

**Thermodynamics for Biological Systems:  
Classical and Statistical Aspects  
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**Lecture – 64  
Thermodynamic Probability for Indistinguishable Particles**

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$$S = k \ln \frac{N! \prod_l g_l^{n_l}}{\prod_l n_l!}$$

$$S = k \ln N! \prod_l \frac{g_l^{n_l}}{n_l!} \Rightarrow \text{Entropy in terms of energy levels.} \quad \text{--- (1)}$$

Boltzmann-Planck

$$S = k \ln W_D \quad \text{--- (2)}$$

Comparing eq<sup>ns</sup> (1) and (2)  $\Rightarrow$  
$$W_D = N! \prod_l \frac{g_l^{n_l}}{n_l!}$$

So, this is this was our first step that we got the thermodynamic probability of the distinguishable particles in terms of the energy levels.

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Now, let's find out  $W_{ID}$

$$\left. \begin{array}{l} \boxed{x|x} \quad \boxed{|x|x} \quad \boxed{|x|x} \\ \boxed{|x|x} \quad \boxed{x|x} \quad \boxed{|x|x} \end{array} \right\} 6 \text{ microstates}$$

$$\left. \begin{array}{l} p \quad q \quad \quad \quad p \quad q \quad \quad \quad p \quad q \\ p \quad q \quad \quad \quad p \quad q \quad \quad \quad p \quad q \\ q \quad p \quad \quad \quad q \quad p \quad \quad \quad q \quad p \end{array} \right\} 9 \text{ microstates}$$

Now let us look at the  $W_{ID}$  now let us find out thermodynamic probability for the indistinguishable particles.

Let us take up a very simple system where we have two particles and my energy state is 3 fold degenerate. So, I have two particles and my energy state is 3 fold degenerate. So, I do have 6 different ways of distributing 2 indistinguishable particles in you know energy state having 3 fold degeneracy. So, in other words I have 6 microstates.

So, if you go back to our previous discussion of distinguishable particles what was the possibility how many number of microstates we could get if the particles were distinguishable. So, let us see so if our particles were p and q so we are we can distinguish the particles as p and q and we had 3 fold, degeneracy. So, here we got 9 microstates.

There was a problem due to which we came across the Gibbs paradox. So, when the particles are not distinguishable which is the case we get 6 microstates for this simple example of two particles distributed in an energy state with 3 fold degeneracy.

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Thermodynamic probability for this state  $\Rightarrow W_l = \frac{(2+2)!}{2! 2!} = \frac{(n_l + g_l - 1)!}{n_l! (g_l - 1)!}$  ;  $(g_l - 1) \equiv$  no. of partitions

$= \frac{4!}{2! 2!} = \frac{2 \times 3 \times 2 \times 1}{2 \times 1 \times 2 \times 1} = 6 \Rightarrow$

$$W_l = \frac{(2 + 2)!}{2! 2!} = 6$$

On generalisation:

$$W_l = \frac{(n_l + g_l - 1)!}{n_l! (g_l - 1)!}$$

So, here my 2 was the number of particles which is  $n_l$  in that particular energy level. So, we can write  $n_l$  factorial the second term we did we said this is the number of partitions here it is 2

because it was 3 fold degenerate see my degeneracy was  $g_1$  so my number of partitions require is  $g_1 - 1$  factorial so where  $g_1 - 1$  is nothing but the number of partitions and on the top we can write  $2 + 2$  as we written so  $n_1$  number of particles +  $g_1 - 1$  factorial. So this is the thermodynamic probability for that particular state in terms of energy levels.

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$$\begin{aligned} \omega_l &= \frac{(n_l + g_l - 1)!}{n_l! (g_l - 1)!} \\ &= \frac{(n_l + g_l - 1)(n_l + g_l - 2)(n_l + g_l - 3) + \dots + (g_l)(g_l - 1)(g_l - 2)}{n_l! (g_l - 1)!} \\ &= \frac{(n_l + g_l - 1)(n_l + g_l - 2)(n_l + g_l - 3) + \dots + (g_l)(g_l - 1)!}{n_l! (g_l - 1)!} \\ &= \frac{(n_l + g_l - 1)(n_l + g_l - 2)(n_l + g_l - 3) + \dots + (g_l)}{n_l!} \end{aligned}$$

$$W_l = \frac{(n_l + g_l - 1)!}{n_l! (g_l - 1)!}$$

Now let us simplify so how we can simplify? We can expand the numerator and if we expand will get  $n_1 + g_1 - 1$  we get  $n_1 + g_1 - 2$  we get  $n_1 + g_1 - 3$  plus this series goes on this series goes on with this number keeps increasing and at certain point this number becomes equal to  $n_l$ .

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$$\begin{aligned} \omega_l &= \frac{(n_l + g_l - 1)(n_l + g_l - 2)(n_l + g_l - 3) \dots g_l}{n_l!} \\ &= \frac{g_l \left[ 1 + \frac{n_l - 1}{g_l} \right] g_l \left[ 1 + \frac{n_l - 2}{g_l} \right] \dots g_l}{n_l!} \\ &= \frac{g_l^{n_l} \left\{ \left[ 1 + \frac{n_l - 1}{g_l} \right] \left[ 1 + \frac{n_l - 2}{g_l} \right] \dots 1 \right\}}{n_l!} \\ &\approx \frac{g_l^{n_l}}{n_l!} \end{aligned}$$

since  $g_l > n_l - 1$   
 $n_l - 2$

$$W_l = \frac{(n_l + g_l - 1)(n_l + g_l - 2)(n_l + g_l - 3) \dots \dots \dots (g_l)}{n_l!}$$

Since  $g_l \gg n_l - 1, n_l - 2 \dots$

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The whiteboard contains the following derivations:

$$W_l = \frac{g_l^{n_l}}{n_l!}$$

$$W_{ID} = \prod_l W_l = \prod_l \frac{g_l^{n_l}}{n_l!}$$

$$W_{ID} = \prod_l \frac{g_l^{n_l}}{n_l!}$$

$$W_D = N! \prod_l \frac{g_l^{n_l}}{n_l!}$$

So

$$W_l \approx \frac{g_l^{n_l}}{n_l!}$$

$$W_{ID} = \prod_l W_l = \prod_l \frac{g_l^{n_l}}{n_l!}$$

$$W_D = N! \prod_l \frac{g_l^{n_l}}{n_l!}$$

So, in other words we like  $w_l$   $g_l^{n_l}$  divided by  $n_l$  factorial is what we get power we get for the thermodynamic probability of a particular energy state. Now if we want to get  $W$  we need to get the product of our all energy states and their energy levels and therefore we take the product over  $w_l$  and that gives us the expression of  $W_D$  as  $g_l^{n_l}$  divided by  $n_l$  factorial. So, that this is our

expression for  $W_D$ ,  $W_{ID}$  thermodynamic probability for the indistinguishable particles in terms of energy levels is equal to product over all energy levels in  $g_l$  to the power  $n_l$  divided by  $n!$  factorial.

And what was our  $W_D$  the thermodynamic probability for the distinguishable particles was  $W_D$  is equal to  $n!$  factorial and in the rest of the remaining part is similar same  $n!$  factorial.