Fundamentals of Statistical Thermodynamics

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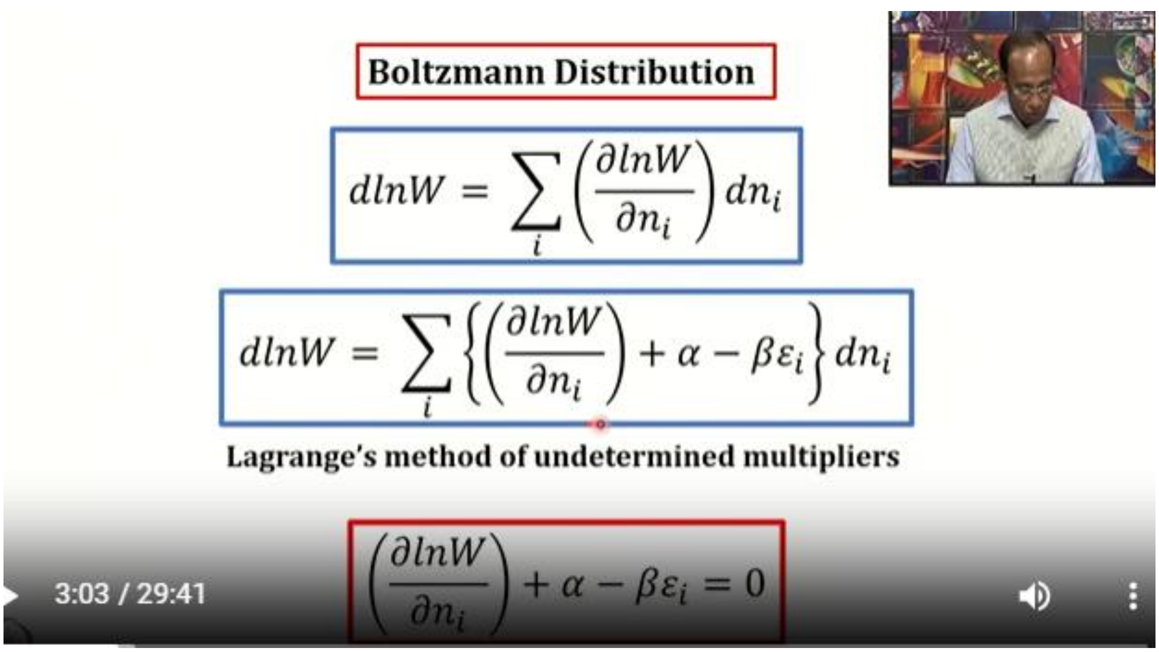
Lecture - 04

Welcome back to the next lecture. In the previous lecture, we talked about the weight of a configuration. We also discussed that instead of working on W, working on log W brings the results more easily. And then we also talked about some constraints which need to be followed because the total number of particles, total number of molecules in a system are constant and the total energy is also constant. Also, keep in mind that we are so far talking about independent molecules. We have not allowed the molecules to interact so far.

So, therefore, let us now proceed further. Now, our next goal is going to be deriving the Boltzmann distribution and in order to derive the Boltzmann distribution, here again, we are going to use certain constraints and we are going to discuss these equations that is you remember. I was talking about that instead of working on W, let us work on d log W. So, we will set up some equations where we will write expressions for d log W and set it equal to 0 and these are going to be constraints. These constraints I am going to discuss with you in details now.

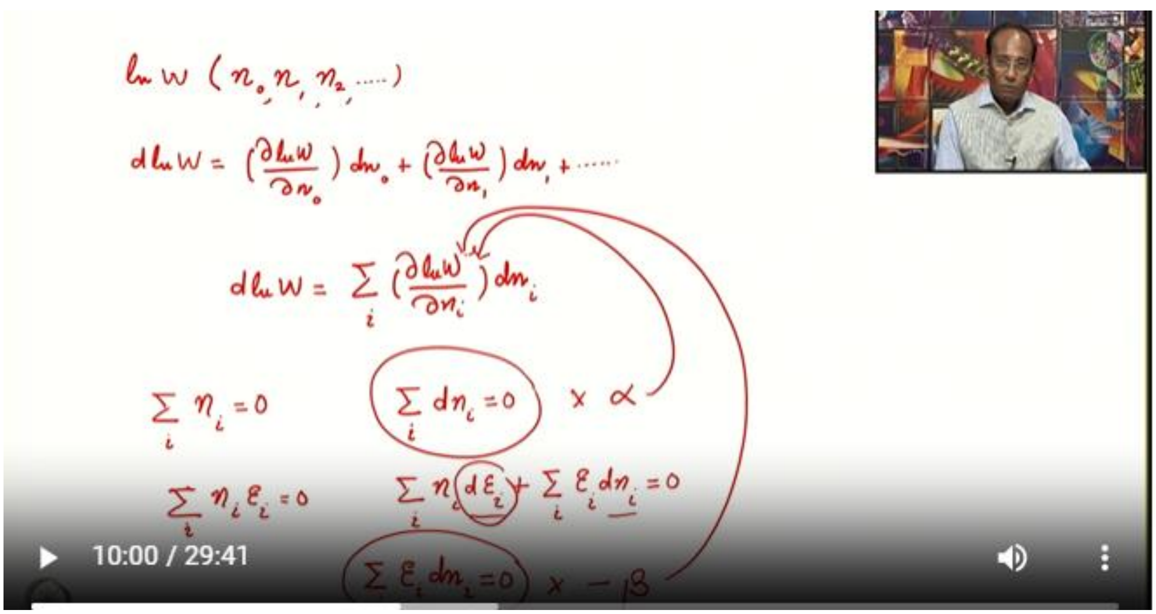


$$dlnW = \sum_i \left(\frac{\partial lnW}{\partial n_i}\right) dn_i$$

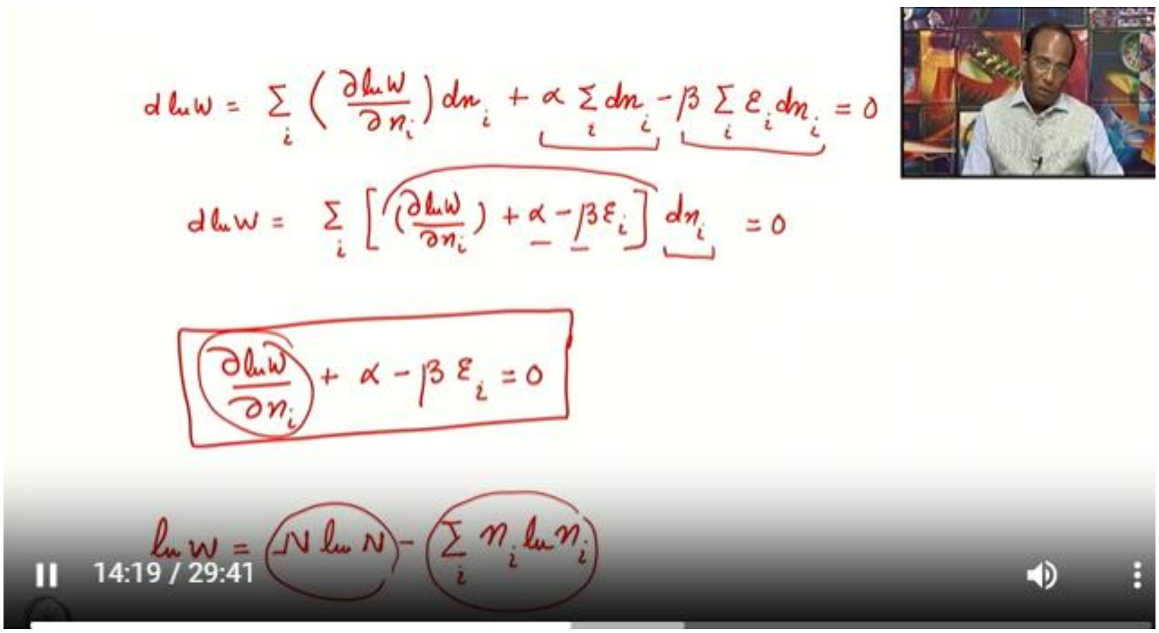
$$dlnW = \sum_i \left\{\left(\frac{\partial lnW}{\partial n_i}\right) + \alpha - \beta\varepsilon_i\right\} dn_i$$

So, the equations that we are going to derive now is are number 1, d log W to be written in the form of partial derivative, and then we will introduce some constraints alpha and beta to transform d log W into another equation where we can set these two you know either dN_i equal to 0 or this bracketed expression equal to 0 if we set d log W equal to 0. And we are also going to use Lagrange's method of undetermined multipliers and eventually we will come up with this expression and let us now go step by step in deriving these equations. So, let us start with log W, log W instead of W let us work on log W. This is a function of N_0, N_1, N_2 etcetera, etcetera. that means I can write d log W is equal to del log w over del n_0 into dn_0 plus del log W del N 1 d N 1 plus you keep on going right

When there is some change you can write the change as d log W and in terms of partial derivatives on the right-hand side these will appear.



So, let us now write d log W equal to I will write summation i del log W by del N_i into d N_i. All these upper you know these various parts of the total sum I have summarized into summation i del log W by del N_i into dN_i. The purpose is to set this d log W equal to 0 we will set this equal to 0. Now suppose that if we set it equal to 0 does that mean that either this del log W by del N_i equal to 0 or d N_i equal to 0 can we set it like that? d N_i is not equal to 0 because there has to be some change.



Then does that mean that del log W by del N i equal to 0? No, the reason is here if you carefully examine the upper steps these dN i's are not independent they are dependent they are appearing with each term. So, therefore, we cannot set either this equal to 0 or this equal to 0 we cannot do that because d N i's are dependent they are not independent. So, therefore, what should be done in such cases so that we can treat d N i's as independent and that is where the method of undetermined multipliers is used. But before I go into the method of undetermined multipliers let us use the constraints let us recall those constraints. So, those constraints first constraint was summation i N $_i$ equal to 0. Then, I write this as for a change summation N dN_i equal to 0.

That means when you add up the sum of all the changes some are positive some are negative everything total sum of all the changes has to be equal to 0. Second one summation i N_i E $_i$ equal to 0 this was the second constraint. So, therefore, I can write for a change N $_i$ or take a derivative N_i dE $_i$ plus summation i E_i d N_i that has to be 0. We know that d N i's cannot be 0 energy levels are fixed energy states are fixed therefore, what is 0 this d E_i is equal to 0. So, what we have here now is summation i E_i d N_i equal to 0.

This is my constraint number 1 this is my constraint number 2. What is the Lagrange's method of undetermined multipliers is that let us multiply these two constraints with some constant. Let us say I multiply this one with alpha and I multiply this with minus beta why minus beta it will become clear soon. See whether you multiply by alpha or beta or minus beta eventually the value is 0 because you are multiplying with 0 only the value is 0. And then if I add these two into both if I add into this expression I am going to do that now in the next step that is d log w is equal to summation i del log w by del N i I had d N_i plus I have alpha into d N_i summation i dN_i the value is 0 minus beta into summation i E_i dN_i is equal to 0. I will set this equal to 0.

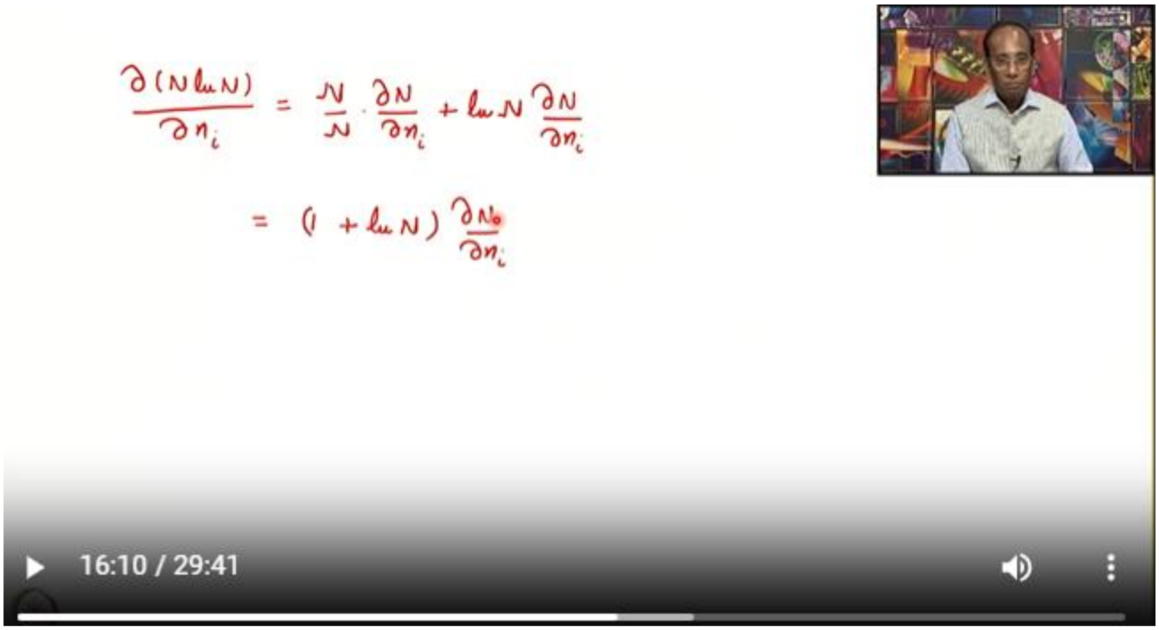
See I have added from one constraint the other constraint both the values of 0. So, it does not make any difference.

Let us rewrite this again d log w is equal to summation i I have del log w del N_i plus alpha minus beta E_i and I will take d N_i out. Now I will set it equal to 0. Remember that these alpha and beta are undetermined multipliers what we are doing is we are introducing some undetermined multipliers such that now we treat these d N i's as independent and then work out for the values of alpha and beta.

So, that is the way to deal with these kind of problems. We have used some undetermined multipliers introduced into our expression now we will treat these as independent and d N i's cannot be 0 therefore, we have to set this equal to 0. That means now our next job is we write del log w del N i plus alpha minus beta E i equal to 0. We have to work on this now. Let us mark this.

We will be using this expression a bit later. Remember log w we have already got as N log N minus summation i N_i log N_i. We have already derived this log w is equal to N log N minus summation N_i log N_i and if we were to find out its derivative then we need to find out the derivative of the first part and then the derivative of the second part with respect to d N_i. Please keep this in mind that now we want to have the derivative of log w with respect to d N_i. So, therefore, there are two parts one is derivative of N log N second is minus summation iN_i log N_i derivative of this.

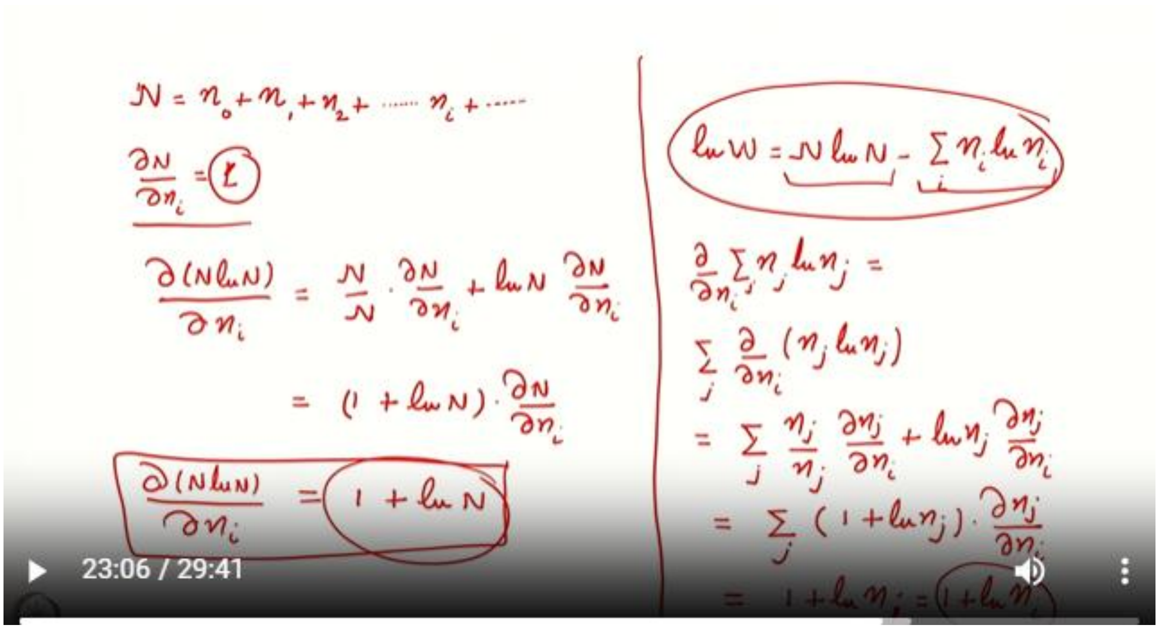
So, we will do this in two steps. Let us first work on the first one. Let us take the derivative of N log N with respect to N_i and see what happens. So, part one del N log N this is what we want to find out. What is this? Now it will be N by N into derivative of N with respect to N i plus log N into derivative of N with respect to N_i.



Can I write like now 1 plus log N into del N by del N_i. So, we need to worry about this N is a constant you know the thing can come in the mind that N total N is constant. So, a cost derivative of a constant should be equal to 0 therefore, this should be equal to 0 this is something which immediately comes to mind, but let us not act fast let us critically analyze. So, what we had is N is equal to N 0 plus N 1 plus N 2 plus so on you have N i plus so on. So, when I take del N by del N i remember that this N 0 N 1 N 2 they do not depend upon each other they are independent of each other.

So, therefore, the derivative of the first term is going to be 0 second term is going to be 0 third is going to be 0 unless you reach N i where del N i by del N i is going to be equal to 1. So, that means this is equal to 1 right. So, we were working on you know del N log N by del N_i, and what we had done is N by N into del N del N_i plus log N del Ndel N_i which is equal to 1 plus log N del Ndel N_i which we just find that this is equal to 1 therefore, this is equal to 1 plus log N. So, del N log N del N_i is equal to 1 plus log N fine. So, first part of that is done.

Now we need to work on the second part and what was that second part let us recall log W was equal to N log N minus summation i N_i log N_i we have worked on the derivative of this.



Now let us work on the derivative of this. So, I am interested in now del del N_i I want to take the derivative of this of summation instead of N i let me use j why I am using j is so that we do not confuse j with i we are taking derivative with respect to i. So, therefore, let me use j as a general term. So, this is equal to what now this is equal to summation j del del N_i of N_j log N_j which is equal to summation j N_j over N_j del N_j del N_i plus log N_j del N_j over del N_i which is equal to summation j in place why have 1 plus log N_j into del N_j by del N_i.

Now when we need to expand when we expand let us say j starts from 0 1 2 etcetera etcetera remember that the number of molecules in let us say i plus 1 is not dependent upon number of molecules in the ground state etcetera they are independently in the different energy states. So, therefore, all the other terms when j is equal to 0 1 2 3 etcetera will disappear till j becomes i only when j is equal to i then del N_i by del N_i is equal to 1. So therefore, the term which will survive is equal to 1 plus log N_i N_i not jN_i when j is equal to i. So, remember that this is equal to 1 plus log N_i. So, we have the expressions for both first part is 1 plus log N second part is 1 plus log N_i and now we can go back and put into this.

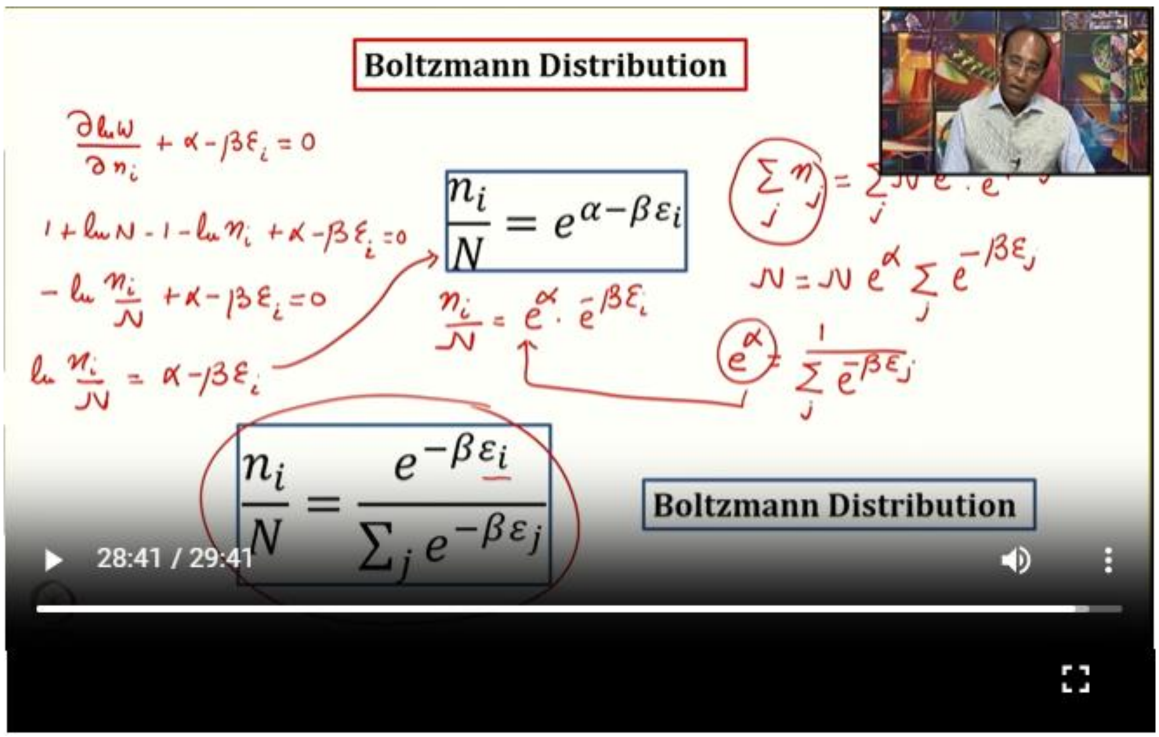
This is what our you know aim was that we take the derivative of this and then work on that forward. All right. So, let me work out here only our aim was del log W over del N i plus alpha minus beta E i equal to 0. And if we just go back del log W by del N i is this minus this right. If we take the derivative of this the derivative of the first part is 1 plus log N the derivative of the second part is equal to 1 plus log N_i.

So, we are going to use that and let us set over here 1 plus log N minus 1 minus log N_i plus alpha minus beta E_i equal to 0. This is equal to minus log N_i upon N right plus alpha minus beta E_i equal to 0. In other words, log N_i upon N is equal to alpha minus beta E_i which I can rewrite as

$$\frac{n_i}{N} = e^{\alpha - \beta\varepsilon_i}$$

We have N_i upon N, N_i upon N is nothing but population. But then if you look at the right-hand side we have alpha, we have beta.

These are the undetermined multipliers and we need to find out the expression for alpha and expression for beta. We can quickly find out the expression for alpha. Let us see how do we proceed. Let me use this space summation j N_j I will use from here instead of i I will use j. This is equal to I am taking summation, summation N exponential alpha into exponential minus beta E_j.



I am writing in terms of j N_i is equal to N into exponential alpha into exponential minus beta. Instead of i I am writing j because I do not want to confuse i with the j. This one is equal to N total number of particles is equal to N it comes out exponential alpha constant comes out summation we have j exponential minus beta E_j. So therefore, what we have exponential alpha is equal to 1 over summation j exponential minus beta E_j. And once you substitute this into this form, remember that I can rewrite this as N_i upon N is equal to exponential alpha into exponential minus beta E_i.

You substitute exponential alpha over here and what you get is this expression

$$\frac{n_i}{N} = \frac{e^{-\beta \varepsilon_i}}{\sum_j e^{-\beta \varepsilon_j}}$$

This is Boltzmann distribution. What this equation tells is the population of an i th state N i is the number of molecules or number of particles in the i th state and N is the total number of particles. Therefore, N i upon N is the population of i th state which can be calculated from the knowledge of energy levels or energy states and this summation. It is a very important result which is called Boltzmann distribution and this will form the basis for our future discussion when I introduce the concept of partition function. It is the partition function which is going to be connected with all the thermodynamic quantities and that will be the focus of discussion in the next lecture.

Thank you very much.