Chemical Principles II
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Calculation with Multi-Level Systems with Fixed Energy
Part – 03

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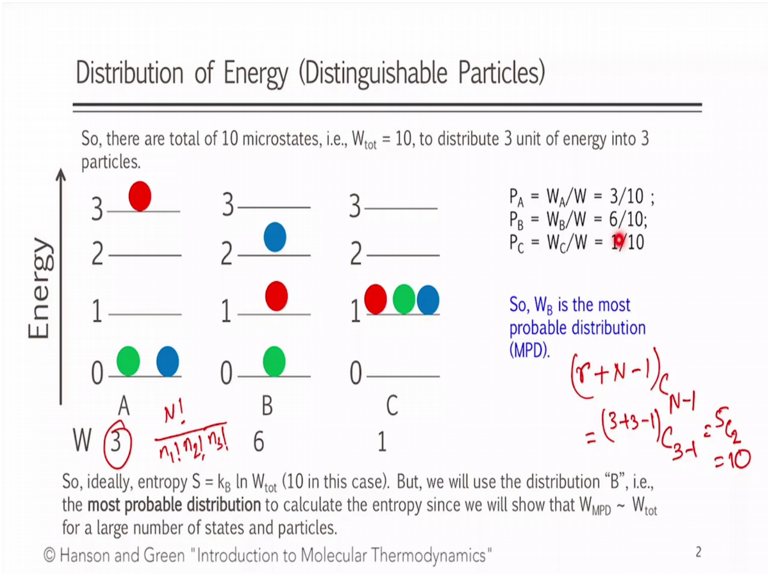

Will continue with the calculations of multilevel systems having a fixed energy, so we still remember that we are still talking about distinguishable particles by that what we mean is that their classical particles, which can be distinguished, I would like to emphasize one particular point here is that, it is not our ability or inability to distinguish a particle as you know, distinguishable or indistinguishable categorization, it is the statistic that comes out of the particular experiment that will eventually tell us whether particles are distinguishable or indistinguishable.

So what I mean by that is that one can do some mathematical calculations with distinguishable particles in distinguishable cells or indistinguishable particles in distinguishable cells and they will eventually give rise to different statistics, now when you do an experiment and see that it is following a particular type of statistics, than we know for sure that it is the this category of particles we are talking about and we will see that today, you know following few slide will bring up that particular issue, that the experiment itself dictated that what kind of particle we are talking about with the background mathematical foundations for understanding them.

So briefly just summarising the what we talked about with 3 particle and you know 3 levels, 3 units of energy, not 3 levels, 3 units of energy, here there are levels are 4 0, 1, 2, 3 and there are 3 possible distributions and the total number of microstates that came out of that is 10 and we know that it is a star bar kind of problem, where indistinguishable particles go into distinguishable cells, here in distinguishable particles means energy, so we are distributing energy which are indistinguishable we do not know whether blue energy or green energy or anything, they are all indistinguishable energy units which is going into distinguishable particles meaning cells.

So again we can map it whichever way we want to, so and that cyber problem with 3 particle and 3 units of energy will give rise to the value of 10 and you can do that calculations simply by, so you know the formula for star bar problem that is number of energy unit is R, particle is N -1 C N -1, so R is 3 here, so 3+3 -1 C3 -1 which is 5 C2 which is nothing but 10, so those are the 10, the total distributions that are here and individually, so the 3+ 6+1 is 10 and individually one can get the 3, 6 or 1 by using the multinomial distributions where you use N factorial the total number of particle by N1 factorial, N2 factorial, N3 factorial and things like that.

So you can see that this 3 is coming from capital N is 3 here where N1 is 1 and N2 is 2, so you can get the factorial by 1 factorial and 2 factorial and you will get the number 3, in this case you will get 3 factorial by 1 factorial, 1 factorial, 1 factorial which will give you 6, here you will get 3 factorial by 3 factorial, 0 factorial, 0 factorial and you will get 1, so that is how you are getting A, B, C and that is we are getting because they are all distinguishable particles as you can see from the color is that and we also talked about that the B is most probable distribution because probability of this particular distribution which is obtained from the number of microstates of B which is 6 divided by total number of microstate which is 10 and that gives us 6 x 10 which is the most probable distribution or MPD in short form.

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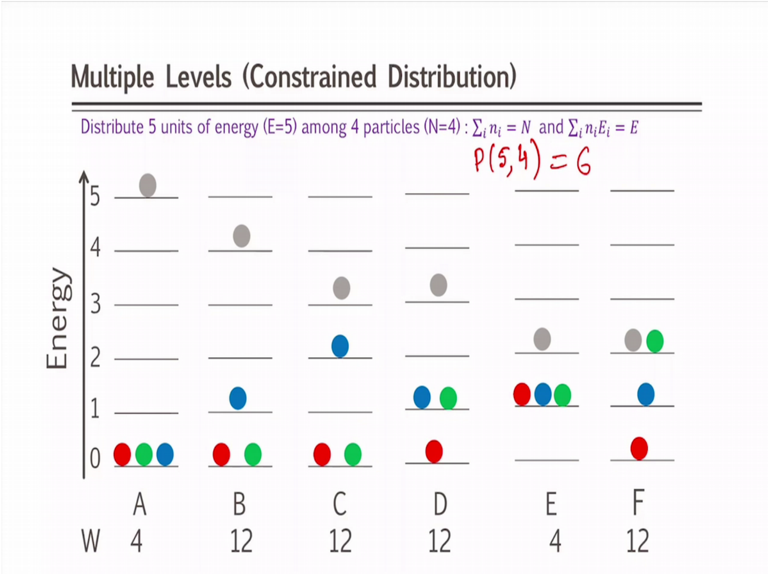

Now this is just 3 particles and 3 units in energy levels, 3 units of energy, not 3 energy levels again, it is 3 units of energy that you are talking about and we are going to go a little bit more complicated system of having 5 units of energy and 4 particles and is also we talked about that you can get these 5 possible distributions, 6 possible distributions and each of them is having different number of microstates, now I already mentioned that the number of distributions and you can get by partitioning an integer into that many number, for example the number of units of energy is 5, so you partition the number 5 into 4 parts.

So you are partitioning 5 into 4 parts in order to get the number of distributions of having 5 units of energy into 4 particles, so basically you are partitioning the 5 into 4 part such that your is part is some energy unit for a particle, so let say if you break 5 into 1, 1, 1 and 2, that means you are giving 1 unit of energy into 1 particle, another 1 unit of energy to another particle, another 1 unit of energy to another particle and 2 units of energy to last particle, if you may break into 3, 2 and 0, 0, then you are giving 3 units of energy will give you 6 partitions.

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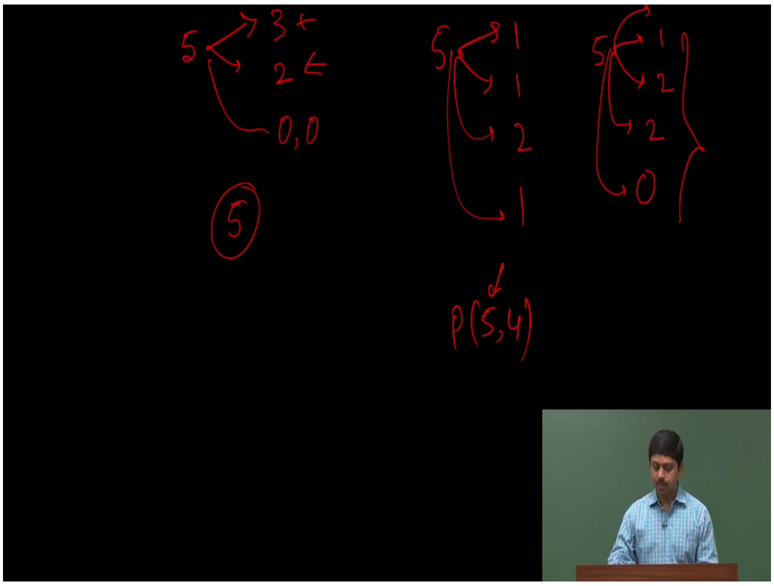

So 6 partitions essentially is 6 distributions, now 6 partitions can be different of kind for example as I said that when I am partitioning 5 units of energy into 6 partition, one of the partition can be 3, 2, which means that one particle is getting 2 units of energy, another particle is getting 3 units of energy, another particles is getting to units of energy and rest of the particle are getting 0 units of energy.

So that is one type of distribution, one can break the 5 into 1, 1, 2 and 1 let say, so 3 particles are getting 1 units of energy, 1 particles is getting to units of energy and that is what it is, 1 distribution we can break 5 into let say 3 2, 2, 1 and 0, so in partition will not get the 0, however, you have to see that whether it is less than the number of particles are not if it is than their last one is getting obviously the 0 units of energy, so this is another type of distribution.

So in order to get the number of distributions we need partitioning of that integer which is equivalent to the amount of energy, for example, partitioning 5 into 4, P5, 4 is number of partitions of 5 up to 4 parts up to, so there can be a partition of like only 5, so that 5 will go to only one particle and the rest of them we get 0, so up to 4 parts, that is more important thing 5, 4 means.

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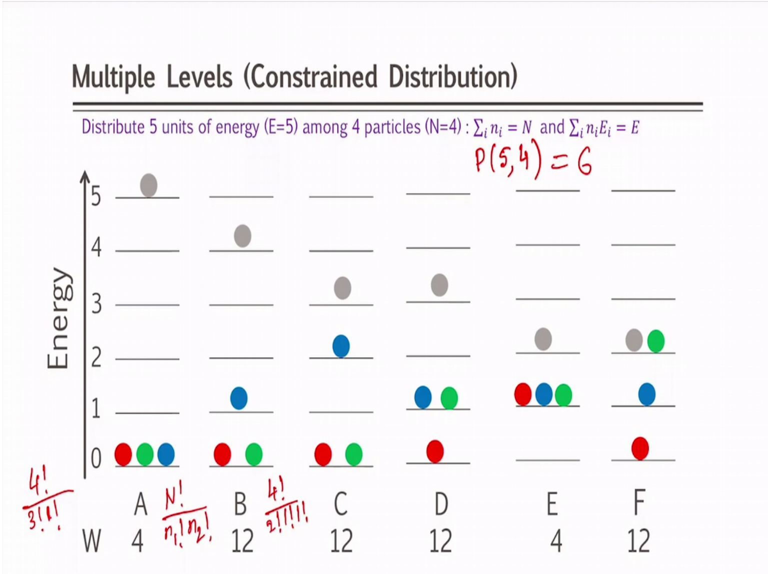

So the N now for each of the distributions, for example distribution A we know how to calculate the number of microstates that is factorial N by N1 factorial, N2 factorial and things like that, and if you do that then you will get 5 factorial by 3 factorial and 1 factorial give you number 4 no, sorry, it is 4 factorial, so number of particles, total number of particles is 4, so 4 factorial by 3 factorial and 1 factorial will give you 4, here 4 factorial by 2 factorial, 1 factorial, 1 factorial will give you 12 and things like that.

Thus will get individual number of microstates for individual distribution and of course the total number of microstate you can get by the formula that is given for star bar system, which indicates that indistinguishable particles putting into distinguishable cells.

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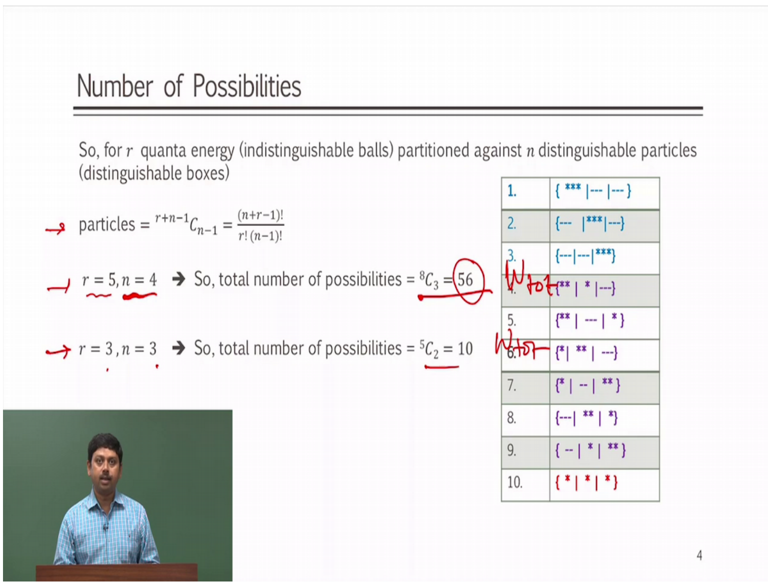

So now that is exactly given here for example, this is a formula for getting total number of distributions and it is mention here if R equals to 5 and N equal to 4, we get 56 possibilities, total 56 possibilities, so all microstates combined, microstates of all distributions together give you 56, so we can call that as a W tot, total number of microstates, now if R units of energy is 3, number of particles is 3 than total W tot we are going to get as 10 as you have shown before and that is again shown in this particular diagram where 3 indistinguishable particles IE energy is distributed among 3 distinguishable cells IE particles and we can see all the 10 for 3 particle and 3 boxes.

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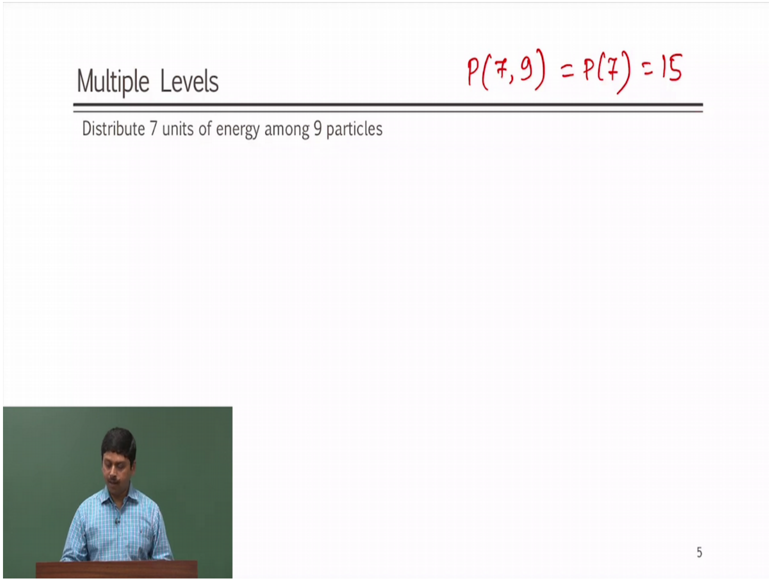

Now let us go to little bit more complicated system and let us now distribute 7 units of energy into 9 particles, again, if I have to tell you that how many number of distributions are there, I would partition 7 into 9 parts, now 7 cannot be broken into 9 parts, so effectively P7, 9 is basically nothing but P 7 that means partition the number 7 to all possibilities and that number is going to give you 15 as you can see from mathematica or you can do it yourself and you can see that.

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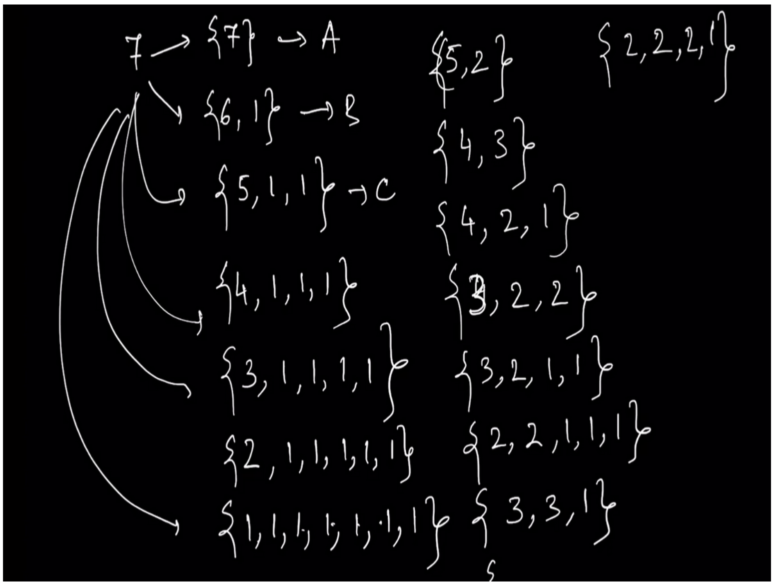

I will give you some examples for let say if you have 7 then how many partitions are possible you can get 7, only 7 which means or one particle is having 7 units of energy and all particles are having 0 units of energy, you can also have 6, 1 which means one particle is having 6 units of energy, another particles is having 1 units of energy and everything else 0, you can get 5, 1, 1, you can get 4, 1, 1, 1, you can get 3, 1, 1, 1, 1, you can get 2, 1, 1, 1, 1, 1, 5 once basically and you can get all 7 once 1, 1, 1, 1, 1, 1, 1 okay.

So there are more possibilities, one possibility will be that you can do 5, 2, that means one particle is having 5 units of energy, another particle 2, you can do 4, 3, you can do 4, 2, 1, you can do 4, 1, 1, 1 is already done, so that you cannot do, then you can do 3, 1, 1,1 is already, so but 3, 2 5, 2 you can do, you can do 3, 2, 1, 1 and you can do 2, 2 4, 5, 6, 7, you can do and to all ones are already done, so let me see how many are there, so 1,2,3,4,5,6,7,8,9,10,11,12,13,

So two more are remaining, let me find out, so 4,1,1,1 is already done 3, 2, 2 are already done 3, 2, 1, 1 is done 2, 2, 1, 1, 1 is done 3, 3, 1 is remaining, anything else 2, 2, 2, 1, is not done okay, now let us count how many? 1,2,3,4,5,6,7,8,9,10,11,12,13,14 and 15, so thus we got all 15 possible distribution, so each one is a distribution that you have to understand, let say you can call it A, you can call it C, I can call it C, so each one is a distribution, each one has a number of microstate associated with that for distinguishable particles.

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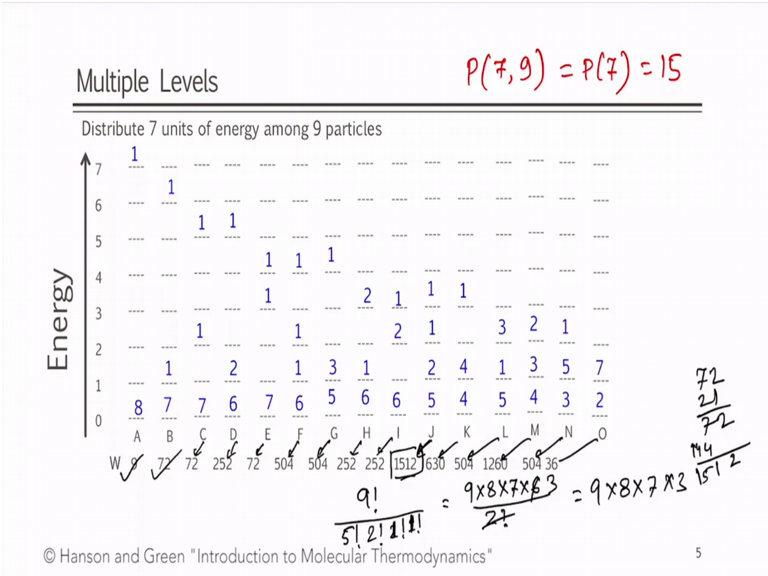

Now let us go back and see how we can do that, so this is our energy distribution from 0 to 7 because there are 70 units of energy not more than that and there are 9 particles, so now this is one particular distribution in which I have to put the particles, so let us start with giving one particle all amounts of, all the energy and then we can build up the other things, so I give 1 units of energy, 7 units of energy to 1 particle and 0 will automatically go to the rest of the particle, so the distribution will be 1 and 8.

Now how many possible microstates can be there, it will be simply factorial 9 by factorial 8 and factorial 1, which will give us 9, now let us go to the 2nd one in which I have brought down the energy of one particle by one level here, I brought down energy of my level I, similarly I have will to pull up one particle to the next level, you see. Now it has become 7, it is 1,1, now many number of possibilities will be in this case 9 factorial by 7 factorial and 1 factorial.

Now go to the 3rd distribution I bring the down this particular 1 by one more step by particularly and automatically I have to pull this one by one more level, so again, that is 7, 1, 1 and it will have the same number of microstates, now let us go to the 4th one distribution, this will let us keep the same level but I bring this one down by one level, so I have to pull up one particle to the higher level, so it becomes 1 to 6, this will have factorial 9 by 6 factorial, 2 factorial and 1 factorial number of microstates.

So, similarly I have 7, 1, 1 I have 1, 1, 1, 6 this is way you can actually get the number of possible distributions, so you breakdown is particle by 1 level and put one particle of, for example here, we brought down one, and I pulled up to 1, so now even if you miss it. That is why I already discussed if you miss it by this way, you can always get by the partitions when confirm whether your number of distributions are matching with this particular way or not, so now G, H and all the other distributions as it is mention here and this is a all 15 possible distributions that are possible and that is mention here, I just remove these because I will show you the number of possibilities for one below.

So here, so that how the 9 comes, similarly 9 factorial by 7 factorial and 1 factorial will give you 72, the C is also 72, D is 252 and things like and if you see here, this is the largest number 1512 and that comes from 9 factorial by, so this is J one is, this one, so 9 factorial by 5 factorial, 2 factorial, 1 factorial and 1 factorial will give you 1512 because I can show it here 9 into 8 into 7 into 6 divided by 2 factorial because we can take care of the 5 factorial already, we took care of so now 2 cancels and give us 3, so it is 9 into 8, 72 into 7 into 3, so 72 into 21, 1512. That is how we get as the number of possible distributions for the Jth one, it is just shifted little bit, so please look at this way the O one is 36.

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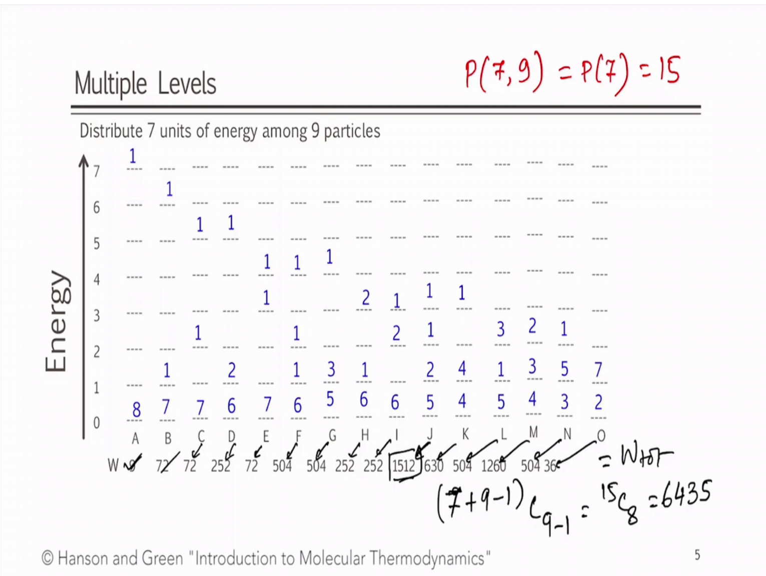

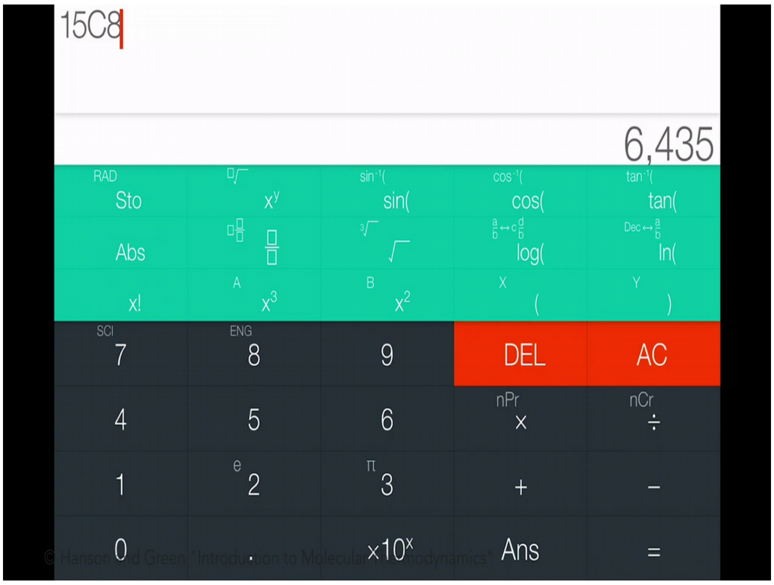

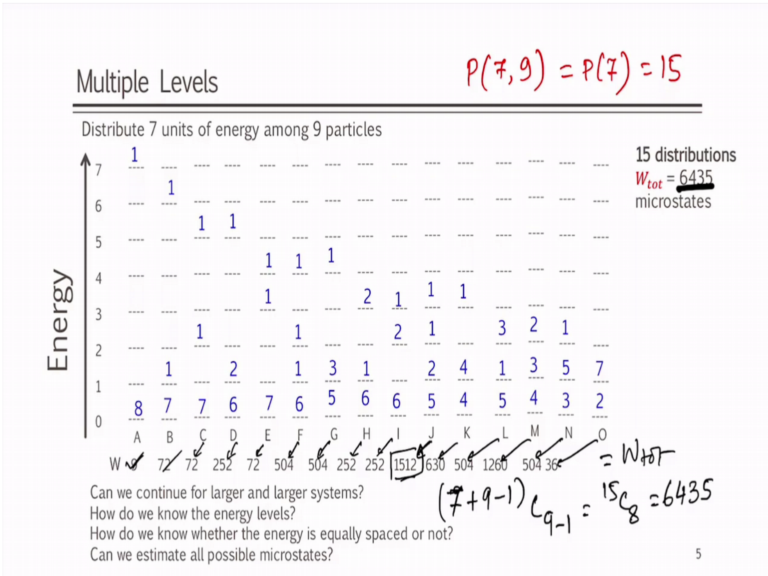

So you see, now that if I add up all the number of distributions than there is a number that I am going to get by summing up this individual distributions, microstates of individual distributions and I can get the W tot which also I can get from the star bar formula that I have 9 units of energy, 7 units of energy in 9 particles which means 7+9-1, it is R +8-1, C9 -1 which is 15 C8 and that will give me 6435, I just do the calculation 15 C8, 6435 – what we are going to get from this thing.

So we can get all possible distributions just, you know in one formula itself, for individual distributions we have to distribute the particles in different level and then calculate it, it is also mention here, now can we continue for larger and larger systems like this, how do we know the energy levels and how do we know whether energy equally spaced not and that is the thing that you have to consider and can you estimate all possible microstates will come back to this questions.

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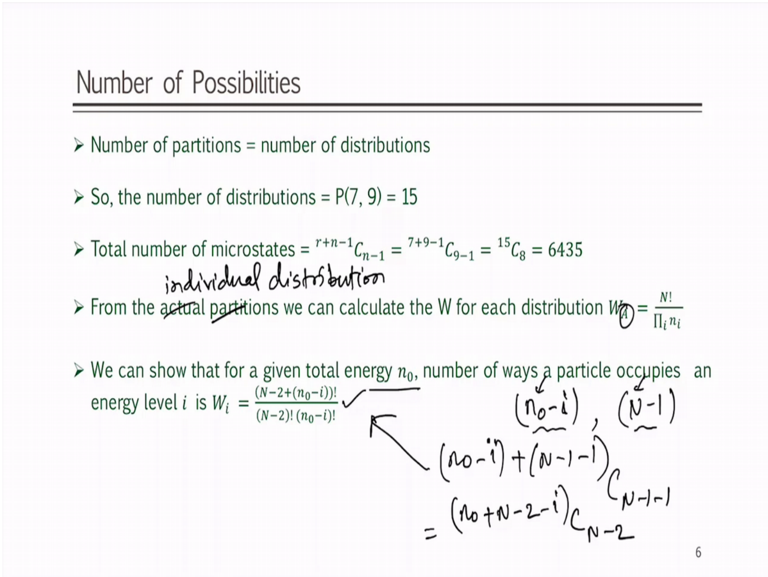

But with some more examples, now here is the summary, so number of partitions is number of distributions, number of distributions is, you know can be partitions 7, 9, 7 into you know 9 partitions maximum and then total number of microstates can be given from this particular formula and for actual, for individual distribution, for I would say individual distribution or for a particular distribution we can calculate the W from this particular formula.

So for distribution A we can get by using this particular formula and now we have to estimate one more thing, we have to estimate that what is the number of microstates possible when a particular particle has, you know having IoT energy because we want to know that many particles are having IoT energy, energy I, so you can show that or I can explain to you briefly that in all possible microstates if I want to calculate that how many particles will have energy I.

So in order to calculate that, what we can do is that, let say the total number of energy, total units of energy, the N0 and I can take out I units of energy and give it to one particle, so I am left with N0 minus I amount of energy and I am left with N -1 particle you see, earlier I had N0 amounts of energy and I had N particle, I have given I amount of energy to 1 particle, so my energy units reduces by I and my number of particle reduces by 1, so that means, now I have a different problem to solve, other one to solve that for N0 minus I units of energy and N-1 particle how many possibilities are there? And that is nothing but this particular formula

N0 minus I plus N -1-1, C N-1-1 which is giving me precisely this particular formula that N0+, minus I plus N -2, C N-2, so I will just write it once more here it will be N0+ N-, sorry this is I N0+ N-2 minus I, C N-2,

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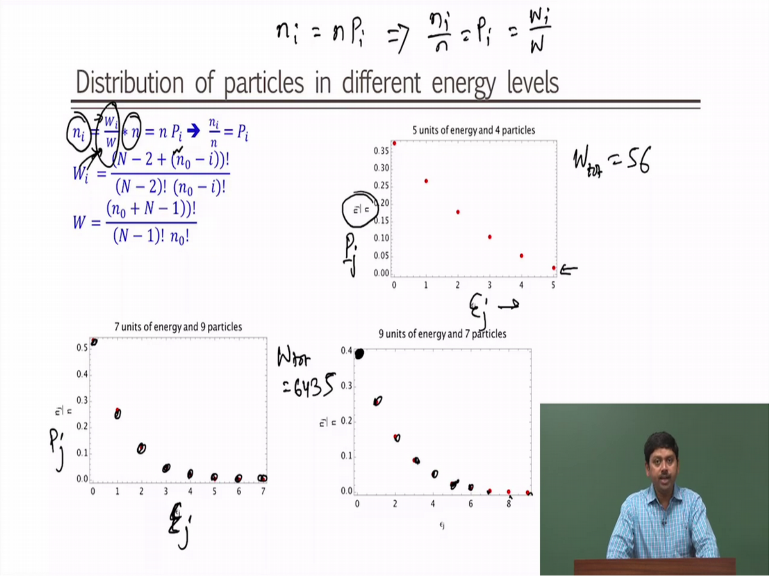

So by using this particular formula you are going to get a number of particles that are there in the IoT energy level, now once we use this particular formula we can calculate that NI is the number of particles in the IoT level, which you can get from the number of microstates corresponding to that particular state that the particle is in the IoT level divided by the total number of W and multiplied by the total number of particles.

Now W I by W we can see that it is a probability of that particular state, so that is nothing but PI, so PI into N is NI which means NI by N is nothing but PI right, is it clear, so what I will write it again here NI equal to N into PI, so which means NI by N, it is PI, so probability of a particular state I to be occupied IoT energy state to be occupied is NI by N, it is given by the number of particles that is there in the IoT energy level divided by the total number of particles.

So N is the so total number of particles, how did I get that? We got there by also calculating the number of microstates corresponding to the particle having IoT energy divided by total number of microstates, so that is, so basically we can see that this is nothing but WI by W, so NI by N is nothing but WI by W, so and we have given the formula of W, we have given the formula of WI and that will be used for 5 units of energy and 4 particles, you see it is going some kind of decaying distribution.

What it means is that? When my energy is smaller NI is bigger, larger, so NI is larger means probability is larger, so particles to fill up the lower energy level is more probable than higher energy level, you see the number of the probability, so this is NI or you know I have written here NJ by N it is same as NI by N, so you see the number of particles or probability of particles filling up higher energy level is less, so this is nothing but probability, it is nothing but PJ, we are denoting it by J, so I and J are dummy symbols.

So we are denoting by J, so the probability of particle occupying Jth level and here it is energy EJ, so as the energy increases, for example here 5 units of energy and 4 particles as the energy increases from 0 to 5 the probability decreases, so which means that it is less and less probable for the particle to occupy higher levels, so there will be more particle the lower level, then less particle, then less, then less, then less, so it will continuously increase as the energy goes higher and higher.

Remember when you initially talked about distribution of particles there was no energy constrained involved, if there is no energy, then particles are equally occupied we have shown you that, for two-level systems, when there were no energy we showed you that the most probable distribution is when the N by 2 particle is there in one state and N by 2 particle in another state, the reason is that at that time there was no energy constraints involved, the energies of both the systems were same.

So they are call degenerated state basically if the energies are same, now even if so if energies are same then particle will like to occupy equally, however we have shown that when the energies are not same for different levels then this probability calculation, just by the calculating the number of microstates itself, just by how we can distribute this total amount of energy into particles, just the number of possibilities, so what we did when we calculated the 15 possible distributions and 6435 number of possible microstates.

So we have all 6435 possibilities are there and what we have done till now is that we have just distributed the particles to satisfy the total energy, so we have satisfied constrains of 2 things, one we have satisfied the total number of particles remained same and the total energy should be also same, with that constrains when you distributed the particles what we finally landed up is that the higher level, energy level will occupy with lesser probability and that is what is shown in this particular graph using 5 units of energy and 4 particles and the formula for getting that is given here.

So this W will give you all possible microstates combining all distributions and this WY will give you the probabilities of a particle occupying or number of microstates in which a particle will occupy IoT energy level, when you do that you get this particular one, similar calculation have been done for other system as well, 7 units of energy and 9 particles we have discussed you and we have seen that in this particular case there were, so in this particular case our W tot was 56 and in this particular case our W tot was 6435.

We did not calculate individual WI though, if you want you can calculate that using this particular formula which you have done it and that is how we plotted this graph, again here you can see we are plotting PJ against EJ, energy of the Jth level and you see it is decreasing as the energy increases, you see it just keeps on decreasing, when the energy is 7 units is very, very less probable, so automatically it is distributed in such a way that low-level will have higher number of particles and higher level is this.

Now here we are just switch be number of units of energy and particle, here 9 units of energy is given to 7 particles, so more energy less number of particles, here there was less energy more particle yes, so you see here also is the same case where this is decreasing as the energy increases, so all the graphs show the same pattern, now remember we are dealing with very few number of particles and few energy states, in actual situation there will be again 10 to the power 23 number of particles and maybe even larger number of energy states.

So there are of course the statistics will be much much much better, here, even with such a simple, you know such a small number of particles and such small units of energy we can still see a pattern, what can a pattern it is? In order to know that we are fitted this to some numerical equations.

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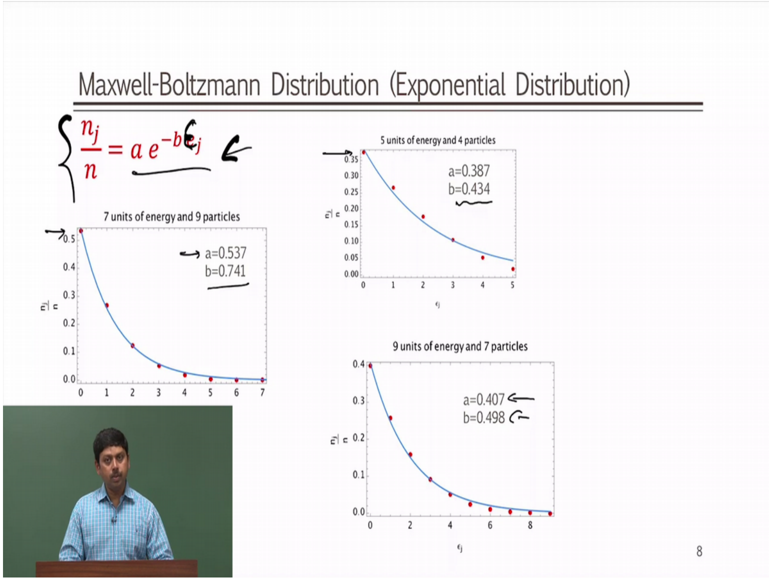

And that equation is typically an exponential question because that is an exponential decaying graph, we can visually see that, so we try to fit that to this particular exponential equations AE to the power minus B EJ, so this E is energy E, this EJ, so it shows that if EJ is higher, in this is larger than term will be smaller and therefore this term also will be smaller, this is call and exponential decaying graph.

A is something like a normalization constant which means when EJ equal to 0 that this quantity will become 1 and it will give you A that is called normalization constant for the 0 energy value, now be fitted this graph to this blue line shows the fitting, you see that it fits beautifully and it gives 0.387 and 0.434 what is the significance of that? When the energy is 0 then NI by NJ probability will be 0.387 and you see here it is very close to 0.35, A is 0.35 and this B 0.434 indicates that how fast the decay will happen, if B is larger than it will take decay much faster, if B smaller than it will decay slowly.

So look at this 7 units of energy and 9 particle, here at 0 energy, the probability is 0.537, you see it is very close to that value and the fit is also looks much better and B is larger, so it falls faster, so it decay so much faster and it decays to 0, so with more number of, more units of energy and more number of particles in decaying faster and but again here you can see that the decay 8 is almost similar and A and B are given here and this also fits very well for 9 units of energy and 7 particles, so all of them follow an exponential distribution.

So what did we learned that? We learn that when there is no energy, you know bias that means that energy is not constrained is not there, then the distributions will be equal or flatter, when there is an energy constrains involved, then for this kind of particles which are distinguishable particles we see an exponential decaying distributions, these are examples coming from the one that we have tried, 7 units of energy, 9 particles, 9 units of energy and 7 particles, 5 units of energy, 4 particles, this is how we constructed it, we calculated it and then we plotted it.

However we need to find much more general, you know example, formula for that I will come back to that and also one more thing you have to note down is that, this we are talking about, for this statistics we are talking about for distinguishable particles, where the particles can be distinguishable and they are typically called, typically classical particles and this distribution is known as Maxwell Boltzmann distribution, will talk about that little more and will show you how to find more general formula of it.

But remarkably this, you know by using this, you know small number of particles and small number of energy level itself, we can see that there is a bias towards lower energy level already for the particle to be there and it is not an equal distributions and that has great implications in all the thermodynamic observation that we see, this probability will dictate all properties that you have observe because those properties will be averaged over by the probability itself, that means the lower one, the properties given by particles in the lower energy level will be more weighted, more important than the properties you get from the particles which are in the higher energy level.

So and okay, so you will come to know it on that these B is not just simply a constant, the B is associated with the temperature and B is in fact 1 by KBT, 1 by temperature, so KB is some Boltzmann constant which will come to know that and then essentially what you are going to get is that NJ by N will be nothing but AE to the power minus EJ by KBT, we will come back to that later on, but, so be is 1 by KBT that is taken in order for the other thermodynamic constraints to satisfy but right now we have use B just as a fitting parameter both A and B, so we see these that from distinguishable particle, the statistics turn out to be Maxwell Boltzmann like which means that there is an exponential distribution.