Fundamentals of Statistical Thermodynamics

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Lecture – 55

Bose-Einstein Statistics

Welcome back, by now we have discussed details of Maxwell Boltzmann statistics and based upon that we have derived various equations connecting to various thermodynamic quantities. Today we are going to discuss Bose Einstein statistics and we will also discuss that what was the need of developing Bose Einstein statistics, what could not be addressed in Maxwell Boltzmann statistics. We will not go through Maxwell Boltzmann statistics again here because we have done that thoroughly, but let us develop some background for discussing Bose Einstein statistics. Earlier I was using the words molecules, particles, etcetera and here in Bose Einstein statistics I will use phase points that particle, molecule, electron, whatever you consider it represents the phase points and the various energy levels we will talk in terms of cell. For example, consider here let us say we talk about two sets of cells, cell i and cell j and let there be some different compartments in the cell i and in the cell j. Let N_i represent the number of phase points in the cell meaning of phase points is I will just write in terms of dot, it can be atom, it can be molecule.

Now why I want to represent as dot because the molecules atoms cannot be distinguished from each other let us say in the gas phase. So, I will represent just as the dot and let us say in any i^th^ cell that there be N_i number of phase points, then the observable properties of the system are determined by the microstate of the system and when we talk about the microstate of the system or observable properties then we think of what is the thermodynamic probability of macrostate. How do you define the thermodynamic probability of a macrostate? It is the number of microstates corresponding to it that is what is the comment here. The thermodynamic probability W of a macrostate is also defined as number of microstates corresponding to it and when we were talking about Maxwell

Boltzmann statistics then the number of microstates were defined as the number of permutations of a given microstate.

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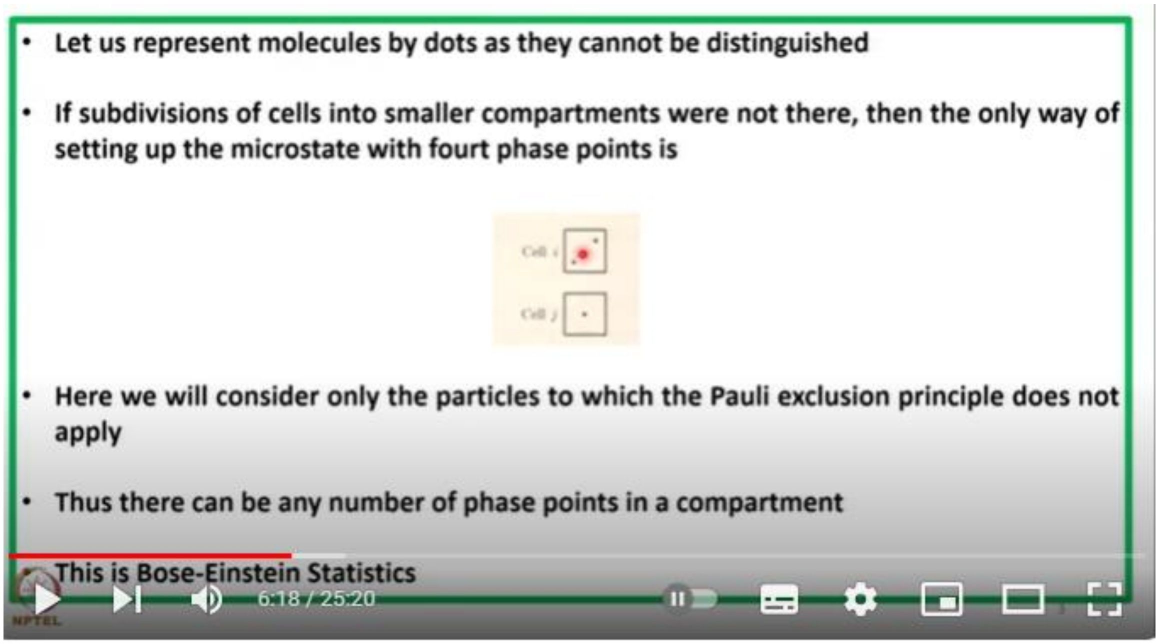

- Let us represent molecules by dots as they cannot be distinguished
- If subdivisions of cells into smaller compartments were not there, then the only way of setting up the microstate with fourt phase points is
- Here we will consider only the particles to which the Pauli exclusion principle does not apply
- Thus there can be any number of phase points in a compartment
- This is Bose-Einstein Statistics

Let us try to discuss in terms of some example. Let us consider these cells cell i and cell j and let us say we have four phase points A B C D although I am saying A B C D we can distinguish letters A B and C and D, but let us assume that these are atoms molecules phase points which cannot be distinguished from each other. Let us consider out of these four phase points three are kept in cell i and one is kept in cell j right. So, we have like you know it is like two energy levels, and in one we have three molecules in the other we have one molecule. So, what is the total number of permutations and combinations? The thermodynamic probability you remember that W was defined as n factorial over n 0 factorial n 1 factorial etcetera etcetera.

So, here I will write W is equal to n factorial total 4 4 factorials in cell i in first one we have 3. So, 3 factorial in the other we have 1 factorial and this is equal to 4 into 3 factorial over 3 factorial into 1 factorial. So, that means, I have W is equal to 4 in this kind of arrangement the thermodynamic probability of the macro state according to Boltzmann Maxwell Boltzmann statistics it gives W equal to 4 this we have discussed earlier. Now, as I earlier said that let us replace a b c d by just dot why by dot because we cannot distinguish between the particles, we cannot distinguish between the phase points. So, let us represent molecules by dots as they cannot be distinguished with just c dots you see cell i put 3 dots, and cell j you just put 1 dot.

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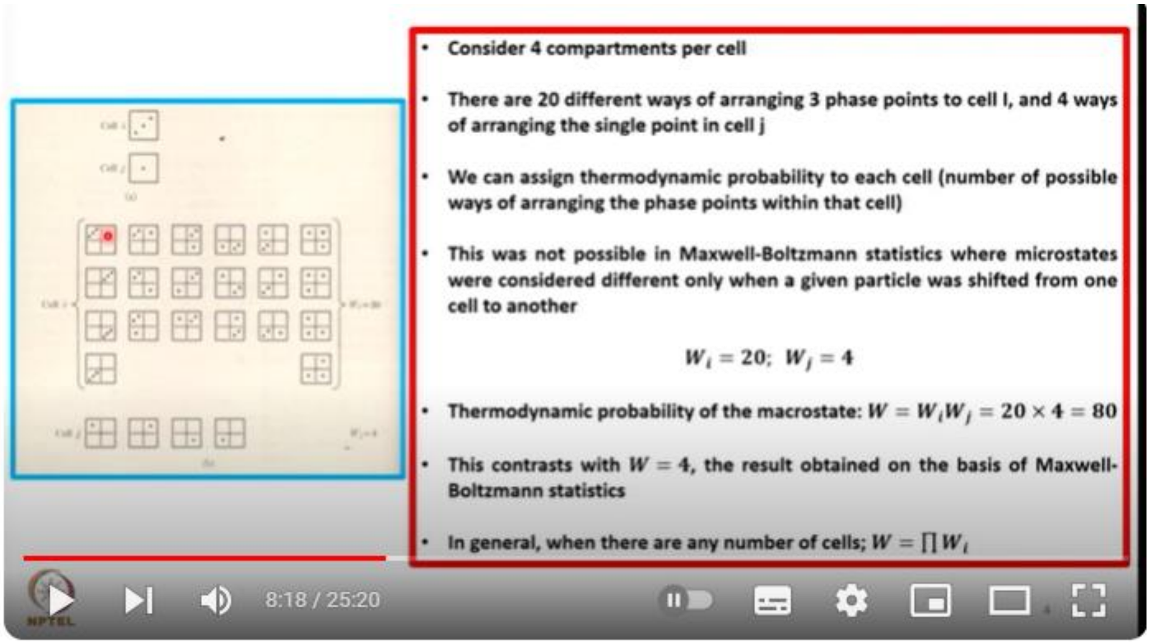

- Consider 4 compartments per cell
- There are 20 different ways of arranging 3 phase points to cell I, and 4 ways of arranging the single point in cell j
- We can assign thermodynamic probability to each cell (number of possible ways of arranging the phase points within that cell)
- This was not possible in Maxwell-Boltzmann statistics where microstates were considered different only when a given particle was shifted from one cell to another

$$W_i = 20;\ W_j = 4$$

- Thermodynamic probability of the macrostate: $W = W_i W_j = 20 \times 4 = 80$
- This contrasts with $W = 4$, the result obtained on the basis of Maxwell-Boltzmann statistics
- In general, when there are any number of cells; $W = \prod W_i$

Now, if the subdivision of cells into compartments were not there then the only way of setting up the micro state with 4 phase points is 3 in i 1 in j when I say the subdivisions of the cells into smaller compartments. That means, within cell i can create further compartments if that is not there then the only way, we can arrange we can have this is 3 in cell i and 1 in cell j. Now, the question is when you are dealing with molecule atoms or when you are dealing with electrons there can be some additional restrictions. For example, there are systems like electrons where poly exclusion principle applies. That means, in that case you cannot have more than 2 electrons together, but in order to avoid that complication which we will worry later on when we discuss Fermi direct statistics.

Here let us only consider the particles to which the poly exclusion principle does not apply does not apply. So, that means, that gives me the freedom to put as many particles in any cell as possible as many phase points in any cell as possible. That is why here you are talking about 3 can be put in I 1 can be in J right. So, that is what the comment thus there can be any number of phase points in a compartment and this is Bose Einstein statistics. Let us discuss little details of this Bose Einstein statistics.

So, we started with this 3 phase points in cell i and 1 phase point in cell j. Now, consider 4 compartments in each cell that is you see here 1 compartment, 2 compartment, 3 compartment, 4 compartment. Consider 4 compartments per cell and now if you carefully examine all these 3 are in one cell 2 in one cell, 1 in another cell and then there are various combinations. There are 20 different ways of arranging these 3 phase points in cell i E and since we had only one phase point is in J and if there are 4 compartments then it can stay here, it can stay here, it can stay here, it can stay here. That means, in this case the thermodynamic probability W is equal to 4.

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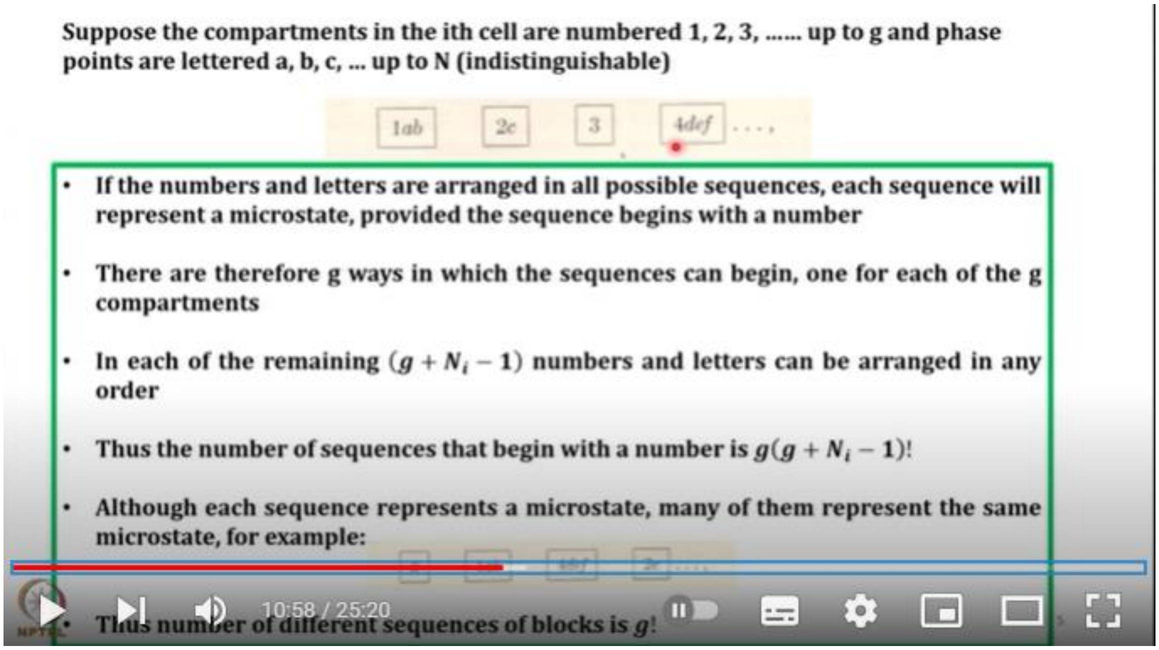

Suppose the compartments in the ith cell are numbered 1, 2, 3, …… up to g and phase points are lettered a, b, c, … up to N (indistinguishable)

- **If the numbers and letters are arranged in all possible sequences, each sequence will represent a microstate, provided the sequence begins with a number**
- **There are therefore g ways in which the sequences can begin, one for each of the g compartments**
- **In each of the remaining $(g + N_i - 1)$ numbers and letters can be arranged in any order**
- **Thus the number of sequences that begin with a number is $g(g + N_i - 1)!$**
- **Although each sequence represents a microstate, many of them represent the same microstate, for example:**
- **Thus number of different sequences of blocks is $g!$**

In the upper case 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20 W is equal to 20. I hope you understood that we consider compartmentalization of cell i, we created 4 compartments and also in cell j and then if you consider the various permutations and combinations. There are 20 different ways of arranging 3 phase points in cell i and 4 different ways of arranging 1 phase point in cell j. Remember that this was not possible in Maxwell Boltzmann statistics, where the microstates were considered different only when a given particle was shifted from one to another. In this case we have W_i equal to 20, W_j equal to 4 therefore, the total thermodynamic probability of the macrostate is going to be product of 2 that is overall W is W_i times W_j, W_i is 20, W_j is 4 so, total it is 80.

If you compare this with the Maxwell Boltzmann statistics, then in that case we got W equal to 4. Here we are getting W equal to 80, see the difference. So, in general when there are any number of cells, then overall W that is the thermodynamic probability is the product of thermodynamic probability of each microstate. So, I hope this is clear. Let us get into little more details.

Suppose we label the compartments now, consider these compartments. We label these compartments as 1, 2, 3, 4 and we can go up to G and the phase points, phase points are being represented by A, B, C, D, E, F. According to this compartmentalization in which the compartment in the i^{th} cell are numbered as 1, 2, 3, 4 etcetera up to G. Let us say the first compartment has A, B molecule, second has 1 molecule, third is empty, fourth has 3 molecules or 3 phase points etcetera. So, what we have here is we have number and we have letters right.

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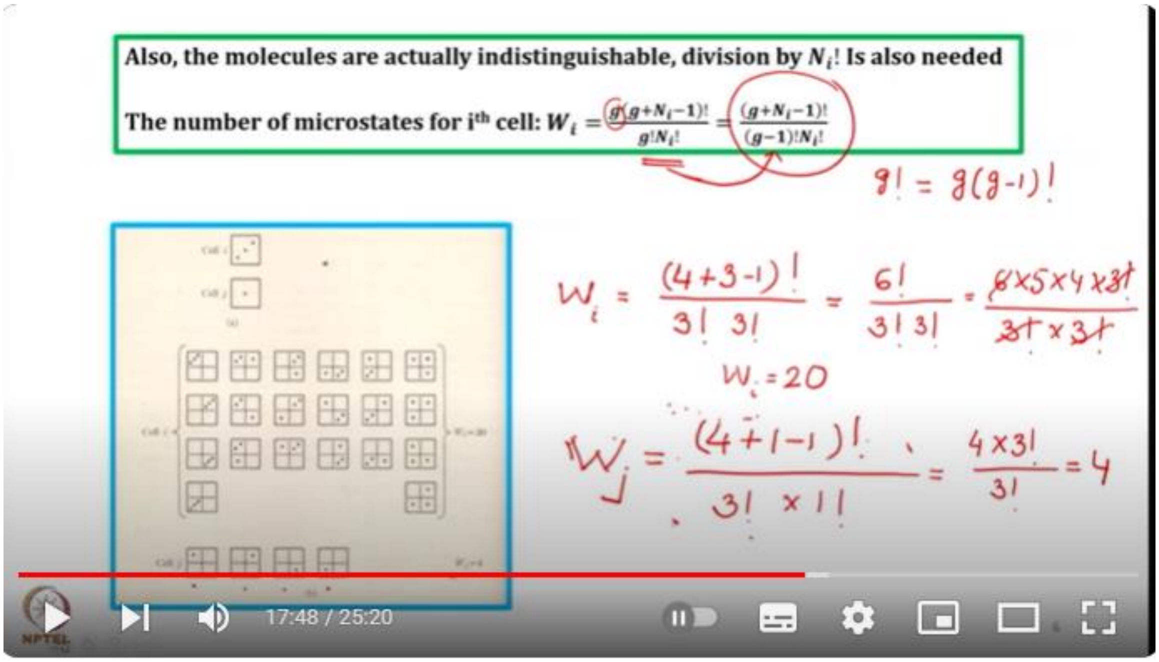

Also, the molecules are actually indistinguishable, division by $N_i!$ Is also needed

The number of microstates for i^th^ cell: $W_i = \frac{g(g+N_i-1)!}{g!N_i!} = \frac{(g+N_i-1)!}{(g-1)!N_i!}$

$$g! = g(g-1)!$$

$$W_i = \frac{(4+3-1)!}{3!\ 3!} = \frac{6!}{3!\,3!} = \frac{6\times5\times4\times\cancel{3!}}{\cancel{3!}\times\cancel{3!}}$$

$$W_i = 20$$

$$W_j = \frac{(4+1-1)!}{3! \times 1!} = \frac{4\times3!}{3!} = 4$$

We have number, we have letters and if the numbers and letters are arranged in all possible sequences, then each sequence will represent a microstate provided the sequence begins with a number. I repeat if these numbers and letters are arranged in all possible sequences, then each sequence will represent a microstate provided the sequence begins with the number and we had these compartments up to G. That means, there are G ways of arranging the sequences. What I mean is there are G ways in which sequences can begin because there are G compartments, one for each of the G compartments. So, there are G compartments, there are N_i number of phase points, the total is G plus N_i and if one starts with one number that means, remaining G plus N_i minus 1 numbers and letters can be arranged in any order.

Try to understand there are G ways in which the sequences can begin because their total number is G here. Then if you count G plus total number of phase points, if you are starting with one compartment that is fixed the remaining G plus N_i minus 1 numbers and letters can be arranged in any order. Therefore, how to calculate the total number of sequences that can begin with the number is G into G plus N_i minus 1 factorial. Although this each sequence in a this represents a microstate, many of these such kind of sequences will be same microstate. For example, if you compare this with this, here you see third is empty, third is empty but it is starting with number 3.

1 a b, 1 a b, 4 d E f, 4 d E f, 3 d E f, 4 d E f, 4 d E f, 5 d E f, 6 d E f, 7 d E f, 2 c, 2 c. Thus, the number of different sequences of the blocks is obviously, G factorial. There are G substances which can be arranged in G factorial ways alright. Now, we have taken care of sequences, but remember that all the phase points that we are talking about they are also not distinguishable, they are indistinguishable. Therefore, we need so that in order to not over count the number of states, we need to divide by N_i factorial.

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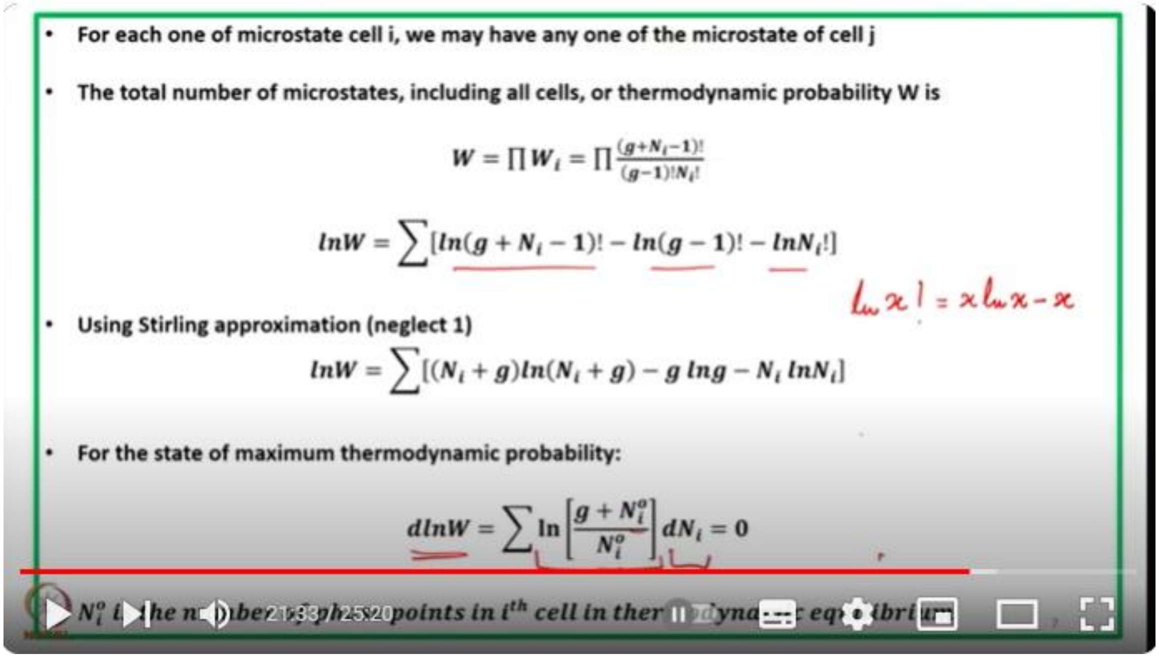

- For each one of microstate cell i, we may have any one of the microstate of cell j
- The total number of microstates, including all cells, or thermodynamic probability W is

$$W = \prod W_i = \prod \frac{(g+N_i-1)!}{(g-1)!N_i!}$$

$$lnW = \sum[\underline{ln(g+N_i-1)!} - \underline{ln(g-1)!} - \underline{lnN_i!}]$$

$$\ln x! = x \ln x - x$$

- Using Stirling approximation (neglect 1)

$$lnW = \sum[(N_i+g)ln(N_i+g) - g\,lng - N_i\,lnN_i]$$

- For the state of maximum thermodynamic probability:

$$\underline{dlnW} = \sum \ln \underbrace{\left[\frac{g+N_i^o}{N_i^o}\right]}\underbrace{dN_i} = 0$$

N_i^o is the number of phase points in i^{th} cell in thermodynamic equilibrium

So, therefore, W_i is equal to g into g plus N_i minus 1 factorial, we divide by g factorial, we divide by N_i factorial. And then your G factorial is equal to g into gminus 1 factorial. So, this gets transformed into this, you are getting rid of this G. Now, let us apply, we will apply to cell i, let us say W_i, this is equal to g plus N_i minus 1. So, g here is 4, so I will write 4.

So, what I will do is, I will write g is equal to 4 plus N_i, N_i is equal to 3 over here minus 1. So, g here is 4, so I will write 4 minus 1 factorial over g minus 1, g is 4, 4 minus 1 is 3, 3 factorials into N_i, N_i is equal to what? N_i is equal to here is 3. So, what I have here is 4 plus 3, 7 minus 1, 6, 6 factorial, 6 factorial over 3 factorial into 3 factorial. So, which is equal to 6 into 5 into 4 into 3 factorial over 3 factorial into 3 factorial. So, 3 factorial is equal to 3 factorial with, cancels with 6, this cancels with 3 factorial that means, W_i is equal to 20, this is what we counted here.

Now, let us say, let us say W_j, W_j here g is 4 plus N_i is 1 minus 1 factorial, g is 4 plus N_i is 1 minus 1 factorial, g is 4 divided by g minus 1, 3 factorial into 1 factorial and this is nothing but this is 4 into 3 factorial over 3 factorial, which is equal to 4, 1, 2, 3, 4. So, therefore, this derived formula is correct. So, now, we have an expression, which can be used to determine the number of microstate for any i^{th} or j^{th} cell. Now, you will see the next treatment is similar to that we discussed in Maxwell Boltzmann statistics. So, what we have now? For each one of the microstate cell i, we may have any one of the microstate of cell j, there is no restrictions, why? So, therefore, how do we calculate the total number of microstates including all cells, cells i, cell j, then the thermodynamic probability is you take multiplication of all these.

If you take the multiplication of all these, then you have multiplication of the ratio of these factorials. Now, let us go back to our discussion in Maxwell Boltzmann statistics. What we talked there was that sometimes it is easier to work with the logarithm of W rather than just will W. So, therefore, when you take the logarithm of W, I take log of W, then this is you know log, when you take log of a product, it can be written as summation, I am not going to get into details because this we have already discussed in Maxwell Boltzmann statistics. So, it will be a summation log g plus N_i minus 1 factorial minus log g minus 1 factorial minus log N_i factorial because g minus 1 and N_i factorial appear in the denominator.

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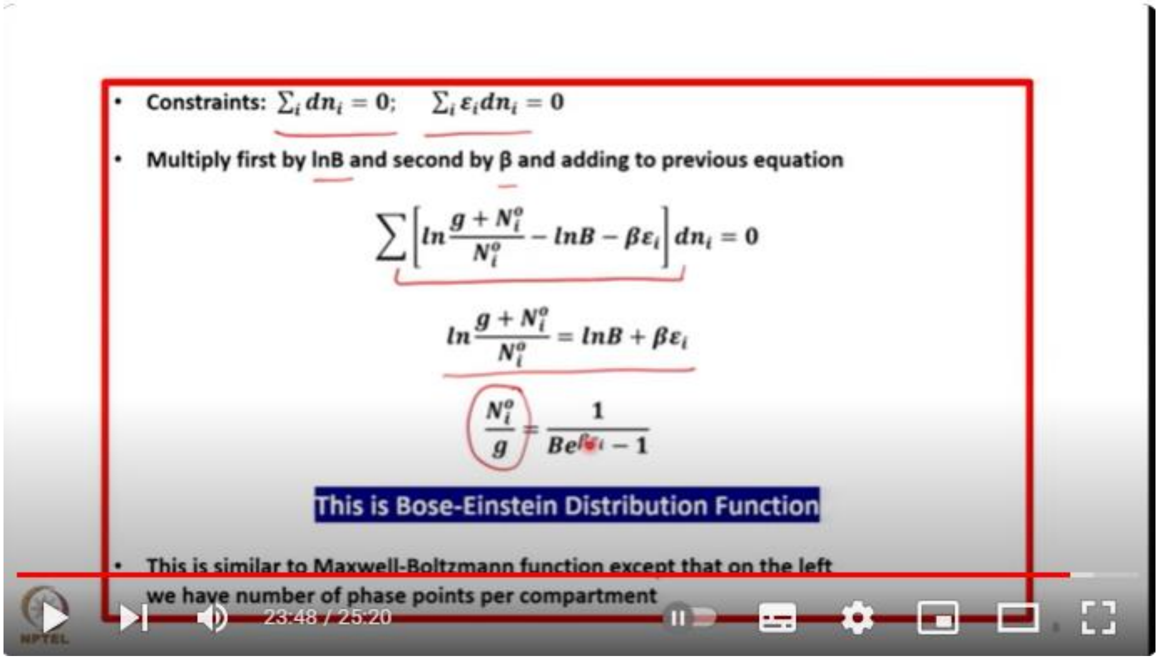

- Constraints: $\underline{\sum_i dn_i = 0}$; $\underline{\sum_i \varepsilon_i dn_i = 0}$
- Multiply first by $\underline{lnB}$ and second by $\underline{\beta}$ and adding to previous equation

$$\underline{\sum\left[ln\frac{g+N_i^o}{N_i^o} - lnB - \beta\varepsilon_i\right]}dn_i = 0$$

$$\underline{ln\frac{g+N_i^o}{N_i^o} = lnB + \beta\varepsilon_i}$$

$$\boxed{\frac{N_i^o}{g}} = \frac{1}{Be^{\beta\varepsilon_i} - 1}$$

This is Bose-Einstein Distribution Function

- This is similar to Maxwell-Boltzmann function except that on the left we have number of phase points per compartment

We can ignore 1 because generally, the number of compartments in the cell is larger than 1, much larger than 1. The number of phase points is also much larger than 1. Therefore, I can drop 1 here, I can drop 1 here. You drop there and then you apply the Stirling approximation. What was Stirling's approximation? We remember that log log x factorial

is equal to x log x minus x.
So, you apply here to all these. Once you apply to all these, then rearrange, then by using Stirling approximation, you have log W is equal to summation N_i plus g log N_i plus g minus g log g minus N_i log N_i going by the same method because we have to now find the state of maximum thermodynamic probability. And what is that maximum thermodynamic probability? Since we have decided to work on log W that means, a derivative of this log W, we should set it equal to 0 and then find out the corresponding expression. So, d log W is equal to summation log g plus N_i° by N_i° into d n i. When you take the derivative of this, you will get this kind of expression. What is this N_i° now here? This is the number of phase points in the i^{th} cell in thermodynamic equilibrium.

Let the equilibrium be there. Now, the question is can we again treat this and this independent? Same way as we discussed in Maxwell Boltzmann distribution. This cannot be treated independent. Therefore, you can treat this independently by using method of undetermined multipliers. What is that method of the undetermined multiplier? For that, you need to have constraints. One constraint is the total number of phase points has to be same that means, all changes in the number of phase points d n i's should add up to 0.
Second summation E_i dN_i should be 0. These are the same thing which we discussed in Maxwell Boltzmann distribution. There we multiplied by α and minus β. Here we will multiply by log β and β. Of course, if you go back, we are adding here and you are adding minus log β minus β E i and now you treat this as 0. Once you treat this as 0, you rearrange you get log g plus N_i° by N_i° is equal to log v plus βE_i and N_i° upon g is 1 over b into exponential b E i minus 1. This is Bose-Einstein distribution function. Remember Bose Einstein distribution function you have N_i° by g, g is the number of compartments, and b exponential β E_i minus 1. Sometimes this 1 can also be conditionally neglected. Now, if you want to further get into this theory of the Bose-Einstein distribution function, you can find out the expression for b.

You can also find out the expression for β which will turn out to be 1 over k T. So, the distribution function that we just derived this is similar to Maxwell Boltzmann distribution function except that on the left-hand side we have number of phase points per compartment and on the right side we have this factor which includes b, β and energy levels. This has the resemblance with Maxwell Boltzmann function, but you see in the Bose Einstein distribution function you have additional consideration for the phase points per compartment. That means, you now start considering the number of compartments in a given cell. So, when you compare with Maxwell Boltzmann distribution, Bose Einstein distribution offer some different features and Maxwell Boltzmann distribution offer some features which were not considered could in the Bose Einstein distribution function.

So, as I said that in this discussion in this treatment, we have not applied poly exclusion principle. If this theory is applied to electrons, then poly exclusion principle has to be adhered to. How that is done that we will discuss in the next lecture. Thank you very much.