Fundamentals of Statistical Thermodynamics

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Lecture – 57

FERMI- DIRAC Statistics

Welcome back. In the previous lecture, we discussed Bose-Einstein statistics and prior to that we have been discussing Maxwell Boltzmann statistics. In Bose-Einstein statistics, we started further sub divided the cell into various compartments. And then what we did was we derived an equation; the final equation was resembling almost similar to the Maxwell Boltzmann statistics. The major difference between the two statistics was highlighted over there and further we also discussed that we will not put any restriction in the number of particles, number of phase points occupying a particular compartment of the cell. In other words, the Pauli exclusion principle was not adhered to, but when we are dealing with the electrons, then we know that you cannot put more than two electrons in a one particular orbital or sub orbital.

Pauli exclusion principle has to be followed. So, in the way we described in Bose-Einstein statistics, here also let us begin by considering N_i number of phase points in the i^{th} cell. So, as usual we fix the number of phase points in the i^{th} cell. These phase points can be electrons, it can be molecule, it can be etcetera, anything else.

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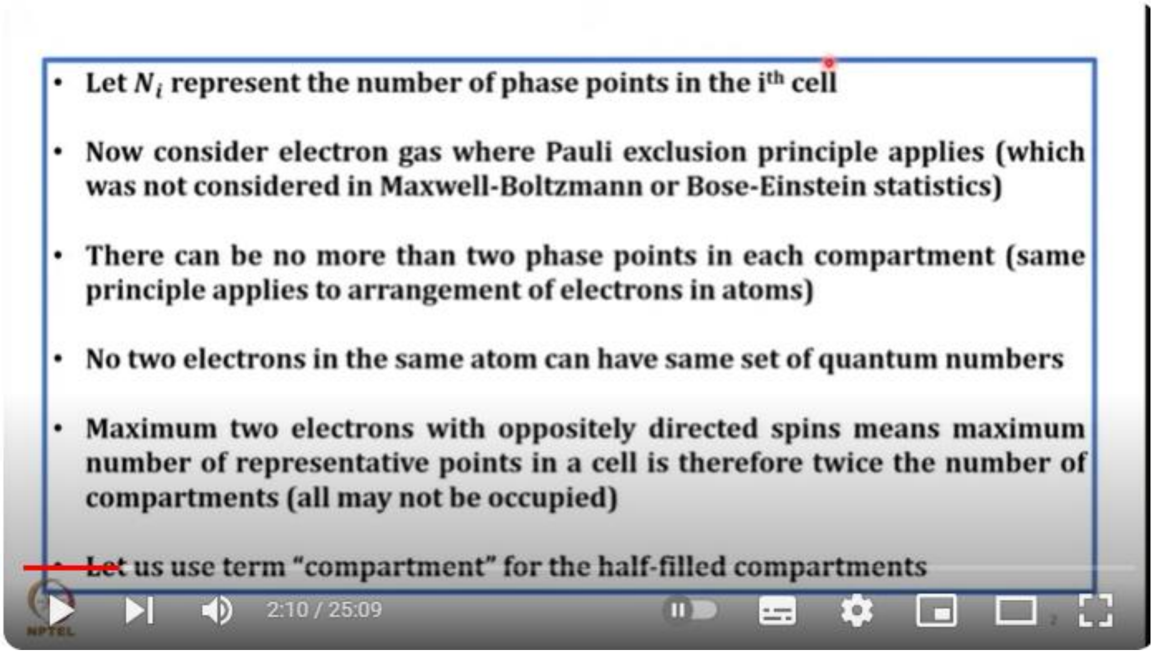

- Let N_i represent the number of phase points in the i^{th} cell
- Now consider electron gas where Pauli exclusion principle applies (which was not considered in Maxwell-Boltzmann or Bose-Einstein statistics)
- There can be no more than two phase points in each compartment (same principle applies to arrangement of electrons in atoms)
- No two electrons in the same atom can have same set of quantum numbers
- Maximum two electrons with oppositely directed spins means maximum number of representative points in a cell is therefore twice the number of compartments (all may not be occupied)
- Let us use term "compartment" for the half-filled compartments

However, when you are specifically considering the electron gas, then see the comment, now consider electron gas where Pauli exclusion principle applies which was not considered in Maxwell Boltzmann or Bose-Einstein statistics, right. So, what it is saying that now you do not want more than two electrons or two-phase points in each compartment, right. So, that means now there can be no more than two phase points in each compartment and this is the same principle that applies to arrangement of electrons in atoms. What it means in other words is that no two electrons in the same atom can have same set of quantum numbers. If all the other quantum numbers are same at least spin will be different.

This is the Pauli exclusion principle that means maximum two electrons with oppositely directed spins means maximum number of representative points in a cell is therefore, twice the number of compartments. You can have a compartment in that you can put maximum two phase points. So, that means if you know the total number of compartments, then the number of representative points in the cell is therefore, twice the number of compartments because each compartment can accommodate two. But now for the representation purpose let us use the compartment term for half-filled compartments. Do not misunderstand when I say two phase points can be put in a compartment, I will further divide that 2 into 1 1 that means half-filled compartment.

So, in each compartment I will put only one phase point. Therefore, now you consider just two cells i and j as usual we have been considering i and j and each divided into four compartments. Now the way I will represent it is you consider let us say I say cell i and then cell j again I will put four sub compartments or four compartments. Now this each compartment means we can only fill one phase point. Remember what we just discussed that let us use the term compartment for half-filled compartments.

So, half-filled means I can put only one in each compartment. So, let us say I put 1 2 3 then you can have the next one you start from here 1 2 3 you can have another one 1 2 3 and there can be another arrangement 1 2 3. There are four possibilities four different ways of arranging these phase points in cell i and in cell j I only want to put only one phase point. So, this can be here this can be here or this can be here or this can be here. So, this is your cell j.

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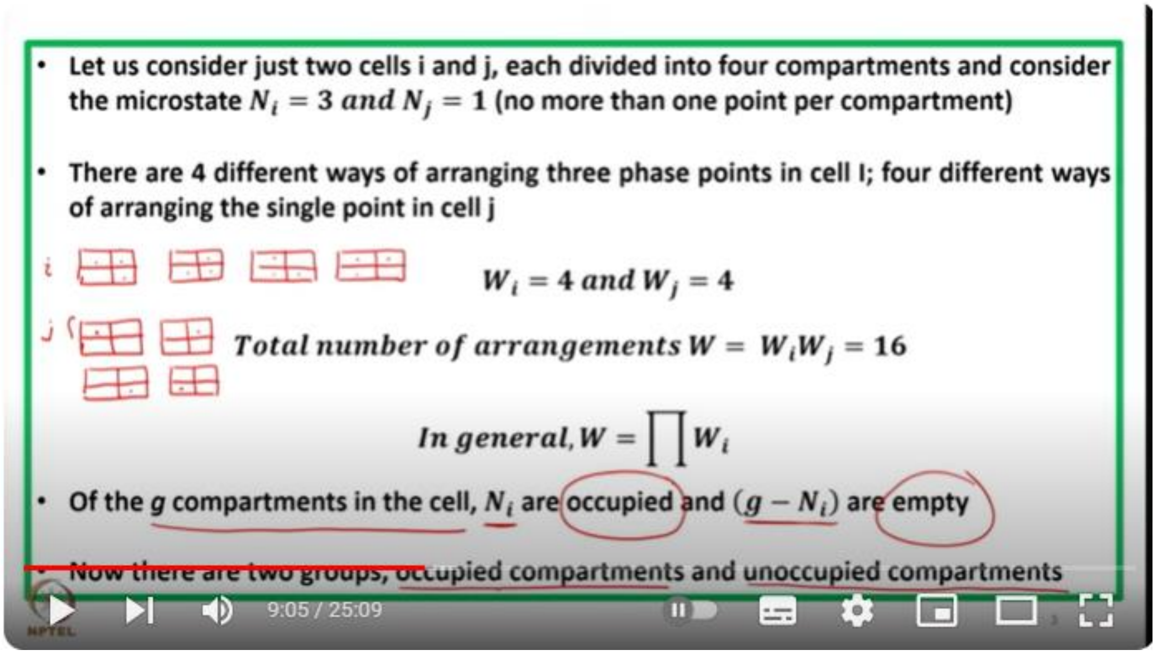

- Let us consider just two cells i and j, each divided into four compartments and consider the microstate $N_i = 3\ and\ N_j = 1$ (no more than one point per compartment)
- There are 4 different ways of arranging three phase points in cell I; four different ways of arranging the single point in cell j

$$W_i = 4\ and\ W_j = 4$$

$$Total\ number\ of\ arrangements\ W = W_i W_j = 16$$

$$In\ general, W = \prod W_i$$

- Of the g compartments in the cell, N_i are occupied and $(g - N_i)$ are empty
- Now there are two groups, occupied compartments and unoccupied compartments

So, what I have 1 2 3 4 W_i is equal to 4 1 2 3 4 W_j is equal to 4. So, therefore, the total number of arrangements is obviously W_i times W_j which is equal to 16. So, 16 possible arrangements with this N_i equal to 3 and N_j equal to 1 with the adherence of poly exclusion principle. That means in general I can write this weight is equal to product of Wi. So, it depends upon the number of cells you have i j k l etcetera if you know the weight of each corresponding to each set of cells then you multiply all those you get the overall thermodynamic probability.

We have talked about four compartments in a cell let us now talk about g compartments in the cell. Let us say we focus on g compartments in the cell N_i are occupied suppose if there are only N_i number of phase points if there are total g compartments in the cell and each compartment can have one phase point. That means if N_i are occupied g minus N_i are empty because there are total g compartments. So, we have occupied and we have empty that means there are two kind of groups there are two groups occupied compartments empty compartments. That means we are talking now occupied compartments and unoccupied compartments.

I hope you realize that how this discussion is proceeding now to slightly different direction earlier when we were talking about the Bose Einstein statistics this kind of restriction was not there. There we could put any number of points in any compartment, but here there is a restriction that if each compartment can only accommodate only half-filled compartment which we are representing as you know only one phase point can be put in each compartment. So, with this treatment now we get down to occupied compartments and unoccupied compartments depending upon the total number of phase points. All right how many compartments are now occupied? One compartment can have only one phase point and if there are N_i phase points then N_i compartments are occupied and remaining g minus N_i these compartments are unoccupied there are total of g compartments. So, once we know how many are total how many are empty how many are occupied then we can assign a thermodynamic probability to this kind of arrangement that is number of ways of dividing compartments into occupied and unoccupied total that is g factorial divided by N factorial divided by g minus N_i factorial this is for I cell of type I.

Similarly there can be J there can be K there can be L etcetera etcetera. Therefore, the general expression for the thermodynamic probability of a given macro state in phase Fermi direct statistics is you need to take product of all these quantities you have W_i you multiply by W_j W_k W_l that means overall product of g factorial divided by N_i factorial into g minus N_i factorial this is the general expression for thermodynamic probability. Now, you know that once we have an expression for thermodynamic probability from that we can now move towards other derivations. For example, you know S is equal to k log W, W can be connected with entropy. We also discussed that W sometimes is not very easy to take forward for derivation of other equations rather it is log W.

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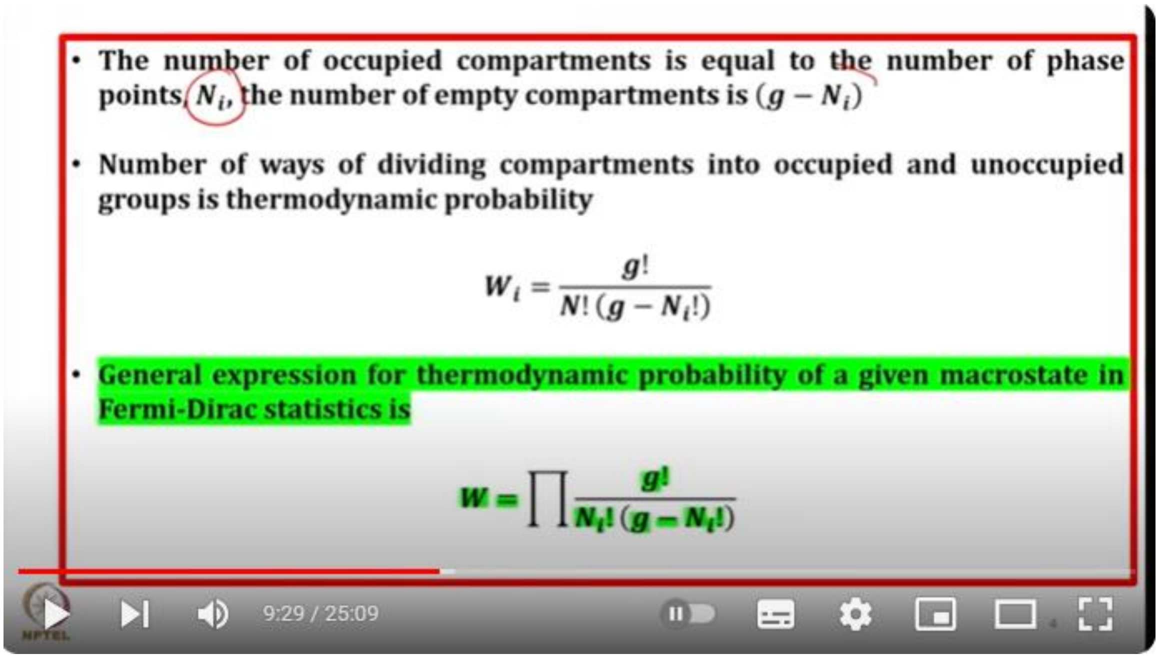

- The number of occupied compartments is equal to the number of phase points, N_i, the number of empty compartments is $(g - N_i)$
- Number of ways of dividing compartments into occupied and unoccupied groups is thermodynamic probability

$$W_i = \frac{g!}{N!\,(g - N_i!)}$$

- General expression for thermodynamic probability of a given macrostate in Fermi-Dirac statistics is

$$W = \prod \frac{g!}{N_i!\,(g - N_i!)}$$

So, instead of W if you work on log W you will see that the derivation of rest of the equations becomes easy. So, once we have W which is product of g factorial over N_i factorial into g minus N_i factorial as usual take the logarithm of this when you take the logarithm of this is product becomes a summation log G_i minus log N_i factorial minus log g minus N_i factorial from this. Now usually the total number of compartments and the total number of phase points is very large in that case we can use Stirling approximation. Let us use Stirling approximation. So, log g factorial is g log g minus g log N_i factorial is N_i log N_i minus N_i.

Similarly, log g minus N_i is equal to g minus N_i log g minus N_i minus g minus Ni. So, anyway when you expand all this eventual resulting equation is log W is equal to summation g log g minus N_i log N_i minus g log g minus N_i plus N_i log g minus Ni. You can easily derive this equation from the upper equation by using Stirling approximation please do try that ok. So, now we have an equation which is in terms of log W. Once we have log W now, we can take it forward how? Same usual procedure we need the state of maximum thermodynamic probability for a maxima as we have already discussed you need to take the derivative it should turn out to be 0.

So, therefore, for a state of maximum thermodynamic probability your d log W d log W it can be represented as log g minus N_i° actually you need to take derivative of this you should end up with this equation and N_i° is the number of phase points in ith cell in thermodynamic equilibrium. The derivation is similar to that we discussed in Bose Einstein statistics and as we have been always discussing that you cannot treat this logarithmic function and dN_i function separately you cannot say either this is equal to 0 or this is equal to 0 and if you cannot say then we need to come up with a method in which you can treat these two independently and then come up with some equation. In order to achieve that what we have been doing is to put some constraints and those constraints are the total number of phase points has to be constant that means, when you add up all the changes that should turn out to be 0 right. This is something which we have done earlier that is summation N_i is equal to N and summation N_i E_i is equal to E right. So, by using these two expressions you can arrive at dN_i summation equal to 0 you can also arrive at summation E_i dN_i equal to 0 and then as done earlier you use method of undetermined multipliers log B term and β term with the appropriate sign then add to this equation when you do that then you have these two parts one is this bracketed part other is dN_i part outside.

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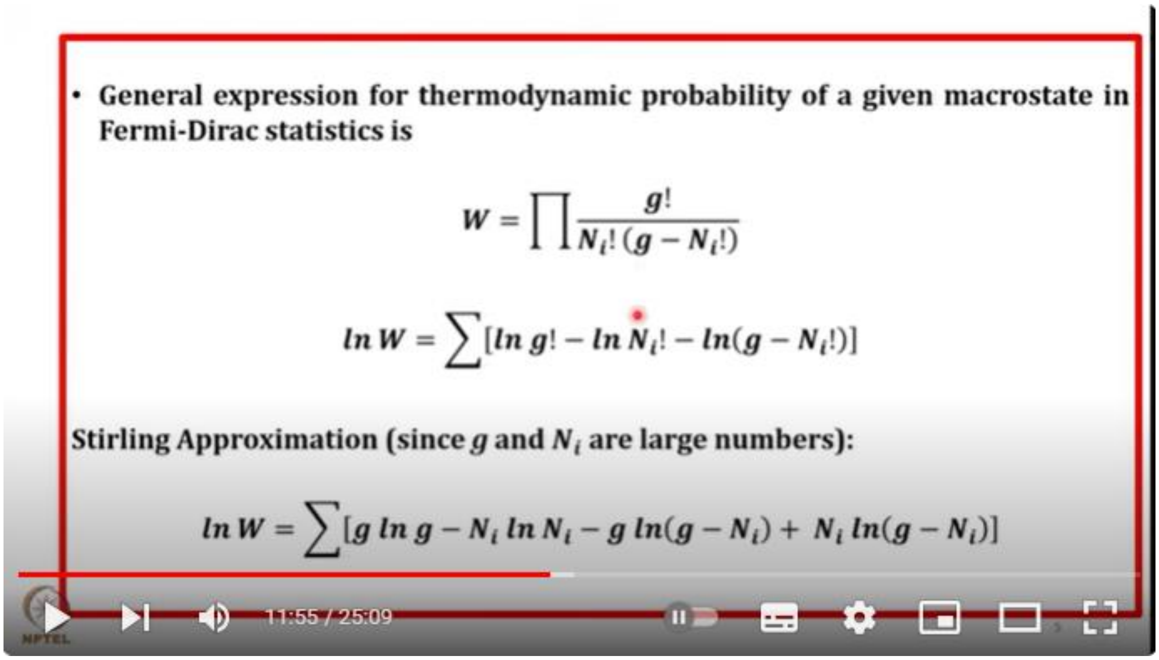

- **General expression for thermodynamic probability of a given macrostate in Fermi-Dirac statistics is**

$$W = \prod \frac{g!}{N_i!\,(g - N_i!)}$$

$$\ln W = \sum [\ln g! - \ln N_i! - \ln(g - N_i!)]$$

Stirling Approximation (since g and N_i are large numbers):

$$\ln W = \sum [g \ln g - N_i \ln N_i - g \ln(g - N_i) + N_i \ln(g - N_i)]$$

Now you can treat these independent and find out for what expression of B and β these can be treated as independent that means, you set this equal to 0 I have log g minus N_i° by N_i° is equal to log B plus β E_i if you set this entire thing equal to 0. Now, we are moving towards closer towards our result from the previous equation we got log g minus N_i° over N_i° is equal to log B plus β E_i once you remove the logs the expression that you get is N_i° upon g equal to 1 plus β exponential β E_i plus 1 here also you remember in Bose Einstein statistic there was a negative sign and here we are getting a positive sign this one is Fermi direct distribution function for the state of maximum thermodynamic probability. So, by now what we have we have three different expressions which can talk about population of various states one is in terms of Maxwell Boltzmann distribution second one was in terms of Bose Einstein statistics and the third one which we talk here is Fermi direct distribution function. When you compare one with the other you will see that in Maxwell Boltzmann distribution you were not considering further compartmentalization of the energy levels whereas, when we started discussing the Bose Einstein statistics that distinction was made, but we said that let us not apply any further restrictions further restriction means no rules like poly exclusion principle etcetera should not be applied we came up with some final equation and then we thought that let us now extend that developed theory for the systems in which the poly exclusion principle is applicable. One such system is electron gas and with that type of arrangement we have this equation which is the Fermi direct distribution function for the state of maximum thermodynamic probability.

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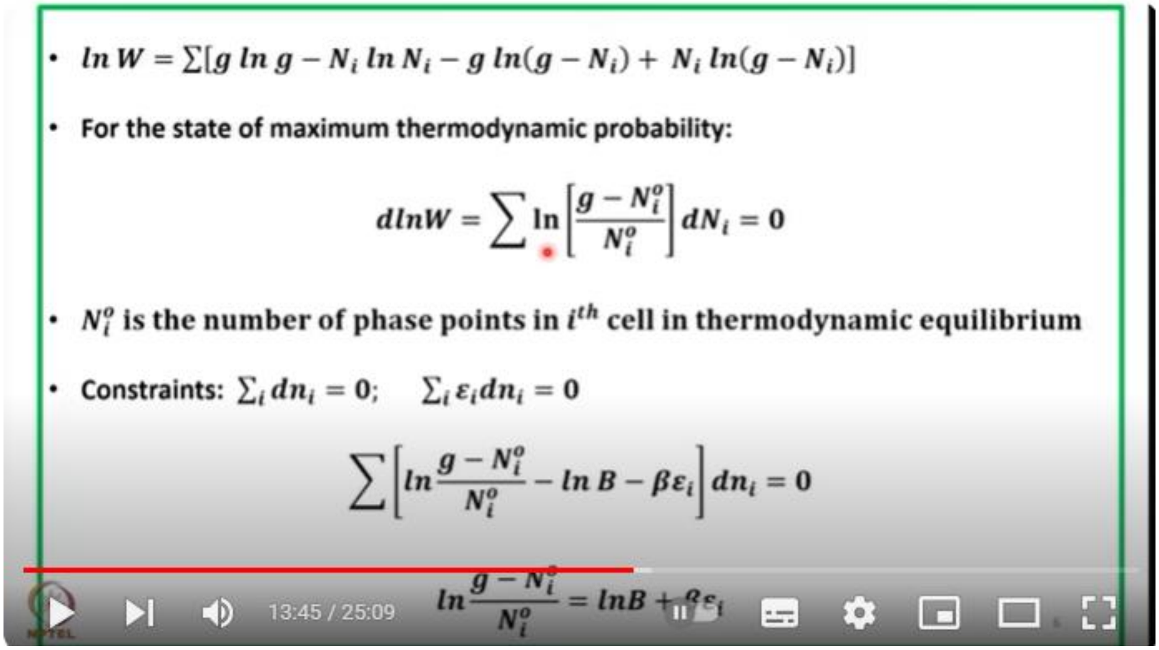

- $ln\,W = \sum[g\,ln\,g - N_i\,ln\,N_i - g\,ln(g - N_i) + N_i\,ln(g - N_i)]$
- **For the state of maximum thermodynamic probability:**

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

- N_i^o **is the number of phase points in** i^{th} **cell in thermodynamic equilibrium**
- **Constraints:** $\sum_i dn_i = 0; \quad \sum_i \varepsilon_i dn_i = 0$

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

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

So, by now we have discussed three different distribution functions, but in details we took forward the Maxwell Boltzmann distribution by using any one of these distribution functions you should be able to establish connection between the number of molecules in a particular set of energy levels molecular partition function and canonical partition function. In statistical thermodynamics when you are focusing on population or you are focusing on any thermodynamic quantities it directly connects you with various energy levels and it also connects you with the temperature it also connects you with degeneracy if there is any. The distribution function under certain circumstances may resemble, but you will appreciate that the overall discussion on statistical thermodynamics whether you talk in terms of Maxwell Boltzmann distribution or you talk about other distribution function the eventual goal is to get thermodynamic quantities in terms of molecular partition function. Why specifically I am not saying in terms of canonical partition function you can have canonical partition function you can have discussion in terms of micro canonical ensemble you can have discussion in terms of grand canonical ensemble, but we said that we will restrict to n v and t because these are the common conditions which are applied. Under constant volume heat supplied is equal to change in internal energy at constant volume derivative of internal energy with respect to temperature is heat capacity.

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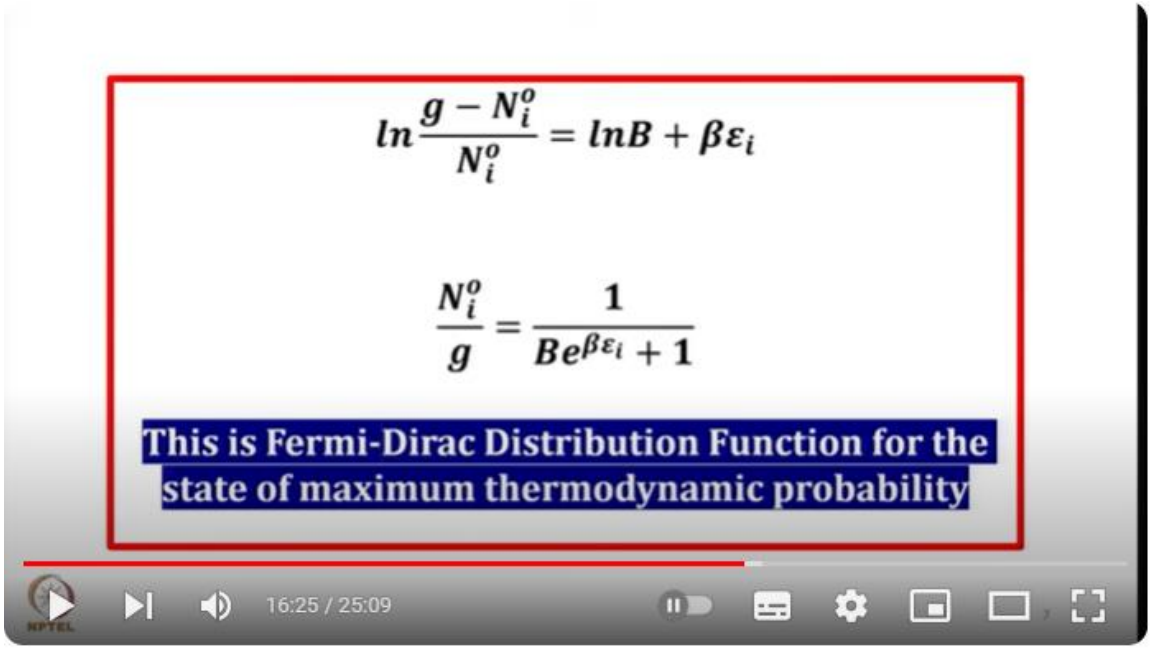

$$\ln\frac{g - N_i^o}{N_i^o} = \ln B + \beta\varepsilon_i$$

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

This is Fermi-Dirac Distribution Function for the state of maximum thermodynamic probability

So, therefore, by applying those restrictions of constant volume NVT we took the discussion forward, but in most of the equations that we derived here or the equations which we discussed taking forward to equilibrium constant were for ideal systems. We have not gone too much into details of non-ideal system because when you consider non-ideal system you have to start considering interaction potential energy which is 0 if the system is not interacting. Therefore, the discussion on non-ideal system or non-ideal gases thus was done based upon the virial coefficients where we talked about second virial coefficient third virial coefficient etcetera etcetera. We did not go too much into details from the virial coefficients although we connected the virial coefficient with canonical partition function or we connected the virial coefficients with the other parameters which were routinely discussed in statistical thermodynamics. While dealing with the various systems we have to be careful about not over counting the number of states.

When I said not over counting the number of states that means, the arrangements which appear again and again and therefore, we applied the factor which is called the degeneracy factor especially you know this was more evident when we were talking for the vibrational contribution to partition function. Therefore, overall, now with the discussion on statistical thermodynamics in terms of all three distribution functions we should be able to connect any thermodynamic quantity with the molecular partition function. As discussed, if you want to go beyond the ideal systems then we need to bring in more parameters we need to talk about virial coefficients. Many problems can be set and solved based upon the Bose Einstein distribution function or Fermi direct distribution function please do those and their connection with thermodynamic properties with thermodynamic functions should be made. We will conclude in today's lecture by accepting by realizing that the various thermodynamic quantities various thermodynamic quantities when I say I mean Gibbs free energy, Helmholtz free energy, pressure, enthalpy, entropy, internal energy can not only be determined by using calorimetry or direct calorimetry, but they can be determined by the knowledge of energy levels by the knowledge of degeneracies in other words by the knowledge of spectroscopic principles.

I hope the discussion was useful and I also hope that as I have repeatedly said that you will be able to connect the molecular partition function or canonical partition function with various thermodynamic quantities and evaluate them. Thank you very much.