Thermodynamics And Kinetics Of Materials

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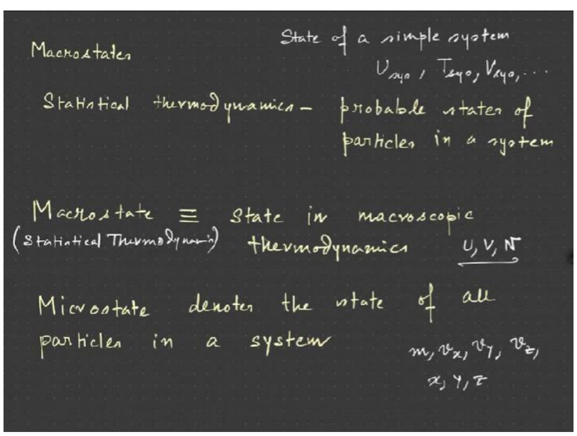
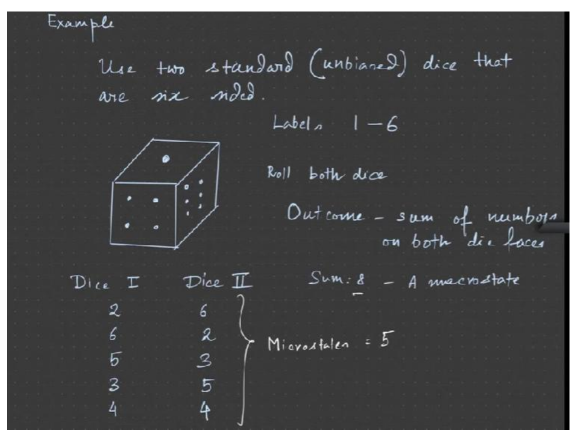
Lecture 15

Concepts of Statistical Thermodynamics – 2

So, as I was talking in the last lecture about macrostate and microstate and macrostate basically is the same as the state that we think about in macroscopic thermodynamics. So, if I am specifying the state of a simple system, then in general, state of a simple system we specify say the internal energy of the system, then we can specify the temperature of the system, we can also specify the volume of the system and so on. So, in macrostate basically this is what exactly what we are also doing, say for example an isolated system that is what we talked about it, an isolated system of gas in equilibrium applying a volume V and however that macrostate has innumerable microstates. These microstates are basically, so this is the point, the microstate notes the microscopic state of all particles in a system. This microstate basically, so for all particles we want to know the mass, then we want to know the velocities vx, vy and vz that is the velocity components and also the position x, y, z. So, this will basically give me the microstate and macrostate is basically the state that we specify or state or condition of the system.

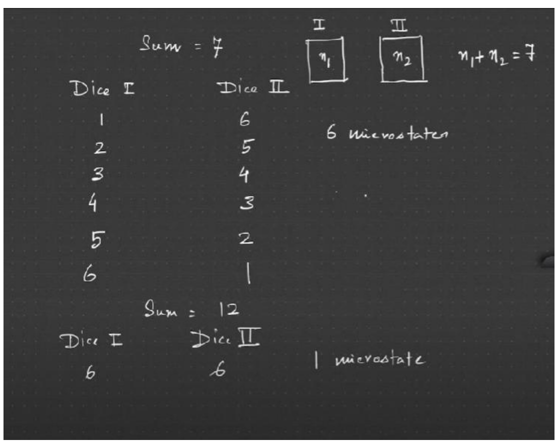


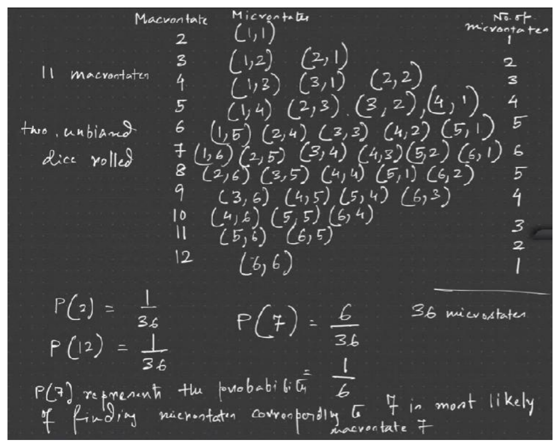


It is like a state or condition of the system. So, for that I gave an example and this example was that of a dice. So, as you can see here, dice has this type of faces, so these are level like you can see here, there is one point here representing 1 and there are 4 points here representing 4 and 6 points here representing 6. So, you have levels from 1 to 6.

Now, you roll a dice, you look at the top face, you look at the number on the top face and you see that that is an outcome. Now, if you roll both, if you roll two of these and these are unbiased and these are unbiased, then what you basically are looking at, you are rolling both the dice and you are seeing the outcome and this outcome, now this outcome is what is equal to provide the constraint and this constraint is basically like I have rolled the dice and there are two dice rolled and we are getting say for example, a sum which is say of this top face numbers, the top face numbers is say 6 and 2. So, the sum is basically 8. So, if I tell that okay, I want all the outcomes to be such that I get an 8. I always get an 8.

The sum of the two top face numbers give me 8. So, that is exactly what I have talked about and that time, so this 8 is the state of this, 8 is the state that I am describing or the constraint that I am describing and that state of 8 is the macro state. So, this is the macro state. So, that sum of these two numbers have to be 8 is a macro state. And for that macro state to be achieved, you have several micro states like 2, 6, 6, 2, 5, 3, 3, 5 and 4, 4.



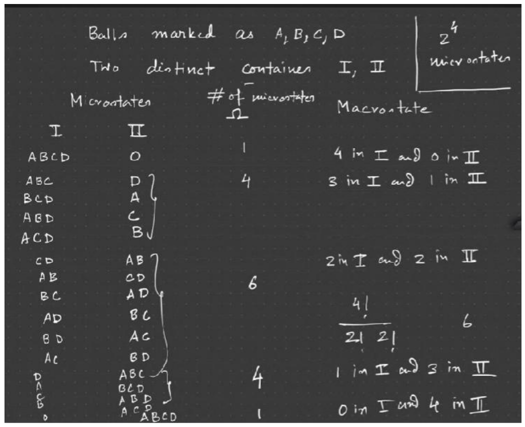


So, basically number of micro states here is 5 which gives you sum of 8. So, this is one example. So, if I tell for example, I want a sum 7 that means my top face of one dice, so this dice 1 and say this is dice 2. The top face should basically have a number, so here the number should be n1 and say here the number should be n2. n1 plus n2 has to be equal to 7. Now, how many ways you can have n1 plus n2 equal to 7? You can have n1 plus n2 equal to 7 in these ways like 1 and 6 gives 7, 2 and 5 gives 7, 3 plus 4 gives 7, 4 plus 3 again 7 and 5 and 2 7 and 6 plus 1 7. So, you have total 6 micro states here, 1, 2, 3, 4, 5, 6. 6 micro states here and the macro state is 7, the number has to be 7. Again if I tell, say now look at an interesting thing when I told the sum is 8, when I told the sum is 8 we get, we got only 5 micro states. When for sum equal to 7 we got 6 micro states.

Now think of sum 12, if I tell sum equal to 12 then basically the only combination that you can get is 6 and 6. So, which basically gives you 1 micro state. So, you are seeing now that different outcomes or different macro states correspond to a different number of micro states. The number of micro states is not the same for all macro states. Some macro states have more micro states and some have very less.
So, if I look at this I have done this. So, there are basically, so what are the macro states possible? So, 1 micro state, so when we have 2 dice rolled, you have 2 unbiased dice rolled. Then you have, what are the micro states possible? 2 is 1 micro state that is possible. 3, 4, 5, 6, 7. So, basically the sum is, now if it is 2 then the only micro state that is possible is 1 and 1. Right? It has to be 1 and 1. 3 you have 2 micro states possible. 4 you have 3 micro states possible as you can see here. Then 5 you have 1, 4, 2, 3, 3, 2 and 4, 1. So, you have 4 possible. 6 you have 1, 5, 2, 4, 3, 3, 4, 2 and 5, 1. So, you have 5 micro states possible. But you look at 7 you have 1, 6, 2, 5, 3, 4, 4, 3, 5, 2, 6, 1. Right? So, there are 6 micro states possible for the micro state of 7. For the micro state of 8 you have 2, 6, 3, 5, 4, 4, 5, 1, 6, 2, again 5. Then again it starts reducing for 9 it is 4. For 10 micro states the number of micro states possible is 3 as you can see here. 4, 6, 5, 5 and 6, 4. You cannot get any other combination. Right? When you roll 2 dice. Now, for 11 it is like 5, 6 and 6, 5. And for 12 again 1 single micro state. So, total number of micro states that are possible is 36. Right? Total number of micro states that are possible is 6. 6 out of these 36 micro states correspond to the micro state of 7.

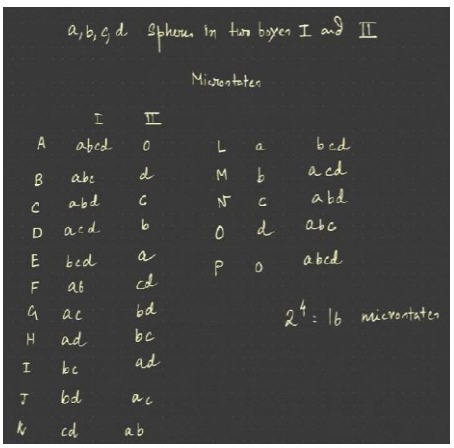
So, therefore using that information I can write the probability of finding a macro state of 7 is basically given by probability of finding a macro state of 7 or probability of finding micro states that will give rise to a macro state of 7. So, this I can write is as P7 represents the probability of finding micro states corresponding to macro state 7. Right? So, similarly I can calculate for example the probability of the micro state having, so what are the micro states that correspond to macro state 2 that probability is 1 by 36. Okay? And for P12 it is still 1 by 36. However, for P7 it is 6 by 36 which is basically 1 by 6.

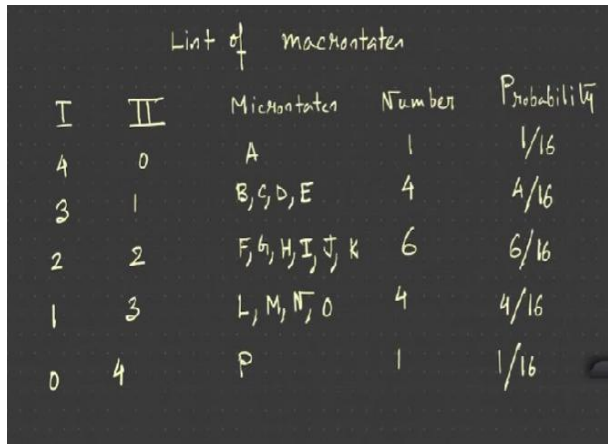
So, as you can see immediately from this chart, as you can see immediately from this chart is that P7 is the most likely outcome because it has the highest number of micro states. Right? It has the highest number of micro states. So, it is the most probable combination that you will see that 7 is the most probable combination that we will see. However, 12 and 2 both are least probable combinations. Right? Both have the same very low probability 1 by 36. Now, this is for a very limited number of outcomes. Right? We have very limited number of outcomes. Now think of this when my numbers become very large then the probability of the most likely micro states or probability of finding the most likely macro state increases to a very large number. It is like a several orders of magnitude greater than the least likely marks. Right? So, this is something that we have to understand. Again, I just give you another example. Say for example I have balls. So, remember here the outcomes that we are talking about where we can basically distinguish that is the thing. So, you are looking at the distinguishable outcomes. So, for example, this ideas of distinguishable is again I can show you that so there are 4 distinct balls A, B, C, D.



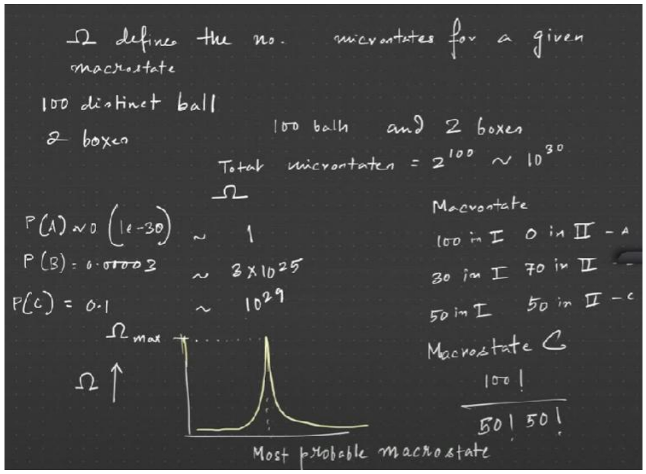
Right? They are marked as A, B, C and D. So, there are 4 distinct balls and there are 2 distinct containers. There are 2 distinct containers. So, they are again labeled as 1 and 2. Now, how can we arrange these 4 balls in these 2 containers? Right? How many ways can we arrange these 4 balls in these 2 containers? So, for example, I can think of the number of microstates like this. Like you have 1 and 2 and the distribution. Right? How the balls will be distributed among this 1 and 2? So, for example, I can have a configuration where all of A, B, C and D are in 1 but 2 has 0. Again, I can also have 3 in 1. So, A, B, C, A, B, C and D or B, C, D and A, A, B, D and C, A, C, D and B. So, these are again this is like 3 balls in 1 and 1 ball in 2. Right? Similarly, I can have 2 balls in each. So, for example, C, D, A, B, A, B, C, D, then B, C, A, D, A, D, B, C, B, D, A, C and A, C, B. Right? So, all of these are possible. Again, you have 6. You see the number. The number of microstates becomes 6. Now, the macrostate here is the state. Right? The state is like 2 balls should be in 1, the box number 1 and 2 balls should be in the box marked as 2. Right? 2 balls should be in the box marked as 1 and 2 balls should be in the box marked with the number 2. Right? And here this microstate is basically 3 in 1 and 1 in 2. And this is like the another microstate. It corresponds to one microstate like 4 in 1 and 0 in 2. And we can also have the same thing like 0 in 1 and 4 in 2. That is again another state. So, however, 2 in 1 and 2 in 2, this is like 2 in the container level 1 and 2 in the container level 2 is where the macrostate that gives you the maximum number of microstates.

The maximum number of microstates correspond to the macrostate. So, maximum number of microstates correspond to the macrostate 2 in 1 and 2 in 2. Right? So, this is the macrostate. Please note that this is the macrostate. Right? 2 in 1 and 2 in 2. And what are the 6 possible microstates? We have C and D in 1 and A and B in 2. Or A and B in 1 and C and D in 2. Right? So, basically if you see one very interesting thing here that there are totally 2 to the power 4 microstates here. Because you have 2 containers or 2 place holders. In each I can have this like you can have means either of like so for each ball you have only 2 containers. Right? So, basically you can go either here or here. Right? There are 2 ways of putting A or B or C or D. Means I can put whatever be the number of distinct balls or distinct objects that I have, I have 2 distinct place holders. Now, in this 2 distinct place holders there are only 2 ways I can put this balls.





I can put A either in 1 or in 2. Similarly, I can put B either in 1 or in 2. It does not depend on whether I have put A in 1 or A in 2. Right? So, again that's an independent event. So, basically if I think of that it basically means that it is like 2. So, A can be put in 2 ways in these 2 place holders. B can be put in 2 ways and C can be put in 2 ways and B can be also put in 2 ways. So, the total, the number of total microstates is 16 and you can if you add them 1 plus 4 plus 6 plus 4 plus 1 you can see that it is 16. So, 16 microstates are possible. What are the microstates? 1, this is 1 microstate, this is 1 microstate, this is 2, third microstate, fourth microstate and fifth microstate. Only 5 states are possible in this experiment. You have only 4 balls and 2 boxes. Again, the number is quite small. Now, think of a larger number. How many? So, basically another important thing I have defined, I have used omega, the symbol omega, you can see here, to represent the number of microstates. To represent the number of microstates for a given microstate.



So, if I have a given microstate, if I have a given microstate, I am trying to say that, so omega defines the number of microstates for a given microstate. So, now think of, just think of this. I have 100 distinct balls. So, again 100 distinct balls or distinguishable balls and I have 2 labeled boxes. Box 1 and box 2. So, 2 boxes that are labeled. Now, I have 2 placeholders and I have 100 distinct balls and I am telling that, okay, what will be the number of microstates? It will be basically, if I go by the previous logic and which is correct logic, it goes to total number of microstates become equal to 2 to the power 100. So, you see the number 2 to the power 100, which is approximately equal to 10 to the power 30. Now, what are the macrostates possible? Like 100 in, so there are several, many macrostates possible. 100 in 1, 0 in 2, 15 in 1, 15 in 2, 13 in 1, 17 in 2, something like that. So, just consider, let us consider 3 macrostates here.

For example, 100 balls in 1 and 0 in 2. That is the macrostate A and then 30 in 1 and 70 in 2, that is the macrostate B, 15 in 1 and 50 in 2, that is the macrostate C. Now, if I have to tell you, how do you find the combination of 15 in 1 and 15 in 2? So, for example, if I want to tell you that, you tell me how do you find 50? So, basically how many ways I can arrange these 100 balls so that 50 balls are in 1 and 50 balls are in 2, what will you do? So, you have 100 balls, right? You have 100 balls but you have 2 boxes. Now, but now I am telling that in 100 balls or in 2 boxes, you are basically looking at how to arrange 50 balls in 1 and 50 balls in 2, right? Or 30 balls in 1, 70 balls in 2. Can you tell me how do you calculate this problem? How do you calculate this number of 100 in 1 or 100, so how do you calculate this number of ways? So, the number of ways basically if I can think of, how many balls are there? 100 balls are there, right? 100 balls are there. From 100, you are picking up only 2 balls if that is so. So, that is not what you are doing exactly. So, can you tell me how do you do this? So, I will tell you the way to do this and then we will come back to this problem, right? We will come back to this problem, how to do this, 15, 1 and 15, 2. Please look at this problem again and try to find out, say for example, here it is a, b, c and d. So, how did we find this number? How did we find this number 4? Okay, and how did we find this number 6? Now, note this that there are 2 boxes here, okay? And there are 4 balls, right? So, you tell, you find out and I will go to, say for example, you see here I have given a formula, so I have given a formula, so I wanted to show you this formula, 4 factorial by 2 factorial, 2 factorial. Similarly, if I tell you that, if I tell you the number of ways I can have 50 balls in 1 and 15, 2, the formula is basically 100 factorial.

So, if I look at macrostate c, how many microstates will correspond to macrostate c? If I have to tell, so it will be like 100 factorial by 50 factorial, 50 factorial. You can try to find that out and you can find out what is the value, but what I am trying to say is that, that number comes out to be 10 to the power 29. Now, you see the, now if you have 10 to the power 29 divided by 10 to the power 30, then basically you get the probability of finding c macrostate and the probability of finding c macrostate is basically 0.1. So, you have 10 to the power 29 microstates that correspond to macrostate c.

Again, this is an approximate calculation. However, look at b which is 100 factorial by 30. Now, you will tell me how did you arrive at this formula. Just wait for a while. I will show you how to count in such a case, in such a condition how to count. Remember, the constraint is that, that total number of balls have to be equal to 100.

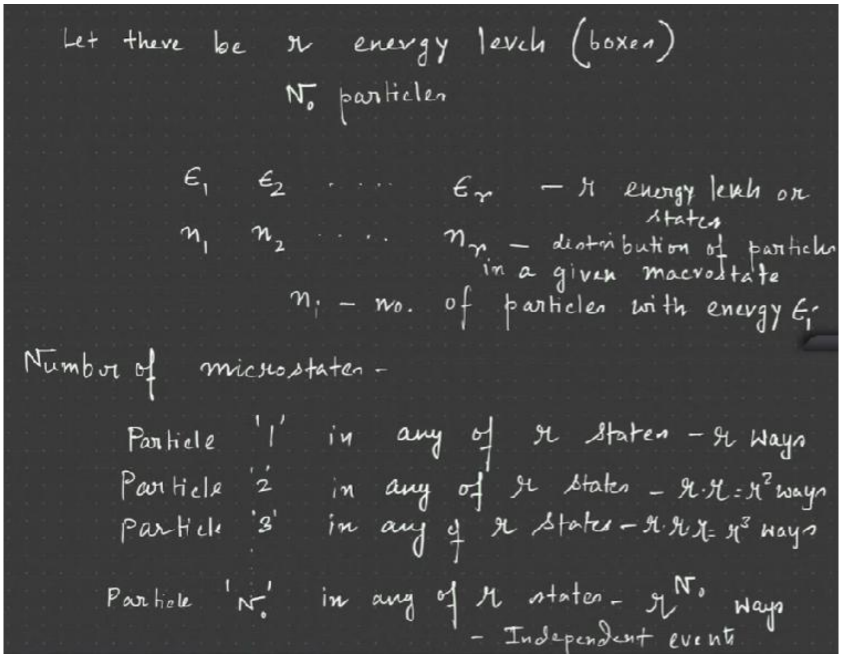
It has to be 100, 70, 30, 100, 0, 50, 50, whatever with the combination. You cannot have a combination of 50, 49. That's the idea. So, this is where the counting, the formula, this formula becomes very, very important. So, basically, if you see there are only two boxes and you can have like, you can think of like this corresponds to by the way, the combination formula which is called 100c2. I will come to that. So, but what I want to show here, if I plot omega, if I plot omega, so here I have plotted omega in the y axis and the most probable macrostate. Now, if you see, obviously, the most probable one is this one. c is most probable one. According to, you can also consider many other macrostates. You will see that the most probable one is the one where you are equally sharing the balls, 50 and 50. And you see that that point one is much, much larger than point 0, 0, 0, 0, 3 or 0. You can see the number of, if say for example, the number of microstates is 1, then the probability is 10, so 1e minus 30 or 10 to the power minus 30. So, basically, this is like, I can, so it is like 10 to the power minus 30, which is very, very, very small. It is like approximately 0.

So, see that it is asymptotically 0, we can tell. So, we can see that when the number, when the numbers increase, the number of species, the number of particles increase, number of distinguishable particles increase, you can immediately see a very rapid change in the most probable macrostate or the number of microstates corresponding to the most probable microstate. The number of microstates corresponding to the most probable microstate is that macrostate which will have the maximum number of, maximum number, omega max means, which will have the maximum number of microstates. So, the macrostate that corresponds to the maximum number of microstates is most likely and it becomes more and more likely if the total number of particles that you are arranging becomes very very large. So, that's why you have a spike here, if you see here, we have given a spike here, there is a spike here because see if you look at it, 10 to the power 29, it is even 4 orders larger than the B macrostate.

The B macrostate is 13,1 and 17,2. This is something, a take home message, this is something that you have to very carefully understand and appreciate. Once you appreciate this idea, then you can understand how this formulation for entropy will be developed using this number of configurations. Remember, if you remember entropy, when we define entropy, we told the maximum dissipation is what is favoured. For example, entropy will change in such a way such that, say for example, the entropy will change in such a way that it is always positive for the natural process or the irreversible process. Think of an irreversible process, again think of a pebble that I have thrown on a pond and the pond has still water.

Now, as soon as I throw the pebble and the pebble impacts water, there are ripples all around it. And you can see a large number of ripples that will be formed as the pebble hits the water surface. Now, think of this, the pebble has to reverse, comes back to your hand and all these waves, all these water ripples come together and become concentrated and the pebble jumps back to your hand. Now, that is a very, very unlikely process. But if you see the process where you have a lot of dissipation of energy, you have like a lot of ripples is the most likely, most likely event.

And that is where the entropy increases. And that entropy increase, as we have told our entropy maximization gives you the equilibrium state. And it also gives you the natural direction of the process. So, that's the idea. So, let us look at this now with n particles and r energy levels. So, you have like, if you think of a gas, for example, you have a lot of particles, this m0 particles let us consider. And there are also several energy levels. Because, for example, if you think of quantum mechanics or something quantum states, you tell that there are several energy levels. And this is not an energy levels are not continuous, but they are discrete energy levels. And some of these atoms, some of the atoms out of this n0 particles, some of the particles will occupy one energy level, some other will occupy another energy level and so on. So, basically, let us think of these energy levels like epsilon 1, epsilon 2 up to epsilon r. So, there are r energy levels or states, r can be 2, r can be 100, r can be 1000, but these are discrete energy levels.

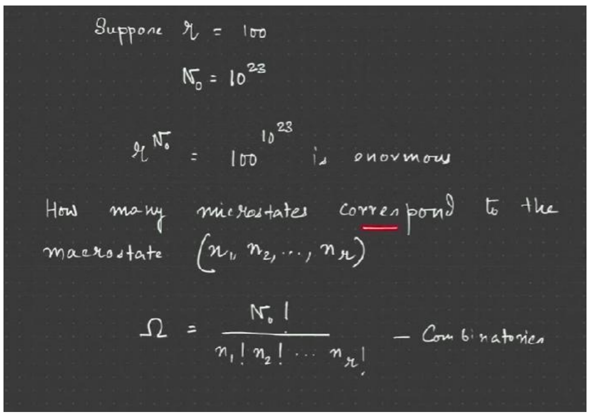


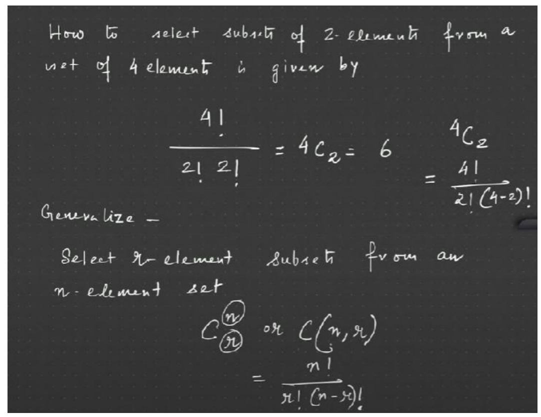
This is not like a continuous energy variation, but discrete energy levels. And each of these discrete energy levels will contain some number of particles. So, for example, n1 particles will go to epsilon 1, n2 particles will go to epsilon 2 and nr particles goes to epsilon r. Okay, so this basically this arrangement of n1 particles going to epsilon 1, n2 to epsilon 2 and nr to epsilon r itself is a state. So, ni is the number of particles with energy epsilon i and i goes from 1 to r. So, basically, if I tell particle 1 in any of the r now, now, if I want to calculate the number of microstates, what I am telling particle 1 can be in any of the r steps, which is r ways.

Particle 2 in any of the r steps, again r ways. So, in any of the r steps, it is possible particle 2, so this r times r which is r square ways. Again, particle 3 in any r step, so again r cube ways. So, basically, if I tell particle n0 in any r way, so it becomes r to the power n0. Now, think of this instead of r equal to 2, if I consider r equal to 10 and if you have particles like 30, you see the number of microstates possible is 10 to the power 30. The number of microstates increase more than, it is very, very fast, they increase very fast, it is more than exponential.

So, you can see as soon as the number of particles becomes large, number of box, number of energy levels become large. Energy, the more the energy levels, the more is the dispersion or dissipation of the energy. Dissipation of energy is more when you have more possibilities or more distribution, means a wider distribution of energy. But what we are considering, these energy levels are discrete.

So, these energy levels correspond to boxes. So, you had two boxes previously, now you have r boxes, r can vary from 2 to, it can be 1, it can be 2, it can be 100. And in general, in these large systems of large number of particles, there can also be a several, means quite a large number of energy states. So, remember when we talk about large number of particles, that is why it is called statistical mechanics, when because we are looking at thermodynamics of these systems with a massive number of particles. So, we have to find out how to calculate and how to understand these quantities that we derive from this description of particles, large number of particles and this large number of energy levels and how to look at these configurations and how to interpret.





So, let us go ahead. So, for example, we can think of r equal to 10 to the power 20, 100, r equal to 100, so 100 energy levels. So, basically 100 energy levels. Now, there are 100 energy levels and let us think of 1 mole of atoms which is like 10 to the power 23 atoms. So, basically r to the power n0 that is possible number of microstates is like 100 to the power 10 to the power 23, it is like enormous, it is so large that it is like infinite.

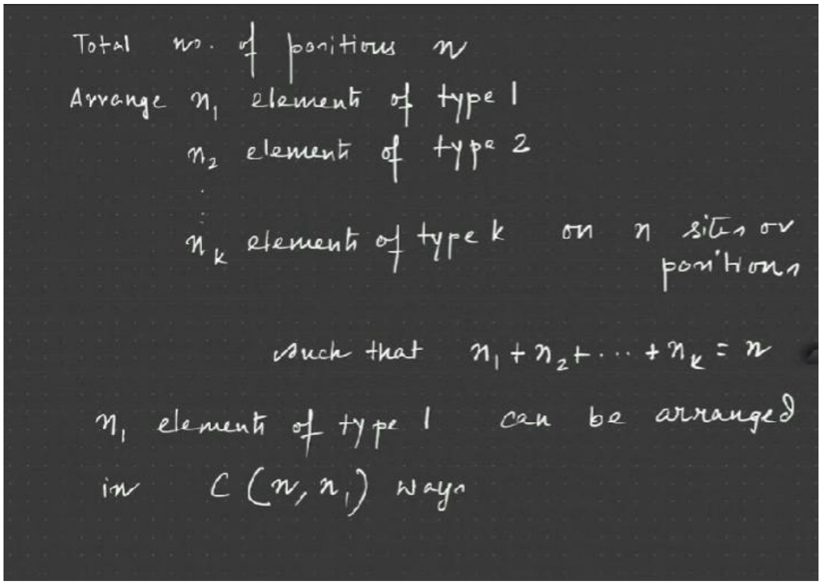
So, the number of microstates is huge. Now, how many microstates correspond to the macrostate? See, the macrostate that we defined is what? n1 particles will occupy energy level epsilon 1, n2 particles will occupy energy level epsilon 2 and so on. So, n3 particles epsilon 3, nr particles epsilon r. Now, if I tell that this is my macrostate, this is one macrostate where we have n1 particles in epsilon 1, n2 in epsilon 2 and nr in epsilon r. Now, in such a case, the number of microstates corresponding to this macrostate can be found by this formula that omega equals to n0 factorial by n1 factorial n2 factorial nr factorial. So, this is basically coming from combinatorics, right? This formula is coming from combinatorics.

This is nothing but this is, so we will see that. So, omega equals to n0 factorial by n1 factorial n2 factorial nr factorial. You will see it comes from a product rule of the combinations, okay? So, I will go to that. Okay, so again before I go to that, I want to show you the definition of this combination, right? Definition of C. So, basically if I have a set, okay, I have a set of n elements. I have a set of, I have set S containing n elements, right? I am going to a very basic combinatorics just to give you an introduction.

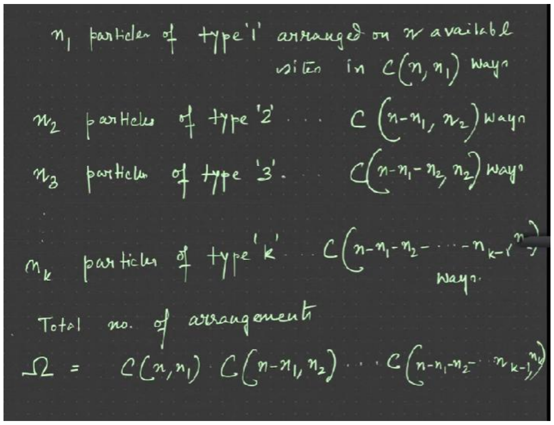
Now, fix a K that is less than n elements to form a K element subset. So, S is the large set of n elements. Out of that, we are fixing some K elements which are less than n to form a K elements subset. So, S for example, is a set of four elements, A, B, C and D. Now, two elements of sets are AB is one subset, AC is one subset, AD is one subset, PC, BD, CD, right? But note that CD on DC, that means the order does not matter.

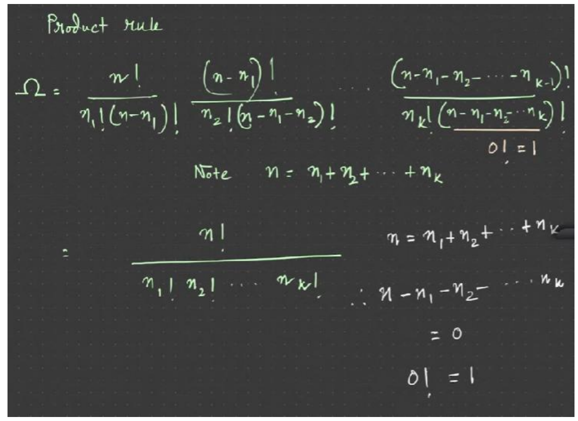
So, C and C, D or D, C are the same. But number of distinct two elements of sets are AB. AB and B are same. So, AB, AC, they are not same, right? AB and AC are distinct. So, AB, AC, AD, BC, PD, CD and so that means we do not care about the order at all. We do not care about the order at all, right? So, how to select the subset of two elements from a set of four elements is given by this four factorial by two factorial, two factorial, which is also written as four. So, we also write this one as 4C2 and 4C2 is nothing but four factorial by two factorial and four minus two factorial.

Okay, so basically, or we can call it like, so select r elements of sets from an n element set is given by C and so n elements set, right? And r elements of set, which is written as Cnr or nCr or Cn,r, which is given by n factorial by r factorial into n minus r factorial. Now, you will tell me, okay, that is fine, but why you have so many factorials here, like n1 factorial, n2 factorial. So, I will use some product rule with this Cnr. So, I will show you that. So, total number of positions, say for example, so if you look at the problem that we had initially, total number of positions, the problem that we told that there are n, n, n positions or n available positions and you have n1 elements of type 1, n2 elements of type 2 and nk elements of type k and they have to be arranged on this n positions or n sides and such that n1 plus n2 plus n, right? So, such that the sum of all these numbers, right? So, you have n1 elements of type 1, n2 of type 2, these types are distinguishable, remember.



So, type 1 is distinct from type 2, is distinct from type k. Now, what we are telling is all these elements that we have, we want to put them on n sides such that n1 plus n2 plus dot dot dot nk, that means n1 plus n2 sum up to nk. So, basically n1, so if I have three elements, n1 is of type 1, n2 of type 3, that type 2 and n3 of type 3 and you have total n sides, we are telling that n1 plus n2 plus n3 equal to n. So, no side is vacant, no side is vacant and all of these, all these elements occupy the sides, okay? So, such that, that's why this constraint, this is called a constraint, the sum of n1 to nk of sum of all elements of different types is going to be equal to the number of sides, right? So, now look at, now start with this, we start with n1 elements, we can start with any other, okay? But we start with n1 elements of type 1 and that can be arranged among n sides. So, you have n sides, n is much larger than n1, so it is basically coming from this combination formula, so cnn1 ways, right? cn, n1 ways and n1 particles of type 1, if you use cnn1 ways, now you have n minus n1 sides remaining and you are now trying to arrange particles of type 2. So, cnn1, n2, that is the, so now we are looking at n2 subset from the remaining elements of the set which is n minus n2.





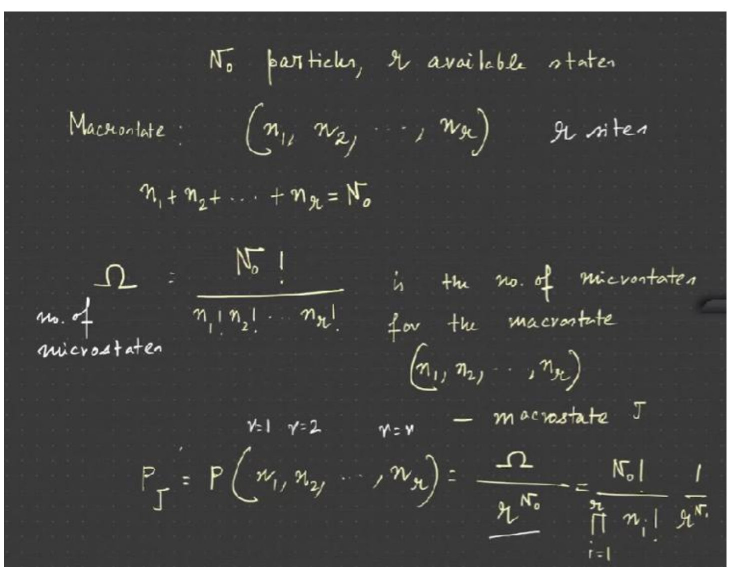
Now, again you have n3 particles, see remember, as soon as n1 and n2 are arranged, now you have n minus n1 minus n2 only remaining. Now, that is your set remaining or that is your positions remaining, in that you want to arrange, okay? Or you want to arrange this number of n3 particles. So, if I have to do that, so this will be obviously, this is wrong, this has to be n3, right? So, you want to arrange n3 particles in the available n minus n1 minus n2 sides. How many ways to arrange them is given again by this combination formula, right? Now, you go on and on and then you have nk particles of type k, so you have, how do you do that? You have filled up to nk minus 1, right? You have filled up to nk minus 1, right? And you are now, whatever sides are remaining, whatever sides are remaining, on that you want to arrange this nk particles, right? So, basically look at this, this is like n minus n1 minus n2 minus up to nk minus 1 and you have nk particles remaining, this itself is nk, right? So, there is this number of ways. So, total number of arrangements if I do, that is the omega is basically, you can use a product like c and n1 and then n minus n1, n2 like that up to n minus n1 minus n2 up to nk minus 1 nk.

Now, if you do that, you get this product rule which is n factorial by n factorial, n1 factorial, n minus n1 factorial. Again, here there is an n minus n1 factorial and here it is n2 factorial and n minus n1 minus n2 factorial. Now, similarly here you have n minus n1 up to nk minus 1 factorial and then here also, so you have n minus n1 minus n2 minus up to nk. So, basically remember that this basically n itself is equal to n itself is equals to n1 plus n2 plus nk up to nk sum. So, that means this last one, so therefore n minus n1 minus n2 minus nk is going to be equal to 0, but 0 factorial equal to 1, right? So, 0 factorial equal to 1.

So, now you see n minus n1 factorial cancels, right? n minus n1 factorial you can cancel with this one, right? The denominator and numerator. Similarly, here and here. Similarly, it means, so all of these will cancel. So, you have n factorial remaining, n factorial will remain and see n1 factorial will remain, n2 factorial remain, nk factorial will remain.

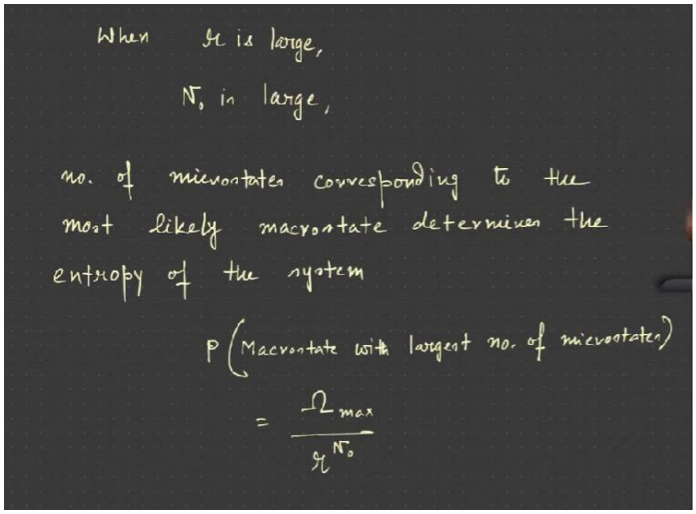
All these other terms will basically get means you can cross them. Say for example, this one and this one are common, right? So, you can remove them, right? Because these are not 0. So, it's 0 by, it's not 0 by 0. So, these are finite numbers or finite numbers, if they are same numbers, so that will be equal to 1, right? So, you can basically do that. So, you can cancel them and you will, so what you cannot cancel, you cannot cancel n factorial, you cannot cancel n1 factorial, n2 factorial up to nk factorial. So, basically, since n is this and this is the constraint and we had n sites available and all these elements were there, out of which n1 particles were of type 1, they were indistinguishable, right? This type 1 particles are indistinguishable among themselves.

However, 1 is indistinguishable from 2, 2 is distinguishable from 3. So, you have this formula n factorial by this. Now, exactly this is the formula that I have been using, whether it is 4C2, whether it is 100C50 or whether it is 100C70, right? So, when we had this one, so for example, this one, I told for macrostate C that the number of ways is 100 factorial by 50 factorial, 50 factorial. So, right? And here we told it is like n0 factorial by n1 factorial, n2 factorial up to nr factorial, right? So, that is the formula that we also derived, okay? Just by using a product rule. So, now come to the probability. Let us come to the probability. So, you have now, now we have come to n0 particles, r available states and the macrostate that we are corresponding is like n1, n2 up to nr and the sum of these is equal to n0. Then we know the number of, so this is basically omega is nothing but the number of microstates. So, it is coming from n0 factorial because n0 particles were there and the n0 sites are also there.



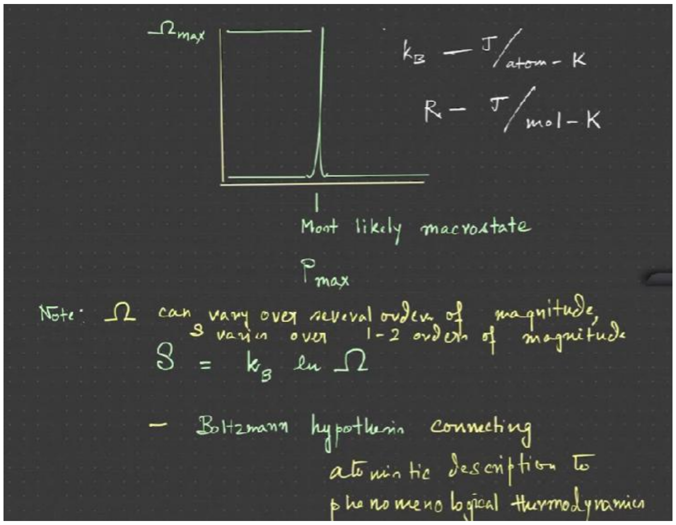
Let us assume that, so no, n0 particles are there. In this case, n0 particles are there. But the number of sites available is r, right? r available states means r available energy states means there are r sites, r sites. And n0 particles, right? n0 particles have to be arranged among r sites. Now, if that is so, the omega comes out to be n0 factorial by n1 factorial, n2 factorial up to nr factorial, right? But remember, this comes because n1, n2 up to nr, if I add them up, we get basically nothing but n0, right? So, this is the number of microstates for the macrostate. So, this is what exactly I am, so number of, so this is, so omega which is given by this is the number of microstates for the macrostate correspond to this, right? This one.

So, let us call this macrostate j. Now, if that is a macrostate j, the probability of finding this macrostate j is like probability of finding a state, probability of finding a state where n1 particles occupy r means energy level epsilon 1 or means energy level 1 and n2 occupies energy level 2, right? So, basically here we can like write like that like here r equal to 1, here r equal to 2 like that, r equal to r, right? So, n1 occupying r equal to 1, n2 occupying r equal to 2, nk or nr occupying r equal to 1. Now, if that is so, you have omega and the number of microstates is r to the power n0, right? These are the number of available microstates, right? So, omega by r to the power n0 is basically like n0 factorial by this is a continued, please note that this is a continued product symbol. So, i equal to 1 to r ni factorial, are you seeing that? So, n0 factorial by ni factorial, right? Because omega is what? n0 factorial by n1 factorial, n2 factorial up to nr factorial divided by r to the power n0, right? That is what is going to be giving me the probability of macrostate j, okay? So, again if I just look at it, just to reprise all this, so you have 16 microstates and you can see that you have like a to p, these are your different microstates, a to p are microstates. But if you look at the macrostates, then basically you are thinking of, because there are two boxes, right? There are two boxes, then you can tell that this is a microstate, this is as I told previously, this is a microstate 1, right? Here you have four particles in 1 and 0 in 2, 3 in 1 and 1 in 2, 2 in 1 and 2 in 2, so these are the number of macrostates.



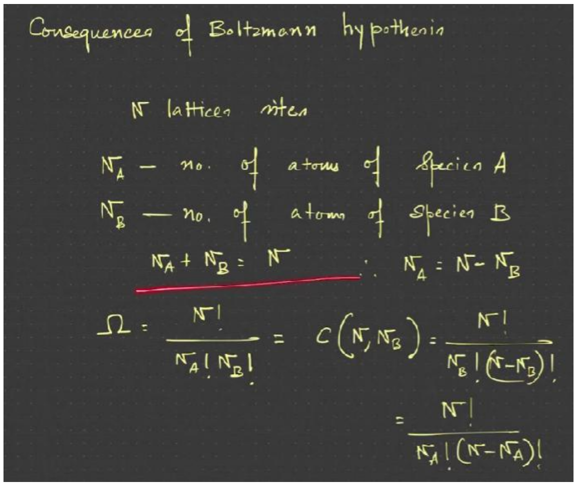
And the macrostates have this type of computation, 4, 0 means it corresponds to the microstate a. And there it corresponds to p, c, d, e. Then f2, k corresponds to 2, 2. Then lm, n0 corresponds to 1, 3 macrostate. And 0, 4 corresponds to p. Now if you see the probability of each, so if you see macrostate, the macrostate number 1, this macrostate, this macrostate, then you have 1 by 16.

And the highest is when 2 and 2 are there, right? So only thing that you have to remember, as I told you from the spike, that when r is large and n0 is large, all of these are large, number of microstates correspond to the most likely macrostate determines the entropy of the system. Because that gives you the maximum number of energy levels, okay, over which the energy dissipation can take place. So number of energy levels available for dissipation have to be maximum, right? And that should determine the entropy of the system. So what determines the entropy of the system? The macrostate, the probability of finding the macrostate with the largest number of microstates, the macrostate that corresponds to the largest number of microstates is that macrostate that determines the, or this number of microstates will, for that particular macrostate is what is going to determine the entropy of the system. So this omega max by rn0, this probability is going to determine the entropy of the system, right? So again, I have drawn the same curve, so as you can see, omega max peaks here, where it is the most likely macrostate.

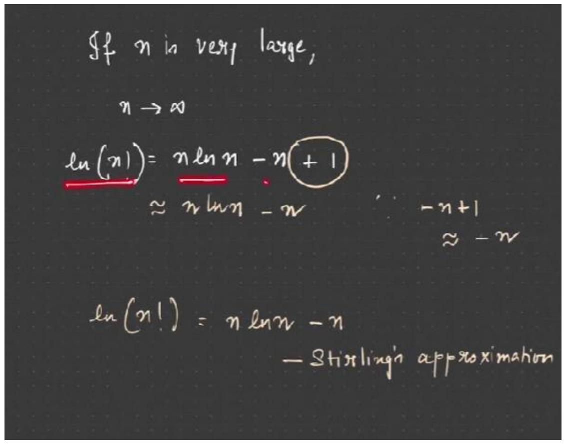


Most likely macrostate is the one where you have the maximum number of microstates, like omega is the number of microstates. So when you have omega max, then basically you pick up here, and see the other ones, the probability of finding other ones are so low, are so low compared to this one, then you have number of particles, number of available sites, all are very large, right? So omega can vary over several orders of magnitude, but s, but see, omega can vary over u, means really several orders of magnitude, but s varies over only a few orders of magnitude, like 1 to 2 orders of magnitude. As a result, you will see that Boltzmann, when he hypothesized that how is it related to omega, or the number of microstates, he used ks equal to kB ln omega. This is typical, because if you see, this is something that a genius like Boltzmann will always think of, because if you see, you have omega which can be very very large, which can vary by over several orders of magnitude, we have seen that, right? 30, 70 was 10 to the power 25, 50, 50 was 10 to the power, even with 2 available states, we had 50, 50, right? Even with 2 available states, we had 50, 50 with 10 to the power 29, right? 10 to the power 29 microstates. And 0, 100 or 100, 0 had 1 microstate, right? If you have 100 particles in box 1 and 0 particles in box 2, then there are only 1, there is only 1 microstate corresponding to that, but if you have 50 particles in box 1 and 50 in box 2, it corresponded to 10 to the power 29, right? 10 to the power 29 out of 10 to the power 30 possible microstates.

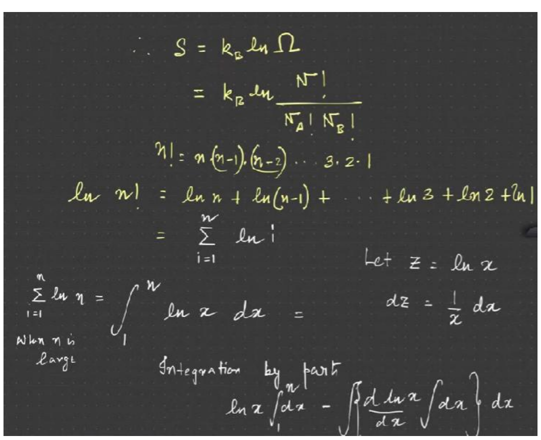
Now, if you see that, that is going to dominate, because 29 orders of magnitude, this is as large as that, but S in general, we have seen, right? We have looked at the problems, S in general does not vary to such like 29 orders, it varies over 1 to 2 orders of magnitude. Now, if you, so the way to think of this or relating omega to S, you require to take help of logarithm, because logarithm reduces, right? Reduces the order of magnitude difference, right? Logarithm makes it smaller, like log of 2 to the power 5 is 5 log 2, correct? But if you think of 2 to the power 5, it is quite large number, so this is the exact, that is why S, so Boltzmann thought S equals to kB ln omega. Another important point, this is something that you think about, is that since entropy is an extensive quantity, kB ln omega, right? But here what we are talking about kB, remember this is Boltzmann's constant, Boltzmann's constant is always per mole, right? So, this S here that we are talking about is per mole, right? Because kB is R by Na, so it is not, it is, so here S is like, you know, like kB, if you think of kB, kB is joules square per mole Kelvin, atom Kelvin, while that is the kB, see me, and if you look at R, it is joules per mole Kelvin, so it is per mole, remember, okay? So, but it is per mole that you remember, but remember that since the magnitude, order of magnitude are so different, okay? But there is another important thing, when we have this extensive entropy, how do you define, so you think about it, how do you define the extensive, because total entropy is extensive, right? Entropy per mole is not extensive. So, here that what we are defining is like, integral per atom or integral per mole, right? So, if you want to define an extensive entropy in terms of the statistical configurations, how do you do that, think about it. So, Boltzmann hypothesis, as you can see, one of the most brilliant hypothesis that you have, it connects the atomistic description, one of the most important hypothesis that you can have, and that hypothesis basically connects the atomistic description, in terms of particles, right? Atomistic description of matter in terms of particles, particles can be like atoms, it can be permeance, it can be bosons, so this atomistic description of particles has, is connected to the phenomenological thermodynamics that we study, right? We study the macroscopic phenomenological thermodynamics, where we have observed quantities or perceptible quantities, and these perceptible quantities are something that we can, means we can perceive, right? We can measure volume using the dimensions of a container, right? So, basically we can measure volume of a system, we can measure temperature of a system, these are basically, and we have this macroscopic or phenomenological description of thermodynamics, but here this is done, Boltzmann connected that to the number of configurations of particles in large systems, right? So, this is a very, very important hypothesis or law, the S equals to K.

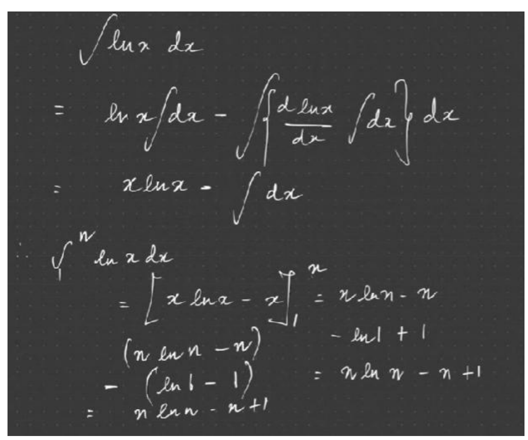


Now, what is consequence of Boltzmann hypothesis, what are the consequence of Boltzmann hypothesis? So, you have N ladyzides, NA is the number of atoms of species A, NB is the number of species atoms of species B, then NA plus NB equal to N, let us assume that you have two species A and B, where NA is the number of atoms of species A and number of atoms of species B is NB and NA plus NB equal to N that means the number of the lattice size have to be occupied by either A or B, then one can write NA equals to N minus NB. Now, omega is N factorial by NA factorial NB factorial, which is again which is nothing but CA and NB which is N factorial by NB factorial N minus NB factorial or we can write it as N factorial by NA factorial into N minus NB factorial because of this relation, this is the constraint. Now, once you have done that, you have S which is equal to K B ln omega and K B ln N factorial by NA factorial NB factorial and you know how the N factorial is, I have just given the formula N times N minus 1 times N minus 2 and it continues up to 1. Now, ln of N factorial, this is called Stirling's approximation, so ln means I will derive Stirling's approximation, so ln of N factorial if I just have to give the logarithm of the N factorial, what do I get? I get ln N plus ln N minus 1 plus ln N 3, ln 2 and ln 1, right or basically I equal to 1 to N, ln I, right. Now, look at this I equal to 1 to N, ln N, the summation can also be written in a continuous way by using an integral, so basically limits are from 1 to N and you have ln X dx.



Now, if you have ln X dx, you can do integration by parts, here I have done integration by parts, so integral of ln X dx, so ln X I have taken as the first function, right and 1 as the second function, so ln X dx and this first function, so d ln X dx dx and this entire thing have to be integrated over dx. So, now you get x ln x minus x ln x minus dx integral and the integral basically the, what are the limits? 1 and N, right. So, this becomes x ln x minus x or so basically this becomes N, ln N minus N, right because x ln x minus x is there, so this becomes N, ln N minus N minus ln 1 which is 0 minus 1. So, this becomes N, ln N minus N and this is minus, so this is minus, right, so this is minus and so this becomes plus, right or you can write this, first you write this, ln minus 1, right, ln minus 1 and which is equal to N, ln N, right. ln minus 1 and which is equal to N, ln N minus N plus 1, right, so that is what, so basically ln of N factorial is N, ln N minus N plus 1, remember that.



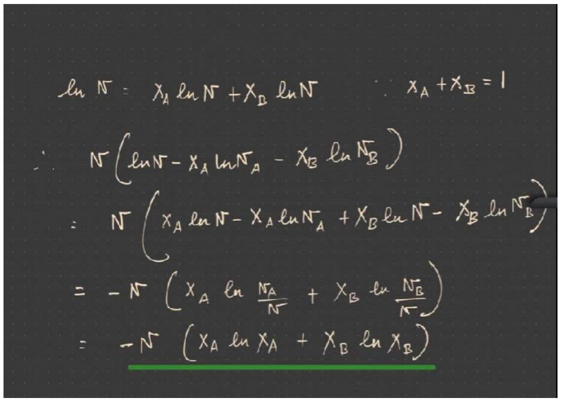
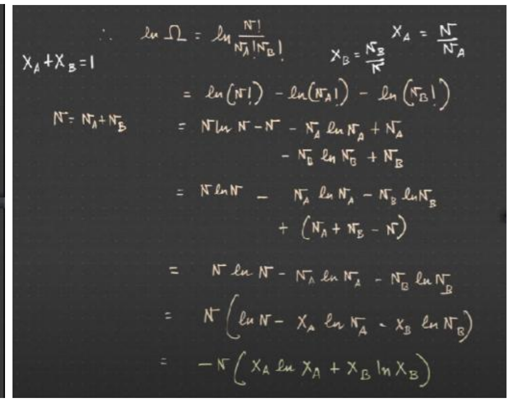


That is what I have derived here. Now, so if N is very large that means say for example N tends to infinity like N equal to 23 then ln N factorial is N, ln N minus N because this plus 1 can be ignored, right, N is so large that plus 1 can be ignored. So, it approximately becomes N, ln N minus N, right, okay because minus of N plus 1 you are adding 1 and that 1 is so insignificant compared to N that minus N plus 1 is nothing but minus N, right. So, you can remove this 1, N is so large that this plus 1 does not make any difference. So, ln N factorial equals to N, ln N minus N is a famous approximation that is used by Sterling and James Sterling and this approximation is something that we will use to find the number of arrangements, okay and also to find out the ln omega. So, ln omega is what we have to find out because a is equal to k, b, ln omega and as you have seen we have used two species A and B and we have N A atoms of A and N B atoms of B and the total number of sites available is N which is N A plus N B.

Now, if you do this you continue doing this algebra, so you have ln N factorial minus ln N A factorial minus ln N B factorial. Now, you continue doing this, so N N N N minus N minus N A N N N N plus N A N B N N B plus N B. So, if you do this you have this term, this term and this term and you have N A plus N B minus N, N A plus N B minus N is nothing but N minus N which is 0. So, you have N N N N minus N A N N A minus N B N N B. Now, you take N form, so you get ln N minus x A ln N A minus x B ln N B. Now, you go further, so ln N, so you have x A ln N, what did I do? So, this goes to 0, right, so this goes to 0, now this guy goes to 0 because N A plus N B equal to N, N minus N equal to 0.

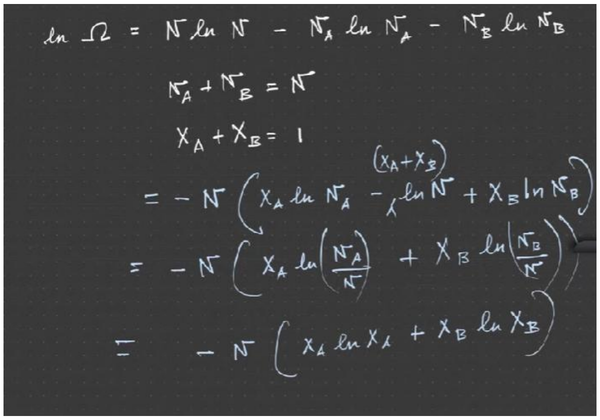
So, you have this term, this term and this term, right, this is the term. Now, I keep N constant, so I get ln N minus x A ln N A minus x B ln N B. Now, I can do, if you see x A is nothing but the mole fraction, x A equals to N by N. So, if I do this, ln N minus x A ln N A. Now, I want to make it like this, I am writing as minus of x A ln N A, right, and this will be minus ln of N.

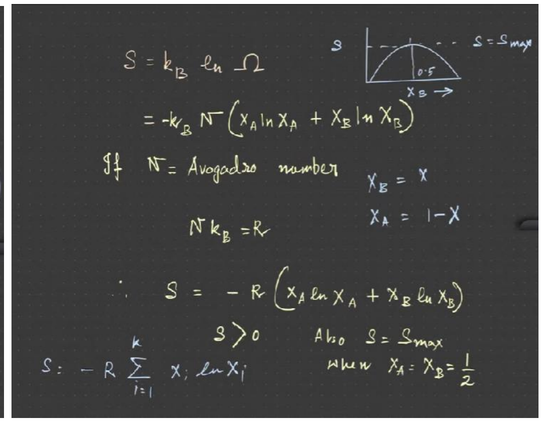
Now, this I will write this ln of minus of ln of N. Now, this can be written as, now this, there is one, so if you see x B goes to N B by N and x A plus x B because you have only two species equal to one, right. So, using that condition, if I put x A plus x B here, so this becomes, say only I am taking these two parts. So, I have minus x A ln N A, so I have taken N common, you can see.

So, x ln N A minus x A plus x B ln N. If I do that, now you can see the other part is also there. So, if I do this, what I get immediately, so I just, I did not just want to make it very clumsy, but you can immediately see, I do not want to make it clumsy. So, if you see, I should show you, you have, so you got ln omega equals to N ln N minus, this is a little bit of algebraic manipulation, minus N B, now N A plus N B, then moles of A and moles of B, mole number of A plus mole number of B equal to N sides, right, that is the constraint. Or if I can define, if I divide both sides, so I get by N, so I get here one and here I get N A by N, which is x A plus x B, this is the mole fractions add up to one, right. Now, I just take, now these are the things, so basically now I take minus N common, and then it becomes minus ln N, and here this will become plus x B ln N B.

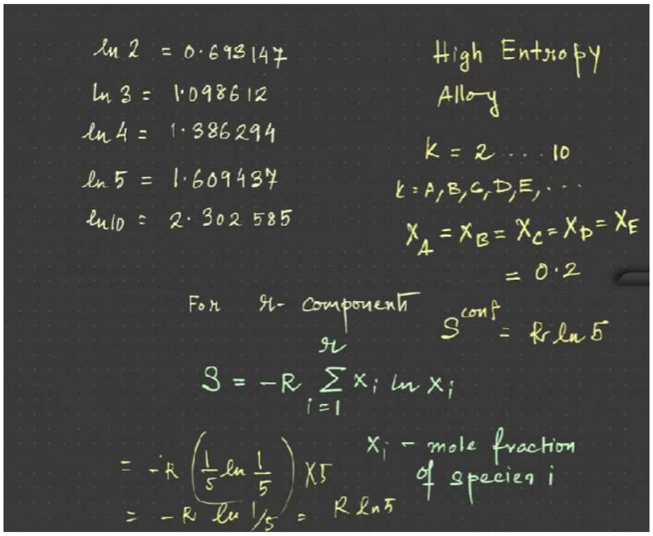
Now, instead of ln N, here you can add x A plus x B, because x B plus x B equal to one. And using this identity, you can now write this as minus N, and you see x A ln N, there is a minus x A ln N, so basically if you see, this is x A ln N A by N, and this will be plus x B ln N B by N. So, this can be written as minus N x A ln x A plus x B ln x B, right, so we got minus N x A ln x A plus x B ln x B, right. So, this is what I have derived, so minus N x A ln x A plus x B ln x B, now S is K B ln omega, so now it is minus K B times N, right, K B times N x A ln x A plus x B ln x B. So, let N be the Avogadro number, if N is Avogadro number, then N times K B is nothing but R, which is the universal gas constant, so S comes out to be minus R, x A ln x A plus x B ln x B. Now, since x A and x B are less than, see remember, when x A equal to one, then ln one is zero, but ln zero is undefined, ln x B is undefined, right, because x B becomes zero.





So, x A and x B have to be less, has to be greater than zero, but less than one, that means they have to be fractional, if they are fractional, then the logarithms are always negative, right, the logarithms are negative, if you have x A, which is fractional, which is less than one, x B, which is fractional, which is less than one, then they are, the logarithms will give you negative values, right. So, negative values with a minus sign here, and there it will also be negative, so as a result, the total sum will be positive, right, S is always greater than, S is greater than zero. Another thing, if you plot this expression, because see x B is nothing but, so you can write this, the same thing we can write as S equals to minus R, I can do it for any number of elements, I can write summation i equal to one to say whatever number of elements if you give, say i equal to one to k, and then I can write x i ln x i, that k is the total number of elements, right. So, k is the number of different species, right, k is the different number of different species. So, now if I plot this, say for binary also, if I plot this, you will see the curve, if you look at this, so remember, so I can take x A equals to, or x B equals to x, then x A equals to one minus x.

Now, if I plot it, if I plot it, then what I will get is, and say this is x B, you will see something like, and you will see that at point five, at point five, means x equal to point five, S you get S equals to S minus, this is basically S equal to S, right. So, this is something that becomes very, very interesting, and if you see that now this new alloys are coming, which are called high entropy alloys, right, you have seen this name called high entropy alloys, many of you have encountered this. Where you basically mix a larger number of elements, like five elements in equal proportion, why equal proportion? Because as I told you, see when it is 50-50, it has the maximum number, maximum entropy. Similarly, maximum configurational entropy, right, because we are looking at entropy here from the standpoint of configurations, how many microstates, like maximum number of microstates, that corresponds to that microstate which is likely, and that microstate is going to determine the entropy, right. So, and that is always going to be the distribution where you have equal number of different species, right, so this is called high entropy alloy concept.



Now, if you see high entropy alloy generally contains like n, which is number of elements, sorry, k, which is like k can be like A, k can be like A, B, C, these are like different atomic species, right, different species, like from the periodic table and so on. And k can generally vary from 2, when I am talking about alloy, then it has to be greater than 1, so 2, 2 you can go to like 10, 12, but generally we look at five components, six component alloys, and if you look at that, immediately you can see this minus R, xi and xi, it just basically becomes, when it is equal proportion, so it becomes, say for example, you have five elements, it becomes minus of R, one fifth ln 1 by 5 and you are doing it like five times, like you are summing it five times, so it becomes into 5, so this becomes equals to minus R ln 1 by 5, which is nothing but R ln 5. So, you have like k, so it becomes R ln 5, so if you have k elements, so basically this becomes, when you have equal proportion, when you have like xa, say I have five elements, equal to xb, xc, xd, xc and these are all have to be equal, so these are equal, sum is equal to 1, so each has to be equal to 0.2. Now, in this case, the entropy S or you can call it S, because there is also a vibrational entropy that is associated, so this is the configuration entropy and that is basically the number, it is determined by the maximum number, the macro state corresponding to maximum number of microstates and then we use Boltzmann hypothesis, what I get is this, S comp is equal to R ln 5.

Now, you see when I have five elements, I get R ln 5, and R ln 5 corresponds to 1.6, whereas ln 2 corresponds to 0.69, so as I increase the number of elements and if I take equiatomic composition, each species has equal proportion, then I get, I maximize the entropy and I also increase the value as I go up and up, means in terms of number of components, like 2 gives me 0.69, 5 gives me 0.6, 10 gives me 2.3. However, it is very unlikely to get a 10 component alloy, if this is because that not only this entropy that is, we will show later, that not only entropy being one of the criteria, there are also different criteria in terms of atomic sizes and electronegativity difference and stuff, right.

So, we will discuss this later, so I will in the next, so basically please note this very important idea that we could derive, right, we could derive and we could connect this atomistic description of matter with the macroscopic description. Okay, so in the next lecture, I will tell how from this atomistic description I can basically calculate useful quantities like C, I have calculated S, now if I can calculate U, right, we know already how to calculate U, but can we calculate Cp, Cv and some, right, and what is ensemble and what is partition function, so I will briefly describe all of these in the next lecture, so thank you for listening to this. Thanks, and if you have any question, please note, if you have any question, please post them in some comment section so that I can basically answer this, okay, I can basically answer this, I can upload a lecture to address some of your queries. Thank you, thank you so much.