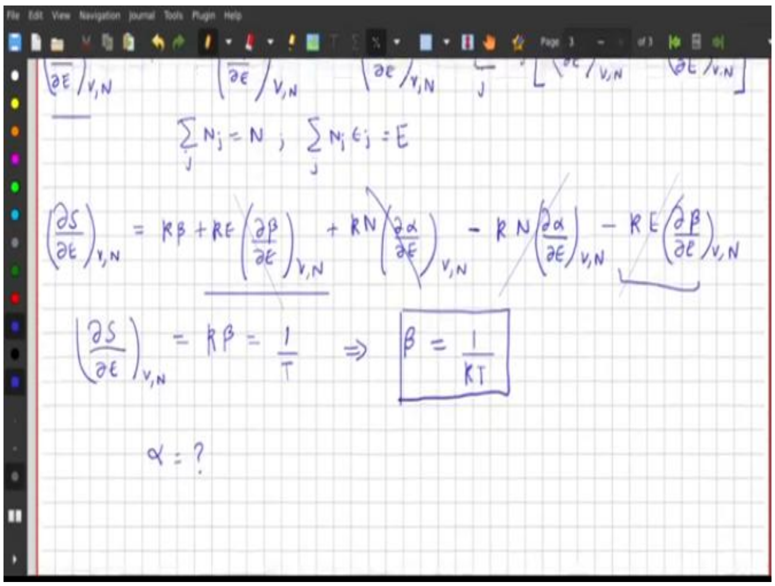
**Statistical Thermodynamics for Engineers**

**Professor Saptarshi Basu**
**Indian Institute of Science, Bengaluru**

**Lecture 29**
**Supplementary Video 10 Problem Solving 2**

(Refer Slide Time: 00:00)




Welcome to another problem-solving session. In this segment, we will be continuing what we were doing in the previous segment. So, if you recall, what we were doing is we were computing the Lagrange multipliers. So, we computed what beta was and there is another Lagrange multiplier which is alpha that is what we will be doing now.

(Refer Slide Time: 00:25)

$$dS(E,V,N) = \frac{1}{T}\,dE + \frac{P}{T}\,dV - \frac{\mu}{T}\,dN$$

$$\left(\frac{\partial S}{\partial E}\right)_{V,N} = \frac{1}{T} \qquad \boxed{\left(\frac{\partial S}{\partial N}\right)_{E,V} = -\frac{\mu}{T}} \qquad \alpha, \beta\,(E)$$

$$S(E,V,N) = k(\beta E + \alpha N) \mp k\sum_j g_j \ln\left(1 \mp e^{-\alpha} e^{-\beta\epsilon_j}\right)$$

$$\left(\frac{\partial S}{\partial E}\right)_{V,N} = k\beta + kE\left(\frac{\partial \beta}{\partial E}\right)_{V,N} + kN\left(\frac{\partial \alpha}{\partial E}\right)_{V,N} \mp k\sum_j \left(\frac{g_j e^{-\alpha} e^{-\beta\epsilon_j}}{1 \mp e^{-\alpha} e^{-\beta\epsilon_j}}\right)\left[\left(\frac{\partial \alpha}{\partial E}\right)_{V,N} + \epsilon_j\left(\frac{\partial \beta}{\partial E}\right)_{V,N}\right]$$

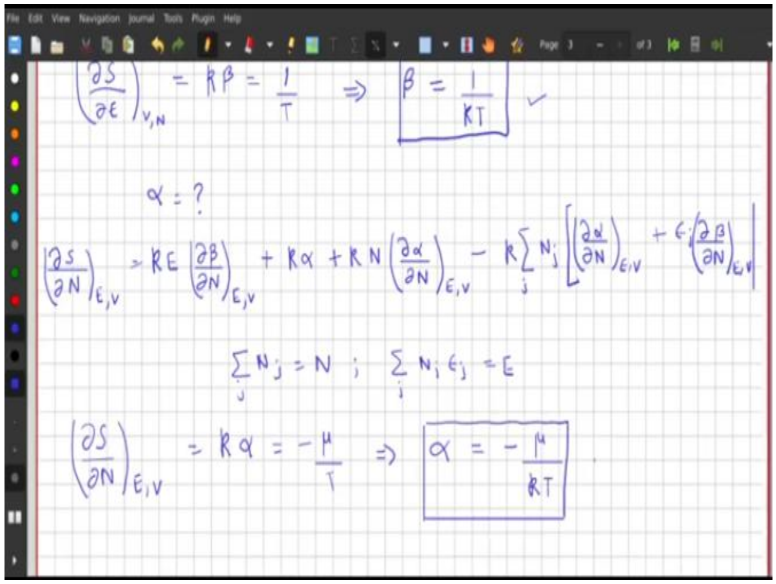
$$\sum_j N_j = N, \quad \sum_j N_j \epsilon_j = E$$

$$\left(\frac{\partial S}{\partial E}\right)_{V,N} = k\beta + kE\left(\frac{\partial \beta}{\partial E}\right)_{V,N} + kN\left(\frac{\partial \alpha}{\partial E}\right)_{V,N} - kN\left(\frac{\partial \alpha}{\partial E}\right)_{V,N} - kE\left(\frac{\partial \beta}{\partial E}\right)_{V,N}$$

$$\left(\frac{\partial S}{\partial E}\right)_{V,N} = k\beta = \frac{1}{T} \Rightarrow \boxed{\beta = \frac{1}{kT}}$$

$$\alpha = ?$$

$$\left(\frac{\partial S}{\partial N}\right)_{E,V} = kE\left(\frac{\partial \beta}{\partial N}\right)_{E,V} + k\alpha + kN\left(\frac{\partial \alpha}{\partial N}\right)_{E,V} - k\sum_j N_j\left[\left(\frac{\partial \alpha}{\partial N}\right)_{E,V} + \epsilon_j\left(\frac{\partial \beta}{\partial N}\right)_{E,V}\right]$$




So, let us see, if you recall again from classical thermodynamics, so if you see here, this equation of the differential of dS from here, we can compute the partial of S with respect to let us say N, so, partial S partial N at constant energy and volume let us say, so, E and V constant so that becomes minus mu over T.

So, we will be using this thing later to evaluate our second Lagrange multiplier, as we saw, we already use this expression to compute the first Lagrange multiplier which is the beta actually. So, now we will be computing alpha and this expression will help us to do. So, what we will do is? We know the right-hand side of this partial S partial N from classical thermo and from statistical thermodynamics we will be able to compute this left-hand side of this expression.

Let us compute partial S partial N just like before where all these things will exactly remain the same just we would differentiating with respect to N now. So, if we do that what we will have is partial S partial N at constant E and V, so E comma V is constant this is k times the energy times partial beta partial N at constant E and V plus k times alpha plus k times N partial alpha partial N at constant E comma V minus the Boltzmann's constant sum over j Nj bracket partial alpha partial N at constant E and V plus epsilon j partial B partial N at E and V, so, if you see the expression for S, we will able to see exactly how this came, so, what we did was a differentiated now with respect to N.

So, here we and again we need to remember that alpha and beta is a function of N here. So, and so what we did here was? kE times partial beta partial N that is kE that is constant because remember this is the Boltzmann constant and this is the total energy just constant multiplied by partial B partial N plus and now this we need to differentiate with respect to N and you see alpha is also a function of N, so, that means you have to use the product rule and hence we will have two terms.

So, the terms k alpha plus kN partial alpha partial N minus k and sum over j and we had this term remember and this term were we (lated) realized was the equilibrium particle distribution which is Nj. This multiplied if you see this was multiplied by the derivative of alphas and betas. So, it says partial alpha partial, but now we are doing with respect to N and then epsilon g partial beta partial N. So, that is this expression.

And now if you just open the brackets, we will be seeing what this will become is recognized again that sum over j Nj is the total N and sum over j Nj epsilon j is the total energy. If you see if you open the bracket, so this kN this will become kN partial alpha partial N EV that will cancel out this term and then we will have minus kE, partial beta partial N E V that will cancel this first term so what we will be left is partial S partial with respect to N at constant E comma V is given by k times alpha.

And from classical thermodynamics we know that this is equal to minus mu over T. From here we computed the second Lagrange multiplier which is alpha equals minus mu by kT. That is the generic method of finding the Lagrange multiplier in case of Bose-Einstein and Fermi-Dirac statistics given when we started with the entropy, this could be done by the way for any other macroscopic thermodynamic variable like for example, the Helmholtz function, the internal energy the Gibbs free energy, but the methodology remains more or less the same.

One of the key important thing that we need to realize here is, is this thing that alpha and beta that the Lagrange multipliers are functions of E V and N and hence when we are doing the partial derivatives we need to differentiate alphas and betas with respect to the individual variables.

(Refer Slide Time: 06:15)

P = ? We know from classical thermodynamics $\quad N_j \quad \epsilon_j$

$$\left(\frac{\partial S}{\partial V}\right)_{E,N} = \frac{P}{T}$$

$$\left(\frac{\partial S}{\partial V}\right)_{E,N} = kE\left(\frac{\partial \beta}{\partial V}\right)_{E,N} + kN\left(\frac{\partial \alpha}{\partial V}\right)_{E,N} - k\sum_j N_j\left[\left(\frac{\partial \alpha}{\partial V}\right)_{E,N} + \epsilon_j\left(\frac{\partial \beta}{\partial V}\right)_{E,N} + \beta\left(\frac{\partial \epsilon_j}{\partial V}\right)_{E,N}\right]$$

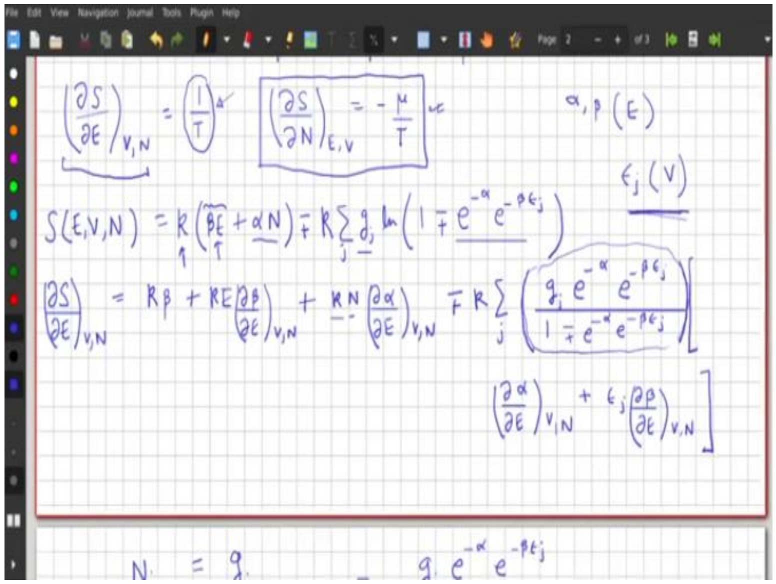

$$\left(\frac{\partial S}{\partial V}\right)_{E,N} = \frac{P}{T}$$

$$\left(\frac{\partial S}{\partial V}\right)_{E,N} = kE\left(\frac{\partial \beta}{\partial V}\right)_{E,N} + kN\left(\frac{\partial \alpha}{\partial V}\right)_{E,N} - k\sum_j N_j\left[\left(\frac{\partial \alpha}{\partial V}\right)_{E,N} + \epsilon_j\left(\frac{\partial \beta}{\partial V}\right)_{E,N} + \beta\left(\frac{\partial \epsilon_j}{\partial V}\right)_{E,N}\right]$$


$$\left(\frac{\partial S}{\partial V}\right)_{E,N} = -k\beta\sum_j N_j\left(\frac{\partial \epsilon_j}{\partial V}\right)_{E,N} = \frac{P}{T}$$

$$\beta = \frac{1}{kT}$$

$$-\frac{1}{T}\sum_j N_j\left(\frac{\partial \epsilon_j}{\partial V}\right)_{E,N} = \frac{P}{T} \Rightarrow P = -\sum_j N_j\left(\frac{\partial \epsilon_j}{\partial V}\right)_{E,N}$$



So, let us say now, we move on to the next part of this discussion where we are (given) so we now know alphas and betas. And now the question is, can we find out a general expression for pressure? So, compute P in terms of entropy basically. So, we can write that from classical thermodynamics, but what we need to write is, so, this we can write we know from classical thermodynamics we know the physical picture behind it but we need to find out in, so, we want to write P's the pressure in terms of the particle distribution Nj the energy states epsilon j.

So, (())(7:06) the thing we need to that we want to write now. If you remember the differential for dS that itself can we can define the pressure. So, you see the partial S with respect to V gives us P over T at constant E and N. So, that means we have a partial of the entropy with respect to V at constant E and N that is equal to P over T.

And that means, let us do the same thing we know the entropy and now we will differentiate with respect to V and again realize that alphas and betas the function of V. So, this expression will become partial S partial V, E comma N and this will become equal to k times E partial beta partial V E comma N plus kN partial alpha partial V E comma N minus k sum over j Nj times the bracketed terms if you remember where is this bracketed term coming from.

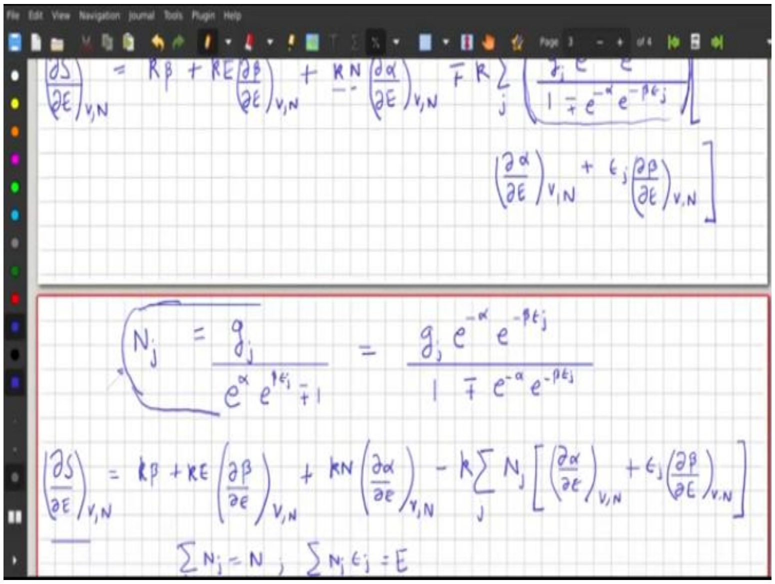
So, if you see this is where the bracketed term is coming from, but now, what we need to realize is? That since we are differentiating with respect to volume now, so, epsilon j the energy is also a function of volume. So, that means, we will have to differentiate with this, we will have three terms of alpha beta and epsilon j.

So, here we will be using the product rule basically. So, everything remains the same just we will have an additional term here. Because epsilon j is a function of, that is the total size of the system that we are dealing with. So, this becomes minus k sum over j Nj partial alpha partial V E comma N plus epsilon j partial beta partial V E comma N and then the product rule second term which is now we keep beta constant and then we differentiate epsilon j with respect to V at E comma.

So, that is the expression for partial S partial V and if you see this, this again using the same ideas before that sum over Nj is N sum over Nj epsilon j is E, this expression becomes so you will see this is kN this will become kN and we will this will cancel this term and then we will have kE partial B partially V that will cancel this first term so what we will be left with is this extra term which we just had now. So, we will have partial S partial V, E comma N and that is minus k beta sum over j Nj partial epsilon j partial V E comma N and if you realize this is what from classical this was P by T.

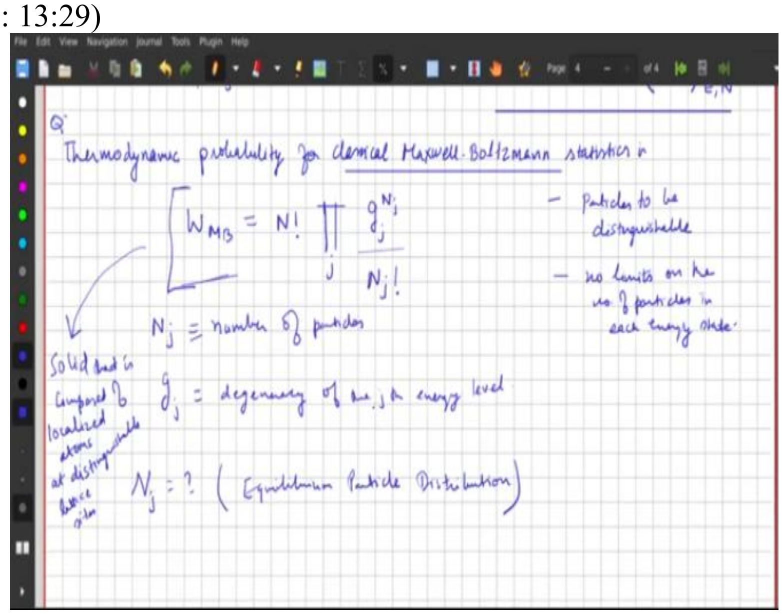
So, and we so if you look at this expression we know what beta is, that we evaluated that was a Lagrange multiplier also, beta was 1 over kT. So, beta is so that is beta is 1 over kT that means k times beta is 1 over T. So, this expression becomes minus 1 over T sum over j Nj partial epsilon j partial V with respect to E comma N and that is equal to P over T and this becomes therefore the pressure, the pressure can be written as P equals minus sum over j Nj partial epsilon j partial V at constant E and N, that is the expression of pressure from a statistical thermodynamics point of view in terms of you see the energy states epsilon j in terms of the particle distribution Nj.

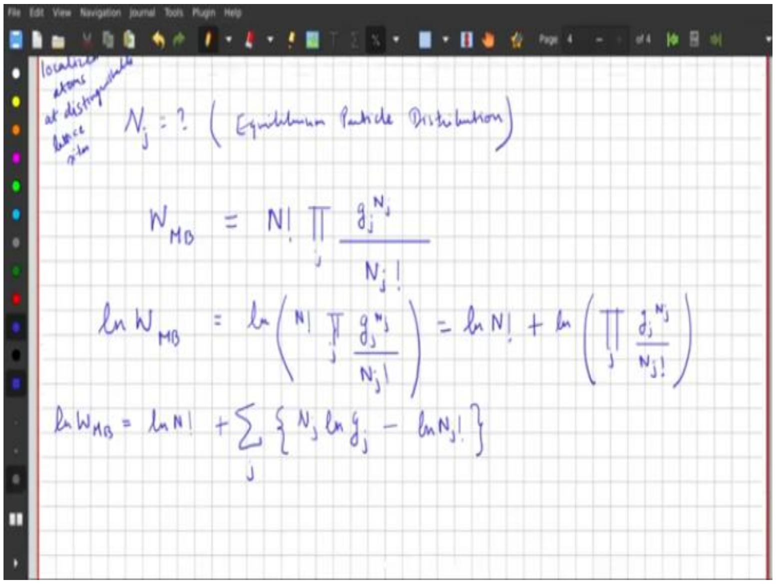
(Refer Slide Time: 12:37)

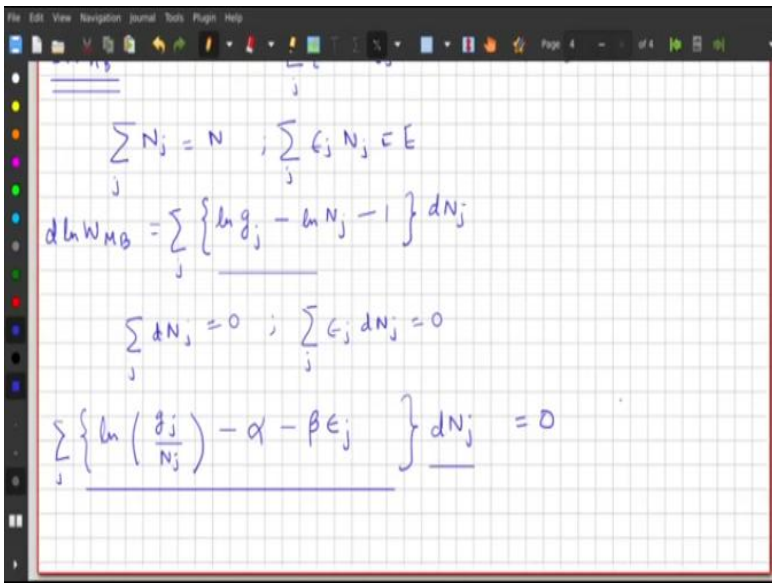


So, here we use this important fact about the particular distribution Nj and this so this we derived in the main lectures if you see if you refer to the main lectures you will see how this Nj was derived and it was derived from the statistical probability and then finding the stationary points of that probability distribution.

(Refer Slide Time: 13:29)






So, now, we will try to do something similar you know that is we will try to find out the equilibrium particle density but not for Bose-Einstein or Fermi-Dirac statistics but, so, the problem that we are trying to deal currently is and to find out the thermodynamic or let us say let us read the question.

So, the thermodynamic this is the question, thermodynamic probability for classical Maxwell Boltzmann statistics W M B and that is given that is N factorial times the product over j gj power Nj divided by Nj factorial and here what we mean by classical Maxwell Boltzmann statistics is been the statistics that was derived by Boltzmann themselves and he assumed the particles to be distinguishable and no limits on the number of particles in each energy state, where we recall Nj is the number of particles in the jth energy state.

So, this is the number of particles and gj is there degeneracy of the jth energy level and the question is what we need to find out is the equilibrium particle distribution? That is you want to find out what is Nj equilibrium particular distribution? That is the question that we want to tackle.

So, (())(15:57) so, this kind of statistics is you can think about an example of this in more practical sense. So, a solid that is composed of localized atoms at distinguishable lattice sites, so, that is an practical example of where the statistics could be handy. So, let us try to find out this equilibrium particle distribution for the classical Boltzmann statistics.

So, given that the thermodynamic probability for the Maxwell Boltzmann statistics classical version of it is N factorial the product of j gj power Nj divided by Nj factorial. Let us take the log of both sides, the log of M B and this becomes log of N factorial product of j gj Nj over Nj factorial and this by using the properties of the logarithm function can be written as log factorial plus log of the product of j gj Nj by Nj factorial.

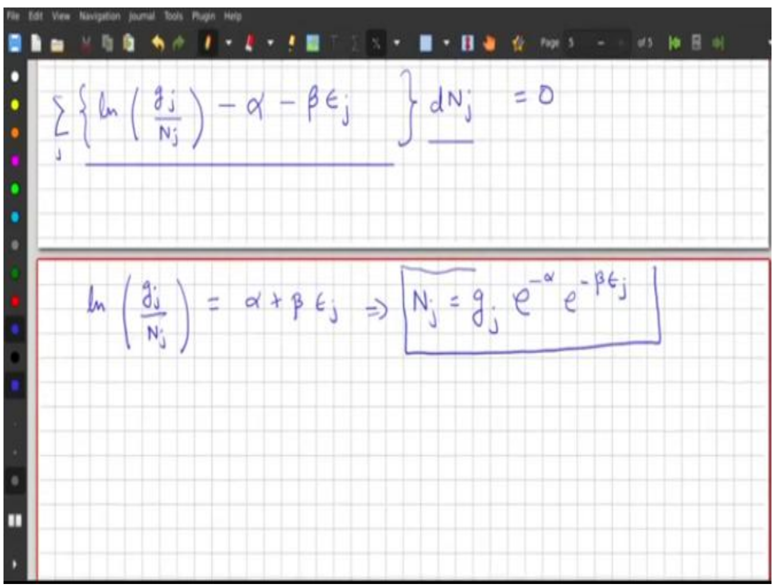
So, this could be again simplified further the logarithm of the Boltzmann probability is log n factorial plus, now, you see this is log of a product and log of a product converts it into a sum, so, this becomes a sum over j and that becomes Nj log gj, so that is coming from this term log of that term minus this is the dominator, so, minus log Nj factorial.

And now, let us see if we use the Stirling's approximation, it says the log of n factorial is approximately equal to n log n minus n for n for n tents to infinity for very large n (())(19:07) technically it should be, this is countable it is greater than 1. So, if you use this Stirling's approximation in this equation this becomes log of W M B and this becomes N log N minus N, so, N log N minus N plus sum over j Nj log gj minus Nj log Nj plus Nj where we use Stirling's approximation here and here both. So, if you see that let us recall the constraint, the constraint is sum over j Nj is N and sum over j epsilon j Nj is E.

So, if we want to find the stationary position for this function, what we need to do is take the differential of that and equate to 0, so, we want d log W M B, you want to maximize that thing that will become sum over j let us do this term first. So, this becomes different, so, we will differentiate with respect to Nj itself. So, this will become (come) log gj minus log Nj minus 1 dNj. Where we recall, so, if we differentiate the constraints themselves so this will become sum over j dNj equals 0 and sum over j epsilon j dNj equals 0.

So now, if you use the method of Lagrange multipliers which we discussed in the previous segments, this will become sum over j log gj by Nj that is coming from this term minus the first Lagrange multiplier times the constraint which is sum over dNj but that will write, so, let me write it like this, so, this is dNj so that is the first Lagrange multiplier times the second set minus beta epsilon j that is the second Lagrange multiplier so this should be equal to 0, if this has to be equal to 0 for arbitrary variations of dNj that means this entire thing has to be 0.

(Refer Slide Time: 22:46)




So, therefore, we have log of gj by Nj equals alpha plus beta epsilon j and hence from here we can write Nj equals gj e to the power minus alpha e to the power minus beta epsilon j that is the equilibrium particle distribution for classical Boltzmann statistics. That is how we do it for any general statistics so we start with the thermodynamic probability for that statistic and this comes from the fundamentals of probability theory, permutations and combinations and once we have this then, what we do is? We take the log of that thing and then log of the factorial.

So, we have log of factorial and then we use basically, you want to convert it into some kind of a continuous version for large ends, what we do is we use the Stirling's approximation we do it converted into a continuous problem and then we use the method of Lagrange multipliers to optimize the function the logarithm of thermodynamic probability under the given constraints and then we use a method of Lagrange multipliers to compute the equilibrium particle distribution.

And once we know the equilibrium particular distribution, you know the equilibrium particular distribution and as it is been discussed in the main lectures we know the partition function that is another important concept, if you know the partition function and Njs basically and basically Nj is related to the partition function basically. So, if so, in principle if we know the partition function, we can compute all thermodynamic quantities in general. So, that is for the segment and we will see you in the next segment. Thank you.