Fundamentals of Statistical Thermodynamics

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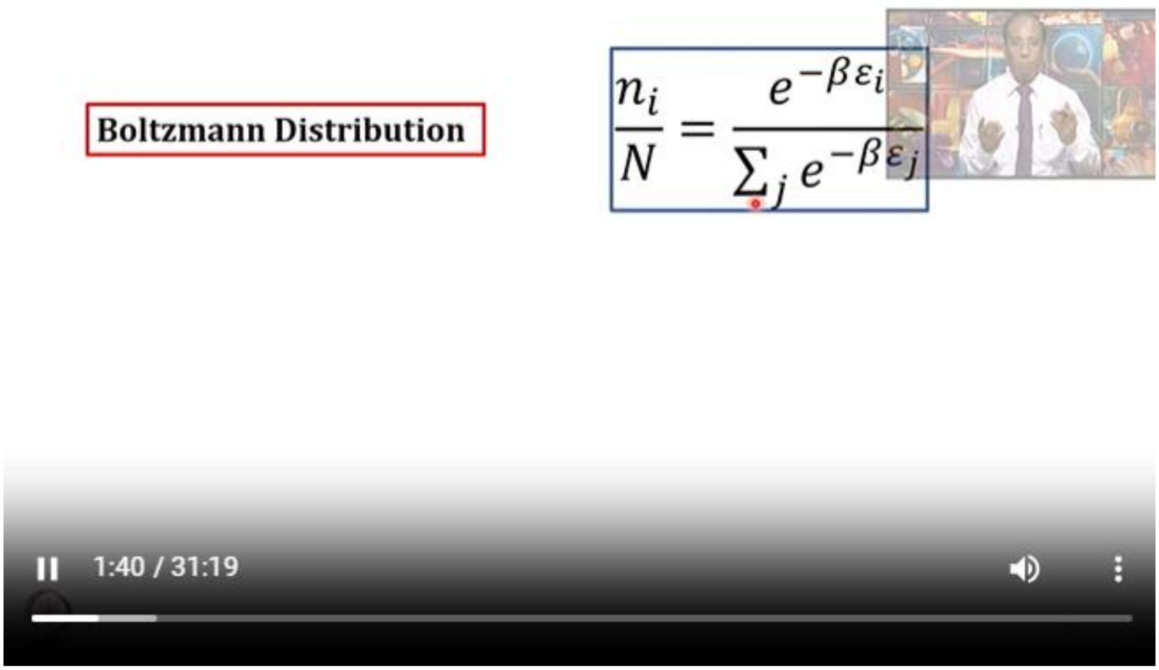
Lecture - 05

Welcome back to the next lecture of Statistical Thermodynamics. Today, we are going to learn about the molecular partition function. In the previous lecture, we have derived expression for Boltzmann distribution and we will move ahead from there. The Boltzmann distribution that is N_i upon N, where N_i is the number of molecules or particles in ith energy state, N is the total number of molecules, exponential minus beta Ei,

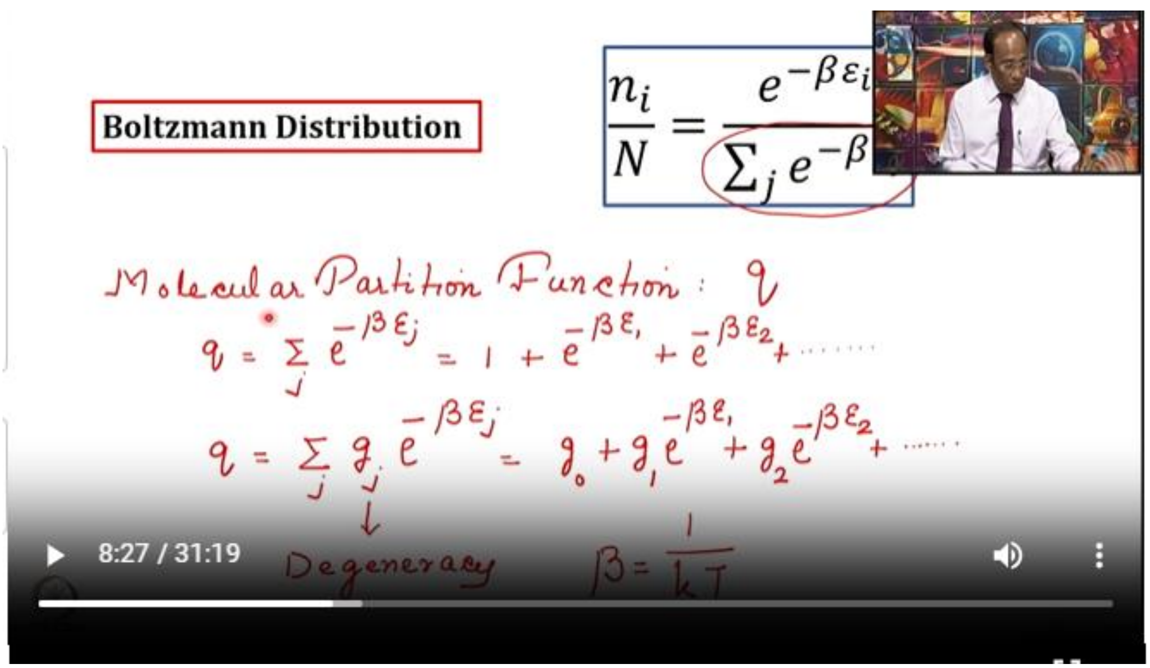


$$\frac{n_i}{N} = \frac{e^{-\beta\varepsilon_i}}{\sum_j e^{-\beta\varepsilon_j}}$$

Ei is the energy of the ith state and then we have this summation j exponential minus beta Ej and that you remember that came for alpha. In the derivation of this expression, we have used method of undetermined multipliers and in that method of undetermined multipliers, we have two constants alpha and beta. Alpha we have already accounted for and we will soon find out an expression for the beta.

Now, I want to specifically draw your attention to the denominator. The denominator which is summation j exponential minus beta ij, this is called the molecular partition function. We will name this as a small q. We will write q is equal to summation j exponential minus beta Ej.

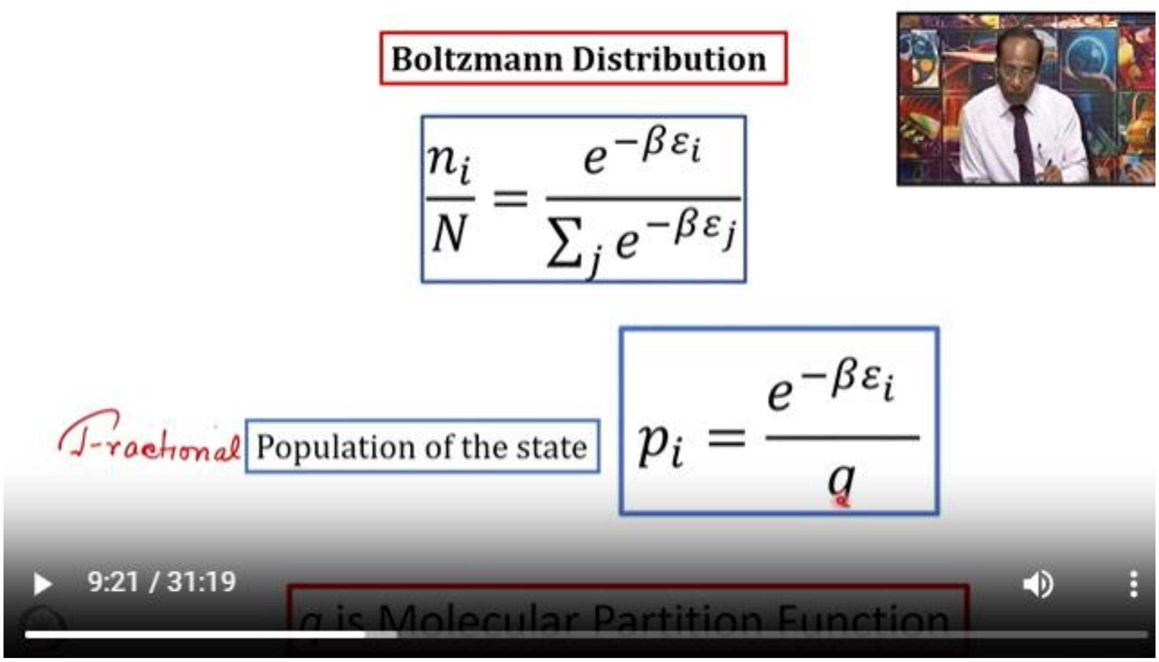
This j can run from 0 onwards that is 0, 1, 2, 3, 4, etcetera. So let us expand this and see what happens. This will be equal to when j is equal to 0, exponential minus beta into 0 is exponential 0. So, first term exponential 0, it is going to be 1. The second term is going to be exponential minus beta E_1. Third term is going to be exponential minus beta E_2 and you keep on going. This is the expansion for the molecular partition function. Where E_1, E_2, etcetera are first excited state, second excited states and so on. Now suppose that two or more states have the same energy. So if different states have the same energy that forms a level. Therefore a particular energy level can be twofold degenerate if two states are having same energy. It can be threefold degenerate. It can be more. So therefore in general what we will do is we will write GJ fold degeneracy. I will include that GJ into my expression now. What I want to say is if two states are having same energy then the same term will appear twice. If three states have the same energy then the same term will apply thrice. Therefore, the way to incorporate this is that let us include g_j exponential minus beta. E_J and that this g_j is the degeneracy of a particular level.



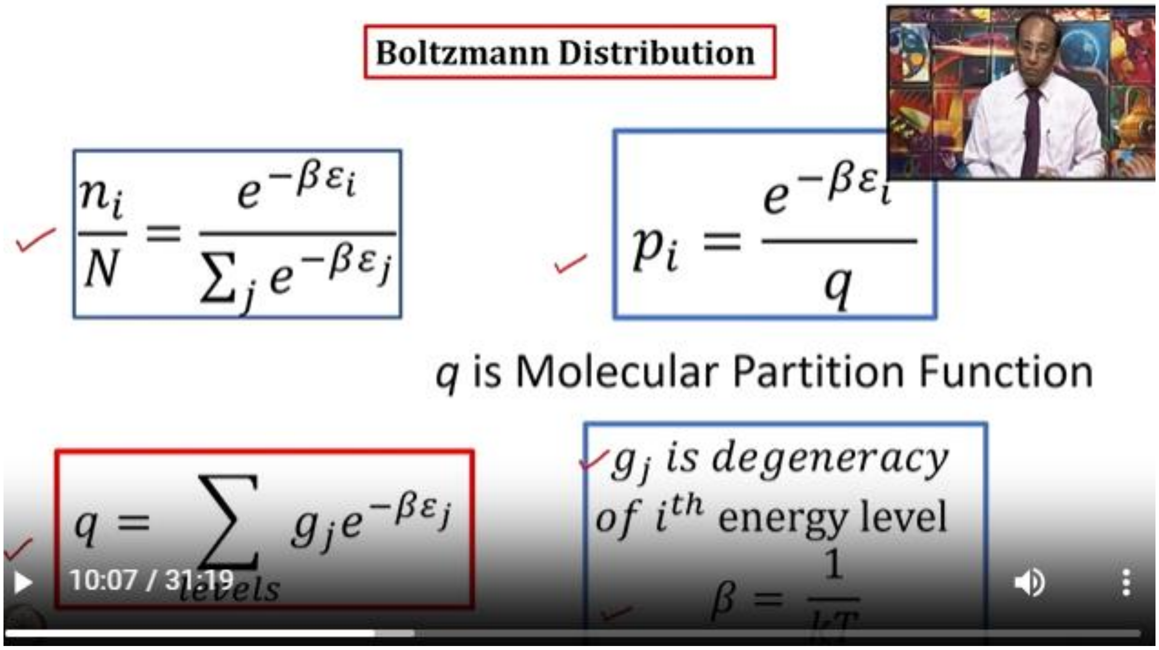
That is the jth level is g_j fold degenerate. So obviously when you expand this g_0 exponential 0 is going to be 1. Then second one g_1 exponential minus beta E_1 plus g_2 exponential minus beta E_2 and then plus will have other terms. So remember that we started from the ratio N_i upon N. What is this ratio N_i upon N? Number of molecules in the ith state divide by the total number of molecules. It represents a fractional population of ith state and I am going to discuss this in more details soon. So obviously a question will come in the mind that earlier we have accounted for alpha.

So what is this beta? Soon we are going to show that this beta is connected with temperature by this expression. Beta is equal to 1 over kT and this k is Boltzmann constant T is the temperature in Kelvin. Sometimes you even say beta as temperature because beta is connected with temperature through this term 1 over kT. So therefore remember that the partition function is given by this expression that is q is equal to summation j g_j exponential minus beta E_J where beta is equal to 1 over kT. What we need to know is the degeneracy of each energy level.

Once we have the values for g, once we have the values of E, therefore we can explicitly calculate the value of the molecular partition function. Also, remember that I am highlighting that this is a molecular partition function because we are talking in terms of individual particles, we are talking in terms of individual molecules. So what we have discussed? We have started with Boltzmann distribution where n_i upon n we refer to as population of the state. To be more precise read it as fractional population of the state because it is n_i upon n. What is this equal to? Exponential minus beta E_I and this denominator we have just discussed that this is molecular partition function.



$$p_i = \frac{e^{-\beta\varepsilon_i}}{q}$$



$$\frac{n_i}{N} = \frac{e^{-\beta\varepsilon_i}}{\sum_j e^{-\beta\varepsilon_j}} \qquad p_i = \frac{e^{-\beta\varepsilon_i}}{q}$$

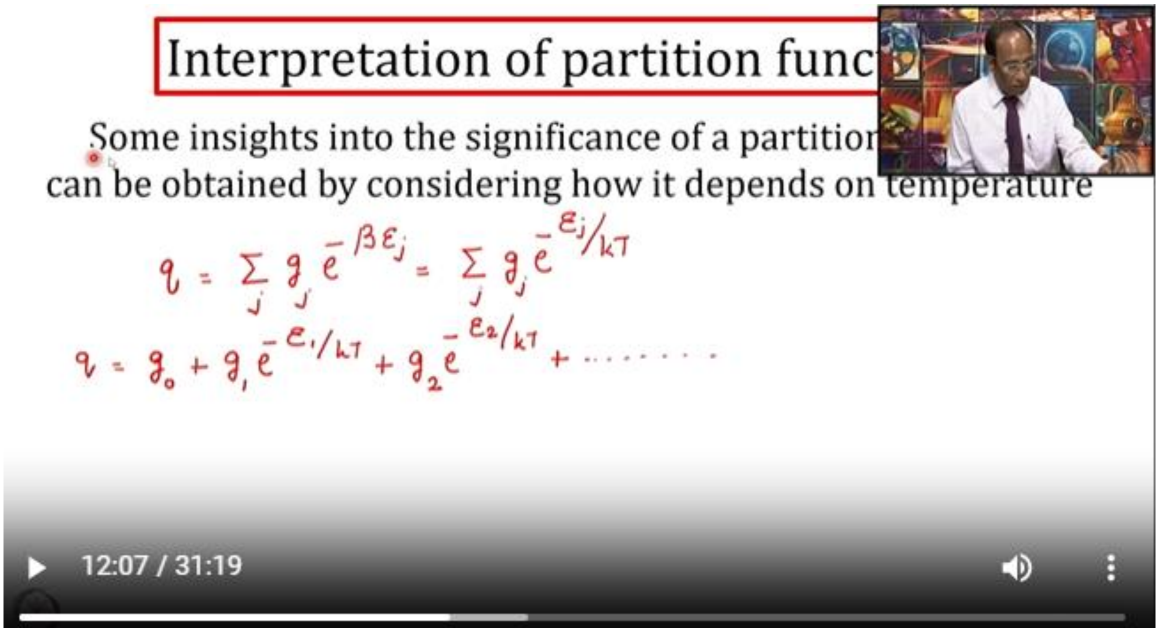
$$q = \sum_{levels} g_j e^{-\beta\varepsilon_j}$$

g_j *is degeneracy*
of i^{th} energy level
$$\beta = \frac{1}{kT}$$

q is Molecular Partition Function

So therefore fractional population of any state can be calculated once we have the information about the various energy levels and also we need to know the temperature and the molecular partition function. Re-emphasizing on the meaning of each term that we have discussed Boltzmann distribution, fractional population of ith state, expressing molecular partition function and also highlighting that the requirement of the degeneracy of the ith energy level and that that beta is connected to temperature by 1 by kT. How it comes? That we will be discussing a bit later.

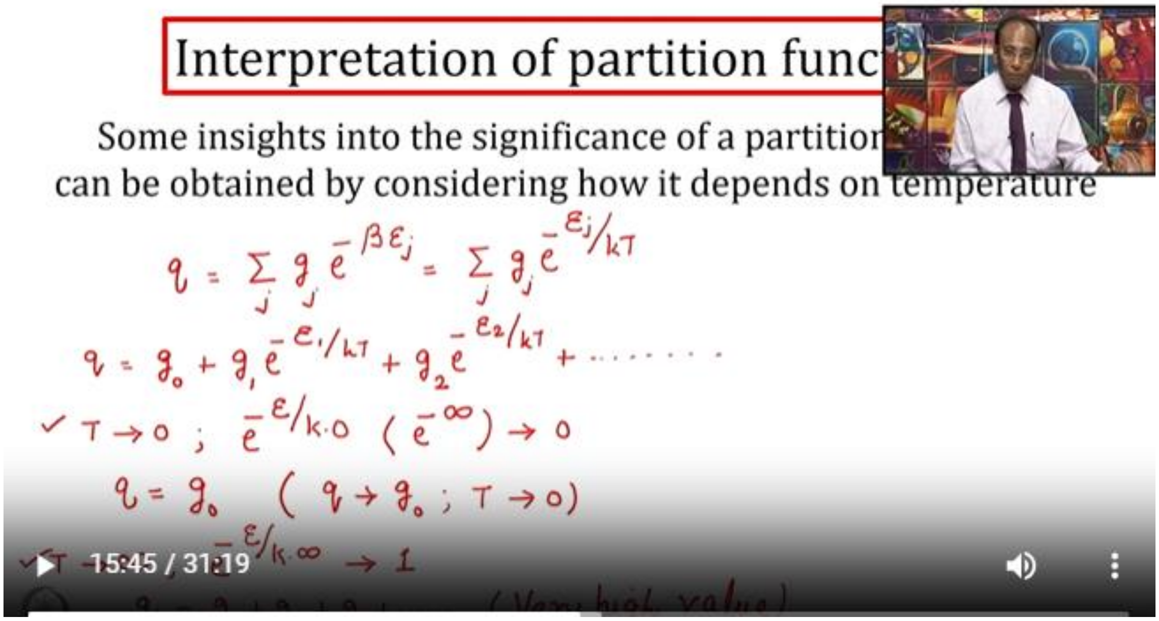
Now let us discuss what is the interpretation of partition function? What does it physically convey? So some insights into the significance of partition function can be obtained by considering how it depends on temperature.



Let us try to understand. Molecular partition function we just discussed is equal to summation j g_j exponential minus beta Ej or permit me to write in terms of temperature g_j exponential minus E_j upon kT. Let us expand it. What we have now? q is equal to put j is equal to 0. So we have g_0 first term E_0 exponential raise to power 0 is 1. Second one we have g_1 exponential minus E_1 upon kT plus g_2 exponential minus E_2 upon kT plus so on.

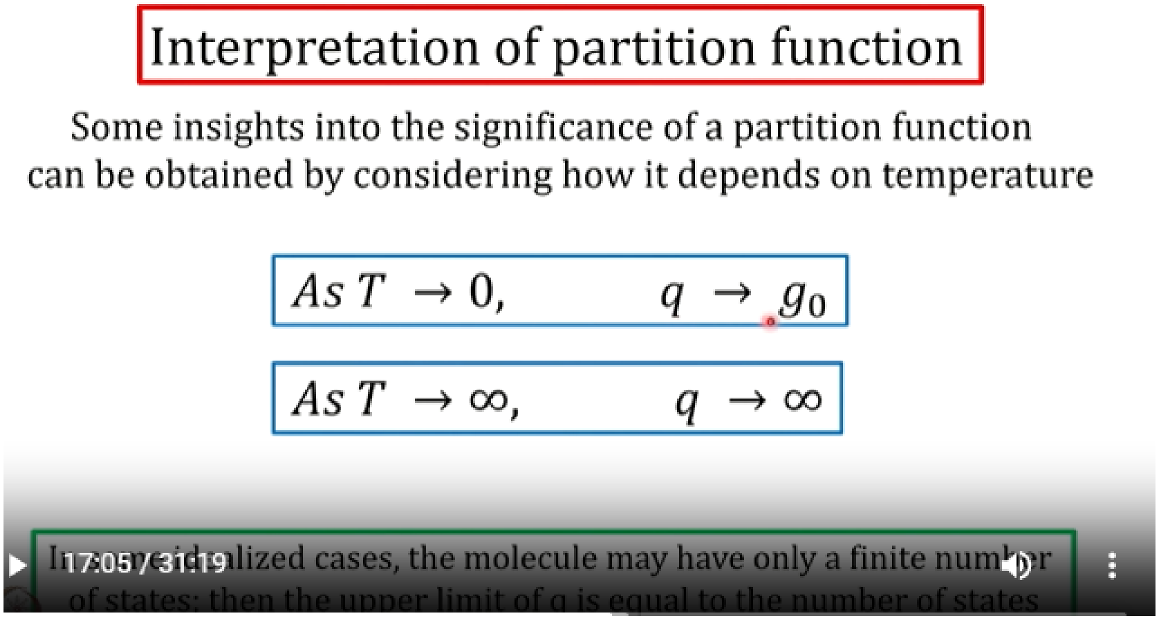
Keep on going. Now if you look at the comment that I made that some insights into the significance of a partition function can be obtained by considering how it depends on temperature. Let us concentrate on that. We want to talk about what is the effect of temperature. So whenever we want to discuss about the effect of temperature the easiest thing is let us first take the extremes. First extreme is when temperature approaches a value of 0. When temperature approaches 0 exponential minus any E upon k into 0. What is this? This is exponential minus infinity. This will tend to a value of 0. So then what will be the value of q? All other terms will disappear. This term will disappear, this term will disappear, all other terms will disappear.

So what will remain is only the first term q is equal to 0 or q approaches 0 when T approaches 0. So let me write this q approaches a value of g_0 as temperature approaches 0. So we have talked about the first extreme. Let us talk about this second extreme now. Temperature approaches a value of infinity.



When temperature approaches a value of infinity exponential minus E upon k times infinity this will approach a value of 1 because its exponential 0 is equal to 1. Therefore this term is going to be 1, this term is going to be 1 and other all other exponential terms are going to be equal to 1. What will remain is g_0 plus g_1 plus g_2 plus so on. So in that case your q will become g_0 plus g_1 plus g_2 plus keep on going that means very high value. I want you to appreciate the discussion that when T approaches 0 your partition function approaches a value equal to the degeneracy of the ground state.

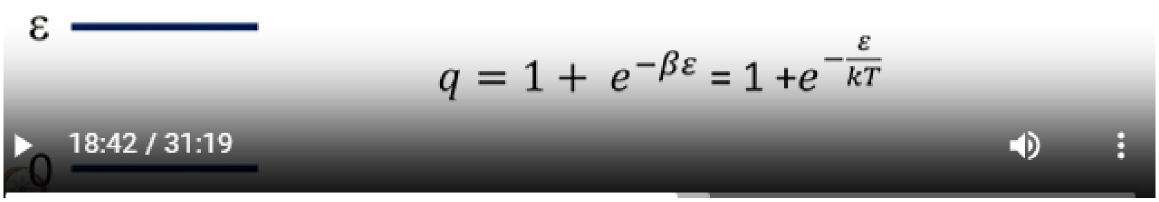
On the other hand when T approaches infinity the value of partition function you see it approaches a very high value. So therefore what do we conclude from this kind of result? That means when the temperature is approaching a value of 0 qis equal to g_0 which is degeneracy of the ground state and when temperature approaches infinity the value of q also increases. It increases to a very high value depending upon the temperature. That means the partition function gives an idea of how many states are thermally accessible at a given temperature. When T approaches 0 only ground state is thermally accessible. When T approaches infinity infinite number of energy states are thermally accessible. Okay.



That is what is highlighted in this slide as T approaches 0 we just discuss that q approaches a value of g_0, g_0 is the degeneracy of the ground state and when T approaches infinity q value also approaches infinity that means very high number many energy states are thermally accessible. So in some idealized cases, the molecule may have only a finite number of states then the upper limit of q is equal to the number of states. Suppose in some idealized states, idealized cases you have only two states available, you have only three states available, or you have only ten states available then the limit of q will be equal to the number of states.

Okay. To conclude this that partition function how do we interpret? partition function gives an idea of how many energy states, and how many energy levels are thermally accessible at a given temperature. Let us take certain examples. Consider only the spin energy levels of a radical in a magnetic field. Spin energy levels. That means in this case there are going to be only two states with the spin quantum number plus half and minus half.

- Consider only the spin energy levels of a radical in a magnetic field
- In this case there will be only two states $m_s = \pm\frac{1}{2}$
- Partition function of such a system is expected to rise to 2 as the temperature increases towards infinity

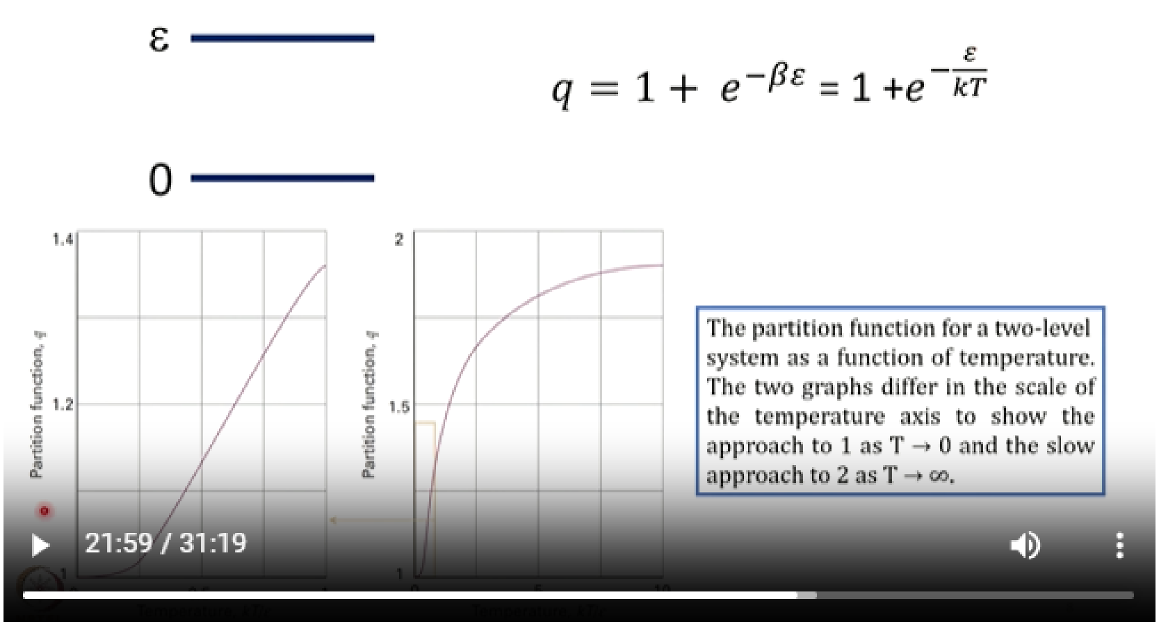


Therefore, how do we interpret that? That the partition function of such a system is expected to rise to a value of two because there are only two states available as the temperature increases towards a value of infinity. Now let us consider another system in which there are only two states available. Look at this. There are ground state energy equal to zero because you know we have discussed in the beginning we will start with the ground state energy equal to zero and then if there is some zero point energy that number can be added if we want to calculate total energy of the system. We will address that a bit later. The second energy state is at a separation of E. How do we write the partition function for this system? q is equal to one plus exponential minus beta E. Q which is equal to summation j g_j exponential minus beta E_j. There are only two states. The degeneracy of the ground state is one and energy is zero. So one into exponential zero is equal to one plus degeneracy of the second state is also one or second level is also one and exponential here the energy is E. That is the expression for the partition function and that is what is written over here and expressing beta in terms of temperature you have one plus exponential minus E upon k T.

$$q = 1 + e^{-\beta\varepsilon} = 1 + e^{-\frac{\varepsilon}{kT}}$$

We should be able to conveniently write the expression for molecular partition function depending upon how many states are there in a system. Here, we are talking about some idealized case in which there are only two states and in that case in that system, the partition function is given by this expression. Let us have a little bit more discussion on this.

So we have these two states. We have this expression for the molecular partition function and we can have some discussion on the effect of temperature. If you plot molecular partition function versus temperature look at this left hand side figure.



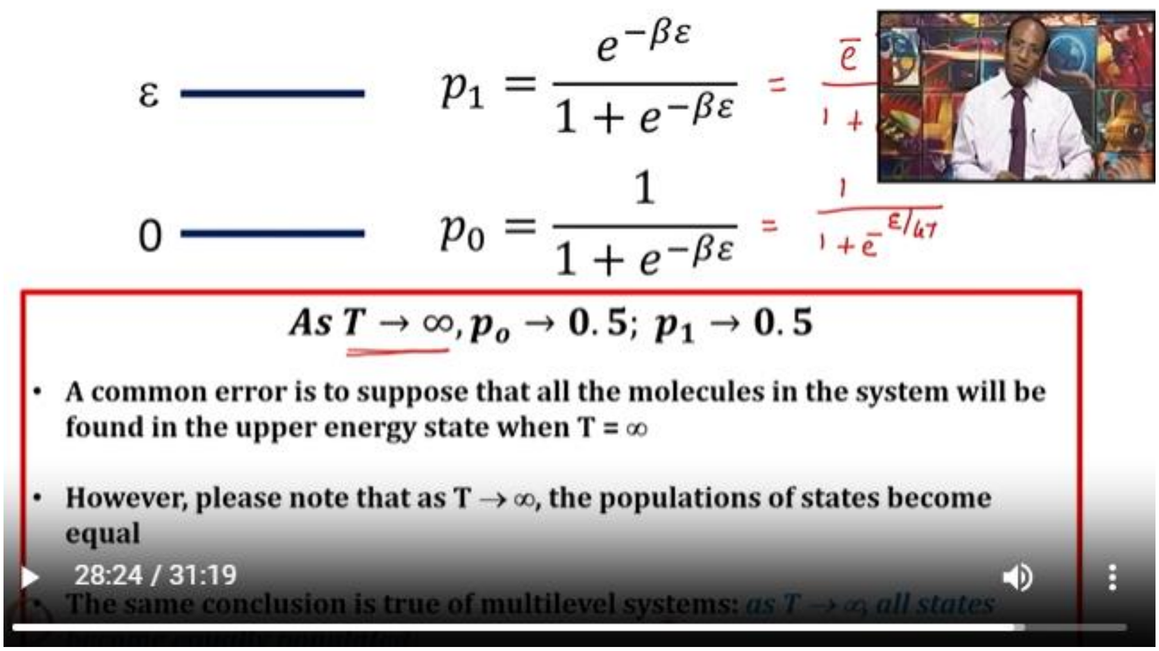
The value when the temperature is zero the value starts from one and then sharply rises. Starts from one which is that one this is one it sharply rises and then if you look at figure which is given on the right-hand side it rises towards a maximum value of two. When temperature approaches infinity it is exponential minus E upon infinity exponential zero that means this part also becomes equal to one.

So one plus one two. The partition function value starts from one and then rises as the temperature becomes very high it goes towards a value of two. So look at the comment. The partition function for a two-level system as a function of temperature is shown in this figures. The two graphs differ in the scale. Note here here zero to about one which is shown in an expanded form over here.

The idea is to show that how the value of partition function will sharply rise and when k T upon epsilon becomes relatively very high the value then moves towards a value of two partition functions a value of two. Still very fast and then a slow approach towards a value of two as the temperature approaches a value of infinity. All right. Now let us talk about the fractional population of each state. P_i is equal to exponential minus beta E_i upon q. We have discussed this. So therefore, we can write P_0 fractional population of the ground state equal to exponential zero which is one upon q and P_1 which is equal to exponential minus beta E. This is the energy upon q. So P_0 is one upon q. q is one plus exponential minus e upon kT or minus beta E and P_1 is given in this form. If I write this as exponential minus e upon kT upon one plus exponential minus e upon k T and this equal to one over one plus exponential minus e upon k T.

When T approaches infinity then this becomes exponential zero that means exponential zero is equal to one. So in that case this is going to be let us say first P 0 this is one over one plus one point five P_0 is point five. In the second case P_1 is also going to be one over two which is point five. As temperature approaches infinity as temperature approaches zero you will see that when temperature approaches zero then in that case what you have P_1 will turn out to be zero P_0 will turn out to be one. But what is important to note in this discussion is followed.

Basically a common error is to suppose that once we increase the temperature and then all the molecules should be pushed to the upper state that is a common error. That is a common error is to suppose that all the molecules in the system will be found in the upper energy state when T is equal to infinity. That is the common assumption. However if you look at this result what does this result say that when T approaches infinity each state is equally populated. Here we have two states and P_0 is also equal to point five that is the fractional occupancy of ground state is point five and the fractional occupancy of the first state first excited state is also point five.



That is what is written over here however please note that as T approaches infinity the populations of states become equal. So we can generalize that the same conclusion is true for multilevel systems. Here we talk about two-level system but the conclusion can be extended to multilevel systems that is as T approaches infinity all states become equally populated. Remember that it is not that when T approaches infinity all the molecules from the ground state are you know populated in the excited state. No, when T approaches infinity all states become equally populated.

So therefore the take-home lesson from this lecture is that the molecular partition function gives an indication of the average number of states that are thermally accessible to a molecule at the temperature of the system. What are the other key points? At T equal to zero only ground level is accessible and g is equal to q is equal to g_o that is molecular partition function is equal to degeneracy. At very high temperatures virtually all states are accessible and q is correspondingly very large that also we discussed. High temperature means this K T is much higher than the energy of that state and q has a very high value and low temperature means K T is much much lesser than energy and q is close to g_0. Therefore let us remember what is the expression for molecular partition function, how to interpret the molecular partition function and how to express the fractional population of a state in terms of molecular partition function.

We will discuss further how to express molecular partition function for states or for the number of states which are more than two in the next lecture.

Thank you.