Thermodynamics of Fluid Phase Equilibria
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Lecture - 33
Multiplicity and Maximizing the Multiplicity

Welcome back, in the last class we developed expressions of multiplicity for simple system. In this lecture, we are going to learn, how this multiplicity and particularly maximizing the multiplicity with or without the constraints are related to physical processes. So, let me just first summarize what we have done.

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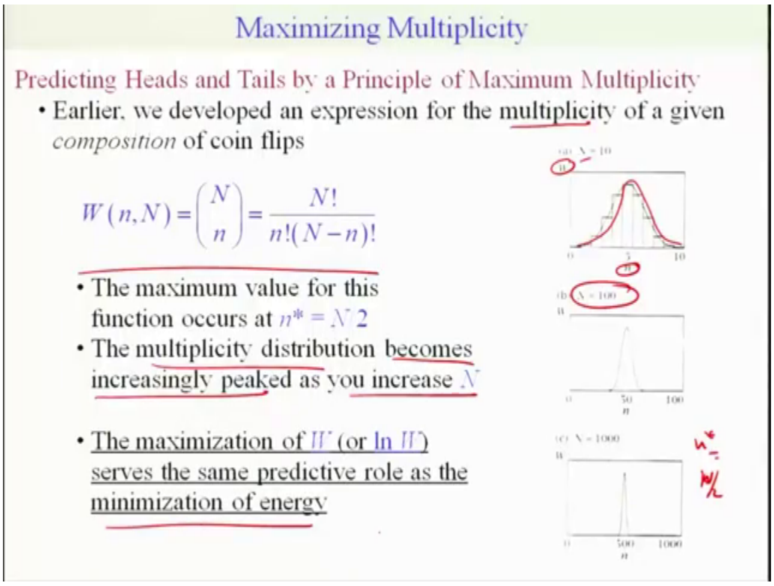

In terms of the development of the expression of multiplicity; we use simple systems such as head and tails systems. And we developed the multiplicity particularly for ah; let us say a composition of coin flips which can be given by this expression where n could be number of head and capital N would be a number of outcomes that includes heads and tail.

So, this is a simple expression of multiplicity; now if you increase n that is it from small number to a large number and let us say you plot the W as a function of small n ok; which again as I said could be number of a heads or number of tails out of capital N outcomes. So, you could see that this expression can be obtained which will look like this if you connect the histogram maximum points.

And here as you increase the capital N what you are going to see is basically the distribution a will be around the n by 2 value as a as shown here and it would be peaked around it which is going to be sharp peak. As clearly from this geometric representation, you can clearly see the maximum workers at n star is equal to n by 2 ok; n star is equal to capital N by 2.

So, the multiplicity distribution becomes or increasingly peaked as you increase n and now why this is important; because we would soon learn that maximization of W or the multiplicity or in logarithmic value of the W serves the same predictive role as a minimization of the energy in order to obtain the optimum value of a variable for a given system.

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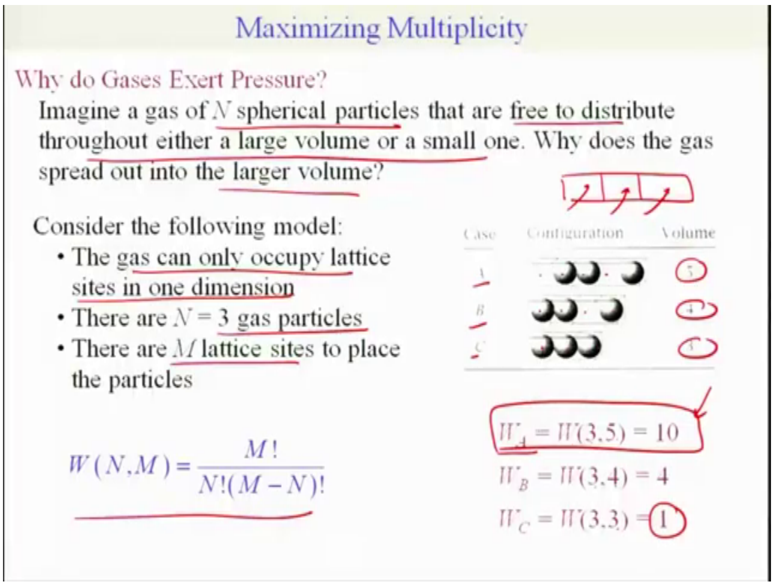

So, with this we can ask a couple of questions and understand the importance of this concept. For example, why do gases exert pressure? Now imagine a gas of N spherical particles that are free to distribute throughout the either large volume or a small volume.

The question would be why does the gas spread out in the larger volume that is something which we have a intuition about it ok, but how do you explain that using the multiplicity concept? So, we are going to consider three systems here; so, let us consider three cases A B C for a given number of gas particles which occupies different volume.

And here the gas can occupy lattice side in one dimension. So, what we have done is the volume itself is divided into different latticed sites. So, this is becomes one lattice site, this is another lattice site and this is another lattice site and the particle which in this case are only three gas particles can occupy only one lattice site. So, let us assume that you have a total number of lattice site is M. And now you have three which can vary depending on the volume which we have and here you have the three cases A B C.

So the volume in the A is going to be 5 because they have 1, 2, 3, 4, 5 1, 2, 3, 4, 5 lattice points here they are 1, 2 3, 4 lattice points and here you have three lattice points. Now considering these one can say that while the number of possible ways to arrange on the multiplicity in this case will vary.

And with vary the same in a form as we have shown earlier. So, in this case what is W A? W A would be 3 out of 5 lattice point, W B would be W 3 out of 4 and W C would be 3 out of 3. So, in this case there is only one possibility.

Because it is in distributed and they show all the particles of same type and hence it is indistinguishable. Now the maximum possibility is basically 10 and hence it tries to expand in order to maximize the number of ways it can arrange itself and this is clearly seen by at the number of W A; this is maximum for the case of A; indicates that the gas like to spread out or the gas particles like to spread out in order to access more sites which it would lead to the increase in the multiplicity.

So, that is the case why the gas spreads out in to larger volume. So, that is a case of case or example 1; another examples and try to explain the similar explain the phenomena based on the maximizing multiplicity concepts.

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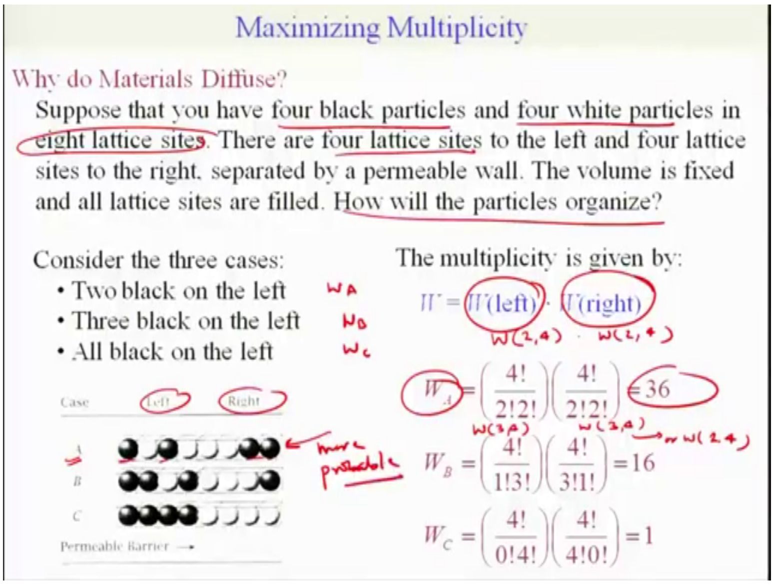

For example why do material diffuse suppose that you have four black particles and four white particles in eight lattice sites. So, there are four lattice sites with the left and four lattice sites with the right and this left hand side regions are separated by a permeable wall.

So, let us say this is the left region this is a right region and this in between there is a permeable wall and as I said therefore, black particles and four white particles; the volume is fixed and all the lattice sites are filled how would the particle organize ? So, what would be the condition for let us say an equilibrium?

So, we consider let us say in order to understand this why particle diffuse or what is the best scenario for an equilibrium condition. We consider a just three cases; in the case A you have two black on the left and of course, two black on the right, in the case B you have three blacks on the left, in the case C you have all the blacks on the left.

And then we ask this question that what is a multiplicity of W A, B and W C. So, this would give an indication that which scenario would be more preferred.

So, we simply since calculate the multiplicity in this case by finding out the multiplicity of the left region multiplied by the right region because these are kind of independent here. So, event A; so, you the number of ways you can arrange in the left multiplied by the number of ways you can arrange in the right would be the total number of multiplicity for the given condition for the given case here.

So, we can simply use the same formulation as we have done earlier. So, this would be your W in this case is 2. 4 multiplied by W again 2, 4 whereas; in this case there are three blacks out of four regions.

So, there should be W 3, 4 and this is again would be W 3, 4 or 1, 4 four or 1, 4 this would be same. And similarly this will be your W 0 4 or 4, 4 and you can clearly see in this case the W A has the maximum multiplicity which indicates that the mixing of this particle or from; initially you had the black in the left region white in the right region.

So, white particle or black particle such that it allows a mixing of this particle, increases the multiplicity and this is the reason that the materials diffuses in order to maximize is multiplicity. So, this means this is more probable scenario at equilibrium.

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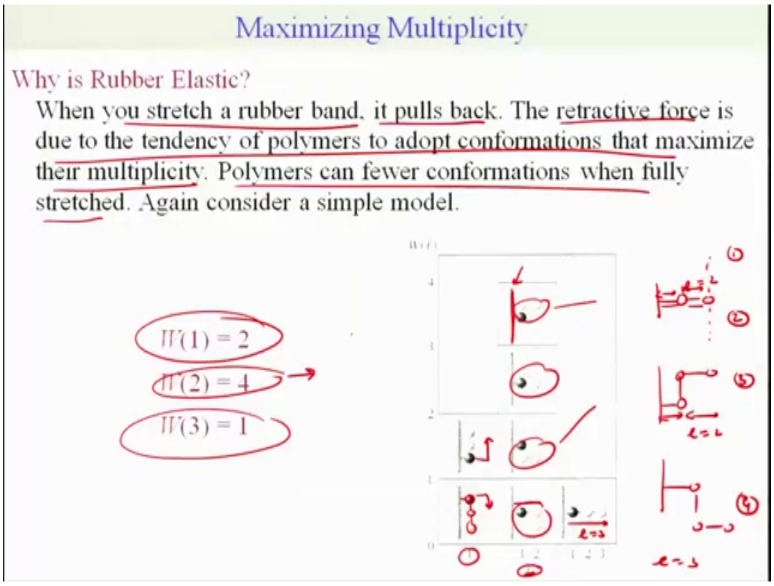

Now, we can also ask a very interesting question that why the rubber is elastic and you know that that when you stretch a rubber band it pulls back does not remain at the initial maximum stretching length it comes back, but it does not go back to the original length ’ it stays in the intermediate length.

The retractive force is due to the tendency of the polymer to adopt conformation that maximizes the multiplicity that is our a session and we are going to show that that intermediate configuration maximizes the multiplicity. And because polymer can have a few confirmations and fully stretch; in order to show that we can consider as a simple model.

So, this model is very simple. So, you have a 3 bit particle which is attached to wall because this wall could be your hand in which you are using it in order to stretch. And now this L is the length away from this wall.

So, when this is one it means you have scenario where the one bond is attached to this and this is related to this. So, there is only two possibilities either you can arrange it in this way or in this way either in this way or in that way the intermediately when you consider let us say 2 that it is going to do; that means, you have scenarios such that the length from here.

So, one and this is another one. So, you can have scenario something like this where you can consider in this way; that means, it has to bend from L L equal to 2. So, this is one length this is another length and it will bend here or in this side that is what it is done here this is one possibility.

The other possibility could be that you have extension here and then it is bend in this way in this will also give us length is equal to 2; that means, this is the intermediate configuration this is what exactly has been done.

So, there are two ways you can arrange in this form and you can arrange this and this in this to form where there is a bending in the first region and the alternative form is this one. So, in total you can arrange this in four ways. So, one in this way; so, this could be 1, the other side would be 2 and here this could be 3.

And if you do the same way it could be 4. Now when you have L is equal to 3 since it is a 3 bit polymer chain this we call it bean. So, there is only one conformation. So, this is going to be L equal to 3 is only one possibility with this the multiplicity having conformation with L equal to 1; that means, close to the wall there are 2 with L equal to 2 this 4 with L equal to 3 there is 1 indicates that this is the most preferred conformation, where the multiplicity is going to be maximum and this is primarily the reason why the when you stretch each comeback whether intermediate length.

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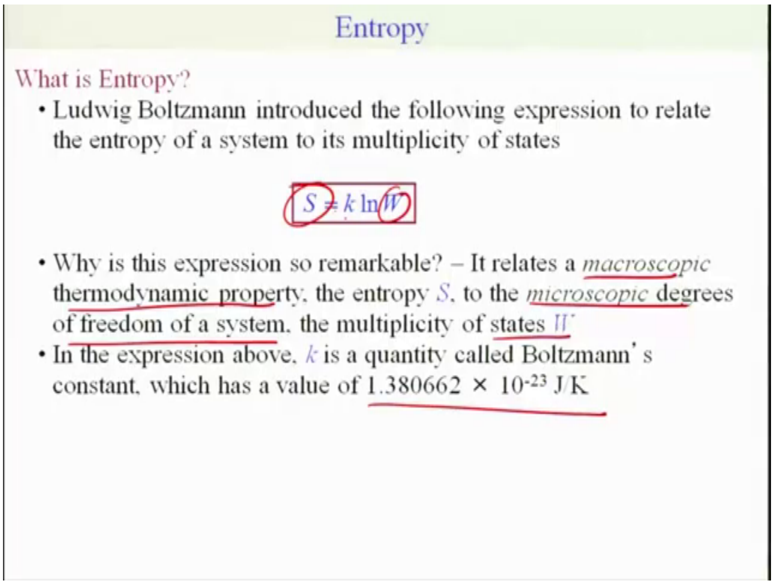

So, with this basic understanding let me just formally define entropy in terms of multiplicity Ludwig, Boltzmann introduced the following expression where entropy is proportional to the logarithm value of the multiplicity where the constant or professionality is k; which is called Boltzmann constant k and this value is given as here.

Now it is very interesting rather it is a remarkable expression because here you have this as a macroscopic thermodynamic property and W is a microscopic degree of freedom of the system or multiplicity. So, this is a relation which connects macroscopic thermodynamic property to a microscopic property and sometimes also called bridge equation.

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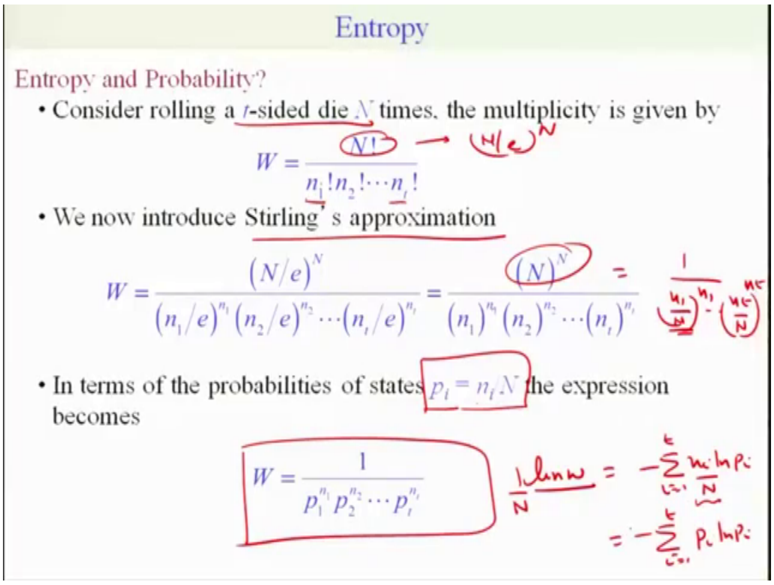

So, now let me connect this entropy to the probability through the expressions of multiplicity. So, let me consider a case of a rolling over three; a rolling of a t sided die N times.

So, using their concept of in the multiplicity we can write this W as N factorial divided by the over counting values of this t sided that would be your n 1 factorial till n t factorial. Now in order to solve this we can use the Stirling approximation which is valid for where the large values of n and here we can write N factorial as N by e to the power N that is what we written here.

Now, you can take out the denominator e to power n and also you can take out from here e to power n one to e to power t and since n is go to some of this n 1 to n t that e in the denominator will cancel out, but remain would be is a simply n one to the power n 1, n 2 the power n 2 and so, forth. Now we can now write down this expression in terms of probability.

So, if we define p i probability of a state i or site i is simply n i divided by N in that case you can divide this by n and this will get cancelled out in the way that it can be written as simply n 1 by N to the power n 1 till n t by N to the power n t which means I can write this expression in this form ok.

Now, this further can be simplified by taking a logarithmic value of W.

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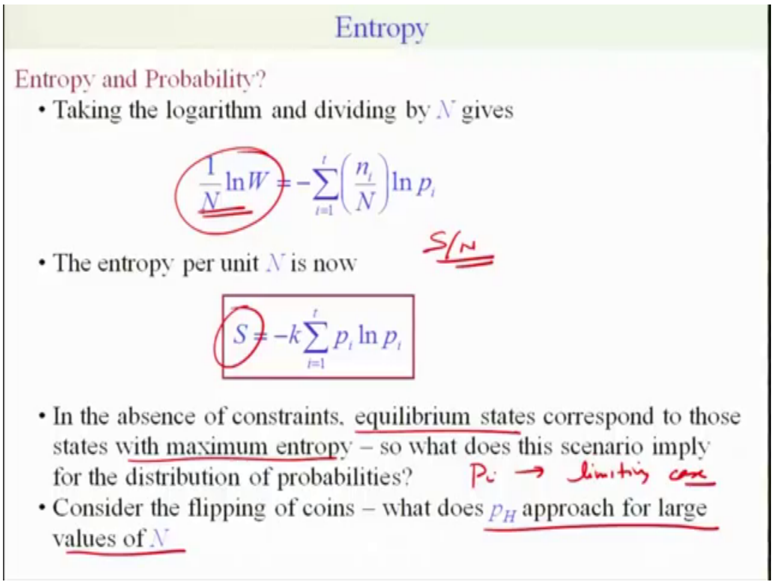

And now using those Boltzmann expression if I divide this by N I can write this as because this if I write it here this will be simply summation and i ln P i phi equal to 1 to t. If I divide by N; I am going to get N here and this is going to be simply P i ln P i i is equal to 1 to t with a negative sign this is what exactly is written here.

Now this expression can be used to in order to get entropy by N which now can be written as here per particle and this is nothing, but this expression. So,; so, we have got an expression of entropy for such a system where it can be connected to the probability of the outcomes of different events here.

So, in the absence of constraints equilibrium states corresponds to those states with the maximum entropy. So, given this what is this scenario imply for the distribution of probability? In other word what would be the P i when in any limiting case; so, now in order to understand this we will consider flipping of coin. So, what does p ph approaches for a large value of n that is the limiting case?

That is what we are asking the question given this information and we know that for the case of no constraints; the maximum entropy would be the case and this is something which we can show that P i approaches toward of course, 1 by 2 that we can we can show that.

But I will come back to this in the later stage, but you we can try to do an example using this expression in order to find the more likely conditions of it is state.

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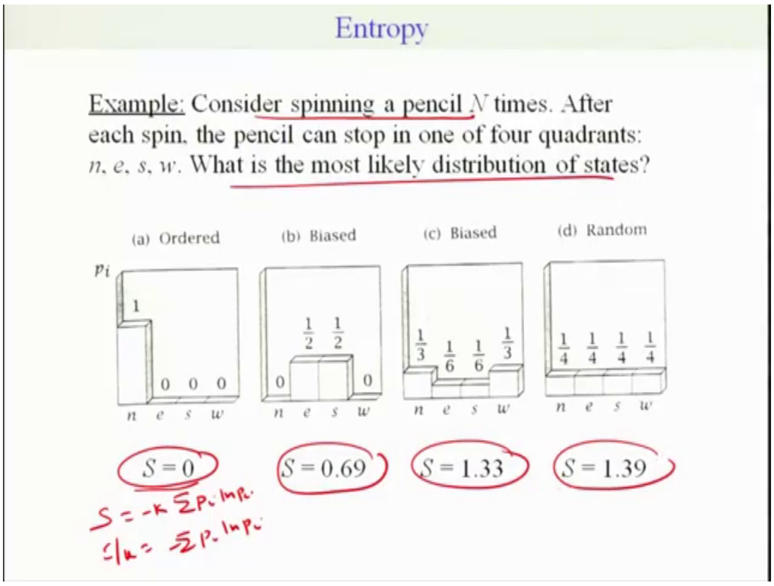

For example, if you consider spinning a pencil N times such that on the table such that it can line in four quadrants and if you define these four quadrants as north, east, south and west. Then let us consider these four different scenario; one will be the order the every time you do that you obtain n in that case your P i is 1. So, this you have done is many many times.

So, you have four different possibilities in this case which we have considered. So, this would be the ordered case if it lands only in east and south with the probability half and half; this will be your bias case and if it is in such a way that it prefers more north and west it will be again a bias case and this is the case where is the random that every quadrant has get every quadrant gets equal chance or we will have the same probability. Now in order to find out the most likely distribution of state in such a case we can calculate entropy.

So, entropy per particle is simply minus k summation P i ln P i or by k is summation P i and P i with a negative sign. So, if you use this information you can clearly see SS S by k is equal to 0 in this case S by k is 0.69 in this case S by k is 1.33 and in this case S by k is 1.39.

And this is a one which has a maximum value of this entropy and does indicate that this is the going to be the likely distribution of state without any constraint put on the system.

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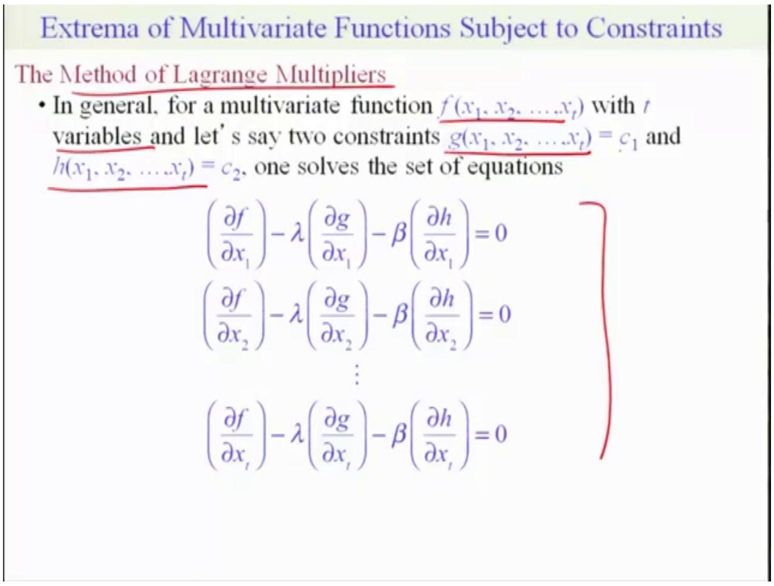

Now we can generalize this by considering cases where you may have constraints. And in such case how do you optimize this function W or in general any function that say f which is a multivariate function which may depends on different variables such as x 1 till x 2.

So, if you consider such a function with t variables and let us say you have two constraint g and h such that g is equal to c 1 g also depends on these variables.

This t variables and h also depends on t variables. So, in order to find this optimized value of the function for this two constraints a given constraints we will be using the method of language multipliers. In such case what we do is basically either we think of.

So, in such case what we do is basically we take the derivative first derivative of this function f with respect to different variables in this form. So, this is this kind of a set of equation to be solved. So, this is for example, del f by del x minus lambda del g by del x 1 minus beta del h by del x 1 and lambda and beta are unknown variables which we need to find.

And similarly we have to take these first derivatives; so, with respect to different variables up till x t and this must be equal to 0. In order to get a maximum value of such a function with given constraints g is equal to c 1 and h is equal to x 1.

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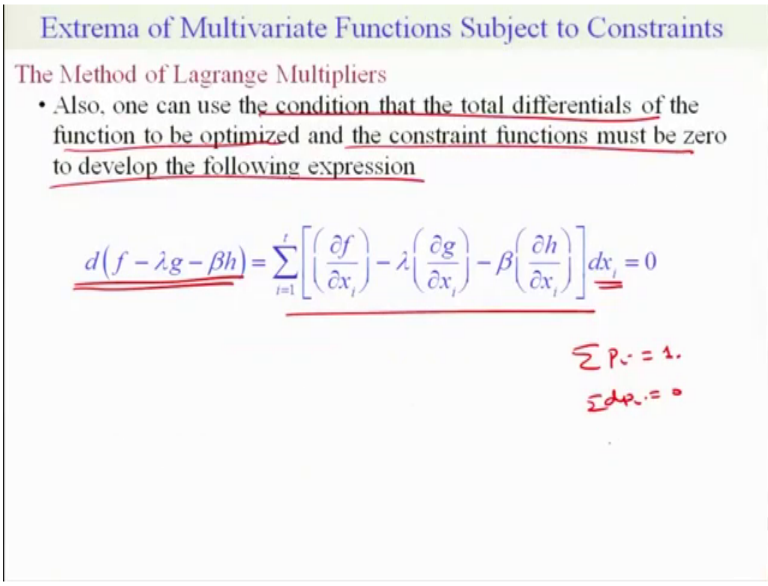

We can simplify this expression by writing in this form that one can use instead of doing this; one can use this condition that the total differential of the function is to be optimized and the constraint function must be 0 to develop the following expression; that means, f minus lambda g minus beta of this differential should be 0 in order to have the or at a maximum value of the variable leading to this function to be do.

And this you can write this expression in terms of the summation of 1 to t t is a number of variables; the first derivative with respect to x i minus lambda and minus beta and del x maximum. This is nothing, but the same expression as do you have got it; if you rearrange this you should be able to get this expression again.

So, this is nothing, but the method of Lagrange multiplier without deriving how this has been approached or obtained; we are just going to use this in order to find out the maximum value of the function or the optimize the function for a given constraint. Now let us look at how to make use of this method in order to find out.

The maximum value of the probability for different conditions; that means, with constraint or without constraints.

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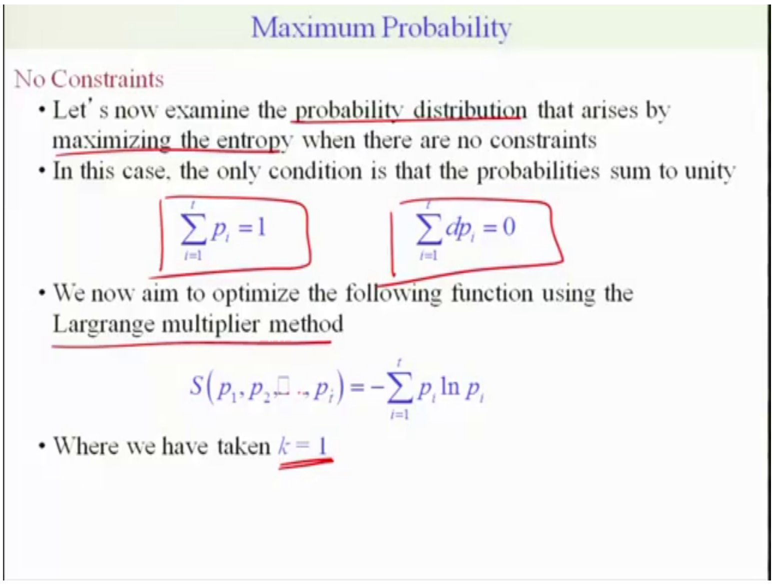

Ok so, let us examine the positive distribution that arises by maximizing the entropy when there are no constraints. So, when we do not have any constraints. So, where; that means, external constraint we still have one particular conditions which must be satisfied that is summation of p i should be equal to one in other word dpi should be equal to 0.

So, we now have to optimize the function using Largrange multiplier method. Now we know that S is equal to summation p i ln p i remember that we are considered in this case as by k and we have taken k is equal to 1 for the sake of simplicity. So, this is this S depends on from p y to pt.

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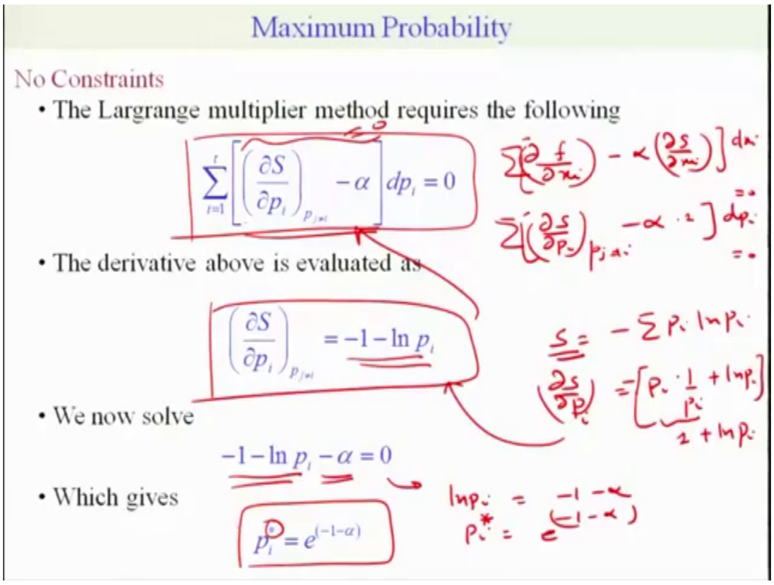

Now, using the Largrange multiplier method we need to remember that what we have done earlier. So, this is your function S here and this is your function the summation p i is equal to 1.

So, if you take a differential of this is going to be simply dpi is equal to 0 that is what it is. So, if you do this exercise use instead of f and f is nothing, but your S here. So, we put here f here ok; so, this is the first derivative del. Remember again and let me just re produce here lambda there is only pne variable.

And this is going to be del g by del x i look at it here alright. And this is going to be the x i this must be 0; so, if you look at the expression this is going to be del x by del p i follow the pj not equal to y minus L lambda and this is going to be simply del g by del p i which is going to be only 1.

So, this would be 1 multiplied by dpi. Now from here M we need to solve this problem this expression now this expression can be evaluated from the fact that you S is equal to S by k k is equal to 1 is minus p i and then p i.

So, if you take the derivative of this you will get del S by del p i is going to be only this expression. Because you are going to differentiate with respect to p i only the rest is going to be 0. So, this is going to be p i 1minus p i with a negative sign here and then this is going to be ln pi.

So, now from we have to get this expression and this expression we can calculate from this the definition of the entropy with as a function of the probability. From here if you take the derivative of S with respect to p i then you can show that this is nothing, but only this one term will remain here and the rest would be 0.

And if you take the differentiation of this part this would be p i multiplied by 1 the pi plus ln p i and this is going to be 1 plus and then pi. So, if you plug in here you get this expression now you in order to solve this you have to plug in this part, but remember that this is this 0 indicates that this will be 0 as well because rest of the i is r different event.

So, if you if this is 0 which means basically this or rather this minus alpha should be 0 and this is the condition which gives us that if you rearrange this itself is going to be ln p i is equal to minus one minus alpha or p i is equal to e to power minus 1 minus alpha.

And this is going to be in optimal value of p i because we have just got an expression which is maximum. And for the probability this that is why we are saying this is the optimum value of p. Now major problem is that we do not know what is alpha ok.

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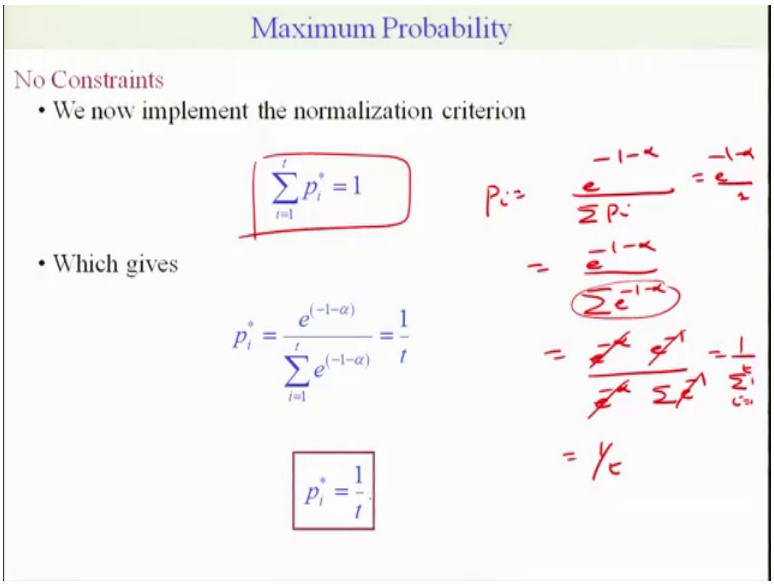

So, in order to get the alpha what we can do is we can go back to the normalization criteria that sum of the p i should be 0 at 1 sum of the p i should be one. So, we plug in this expression p i we know that is sum of this p i should be 1.

So now if we consider this it to be e to power minus 1 minus and; so, I can write this as p i because this is equivalent of saying this is lambda to 1 to power 1 and now i can get rid of alpha this is going to be summation e to power minus 1 minus alpha.

Alpha being constant here it we I can take it out e to the power minus alpha e to power minus 1 and this is going to be e to the minus alpha summation e to the power minus 1 so, this gets cancelled.

So, what do I have is basically this will also get cancelled and this is going to be only summation 1 i is equal to 1 to t which is nothing, but 1 by t. So, in such case your product distribution says that it is 1 by t or normalized or basically the random or equal probability for all the side. So, this is something which we have seen the case when we have this pencil randomly rotated for this four quadrant and we obtained 1 by 4 as an option.

Similarly, if you consider two events such as head and tail if it is non biased, you will see that psi is going to be 1 by 2. For all this case if you have t outcome and you are looking at the normalization or limiting condition, where this p is going to be optimized where the entropy is going to be maximum for such a p this p is going to be simply 1 by t.

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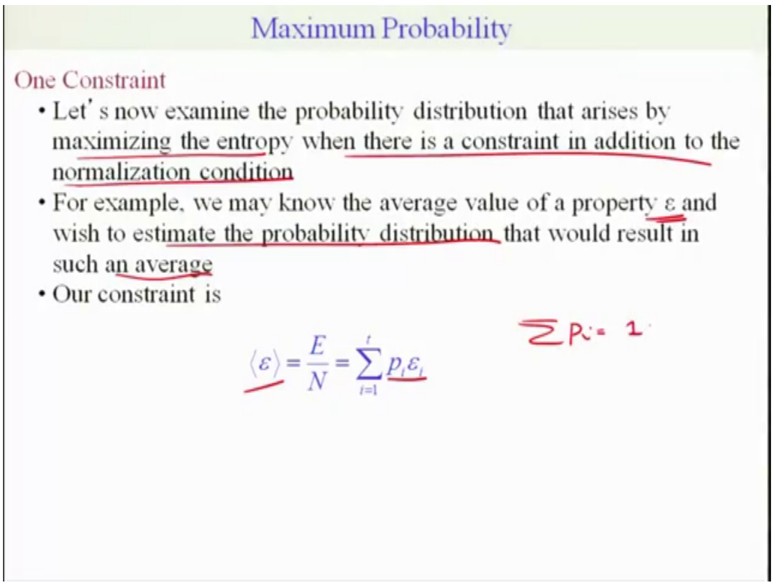

So, we can extend this exercise now instead of considering and without any constraint we consider with one constraint. So, let us examine the probability distribution that arise by maximizing the entropy when there is a constraint in addition to normalizing normalization condition. So,; so, what is the constraint?. So, let us say we are aware of average property of energy ok.

And we wish to estimate the probability distribution that would result in such an average. So, you have to optimize the entropy, but now the delta e is given to you and we have to find out the probability which would lead to such a condition where the delta e would be the final value of the average energy.

So, what is the delta e average value of E? Is E by N and that can be written as simply the weighted average of this the first moment of the probability distribution which is p i epsilon i.

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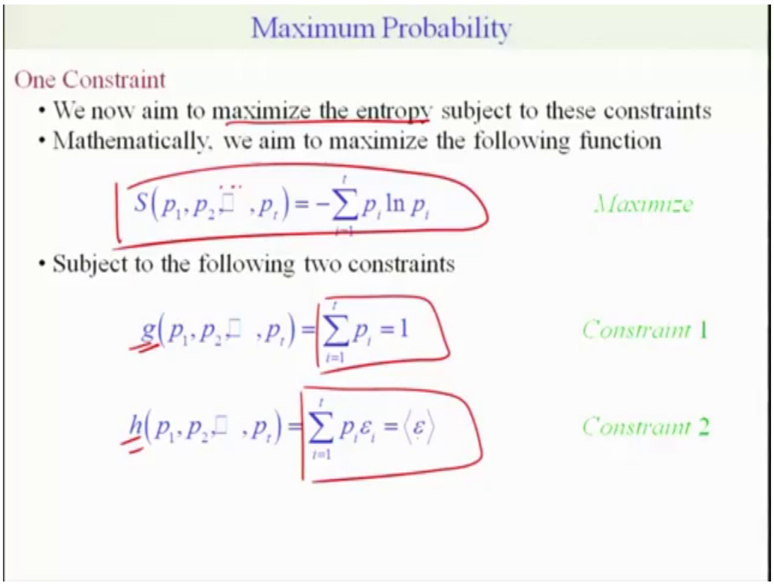

Because assuming that p i is normalized. So, now we have to consider maximize entropy. So, this is p 1, p 2 and this is dot dot to the p t this is we know this is we have to maximize, but with the constraint that summation p is going to be 1 that is your g function and h function is that summation p i epsilon i is known value which is average value of E.

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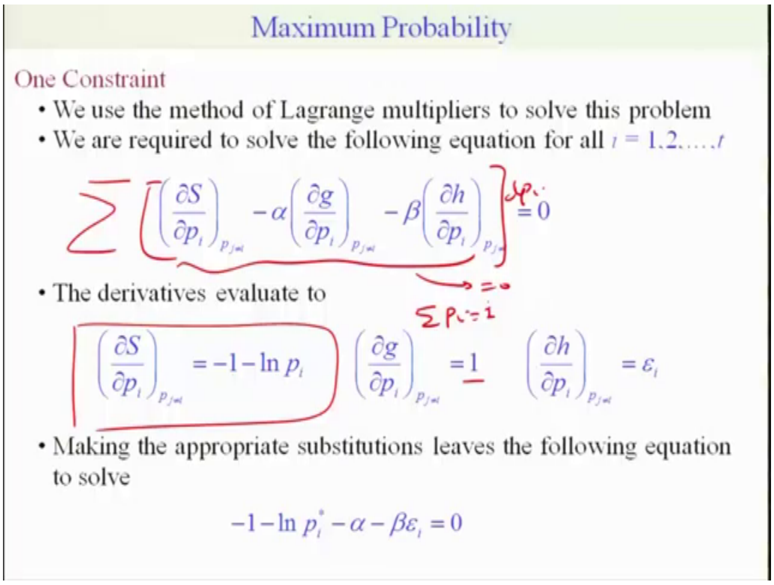

So, now, we go back to the same expression of the Lagrange multiplier here; I remember that for the Lagrange multiplier for each term we have written this right dpi. So, this internal or this part will must be 0; this part must be 0.

Now we have to find out the first derivative S, g and h. So, what is the first derivative h S will remain the same as we have obtained for the case of non constrained which will be simply minus 1 minus lnpi; what about g? This is going to be 1 because this is the summation p i equal to 1 and what about the h this will be simply epsilon i.

So, if you take a derivative of this expression with respect to the p i is going to be only epsilon i. So, we plug in this expression and we got this expression this is due to the first term, this is the second term and this is the third term.

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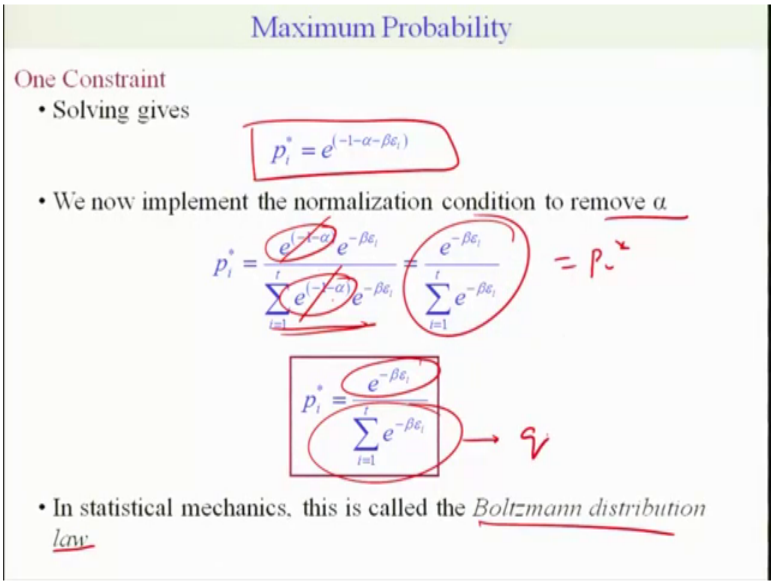

Now we got an expression of p i now which comes from here if you if you take from here the last one, you are going to get e to the minus 1, minus alpha, minus beta epsilon i.

Now again we make use of this normalization condition in order to remove the alphas. We consider summation p i equal to 1; that means, this we divided by this expression and here we separate this part, this part and this part and for numerator the same part which gets cancelled.

So, what remain is this and this is nothing, but p i star. Now this expression is a very well known expression, this expression is called Boltzmann distribution. And what we have seen and what we have develop here is basically that the probability of a state having energy e is nothing, but the Boltzmann factor which is epsilon exponential of minus beta epsilon divided by the normalized the sum of the all the probabilities.

Whether; the word the probability distribution is nothing but the normalized value of the Boltzmann factor because this is the sum of the probability of all other states. So, this is beautiful expressions which have come for the constraint values. Now this expression is also called sum as partition function.

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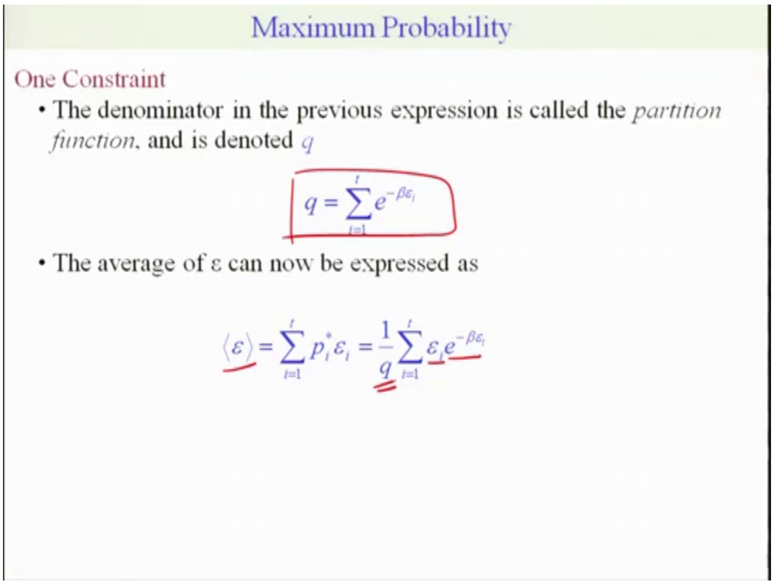

This is also call the partition function and now we can write this epsilon average e as simply p i star epsilon i which can be written as e epsilon i multiplied by the Boltzmann factor divided by the partition function.

So, this is now the way to calculate epsilon for this concern system having a construct. Now this is a common approach in statistical mechanics now we can apply to many different systems. So, in the next lecture I will formally define this statistical mechanics and we will be using this such an expression for molecular systems.

So, with this I will stop today's lecture. So, see you next time.