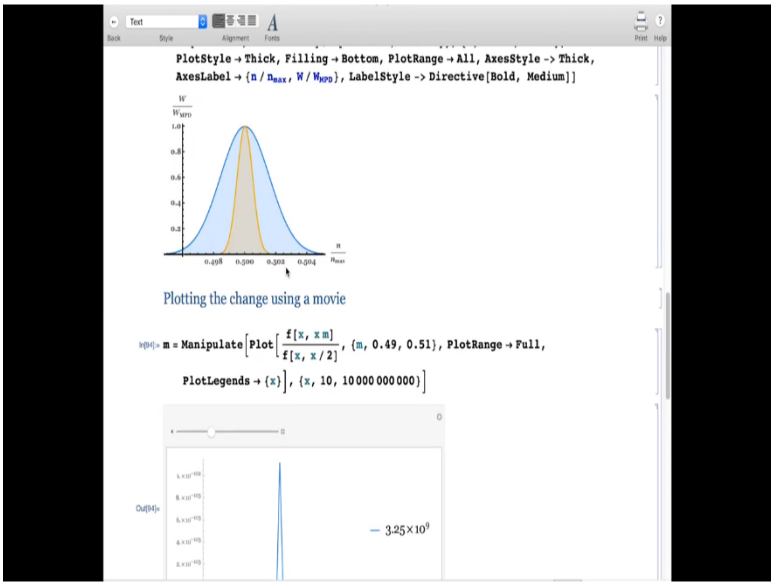

And that’s what here I have shown the same plot that was there, so here all calculated from Mathematica as you can see here.

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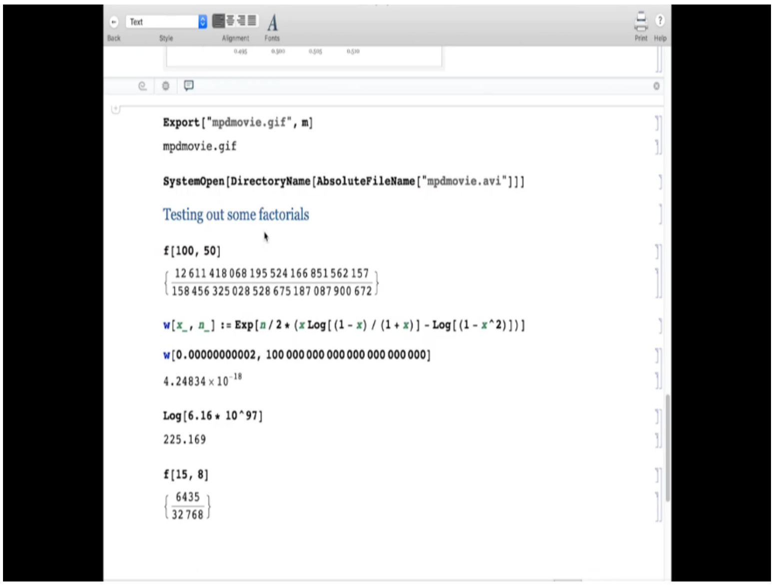

And the number that I told you about this is 10 to the power 23, this number. And this is like that much fractional deviation and that gives you. And this is the formula that I used I have shown you. So if you use this formula you can get the same value.

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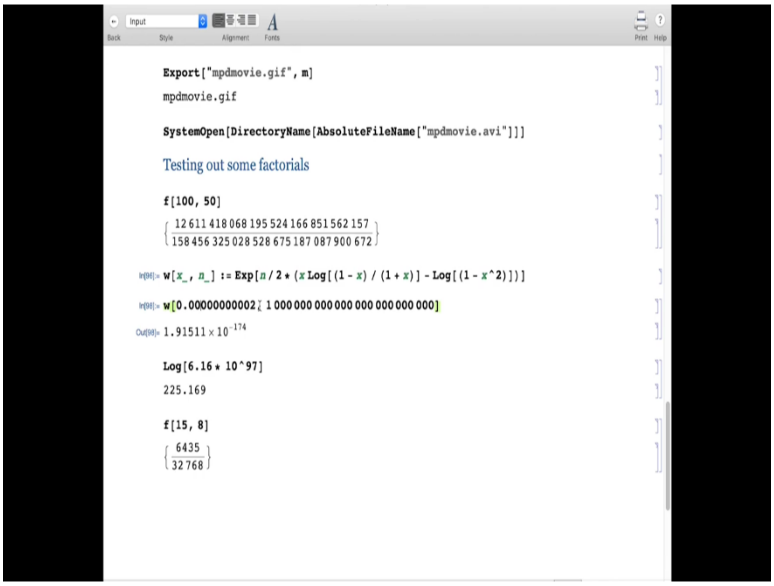

So for example I will show you this one and if this is my function and then I can use this and get the same number. Now this 10 to the power 23 if I use one more zero, let's see how much you get. So as you can see I am getting 10 to the power minus 174. So when the number of particles is 10 to the power 4, you can see here then it drops to 10 to the power minus 174 for that much deviation 0.0000 0000 there are 8 zeros there.

3, 4, 5, 6, 7, 8, 9, 10 zeroes which means 8 zero 2 percent because 2 zeros are less for the percent, okay. So you can see that for huge number of particles it is just suffices to say that distribution is just half half.

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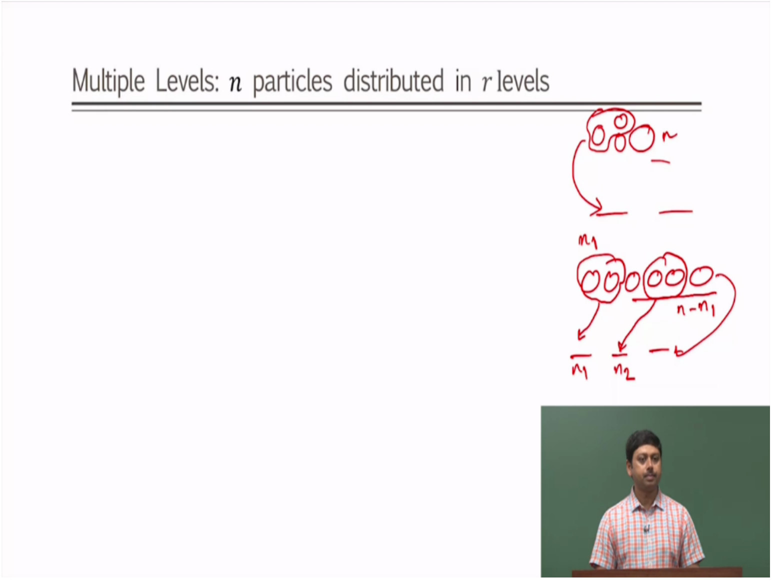

So we talked about two-level system now we are going to about multilevel systems. What if the particles, n particles are distributed in 3 levels or 4 levels what will happen in that case? and again we are talking about distinguishable particle and distinguishable levels, okay. So let's say we had n particle earlier and we had 2 levels. So we chose from n particles n1 number of particle and put it in one level and rest of the particle automatically we have chosen for the 2nd level.

Now let's say if we have 3 level system. And then what I can do is that, I can choose some n1 number of particles first level that leaves me in minus n1 and out of this in minus n1 I can choose another n2 for the 2nd level and the rest will automatically go to the 3rd level. So you see, the way it will work is.

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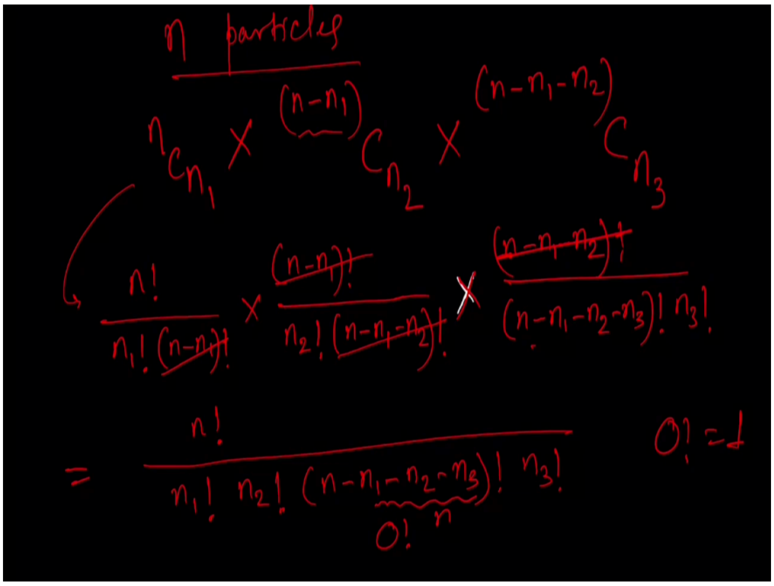

That lets say I have n particles. So I choose n1 particle from the n particle that leaves me with n minus n1 particle, I choose from there some n2 particle that leaves me with n minus n1 minus n2 particle and from that I choose let's say n3 particles. So there are 3 levels n1, n2, n3 but the condition is that n1 plus n2 plus n3 should be equal to n. So what happens is here is that from this what we get is, ncn1 is factorial n by n1 factorial and n minus n1 factorial multiplied by I have n minus n1cn2.

So it is n minus n1 factorial divided by n2 factorial and n minus n1 minus n2 factorial. Now in the 3rd case I have n minus n1 minus n2 factorial divided by n minus n1 minus n2 minus n3 factorial multiplied by n3 factorial, okay. This is clear? So now what is going to happen is that, n minus n1 factorial cancel, n minus n1 minus n2 this part also will cancel leaving me with n factorial divided by n1 factorial, n2 factorial and these 2 quantities which is n minus n1 minus n2 minus n3 factorial and n3 factorial.

Now you know that n1 plus n2 plus n3 equal to n, right? So this quantity is nothing but 0 factorial and 0 factorial is also 1, so we can finally write the formula as, I will erase this part and I can write it.

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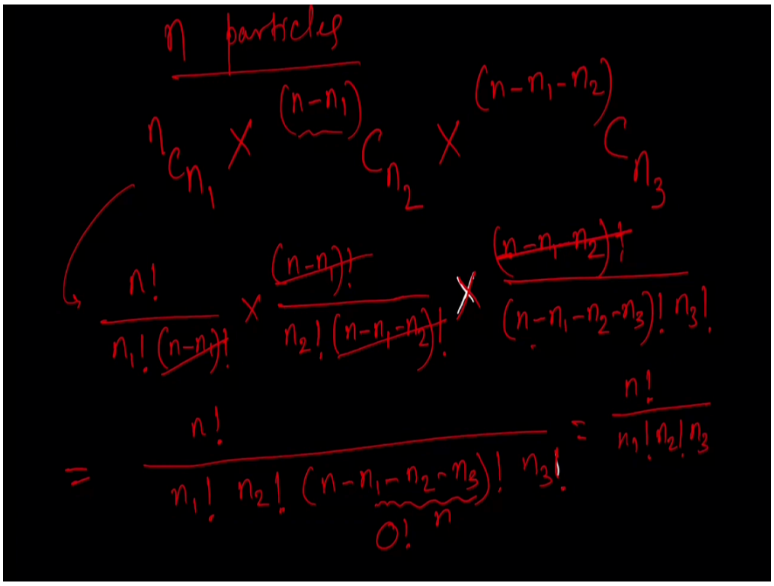

This gives me n factorial by n1 factorial, n2 factorial, n3 factorial. So I remember earlier what was the situation? It was n factorial by n1 factorial and n2 factorial and now we get n1 factorial, n2 factorial, n3 factorial, so this is called multinomial distribution. Instead of binomial it is multinomial.

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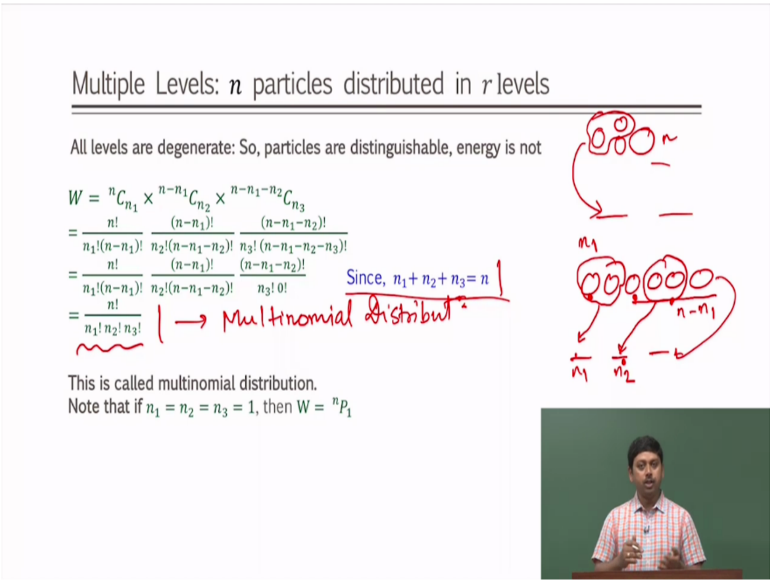

So it is exactly here as you can we arrive at this particular situation where it is n factorial by n1 n2 n3. Remember we are only talking about 3 level system and this multiple levels this is called multinomial distribution. Bi means 2, multi-means more than 2, this is the condition, okay. I have written that here.

Now interestingly you will notice that, if all my n1 n2 n3 where all one then I will choose just one by one, right? For levels and I will arrive at something called nP1 or n factorial only because if all if all n1 n2 n3 are equal then I am going to get n factorial only and n factorial is nothing but permutations of n particles nP1 which means essentially I am choosing one particle and putting in the first level.

Choosing the 2^{nd} particle and putting in the 2^{nd} level, choosing the 3^{rd} particle and putting in the 3^{rd} level, choosing the 4^{th} particle and putting in the 4^{th} level, choosing the neth particle and putting in the neth level that means nothing but it's a permutation of those particles and therefore it is np1 because I'm choosing 1 or all of them to put that in the different level, it is just a digression to that.

So this is the formula that needs to be used when we are talking about distinguishable particle and multiple levels. Still, you see, we have only one constraint here that is the total number of particles that has to be you know some value n. However we don't have here any energy constraint or anything. So this formula is typically applicable when we have already generated energy's that means all energies are equal.

So therefore there is no preference for putting in one level versus other because essentially ultimately the total energy will be n multiplied by energy of that particular level. Either it is zero then it will be zero, if it is f silent b n f silent. So, n f silent will be the value of the total energy anyway because all particles are degenerated, so wherever you put the particles will get the same energy. So in future we will talk about where that is not the case, okay.

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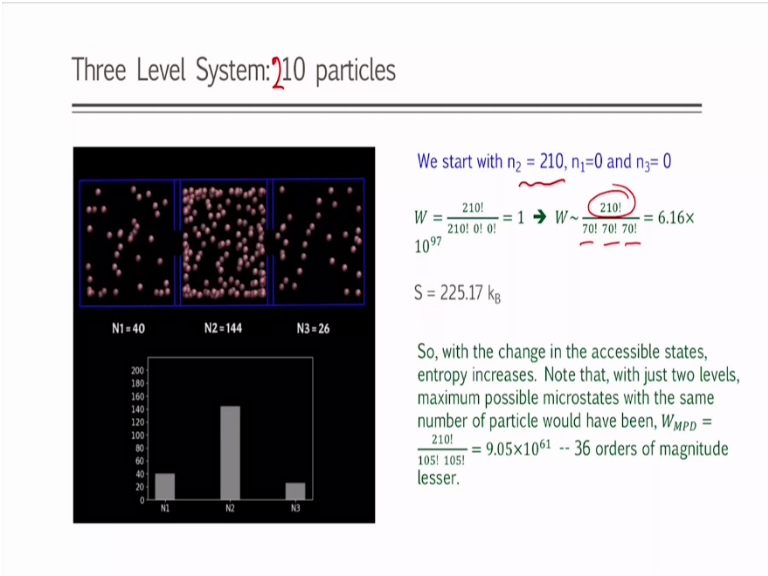

So let's see, now the thing is that, what you have seen is that, we went from 2 level system to 3 level system. What is the consequence of going from two-level system to 3 level system, may I know ensuring the same number of particles. We are showing you one of the consequences here. We have taken 10 particles and put into 3 levels and as you can see the 10 particles initially started from here and they will defuse into both the boxes.

And the bar chart will show you that it is going to different boxes, so we start with n2 equal to 10 n10 and n30 and essentially what you're going to get is that, initial value was one because all of them went to the same box we expect them to be equal attributed because as we have seen that for two-level system n1 equal to n2 equal to n by 2. Similarly for 3 level system it will be n1 equal to n2 equal to n3 equal to n by 3.

However here I cannot divide by 3, so I am just taking the best possible value 334 and that number is 4200 is not that great of a number yet. It will give you only 8.3kb not enough for really distributing them equally and that's why you can see some boxes remain empty. Let's do the same thing with more number of particles, so the number of particles is 210 here.

Initially all 210 particles wherein in the middle box and the other 2 boxes were empty. Now you see, as the simulation is progressing the particles is distributing in all the 3 boxes naturally. Again these particles does not have energy, so they have no preference to go to either of the boxes though no reasons for the particle to go because they are not gaining anything energetically by going to other boxes but still they are going why?

Because that is only more probable, you have 3 boxes available, why you want to be constraint in one box, it is like as I said again and again if you have a whole campus to move, why you will be constraint in a room? It is just entropy that will take you out of your room. Just by unless you force yourself to be, that's a different thing that work against entropy we will come back to that at some point.

But however if you're like a free particle who has no free will then naturally it will be found everywhere else because that is what is more probable and you can see all the 3 boxes have now similar values. At the end when the equilibrium reaches all of them will have similar values? The reason is that there is overwhelming number of possibilities when the particles distribute equally in 3 boxes.

You can see from here, W is one when all particles are confined in one box. However that W becomes 10 to the power 97 when it gets equally distributed as 70 70 70 just a factorial calculation. A simple multinomial calculation the formula that we just now discussed that 210 n factorial by n1 factorial n2 factorial n3 factorial and this is the only most probable distribution.

There are all possible distributions possible I can have one particle in one box, 2 particle in the other box and rest of 207 particles in other box like that there are so many other possibilities. How many, we are going to discuss? How many possibilities will be there if there are n number of particles and n number of levels available? That's a different problem altogether but here I'm just talking about only one possible values which we know to be the most probable distribution dividing them equally and that's what we see again and again in this movie. This movie is showing you that that it has naturally happened.

So now here S is 225.17kB although the notice one thing that although the W is huge S is not that much. The reason is that the ln function, you know it brings it down and drastically that that usually and there is a good reason for that actually. As you know that this is not only the most probable distribution there are percentage deviation will be huge means the change in W due to the small percentage deviation will be here.

But there will be still many around the most probable distribution will contribute but even if you take thousands of them around that is now going to change the value of S significantly because again the ln function. Even if you have 10 to the power 3 around your most probable distribution if you take is going to just add to ln 10 to the power 3, it is not much ln it will not be much.

So therefore again taking most probable distribution is okay means is enough that one can get the values by that and we will of course tell you that importance of most probable distribution that it is not possible for us to calculate all possible distributions anyway for realistic systems. So therefore most probable distribution will be always helpful, okay.

So now what you see here, that with the change in the number of accessible states, so earlier there are accessible states that means boxes where only 2. Now we have 3 boxes, so with the change in the accessible states entropy increases. Note that with just 2 levels maximum possible Micro state could have been 9.05 into 10 to the power 61, so what I did is that, I took most of probable distribution with 2 boxes.

That means dividing 210 particle into 105 105 that gave us 10 to the power 61. Now when you divide into 3 boxes I'm getting 70 7070 that gave me 10 to the power 97, so 36 orders of magnitude larger W we get by dividing into 3 boxes. So you can naturally know that if I divide into 4 boxes, 5 boxes, 6 boxes entropy will only keep on increasing. So entropy increases with number of accessible states.

By that we mean that entropy increases by number of choices, number possibilities, if I have 5 possible places to go the entropy will be of course more for example a coin has only 2 possibilities, a dice has 6 possibilities, so entropy of one die will be larger than entropy of a coin. Figuratively speaking there the entropy is not quite applicable but choices are still applicable.

In chemistry we use that with the help of kB otherwise without the kB it is just a number with the kB we can associate with the chemistry.