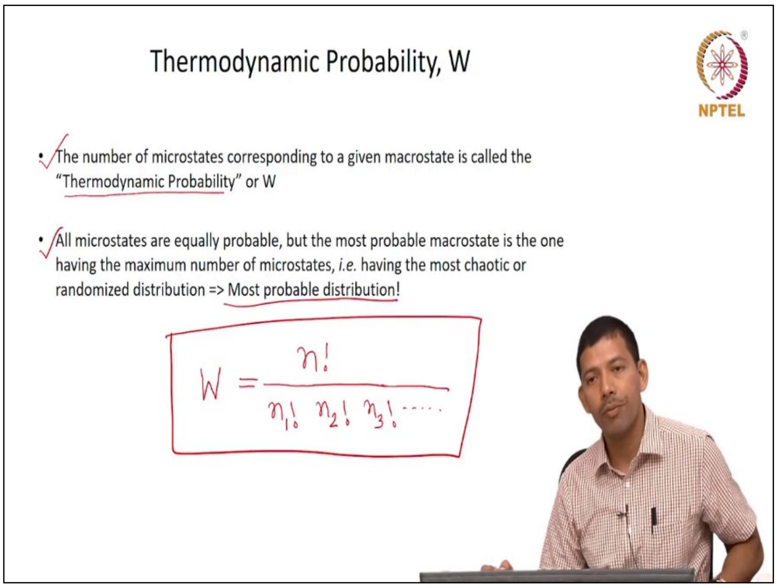
Thermodynamics for Biological Systems:
Classical and Statistical Aspects
Prof. Sanjib Senapati
Department of Biotechnology
Indian institute of Technology - Madras

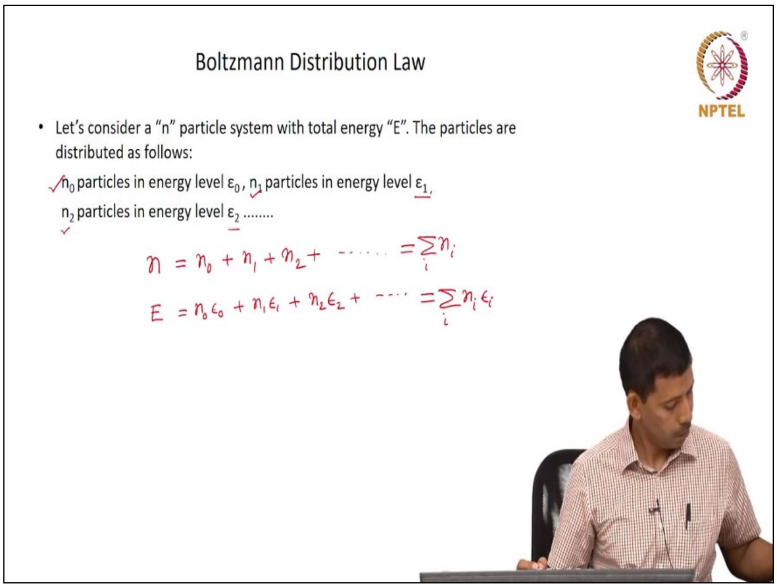
Lecture – 57
Boltzmann Distribution Law

(Refer Slide Time: 00:34)



Alright, so, now we will, so, so far we have seen the definition of statistical thermodynamics, we have seen the difference between thermodynamics and statistical thermodynamics. We have taken one example for a biological system and we have defined distribution of states and from there. We have defined the thermodynamic probability depth.

(Refer Slide Time: 00:54)



Now, now let us look at Boltzmann Distribution Law, the very important law in statistical thermodynamics. And we will derive the Boltzmann distribution law. So, let us consider our n particle system with total energy E, so they set the total energy I will be defining as capital E and energy for the states will be defining as epsilon. So, for the ith state the energy I'll take as epsilon i. So, we have a n particle system with total energy E. And the particles are distributed as follows:

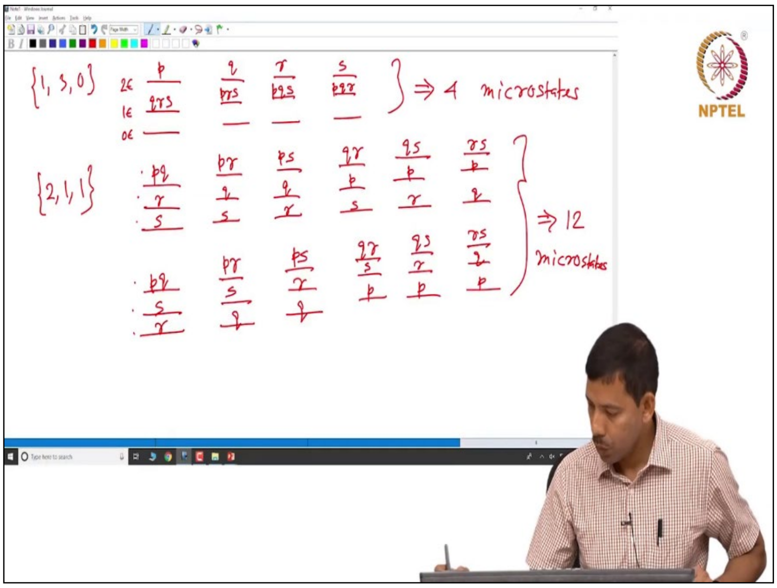
$$n = n_0 + n_1 + n_2 \;\ldots\ldots\; = \sum_i n_i$$

And

$$E = n_0\varepsilon_0 + n_1\varepsilon_1 + n_2\,\varepsilon_2 \ldots\ldots = \sum_i n_i\varepsilon_i$$

So, number of particles in energy level ε_0 have n_0 number of particles, energy level ε_1 have n_1 number of particles, , energy level ε_2 have n_2 and so on so forth. So, my total number of particles n is sum over n_0 plus n_1 plus n_2 plus all other terms which we write as sum over i n_i. Likewise our total energy E you can write as sum over i n_i E_i, okay.

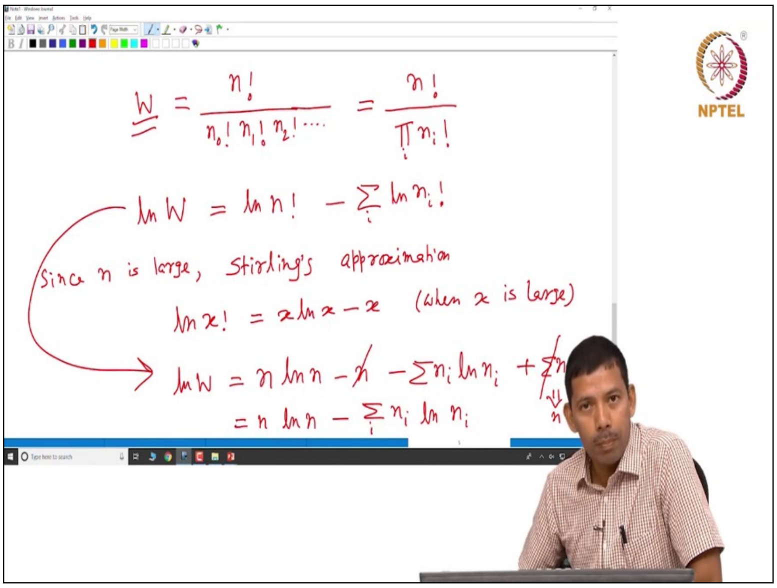
(Refer Slide Time: 02:52)



So, as you have seen thermodynamic probability W is

$$W = \frac{n!}{n_1!\; n_2!\; n_3! \ldots\ldots}$$

(Refer Slide Time: 03:01)



n factorial divided by n0 factorial, n1 factorial, n2 factorial and so on, so forth and this we can write as n factorial which is total number of particles and this we can write as product over all ni's. So, this is my W can be written as–

$$\mathrm{W} = \frac{\mathrm{n}!}{\prod_i \ \mathrm{n_i}!}$$

so if I take Lon,

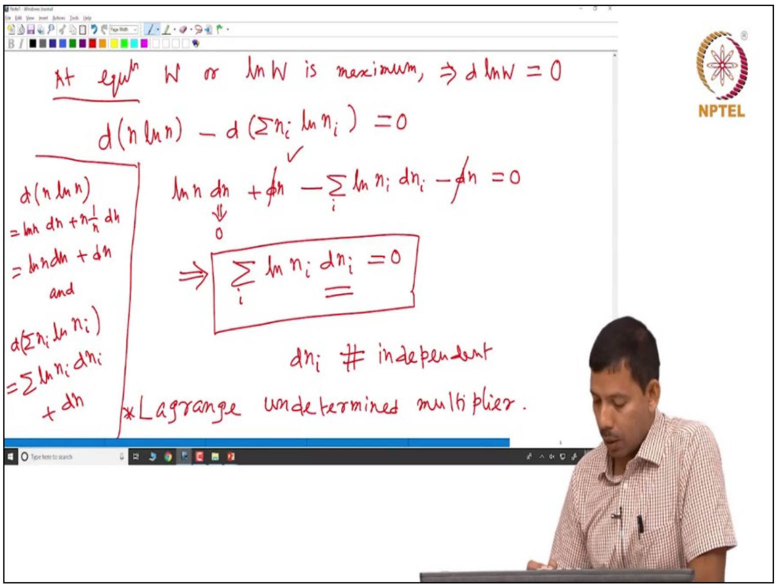
$$\ln\mathrm{W} = \ln\ n_i! - \sum_i \ln n_i!$$

Since, n is your total number of particles which is very large we can apply Sterling's approximations. So, after Sterling approximation we can write–

$$\ln\mathrm{W} = \mathrm{n} \ln\ n\ - \sum_i n_i \ln n_i$$

And that thermodynamic probability changes all the time since particles are moving up and down. So, since particles go up come down, so, as they move up and down, the thermodynamic probability also changes. And thermodynamic probability becomes maximum at equilibrium.

(Refer Slide Time: 07:11)



So, at equilibrium so at equilibrium W or lon W is, is maximum. So, at equilibrium W or lon W is maximum and therefore derivative of lon W is zero. So, we can take the derivative of the previous expression where we had d just, so we had d of n ln n minus d of sum over ni lon ni and that is equal to zero. So, now if we simplify the n ln n, so, how do you get?

$$d \ln W = 0$$

$$d(n \ln n) - d\left(\sum_i n_i \ln n_i\right) = 0$$

$$\sum_i \ln n_i \, dn_i = 0$$

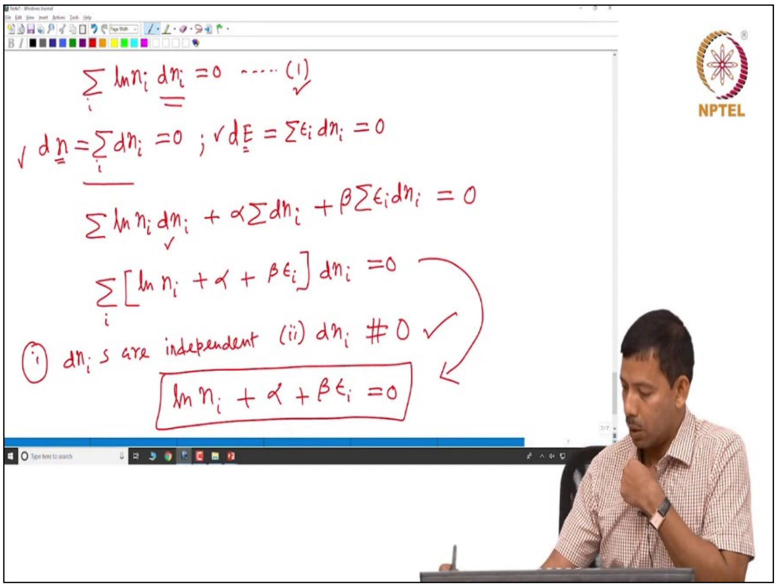
Particles are spontaneously and continuously moving up and down and therefore d n_i is not independent. So, how to simplify this expression? So, to simplify this expression we will be calling some important mathematical method, proposed by Lagrangi which is called Lagrangi undetermined multiplier.

$$d(n \ln n) = \ln n \, dn + n \frac{1}{n} \, dn$$

$$= \ln n \, dn + dn$$

And $d(\sum_i n_i \ln n_i) = \sum_i \ln n_i \, dn_i + dn$

(Refer Slide Time: 11:55)



So we will be making use of Lagrangi undetermined multiplier. So, the expression we got

$$\sum_i \ln n_i \, dn_i \; = 0 \; \ldots\ldots\ldots (1)$$

$$dn = \sum_i dn_i = 0 \, ; dE = \sum_i \varepsilon_i dn_i = 0$$

$$\sum \ln n_i \, dn_i + \; \alpha \sum dn_i + \; \beta \sum \varepsilon_i \, dn_i = 0$$

$$\sum_i [\ln n_i \; + \; \alpha + \; \beta \, \varepsilon_i] \, dn_i = 0$$

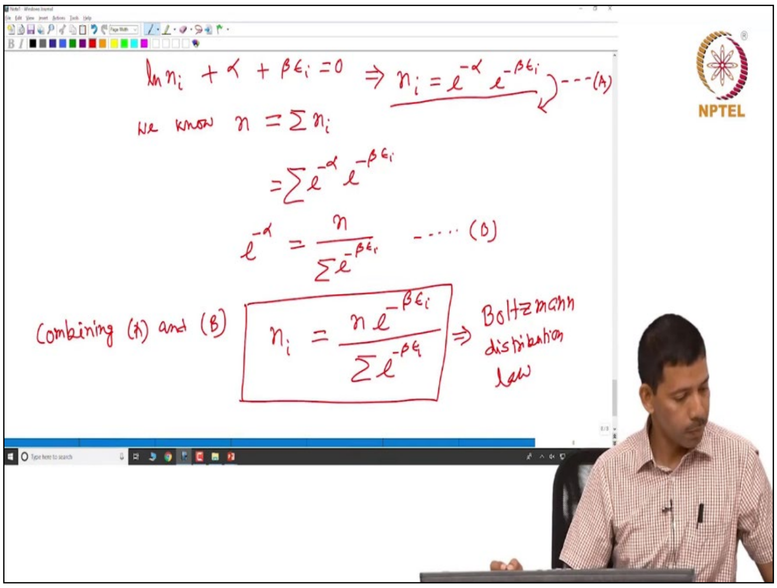
After that if we add those two expressions with our parent equation, then, the variables become independent. So, at the moment our dni's are not independent. So, now following the Lagrangi multipliers, what we are doing were basically multiplying constant one by a constant alpha dni and then adding to this expression multiplying the second constant with another constant beta adding the adding those two up in my parent expression one and they sum up to zero.

So, now according to Lagrangi now dni's become independent okay. So, we can write this as ln ni + alpha + beta epsilon i dni is equal to 0. So, now here there are so, now the restraining condition that dni's are not independent is gone. So, due to Lagrangian multipliers my dni's are, are now independent, independent, independent.

$$dn_i \; \neq 0$$

It cannot be 0 because particles are always moving up and down.

(Refer Slide Time: 16:48)



Hence $$\ln n_i + \alpha + \beta\,\varepsilon_i = 0$$

$$n_i = e^{-\alpha} e^{-\beta\varepsilon_i} \quad \ldots\ldots\ldots\ldots\ldots\ldots \text{(A)}$$

We know that

$$n = \sum n_i$$

$$= \sum e^{-\alpha} e^{-\beta\varepsilon_i}$$

$$e^{-\alpha} = \frac{n}{\sum e^{-\beta\varepsilon_i}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(B)}$$

By combining A and B finally we will get the

$$n_i = \frac{n\, e^{-\beta E_i}}{\sum\ e^{-\beta E_i}}$$

This is the famous Boltzmann distribution law.

So, what this distribution law says, that number of particle in the state with energy epsilon i is n_i. So, n_i is number of particles having energy epsilon i at equilibrium. So, Boltzmann distribution basically dictates the distribution of particles across energy states.