Statistical Thermodynamics for Engineers
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Lecture 11
Supplementary Video 3 Equilibrium particle distribution

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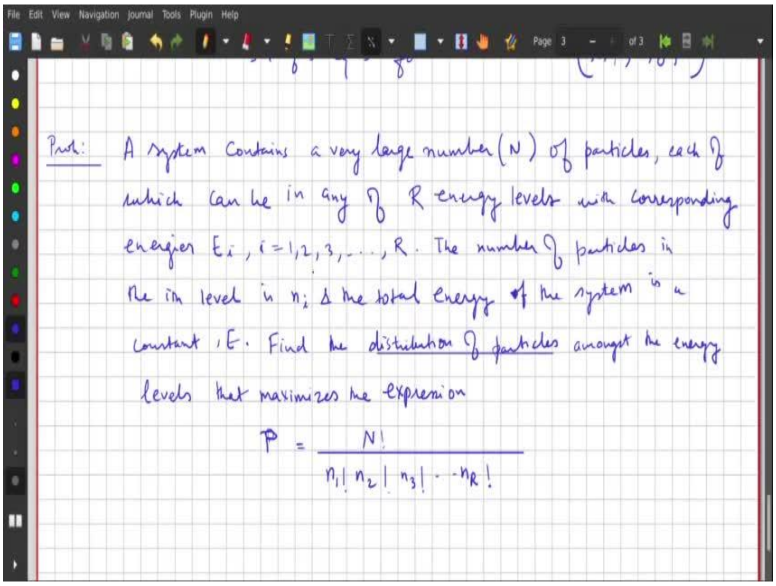

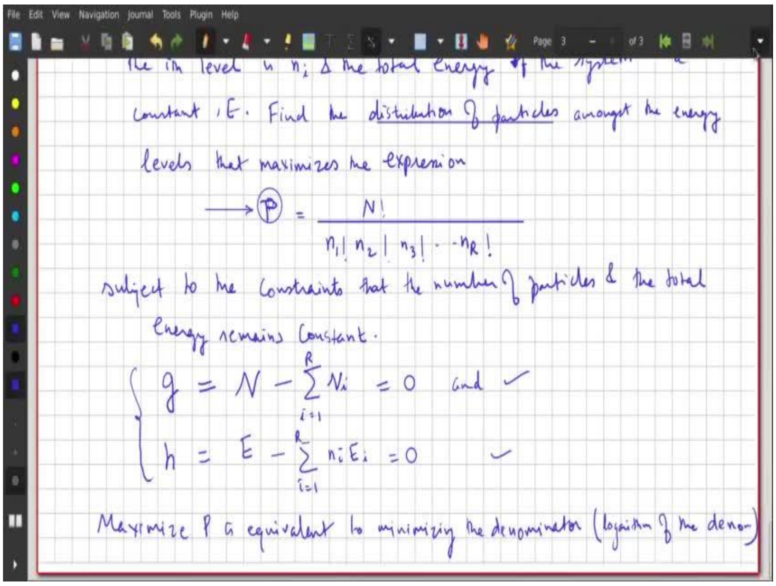

Welcome everyone to another segment of supplementary video. So in this video we will see an example of where we will be using the method of Lagrange multipliers that we discussed in the previous segment to our practical problem in statistical mechanics, so let us consider this problem.

So the problem that we have in our mind is so let us say we write it down. So let us say we have a system that contains a very large number N of particles, a system has a very large number of particles which we are denoting by N each of which, each of which can be can be in any of R energy levels with corresponding energies E sub i, where i can go from 1, 2, 3, dot dot dot up to R.

The number of particles in the ith level is given by n sub i, that means it is n 1, n 2, n 3, and so on for different energy levels and the total energy of the system is a constant given by E, so that is the total energy of the system. So the problem that you want to solve is find the distribution of particles amongst the energy levels that maximizes this is the expression P equals N factorial divided by n 1 factorial, n 2 factorial, n 3 factorial, dot dot dot, n R factorial. So if you see this what we want is we want to find out what should be the particle distribution or let us say what is the distribution of particles among the various energy levels such that this expression is maximized.

So and if you see this is P, what is P denoting is telling us the number of ways in which we can arrange N particles in i, or let us say R energy levels. So that is the expression for the total number of ways that we can do it. And if you want to maximize this, that maximization brings us to the idea of the most probable distribution that we have, that we will see in the parallel lecture videos. So we want to pose this problem as an optimization problem.

So let us write that, so we want to maximize this expression, given what are the constraints, so subject to the constraints, what are the constraints? That, subject to the constraint that the number of particles and the total energy remains constant. So what we essentially imply is we want to preserve mass conservation and energy conservation. So we want to deal with an isolated system basically.

So we can write the constraint in this way, so what we want is let us write g equals N minus sum over N i, i is equal to 1 to R, and that condition needs to be true, that is one constraint and another constraint is h equals E minus sum over i is equal to 1 to R, n i E sub i equals 0. So this is the mass conservation and this is the energy conservation basically, those are the two constraints. So what we need to do, so we got our optimization problem, we want to maximize this expression P subject to these two constraints. So here you see where we will be able to apply method of Lagrange multipliers to find out the most probable distribution.

So let us, so some one thing so if you want to maximize P, what do you want to do is basically minimize the denominator. So and minimizing the denominator is same as minimizing the logarithm of the denominator, and why we want to do the logarithm? Because you saw in the previous segment about we want to use Stirling's approximation because we want to use calculus, that means we want to convert these discrete objects into a continuous function. So there comes why we take logarithm.

So we want to maximize P, so maximize P is equivalent to minimizing the denominator or the logarithm of the denominator, so that is the denominator, that is the general idea. So what we need to do is, we want to find, so we cast this problem P rather as a maximization problem, as a minimization problem, because we want to minimize the denominator basically.

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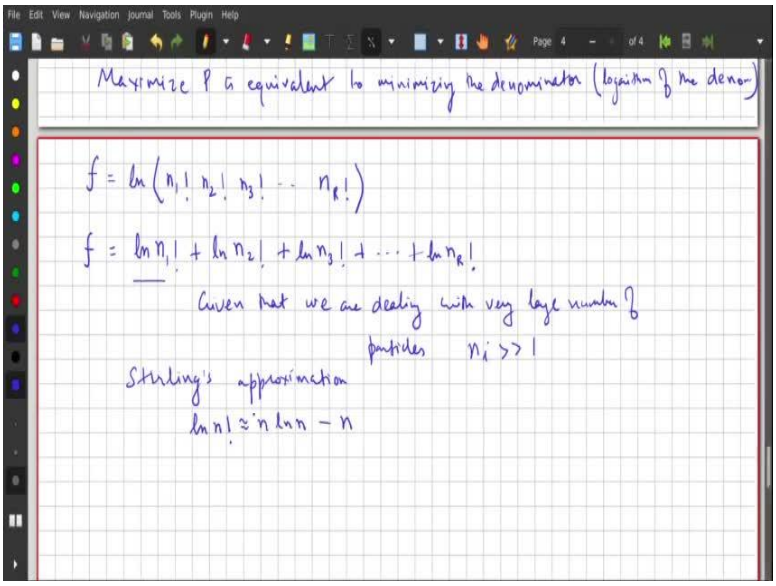

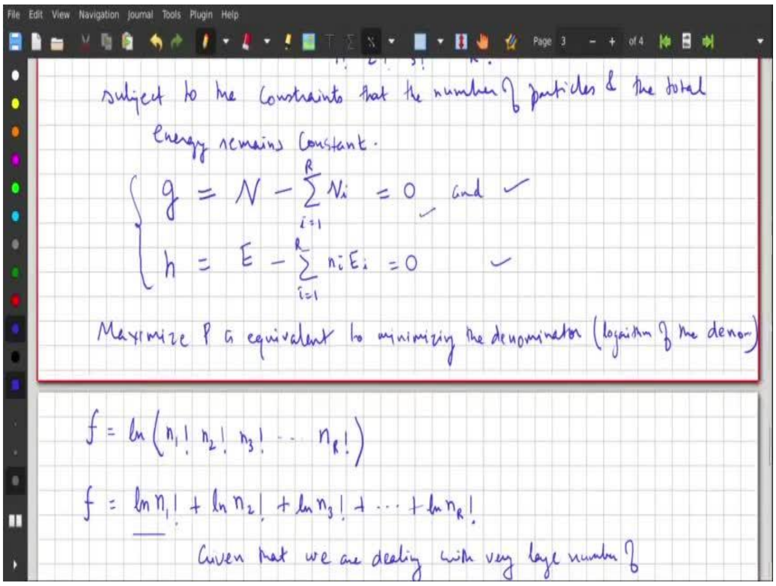

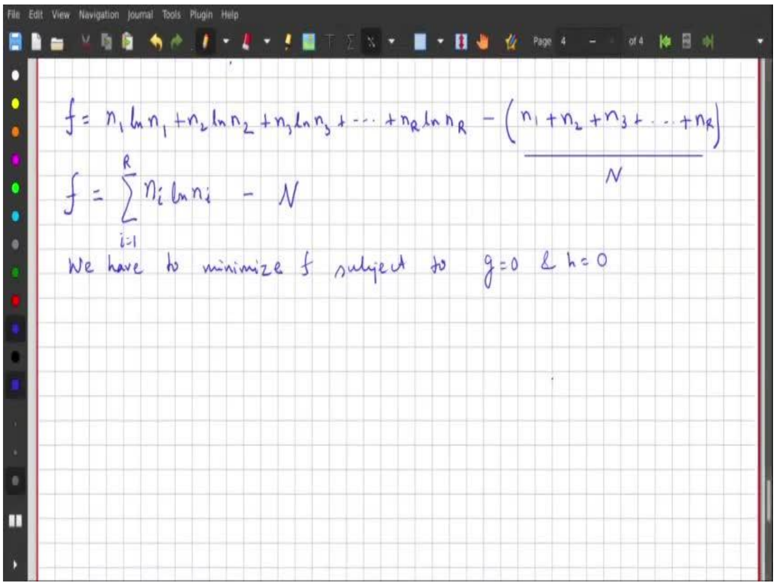

So the function that we are trying to minimize this F is log of n 1 factorial, n 2 factorial, n 3 factorial dot dot dot, n sub R factorial and using the properties of logarithm, where the log of the product of quantities could be converted into additive quantities, we can write this as n 1 factorial plus log of n 2 factorial plus log of n 3 factorial plus dot dot dot log of n R factorials. And now, given that we are dealing with very large number of particles that means, any arbitrary n sub i is much-much larger than 1, and hence, we can use the Sterling's approximation.

So what we will do is here we will use the Stirling's approximation, Stirling's approximation. So what does Stirling approximation say? It says that, you can write the log of the factorial of n is approximately equal to n log n minus n. If we use this expression for each of the individual terms for n 1, n 2 and n 3, our function becomes f equals n 1 log n 1, plus n 2 log n 2 plus n 3 log n 3 plus dot dot dot, n r log n r minus n 1 plus n 2 plus n 3 plus dot dot dot n R. That is our function, which we want to minimize subject to the constraints of a fixed number of particles n and a fixed total energy E.

So we can write this function f in terms of a summation notation. So where we can have write this as n sub i log n sub i, where i is the running index that runs over i equals 1 to R minus and this is basically the total number of particles so that is basically N, so that is the function that we are trying to optimize. So P, so this f that means we have to minimize f subject to g equals 0 and h equals 0, where remember what was g and h? g and h was given by these two constraints. So the particle conservation or mass conservation and energy conservation basically.

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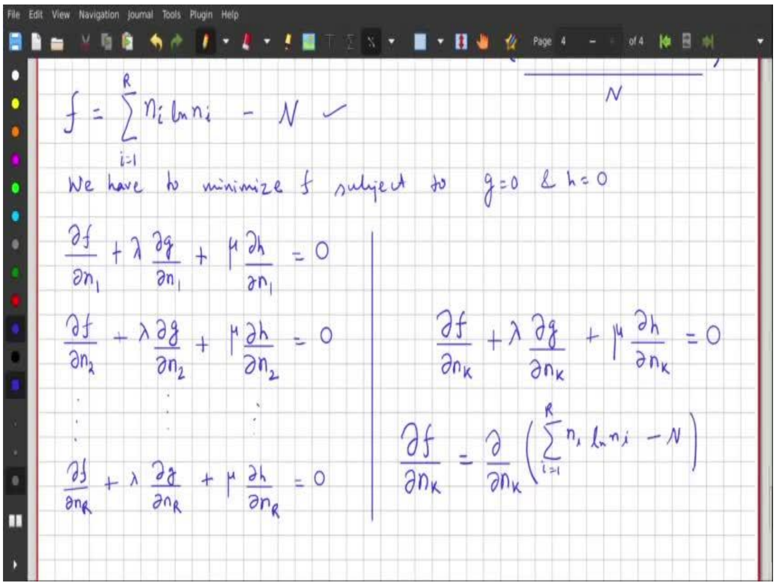

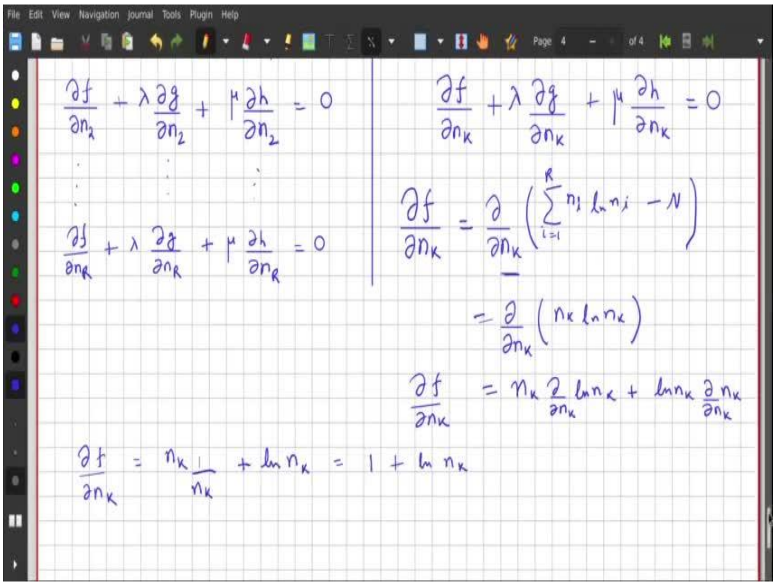

So now we will see (())(10:36) problem basically. So we have two constraints as you can see, and we have you see this R basically this function. So you can see there are R it can minimize with respect to R variables basically. So let us write all the constraint equations, it will become partial f, partial n 1 with respect to n 1, so we vary just n 1, as Lagrange first Lagrange multiply lambda times partial g partial n 1 plus mu partial h partial n 1 equals 0. So that is the first equation like that we can write partial f partial n 2 plus lambda partial g partial n 2 plus mu partial h partial n 2 equals 0, and this we can write for all of the R states, energy states. Partial f partial n r plus lambda partial g partial n R plus mu partial h partial n R equals 0.

If you see there is a commonality, common pattern among all these constraint equations. So we can write a general version of these constraints. So you can write this as partial f partial n sub k plus lambda times partial g partial n sub k plus mu times partial h partial n sub k equals 0. So now, if we use the individual values for f, this is what f is and g and h just compute each of these derivative. So let us compute partial f partial n sub k. So partial f partial n sub k is partial with respect to n sub k and remember what f was. So f is the sum of i equals 1 to R n sub i log n sub i minus N.

So remember n 1, n 2, n 3, all those are independent variables it could you can vary all this a number of particles in the each of the energy states independently. So the only derivative we are concerned about is the kth is derivative basically. So what this will become is, partial with respect to n sub k of n sub k log n sub k and now, we can use the product rule of derivative.

So n k as it is and the derivative of log n sub k, this will become the derivative of log n sub k plus log n sub k derivative with respect to n sub k of n sub k itself. So this will become this is partial f partial n sub k. See what is partial f partial n sub k? Partial f, partial n sub k is n sub k and the derivative of log n sub k is 1 over n sub k. And then this becomes log over n sub k, so this becomes 1 plus log of n sub k, so that is partial f partial n sub k.

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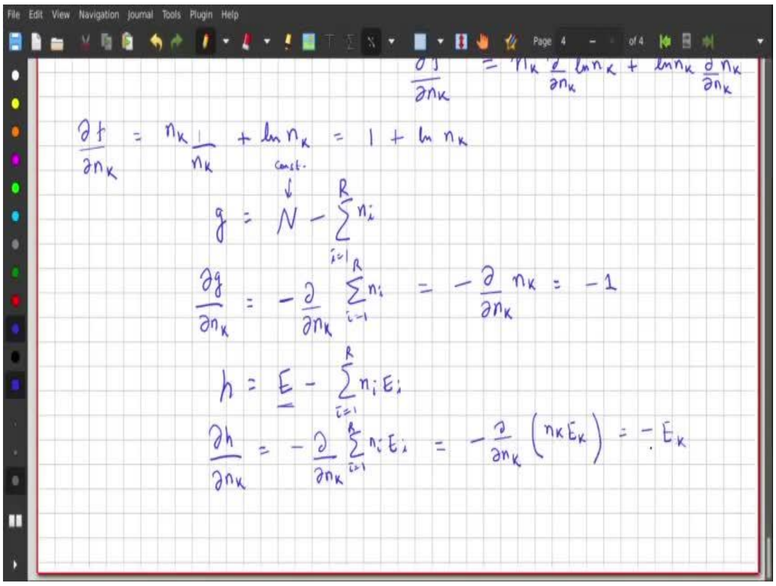

And let us figure out now the second term is partial g partial n sub k. So let us write what g was? The g was the particle conservation basically. So this was g equals N minus sum over i is equal to 1 to R n sub i. So what we want is partial g partial n sub k. If you see this derivative have N but this is constant remember, because we are dealing with an isolated system, so the derivative of that is 0, so this will become minus the derivative with respect to n sub k of the sum i equals 1 to R n sub i and the only term that will contribute is the kth term. So this will become minus derivative of n sub k with respect to n sub k, which is minus 1.

And let us write what is h? So h was E minus sum over i is equal to 1 to R, E sub i n sub i that was n sub i, e sub i, and if you write partial h with respect to n sub k. Again, given that we are dealing with an isolated E is constant that is 0, so what we have is negative partial with respect to n sub k sum over i equals 1 to R, n sub i, e sub i and the only term that will contribute again is the kth term is minus partial with respect to n sub k of n sub k E sub k. So this becomes minus E sub k. So we have all the derivatives now.

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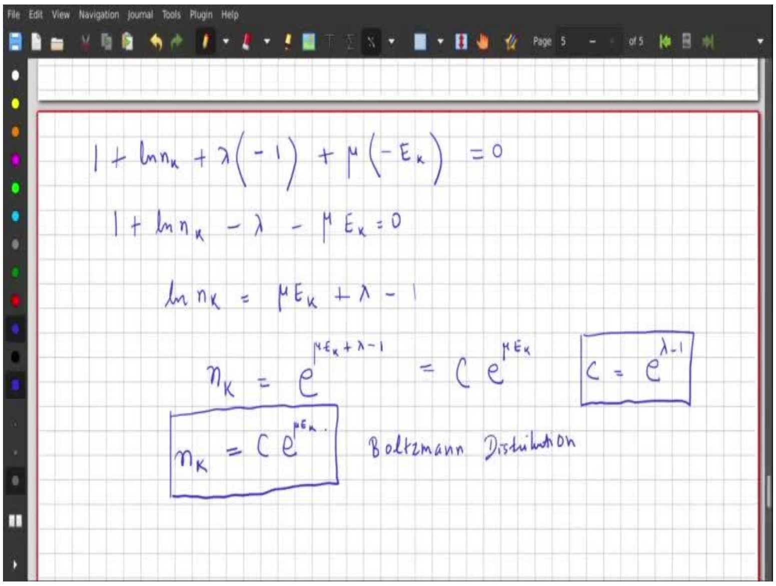

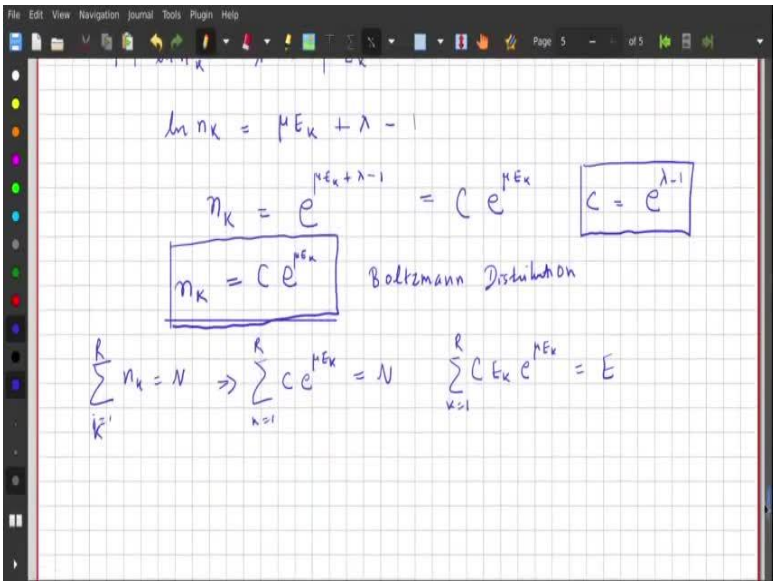

So we have all these derivatives and now, let us combine all these derivatives so partial f partial n k that is 1 plus, so that is write it in a new page. So that is 1 plus log n sub k that is the first term partial f partial n sub k plus lambda times partial g partial n K which was minus 1, plus mu times partial h partial n sub k which is minus E sub k and that is worth 0. That is the general expression that we found out. So if you see, what this becomes is on simplification 1, plus log n sub k minus lambda minus mu E sub k equals 0, or we can write this as log of n sub k equals mu E sub k plus lambda minus 1 R. n sub k is e to the power mu E sub k plus lambda minus 1 or this could be written in now where C e to the power mu E sub k, where C is e to the lambda minus 1.

So we found out n sub k that is the particle distribution, number of particles found in the kth energy state will be given by C e to the power mu E sub k. So that was the thing that we were looking for. And this distribution is very important in statistical mechanics and it is so important that this has a name to it, basically and this is known as the Boltzmann distribution.

And the constants mu and C could be evaluated from the constraints that sum over i is equal to 1 to R, n sub k is N, and if we use it using this n sub k, this will become sum over this is K, K equals 1 to R, C e mu E sub k that is equal to N. And similarly for the energy sum over K equals 1 to R, E sub k, e mu E sub k because it was based on these two constraints the constraints could be figured out. But this was the expression that we were looking for the distribution of particles basically and you see how we got it. It is came from the natural idea of function optimization problem, subjected to constraints.

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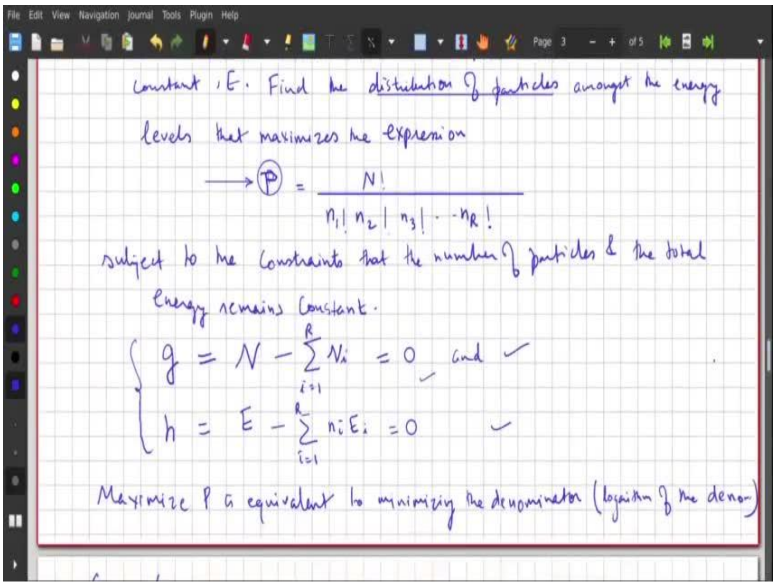

$$f = \ln\left(n_1!\, n_2!\, n_3! \cdots n_R!\right)$$

$$f = \ln n_1! + \ln n_2! + \ln n_3! + \cdots + \ln n_R!$$

Given that we are dealing with very large number of particles $n_i >> 1$

Stirling's approximation

$$\ln n! \simeq n \ln n - n$$

$$f = n_1 \ln n_1 + n_2 \ln n_2 + n_3 \ln n_3 + \cdots + n_R \ln n_R - \underbrace{\left(n_1 + n_2 + n_3 + \cdots + n_R\right)}_{N}$$

$$f = \sum_{i=1}^{R} n_i \ln n_i - N \checkmark$$

$$f = n_1 \ln n_1 + n_2 \ln n_2 + n_3 \ln n_3 + \cdots + n_R \ln n_R - \underbrace{\left(n_1 + n_2 + n_3 + \cdots + n_R\right)}_{N}$$

$$f = \sum_{i=1}^{R} n_i \ln n_i - N \checkmark$$

We have to minimize f subject to $g=0$ & $h=0$

$$\frac{\partial f}{\partial n_1} + \lambda \frac{\partial g}{\partial n_1} + \mu \frac{\partial h}{\partial n_1} = 0$$

$$\frac{\partial f}{\partial n_2} + \lambda \frac{\partial g}{\partial n_2} + \mu \frac{\partial h}{\partial n_2} = 0$$

$$\vdots$$

$$\frac{\partial f}{\partial n_R} + \lambda \frac{\partial g}{\partial n_R} + \mu \frac{\partial h}{\partial n_R} = 0$$

$$\frac{\partial f}{\partial n_k} + \lambda \frac{\partial g}{\partial n_k} + \mu \frac{\partial h}{\partial n_k} = 0$$

$$\frac{\partial f}{\partial n_k} = \frac{\partial}{\partial n_k}\left(\sum_{i=1}^{R} n_i \ln n_i - N\right)$$

$$\ln n_k = \mu E_k + \lambda - 1$$

$$n_k = e^{\mu E_k + \lambda - 1} = C e^{\mu E_k} \qquad \boxed{C = e^{\lambda - 1}}$$

$$\boxed{n_k = C e^{\mu E_k}}$$ Boltzmann Distribution

$$\sum_{k=1}^{R} n_k = N \Rightarrow \sum_{k=1}^{R} C e^{\mu E_k} = N \qquad \sum_{k=1}^{R} C E_k e^{\mu E_k} = E$$

So we wanted to remember what we did, we wanted to maximize this term P subjected to the constraint of a given number of particles and a given total energy. And how we did it? We did it by so we dealt with the logic that if we want to maximize P, we want to minimize its denominator and we want to minimize the denominator that is same as minimizing the logarithm of the denominator.

And so this was the function that we started with. And we took logarithm for a reason because we wanted to convert the factorial to, factorial functions to continuous smooth functions using the Stirling's approximation. And that is what we did, we converted f using the Stirling's approximation, this was f and then we had the constraints g and h. And based on the constraints, we wrote the optimization problem using the Lagrange multipliers lambda and mu. And based on that, we were able to figure out the particle distribution for the Kth energy state and the constants the Lagrange multipliers themselves could be figured out from the constraints themselves.

So this was when we are able to show how the Boltzmann distribution is a result of an optimization problem, basically. So this is related to a finding out the most probable number of ways of arranging N particles and let us say Rth, R number of energy states and the best way to do it. And the, the equilibrium particle distribution is given by the Boltzmann distribution, and that is what we derived here. So this was the Boltzmann distribution. So that is for the segment. Thank you.