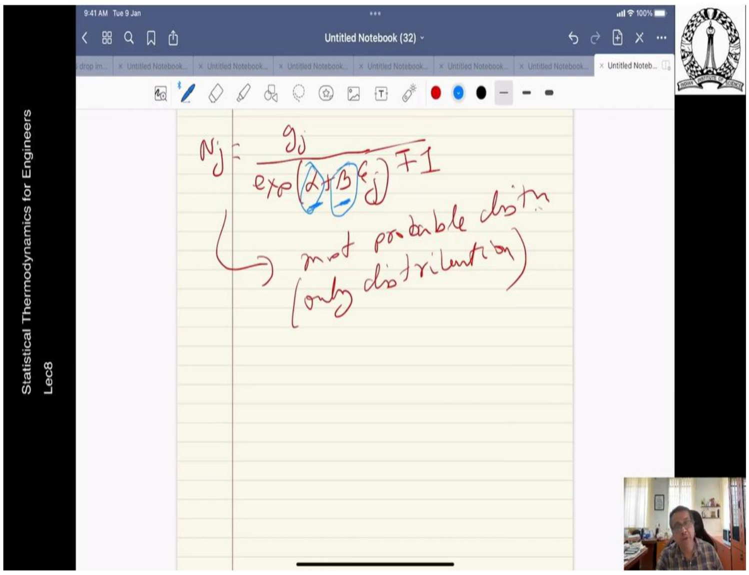
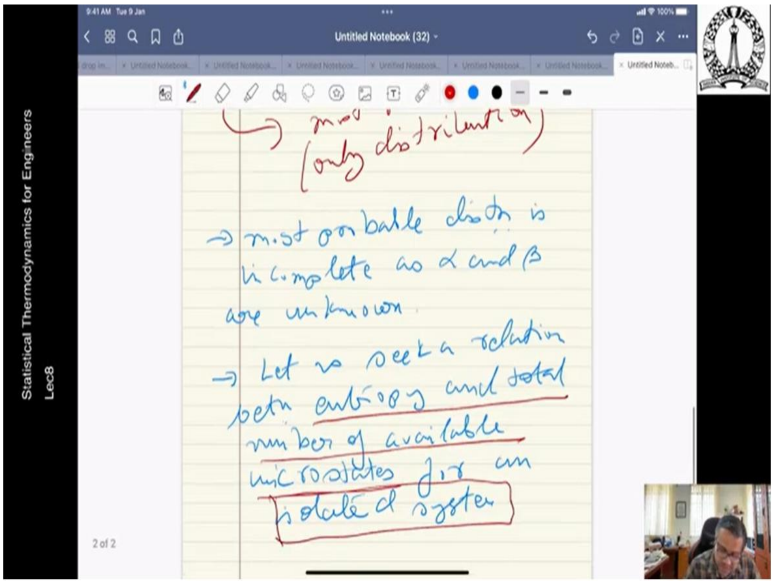
Statistical Thermodynamics for Engineers
Professor Saptarshi Basu
Indian Institute of Science, Bangalore
Lecture 08
Entropy and the Equilibrium Particle Distribution

(Refer Slide Time: 00:09)



$$N_j = \frac{g_j}{\exp(\alpha + \beta \epsilon_j) \mp 1}$$

→ most probable distn
(only distribution)



→ most
(only distribution)

→ most probable distn is incomplete as α and β are unknown.

→ Let us seek a relation betn entropy and total number of available microstates for an isolated system

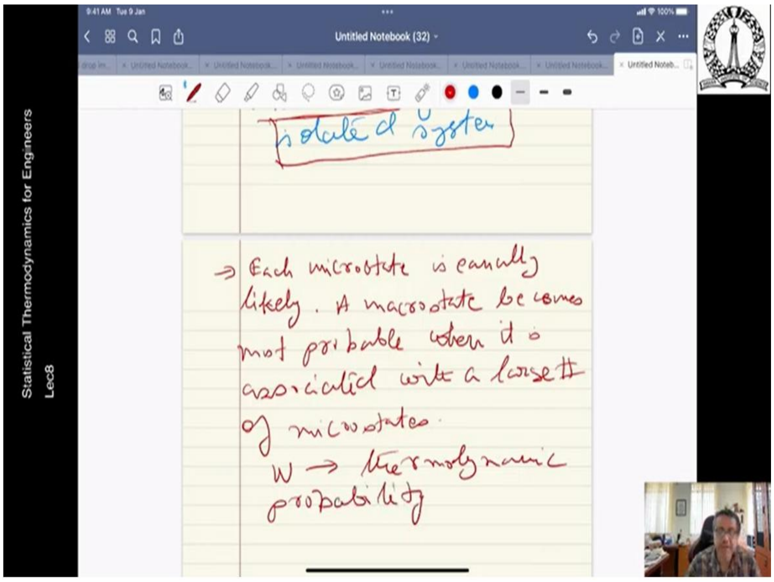
So, welcome to lecture 8 of The Statistical Thermodynamics for Engineers. If you recall in the last class, the last lecture, we said Nj is equal to gj exponential alpha plus beta ej minus plus 1. This was the most probable distribution, most probable distribution and this was perhaps the only distribution.

But there are a few points that we mentioned over there, one was this alpha and beta, these two, these two LaGrange multipliers were actually unknown, right, they are not known at all.

So, we decided that how to get around it. So, the most probable distribution, most probable distribution is incomplete, is incomplete as alpha and beta unknown.

So, let us now therefore do a, do a simple thing, because we have to find this in some way. So, let us seek a relation, relation between entropy and total number, total number of available microstates, available microstates for an isolated system. So, that is let us do that between entropy and the total number of available microstates for an isolated system.

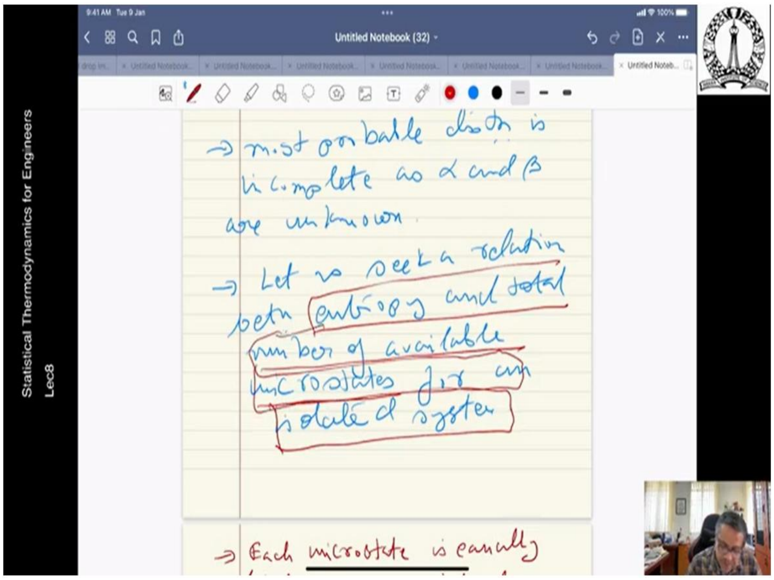
(Refer Slide Time: 02:15)



isolated system

→ Each microstate is equally likely. A macrostate becomes most probable when it is associated with a largest of microstates.

W → thermodynamic probability



→ most probable distn is incomplete as α and β are unknown.

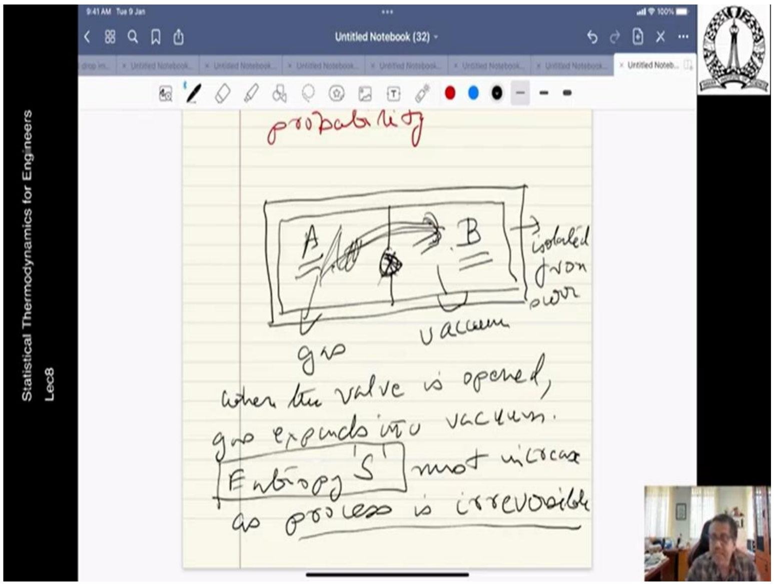
→ Let us seek a relation betn entropy and total number of available microstates for an isolated system

→ Each microstate is equally

We also know that each microstate, microstate is equally likely, equally likely. A macrostate, a macrostate becomes most probable, most probable, probable, when it is associated, when it is associated, associated with a large number of, large number of microstates, microstates. So, W is basically what we call thermodynamic probability, in any probability.

So, this is the journey we are going to undertake that we have to find out the alpha and the beta, but at the same time we have to find out the relationship between entropy and the total number of available microstates in an isolated system.

(Refer Slide Time: 03:26)



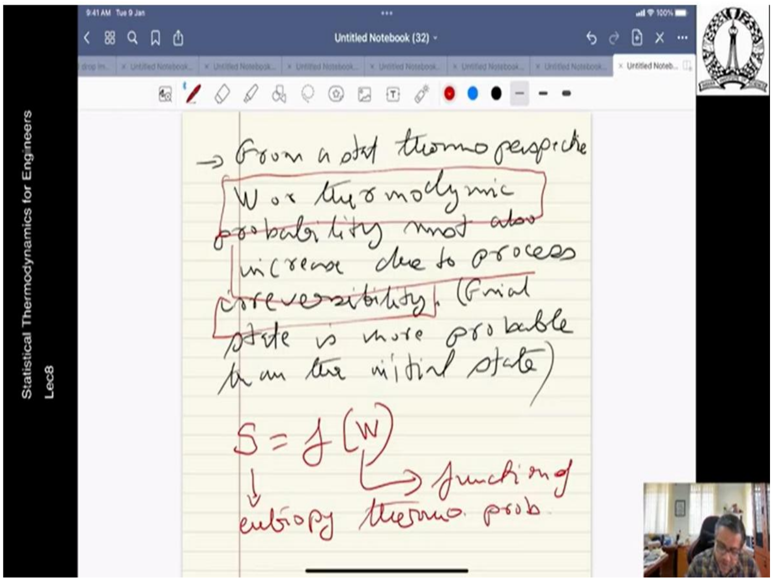
when the valve is opened,
gas expands into vacuum.
Entropy 'S' must increase
as process is irreversible

So, for doing that, let us assume this kind of configuration, let us assume that this a chain board, that is completely isolated, isolated, isolated from surroundings, surroundings. So, this is got valve, so, there is a A part of the chamber and there is a B. A has got a gas, B is vacuum. So, this is a valve, separating the A, the chamber A from chamber B which is separated by this valve and there is a gas in chamber A.

So, when the valve is opened, valve is opened, what will happen? Gas expands into the vacuum, vacuum. So, the gas from here will expand and go there. So, entropy as we know, entropy S from your macroscopic understanding must increase, must increase as the processes is irreversible.

So, you have suddenly opened the valve, it is not like a slow transition, we can go back. So, you have just opened the valve suddenly and so, the gas will expand and go from chamber A to chamber B because B is vacuum and so the gas expands and the process is irreversible. So, therefore, entropy, the quantity entropy must therefore increase. So, this is gas.

(Refer Slide Time: 05:34)



→ From a stat thermo perspective

W or thermodynamic probability must also increase due to process irreversibility. (Final state is more probable than the initial state)

$S = f(W)$

↓ entropy

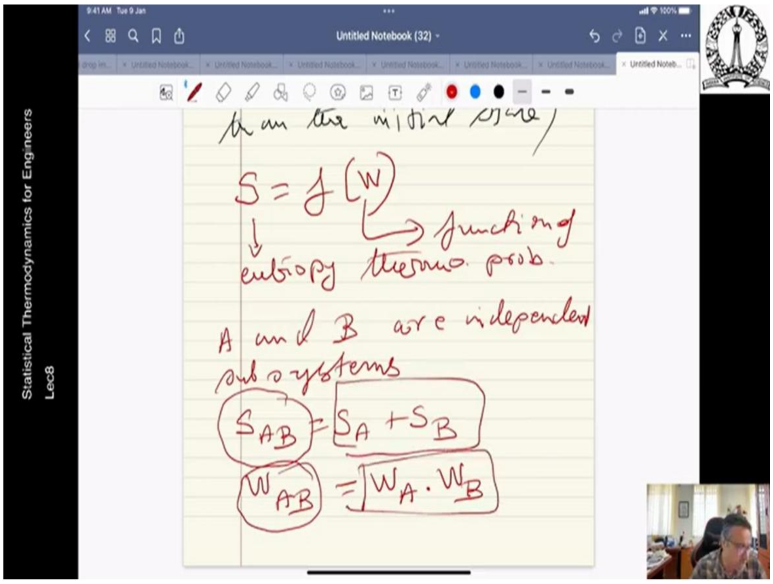
→ function of thermo. prob

Now, from a stat thermo perspective, stat thermo perspective, perspective, that view, or the thermo probability, probability must also increase, also increase due to process is irreversibility. Correct? Process irreversibility. This is the simple reason her is the final state, final state is more probable, probable than the initial state, than the initial state.

Initial state is that the gas remains in chamber A and it is not going to chamber B. So, that is also not a probability, but obviously, the final stage which is a gas fills the whole container both A and B is a much more probable scenario. So, therefore the thermodynamic probability or W must also increase due to this process irreversible, that is supposed to happen.

So, therefore what we can say is that entropy is definitely therefore a function of this thermodynamic probability. So, if this is a entropy, we do not know what function it is, it is definitely a function of, function of this thermodynamic probability. All right? So, the entropy should be a function of this thermodynamic probability and as entropy increases, the thermodynamic probability also increases. We do not know whether they, how they are correlated with each other, but we definitely know that this should be the situation.

(Refer Slide Time: 07:39)



than the initial state)

$S = f(W)$

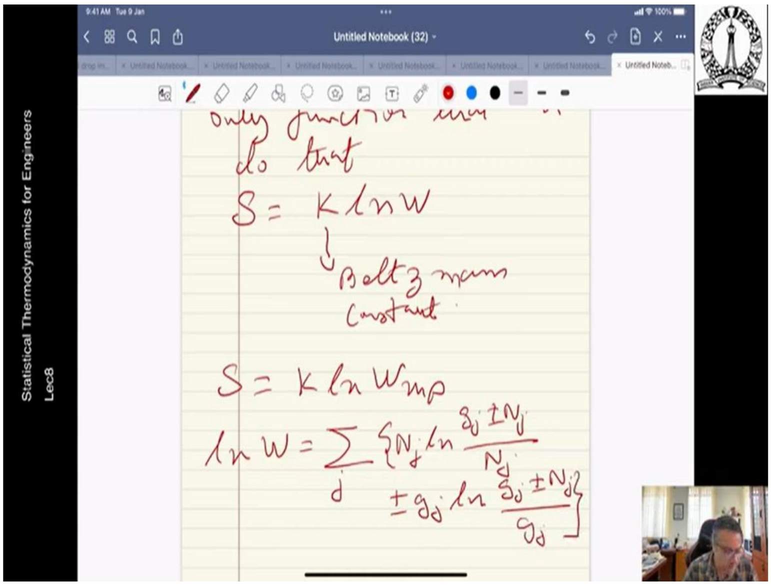
entropy

function of thermo. prob.

A and B are independent subsystems

$\boxed{S_{AB}} = \boxed{S_A + S_B}$

$\boxed{W_{AB}} = \boxed{W_A \cdot W_B}$



Only function that can
do that

$S = k \ln W$

Boltzmann constant

$S = k \ln W_{mp}$

$$\ln W = \sum_j \left\{ N_j \ln \frac{g_j \pm N_j}{N_j} \pm g_j \ln \frac{g_j \pm N_j}{g_j} \right\}$$

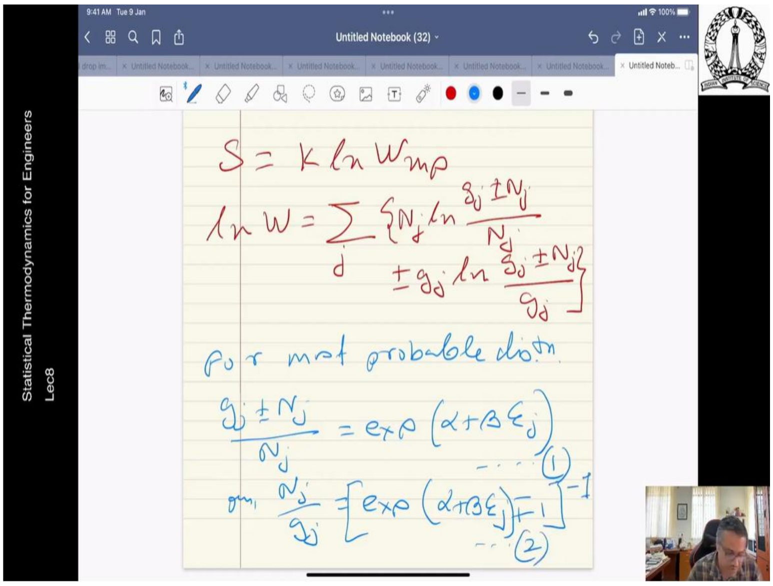
Now, since A and B are independent, independent subsystems, independent subsystems, therefore the entropy of A and B is basically entropy of A plus entropy of B, whereas the probability of A and B, thermodynamic probability because we are independent, S must be WA into WB.

So, what we are stating over here, that this entropy must be related to this, but this is an additive quantity and this is a multiplicative quantity, the only function that can actually do that, only function that can do it, do that is basically your S is given as klnw, because logarithm is the only operator which can do that multiplicative to additive.

So, SA plus SB is actually equal to klnwA plus klnwB so, which is the logarithmic science, you know that they can be multiplicative. So, this k, a constant that sits, is basically called the

Boltz Moon Constant. So, in other words, we can say that S is therefore kln the most probable distribution. So, klnw, as we already got is summation over j Nj ln gj plus minus Nj by Nj plus minus gj ln gj plus minus Nj divided by gj goes in the bracket. All right? So, this is how it goes.

(Refer Slide Time: 10:03)



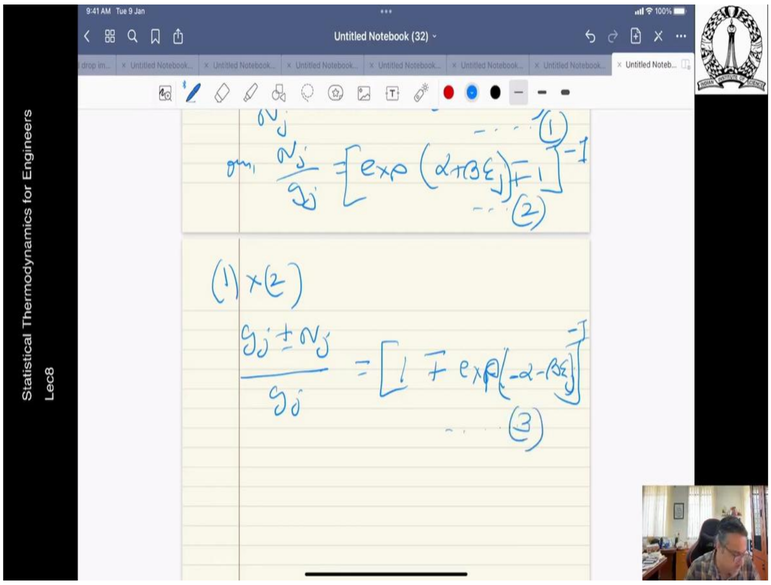
$$S = k \ln W_{mp}$$

$$\ln W = \sum_j \left\{ N_j \ln \frac{g_j \pm N_j}{N_j} \pm g_j \ln \frac{g_j \pm N_j}{g_j} \right\}$$

For most probable distn

$$\frac{g_j \pm N_j}{N_j} = \exp(\alpha + \beta \varepsilon_j) \quad \text{---} (1)$$

$$\text{or, } \frac{N_j}{g_j} = \left[\exp(\alpha + \beta \varepsilon_j) \mp 1\right]^{-1} \quad \text{---} (2)$$



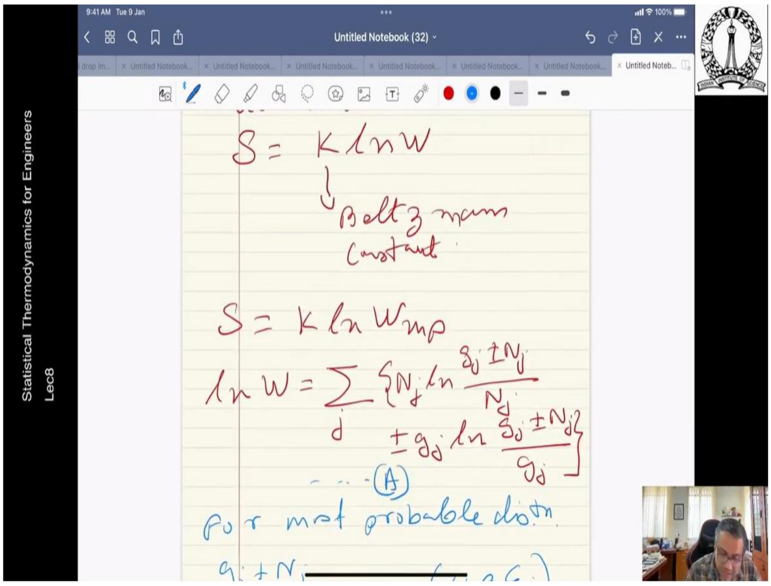
$$\text{or, } \frac{N_j}{g_j} = \left[\exp(\alpha + \beta \varepsilon_j) \mp 1\right]^{-1} \quad \text{---} (2)$$

$(1) \times (2)$

$$\frac{g_j \pm N_j}{g_j} = \left[1 \mp \exp(-\alpha - \beta \varepsilon_j)\right]^{-1} \quad \text{---} (3)$$

So, the most probable distribution, most probable distribution gj plus minus Nj by Nj, this we already know, exponential alpha plus beta ej, let us call this 1or in other words we can call this Nj by gj is equal to exponential alpha plus beta ej minus plus 1 is to the power of minus 1. So, this is 2, relationship 2. If you multiply 1 multiplied by 2, you get, you get gj plus minus Nj divided by gj is equal to 1 minus plus exponential minus exponential minus alpha minus beta ej close bracket minus 1. So, this is basically your expression 3.

(Refer Slide Time: 11:53)



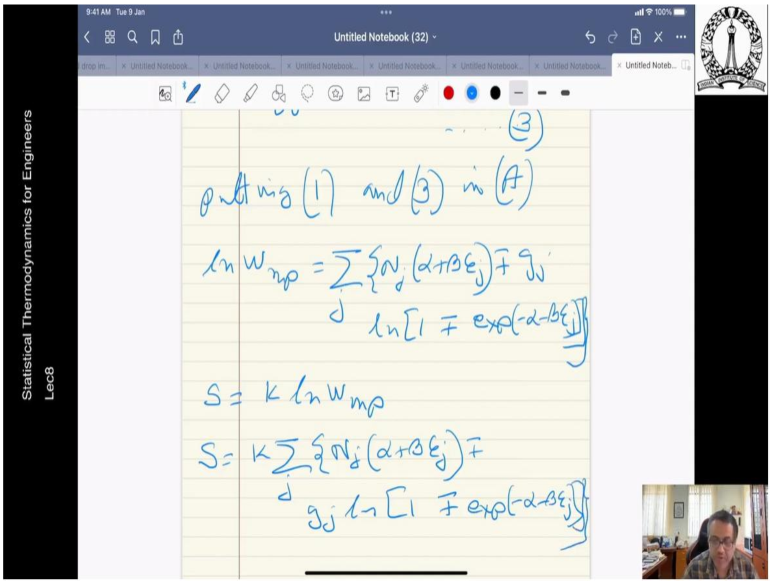
$S = k \ln W$

Boltzmann Constant

$S = k \ln W_{mp}$

$$\ln W = \sum_j \left\{ N_j \ln \frac{g_j \pm N_j}{N_j} \pm g_j \ln \frac{g_j \pm N_j}{g_j} \right\} \quad \text{---} (A)$$

For most probable distn



--- (3)

putting (1) and (3) in (A)

$$\ln W_{mp} = \sum_j \left\{ N_j (\alpha + \beta \varepsilon_j) \mp g_j \ln [1 \mp \exp(-\alpha - \beta \varepsilon_j)] \right\}$$

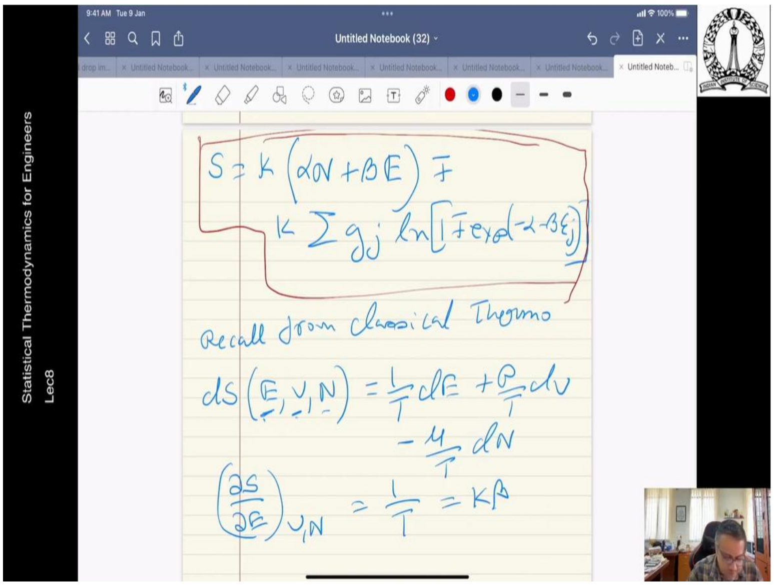
$S = k \ln W_{mp}$

$$S = k \sum_j \left\{ N_j (\alpha + \beta \varepsilon_j) \mp g_j \ln [1 \mp \exp(-\alpha - \beta \varepsilon_j)] \right\}$$

So, now, now, so, if we name this expression now which we have over here as A, let us put it as A, so what you can do is that putting, we will put, putting 1 and 3 in A, in expression A, we get the most probable distribution equal to summation j Nj alpha plus beta ej minus plus gj ln 1 minus plus exponential minus alpha minus beta ej close bracket, this.

Now, since, your S is equal to klnwmp so, therefore S is equal to k summation j Nj alpha plus beta ej minus plus, minus plus we will write it in next line gj, gj ln 1 minus plus exponential minus alpha minus beta ej. So, that is what you get. And then you can simplify this a little bit further.

(Refer Slide Time: 13:26)



$$\boxed{S = K(\alpha N + \beta E) \mp K \sum_j g_j \ln\left[1 \mp \exp(-\alpha - \beta \varepsilon_j)\right]}$$

Recall from classical Thermo

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

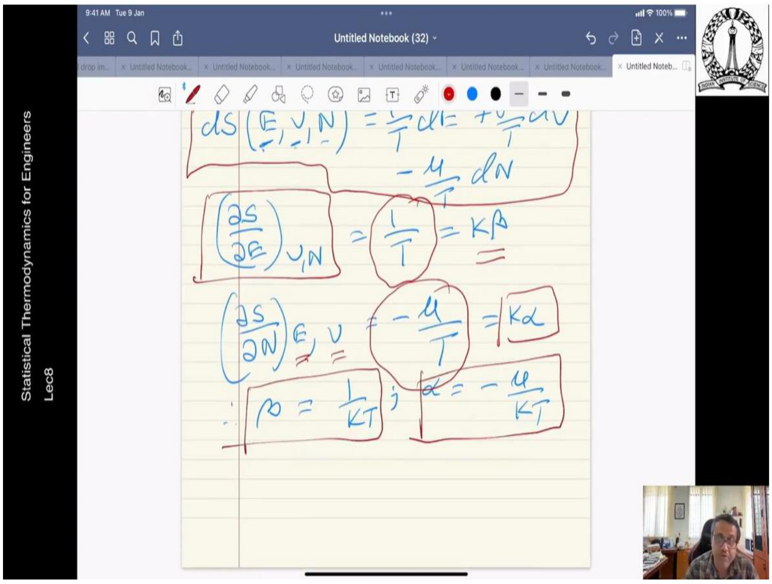
$$\left(\frac{\partial S}{\partial E}\right)_{V,N} = \frac{1}{T} = K\beta$$

K N beta E as you can see minus plus K gj ln 1 minus plus exponential minus alpha minus beta ej bracket close this. So, this what you get as a expression for entropy. But again, you still retain the terms alpha and beta as you can see. So, those are not yet anchored that what you should do about it.

So, in that particular case, if you recall from classical thermodynamics now, classical thermos, what you will call, that your, this you know from your classical that this is how entropy changes, so, it is in terms of the three variables energy, volume and number. So, this is what it is.

So, therefore, dS into dE if you keep so, this is a partial keeping V and N constant is equal to 1 over T which is nothing but K beta. So, if you differentiate now with respect to V and N you will get constant, you will get 1 over T. So, that is what is your K beta, K beta. You understood the point.

(Refer Slide Time: 15:30)



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

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

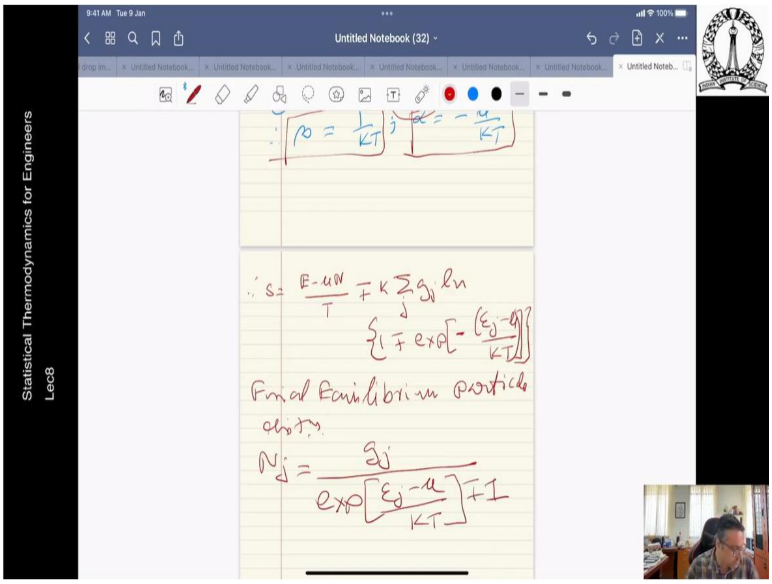
$$\left(\frac{\partial S}{\partial N}\right)_{E,V} = -\frac{\mu}{T} = k\alpha$$

$$\beta = \frac{1}{kT}; \quad \alpha = -\frac{\mu}{kT}$$

And similarly, dS by dN with E and V constant is equal to minus mu over T which is equal to k alpha. So, k alpha and k beta so, this gives an unique opportunity that now you know that what is, what is the value of A, constant alpha and beta you know. So, therefore you beta is equal to 1 over Kt, alpha is equal to minus mu over kT. So, you see that what we have done over here, we have taken the macro equilibrium, or we have taken the definition of entropy and then once you differentiate it with respect to V and N to give the two constant, you get this is dT, because that is what you are differentiating. And this should a k beta. This should be their k beta, to begin with.

Similarly when you actually differentiate it with respect to E and V, with respect to and keeping E and V constant in this because minus mu by T so, that becomes your k alpha then, k alpha. So, this gives us then a unique opportunity to find out what will be the value of data and what will be the value of your outcome.

(Refer Slide Time: 17:10)

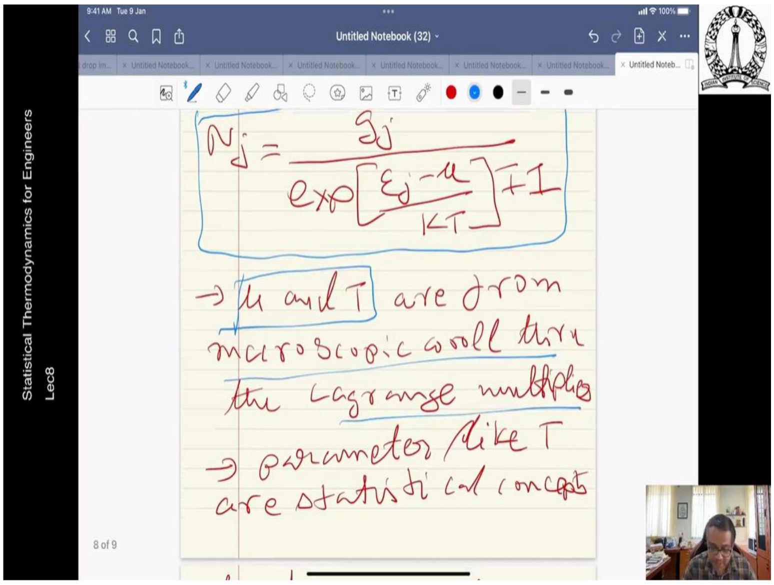


$\therefore \boxed{\beta = \frac{1}{KT}}; \boxed{\alpha = -\frac{\mu}{KT}}$

$\therefore S = \frac{E-\mu N}{T} \mp K \sum_j g_j \ln \left\{1 \mp \exp\left[-\frac{(\epsilon_j-\mu)}{KT}\right]\right\}$

Final Equilibrium particle distn.

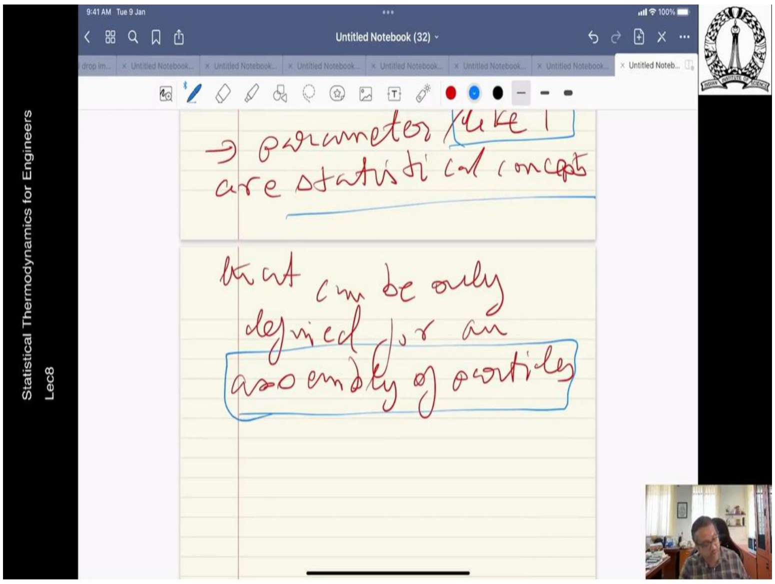
$N_j = \frac{g_j}{\exp\left[\frac{\epsilon_j-\mu}{KT}\right] \mp 1}$



$$\boxed{N_j = \frac{g_j}{\exp\left[\frac{\epsilon_j-\mu}{KT}\right] \mp 1}}$$

→ μ and T are from macroscopic world thru the Lagrange multiplier

→ parameter like T are statistical concepts



→ parameter like T are statistical concepts

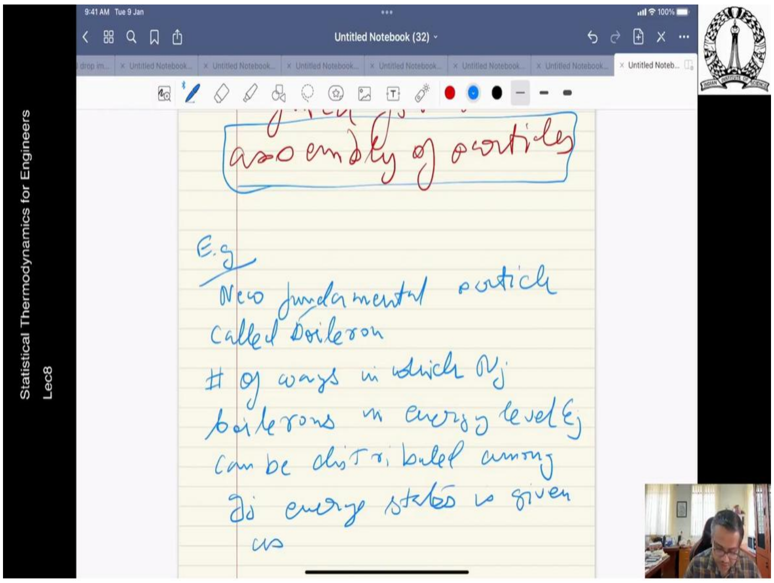
that can be only defined for an assembly of particles

So, therefore, we will go to the next page, therefore, S is written as E minus mu N by T, now you can substitute. Therefore, T minus plus k summation j gj ln I am writing this ln in the bracketed terms down minus plus exponential minus now we have everything, ej by mu by kT close he bracket, close the second bracket, close the third bracket. So, the final equilibrium article distribution, final equilibrium article distribution, article distribution becomes Nj is equal to gj divided by exponential Ej minus mu divided by kT minus plus 1.

So, in this particular case your mu and T are from macroscopic world, macroscopic world, world through the LaGrange multipliers. So, parameters, parameters like temperature are therefore statistical concepts, statistical concepts, concepts. That can be only defined, only defined for an assembly of particles, for an assembly of particles.

So, what we have done over here, just to have a quick recap, this becomes your final equilibrium particle distribution depending on whether it's (inaudible) and mu and T the chemical potential and temperature are from the macroscopic world through the enters through the LaGrange multipliers and the equivalent concept is that parameter like temperature is basically a statistical concept that can be only defined for an assembly of particles. So, this is like a new insight of what temperature is so what temperature can be.

(Refer Slide Time: 20:17)

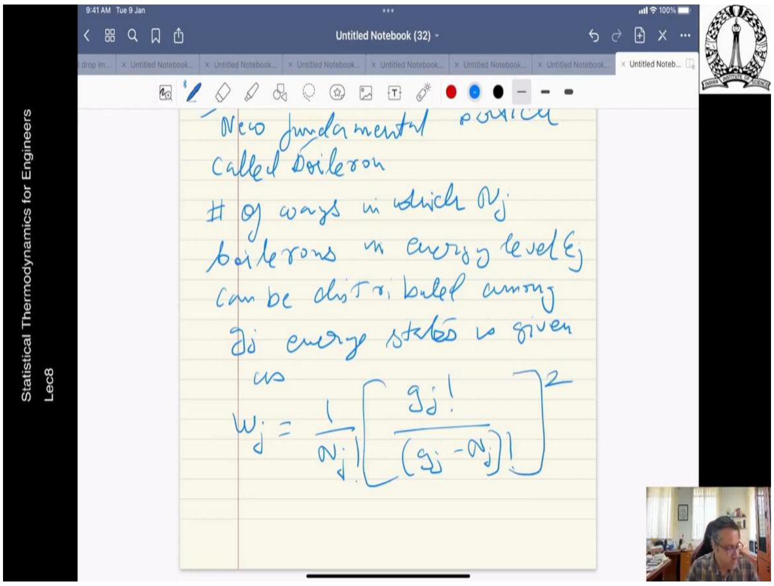


assembly of particles

E.g.

New fundamental particle called boileron

# of ways in which N_j boilerons in energy level E_j can be distributed among g_j energy states is given as

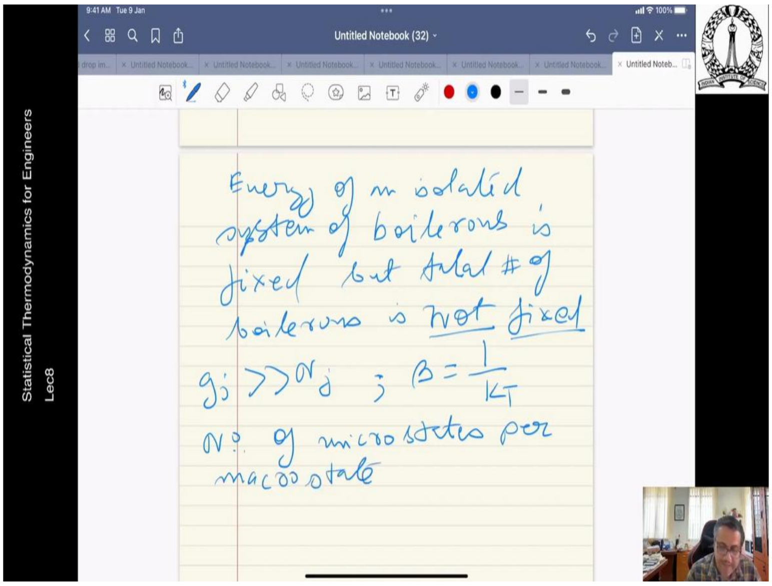


New fundamental particle
called Boileron
# of ways in which N_j
boilerons in energy level E_j
can be distributed among
g_j energy states is given
as

$$W_j = \frac{1}{N_j!}\left[\frac{g_j!}{(g_j - N_j)!}\right]^2$$

So, let us see an example problem so, that you understand it the best. Example problem. So, there is say a new fundamental particle called say Boileron, Boileron. So, number of ways, so, this is just a, this particle may not be there in the real life, this is just an example. Number of ways in which Nj Boilerons, in energy level Nj can be distributed, can be distributed among gj energy states, energy states is given as, so, we are giving you the distribution given as wj is equal to 1 over Nj bar, gj bar gj minus Nj factorial whole square.

(Refer Slide Time: 21:40)



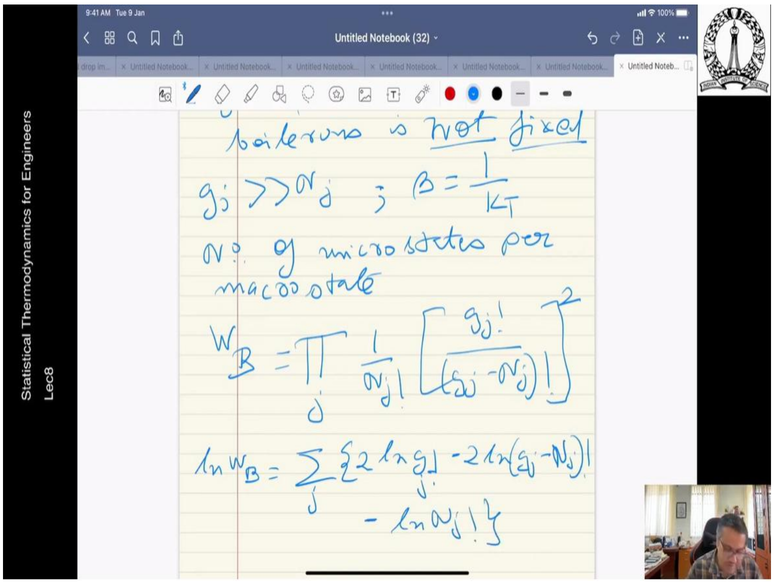
Energy of an isolated
system of boilerons is
fixed but total # of
boilerons is not fixed

$g_j >> N_j$; $\beta = \frac{1}{kT}$

No. of microstates per
macrostate

So, now the energy, what we know, the energy what we know, the energy of an isolated energy of an isolated system of boilerons, boilerons is fixed, is fixed but total number of boilerons is not, not fixed. And of course your gj is much, much greater than your Nj, and off course your beta is therefore 1 over k T. So, the number of microstates, microstates for such boilerons, microstates, per macrostates.

(Refer Slide Time: 22:39)



boilerons is not fixed

$g_j >> N_j$; $\beta = \frac{1}{KT}$

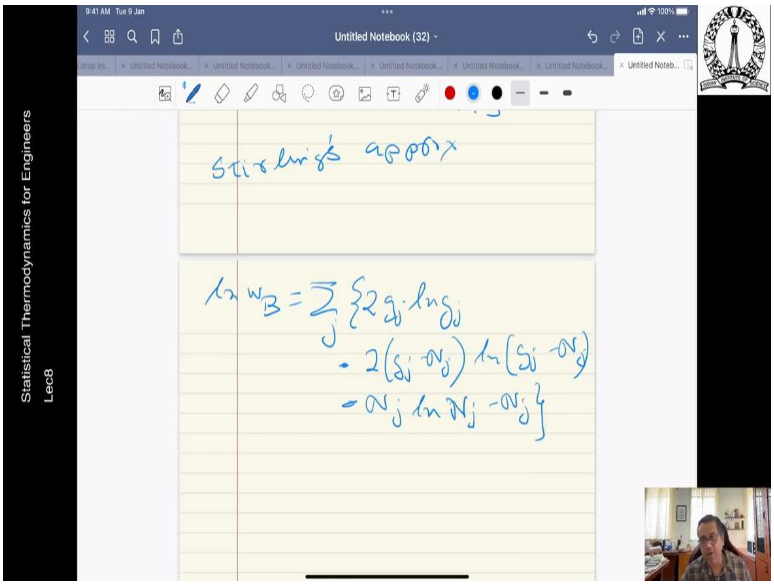
No. of microstates per macrostate

$$W_B = \prod_j \frac{1}{N_j!} \left[\frac{g_j!}{(g_j - N_j)!} \right]^2$$

$$\ln W_B = \sum_j \{ 2 \ln g_j! - 2 \ln (g_j - N_j)! - \ln N_j! \}$$

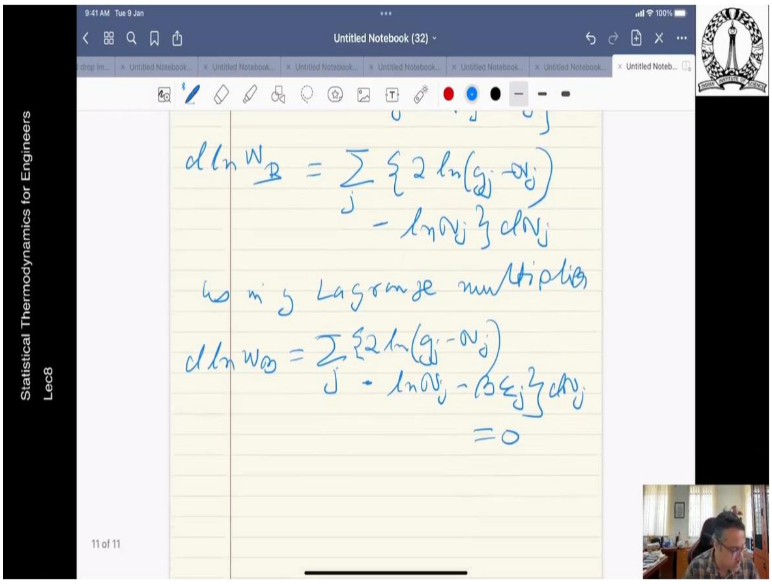
How is it given then? Its WB multiplicated over j 1 over Nj factorial gj factorial gj minus Nj factorial square. Now if you take a log of WB we will now have a summation j and this 2 comes out, 2 ln gj factorial minus 2 ln gj minus Nj factorial minus ln Nj factorial.

(Refer Slide Time: 23:28)



Stirling's approx

$$\ln W_B = \sum_j \{ 2 g_j \ln g_j - 2 (g_j - N_j) \ln (g_j - N_j) - N_j \ln N_j - N_j \}$$



$$d \ln W_B = \sum_j \{2 \ln(g_j - N_j) - \ln N_j\} dN_j$$

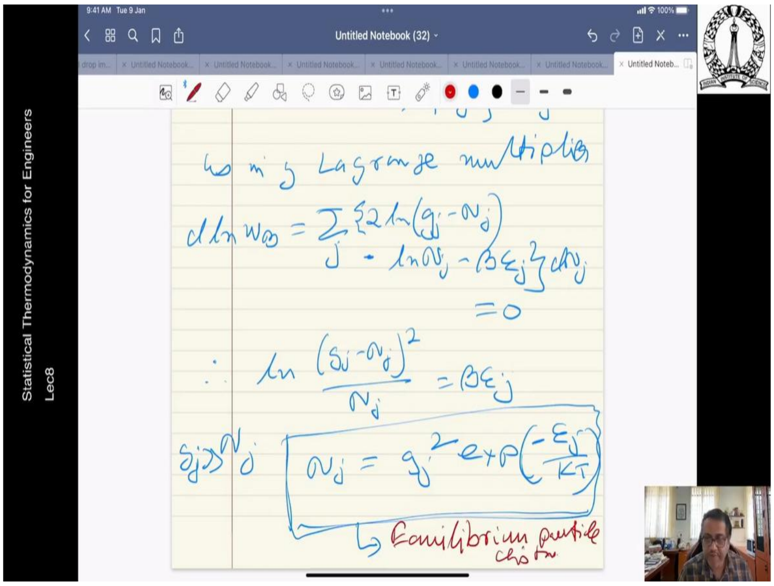
Using one Lagrange multiplier

$$d \ln W_B = \sum_j \{2 \ln(g_j - N_j) - \ln N_j - \beta \varepsilon_j\} dN_j = 0$$

So, next what we do, we apply Sterling's approximation. So, there can be numerous problems like this obviously, where we say that ln WB is equal to summation j 2 gj ln gj minus 2 gj minus Nj ln gj minus Nj minus Nj ln Nj minus Nj. So, it is a very long expression as you can see. So, now what you do, you differentiate, differentiate so, in the differentiation what happens minus 2 ln gj minus Nj minus ln Nj d Nj, bracket.

Now, there can be only one LaGrange multiplier, using LaGrange multiplier, only one LaGrange multiplier in this case. So, that is given as d ln WB j 2 ln gj minus Nj minus ln Nj minus beta Ej d Nj is equal to 0.

(Refer Slide Time: 25:13)



Using one Lagrange multiplier

$$d \ln W_B = \sum_j \{2 \ln(g_j - N_j) - \ln N_j - \beta \varepsilon_j\} dN_j = 0$$

$$\therefore \ln \frac{(g_j - N_j)^2}{N_j} = \beta \varepsilon_j$$

$g_j \gg N_j$

$$\boxed{N_j = g_j^2 \exp\left(-\frac{\varepsilon_j}{KT}\right)}$$

↳ Equilibrium particle distn.

Therefore, ln gj minus Nj square 1 Nj is equal to beta Nj since gj Nj is much much greater than Nj. So, therefore, Nj becomes equal to gj square because this is a much smaller number and exponential minus Ej by kT. So, this is, this is a fantastic piece of thing which shows that, if you have a situation where an unknown particle is given but you know the rules of this is energy distribution, etcetera, etcetera, particle distribution, you can find out what will be the equilibrium particle distribution. So, this is the equilibrium particle distribution.

So, that is, that is what it is. So, this is the equilibrium are the most probable particle distribution. So, that is, that is that so, next we will try to see that what else we can do with the Einstein and (inaudible) Einstein, statistics. Now we want to know that what will be the for independent isolated particles, what else can we do? For example, let us look at what we call a (inaudible) approximation. So, that is what we are going to cover in the next lecture. I think you have understood now from this lecture, that what are the -- how to proceed to solve problems like this. So, thank you.