Fundamentals of Statistical Thermodynamics

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Lecture59: Recap-1

Welcome back for further discussion on Statistical Thermodynamics. By now we have covered almost the whole course content which were targeted to be achieved at and in between along with discussion on various concepts, deriving various equations, explaining various further developed equations we have also solved some numerical problems. So, after covering the entire syllabus we should now recap what we have done and also try to note down what are the most important points that we should keep in mind. Whenever we derive any relations any equations sometimes lot of mathematics goes into it, lot of concepts go into it and finally, we arrive at some final equation. That equation is very important however the steps which lead to derivation of that equation are equally important. Let us recap some of the things what we have done in this course.

Our goal was to address thermodynamic principles from statistical point of view. We started by assuming that we know chemical thermodynamics. In chemical thermodynamics I am sure that all of you have gone through that course you were taught how to experimentally measure or obtain various thermodynamic quantities and what is the meaning of those thermodynamic quantities. For example, if we talk about the heat change when something reacts with something or the process undergoes change from state 1 to state 2 the enthalpy changes can be measured with the help of calorimetry.

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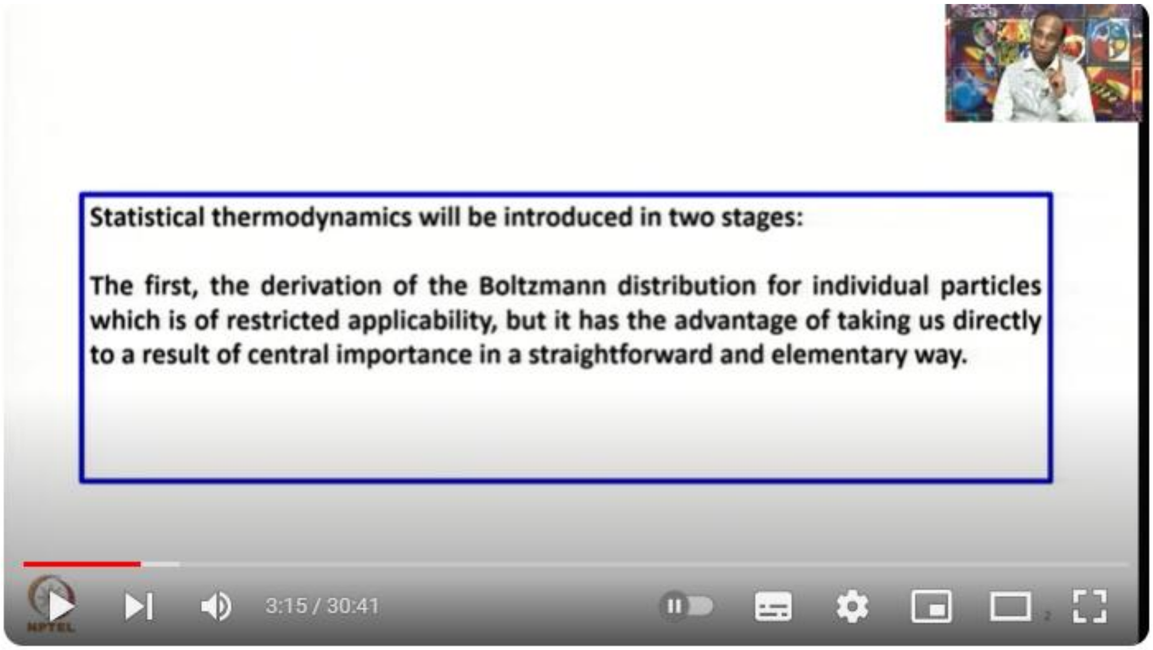

Statistical thermodynamics will be introduced in two stages:

The first, the derivation of the Boltzmann distribution for individual particles which is of restricted applicability, but it has the advantage of taking us directly to a result of central importance in a straightforward and elementary way.

And in statistical thermodynamics we wanted to highlight and address then the same thermodynamic quantities can be obtained by using spectroscopic approach. So, what we did was we started by discussing that statistical thermodynamics will be introduced in two stages. One was the derivation of Boltzmann distribution of individual particles. Remember that we started with individual particles. Of course, that individual particles means of restricted applicability, but that was the beginning point.

And then we brought in interacting particles how that was achieved by considering ensembles. We will go to that discussion also bit later. But before we derived any particular equation which were connected to the thermodynamic quantities, we talked about the configurations instantaneous configurations and their weight. Remember that when we said instantaneous configuration this type of arrangement we referred to as instantaneous configuration. We said that N_0 means N_0 number of molecules in ground state n 1 molecules in first excited state so on and so on.

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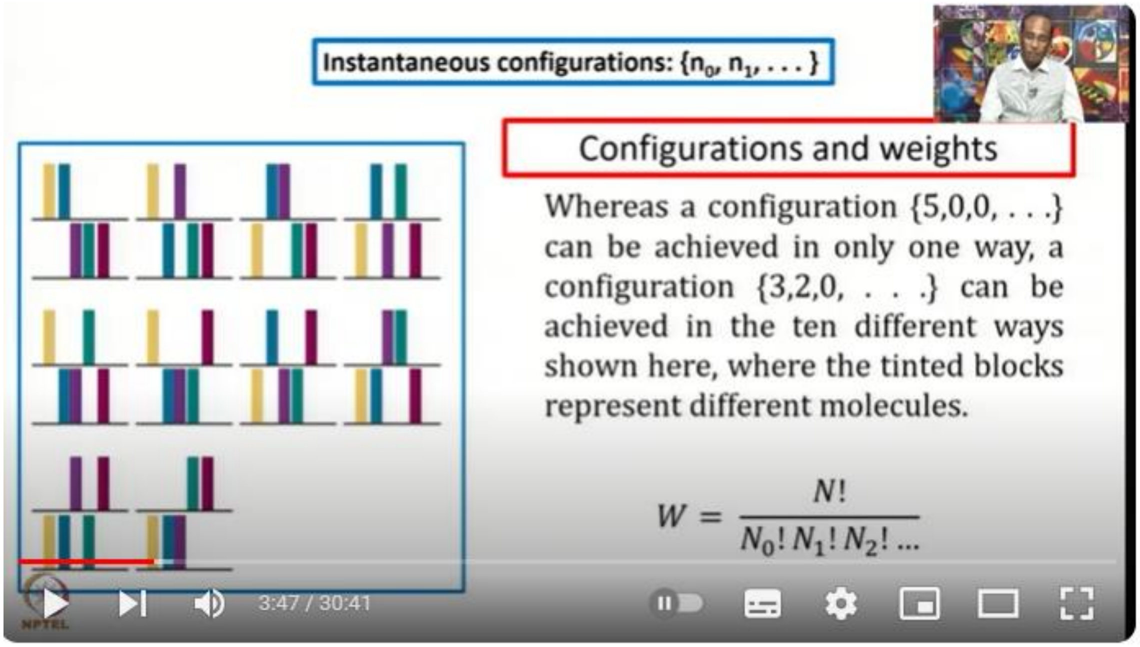

Instantaneous configurations: {n_0, n_1, . . . }

Configurations and weights

Whereas a configuration {5,0,0, . . .} can be achieved in only one way, a configuration {3,2,0, . . .} can be achieved in the ten different ways shown here, where the tinted blocks represent different molecules.

$$W = \frac{N!}{N_0!\,N_1!\,N_2!\,\ldots}$$

The weight of a configuration we discussed can be given by this formula where weight of a configuration is n factorial n is the total number of particles N_0 is the number of particles in ground state N_1 in the state corresponding to E_1 energy N_2 in the state corresponding to E_2 energy and so on. This was very important point to begin with that once you have instantaneous configuration there can be several configurations possible. So, that means, the number of ways those molecules those particles can be arranged can be numerous fine. So, what we decided another important point that instead of W statistical weight why do not we work on log W. Log W takes up this form we also discussed at that point that sometimes if you slightly transform the representation of an equation, you get the desired results easily.

You might remember that at one point I said that whenever we deal with internal energy we generally talk about temperature and volume. Because if you express internal energy in terms of temperature and volume and then you further derive equations from this it becomes easier to connect with the experimentally measurable properties. And that is why that is why we decided at that point that instead of W if you work on log W then the further derivations become important. And one such intermediate step was log W is equal to n log n minus summation N_i log N_i. This kind of equation was used multiple times in derivation of other equations.

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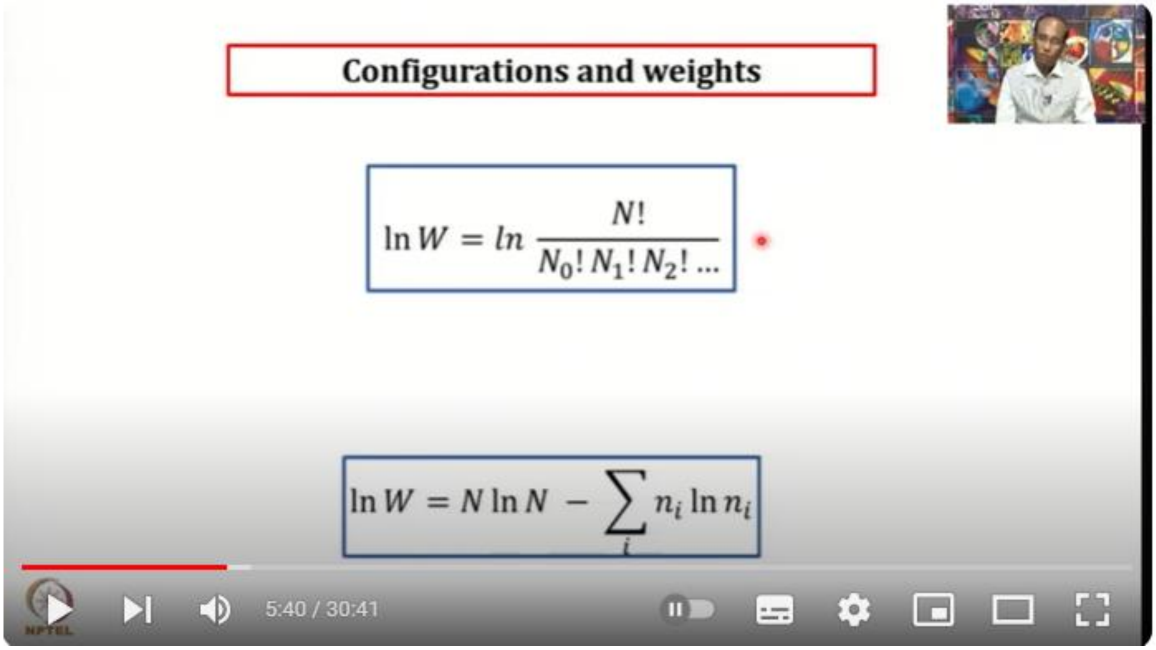

Configurations and weights

$$\ln W = ln\,\frac{N!}{N_0!\,N_1!\,N_2!\,\ldots}$$

$$\ln W = N\ln N - \sum_i n_i \ln n_i$$

But then we discussed that although several configurations are possible several instantaneous configurations are possible, but all of them may not be acceptable. There have to be certain acceptable configurations and then we decided that there should be some constraints. What are those constraints? That the total energy of the system has to be constant. Unless you supply external heat the total energy of the system will remain constant. Summation i N_i E_i is equal to E this is first constraint.

Second is constant number of molecules the number of molecules in a system will remain constant. With these two constraints the next step was to find dominating configuration because there are so many configurations which are possible. So, there has to be one configuration which is most dominant. That is where we decided to bring in the concept of maxima that is if a function f its maxima is to be found out take its derivative and set it equal to 0. So, instead of log W later on we started working of d log W that is the derivative of log W.

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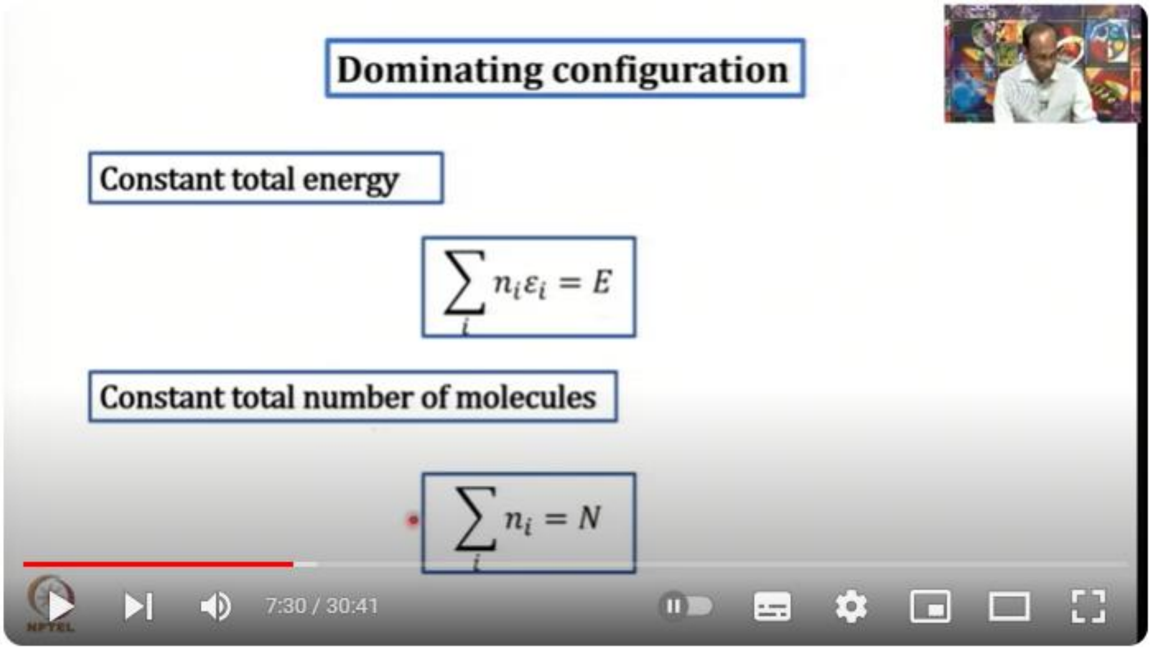

Dominating configuration

Constant total energy

$$\sum_i n_i \varepsilon_i = E$$

Constant total number of molecules

$$\sum_i n_i = N$$

And derivative of log W can be expressed in this summation form and the idea was to take the derivative and set it equal to 0. This is an important step of the recap process. We said that the derivative of log W should be set equal to 0 and if I set this equal to 0 that means can I treat either the first bracketed term equal to 0 and d N_i equal to 0 no because they are not independent of each other. And then we brought in a very important method of undetermined multipliers this is called Lagrange's method of undetermined multipliers. In that you choose two parameters one is alpha another is β and then transform this equation in such a form that this bracketed term along with alpha and β E_i can be taken equal to 0 and then find out for what expression of alpha and what expression for β this can be set equal to 0.

This is called Lagrange's method of undetermined multipliers. Why we were doing this because we wanted to derive equation for Boltzmann distribution. With this treatment we were able to derive this equation which is for Boltzmann distribution N_i is the number of molecules in i^{th} state n is the number of particles or molecules total this is equal to exponential minus β E_i divided by summation of j exponential minus β E_j that is where we recognized that this denominator is equal to molecular partition function. We also included the degeneracy term over here. So, the molecular partition functions definition was introduced at that time summation over all the levels g_j exponential minus β E_j and later on we showed that this β is equal to 1 over k T.

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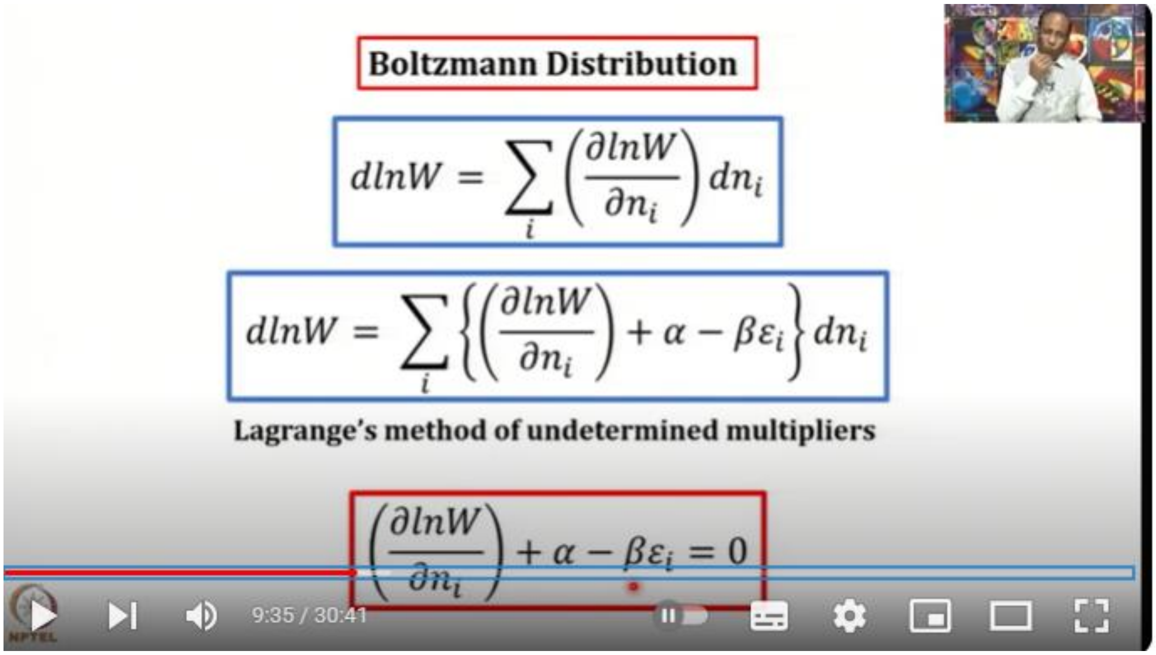

Boltzmann Distribution

$$d\ln W = \sum_i \left(\frac{\partial \ln W}{\partial n_i}\right) dn_i$$

$$d\ln W = \sum_i \left\{\left(\frac{\partial \ln W}{\partial n_i}\right) + \alpha - \beta\varepsilon_i\right\} dn_i$$

Lagrange's method of undetermined multipliers

$$\left(\frac{\partial \ln W}{\partial n_i}\right) + \alpha - \beta\varepsilon_i = 0$$

So therefore, many times you will come across the temperature also is you know represented just as β β is equal to 1 over k T in this expression k is Boltzmann constant. So, β is inversely proportional to temperature all right. We had the definition of molecular partition function then we were interested in understanding we know the mathematical expression for molecular partition function, but what does it physically mean does it have any meaning. To understand that we invoked two conditions generally we invoke these these kind of two extreme conditions which is one is the temperature approaching 0 and the second is temperature approaching infinity. We observed that when temperature approaches 0 the molecular partition function approaches a value of degeneracy of the ground state and when temperature approaches infinity molecular partition function approaches a value of infinity.

So, based upon this discussion this two constraints that we put two extreme constraints that is T approaching 0 and T approaching infinity. The conclusion that we drew from this discussion was that the molecular partition function gives an idea of number of thermally accessible states in a system. When temperature approaches 0 only ground state is available. When temperature approaches infinity the molecular partition function also approaches infinity that means almost all the energy levels are accessible to the particles or to the molecules. This is how we started interpretation of molecular partition function.

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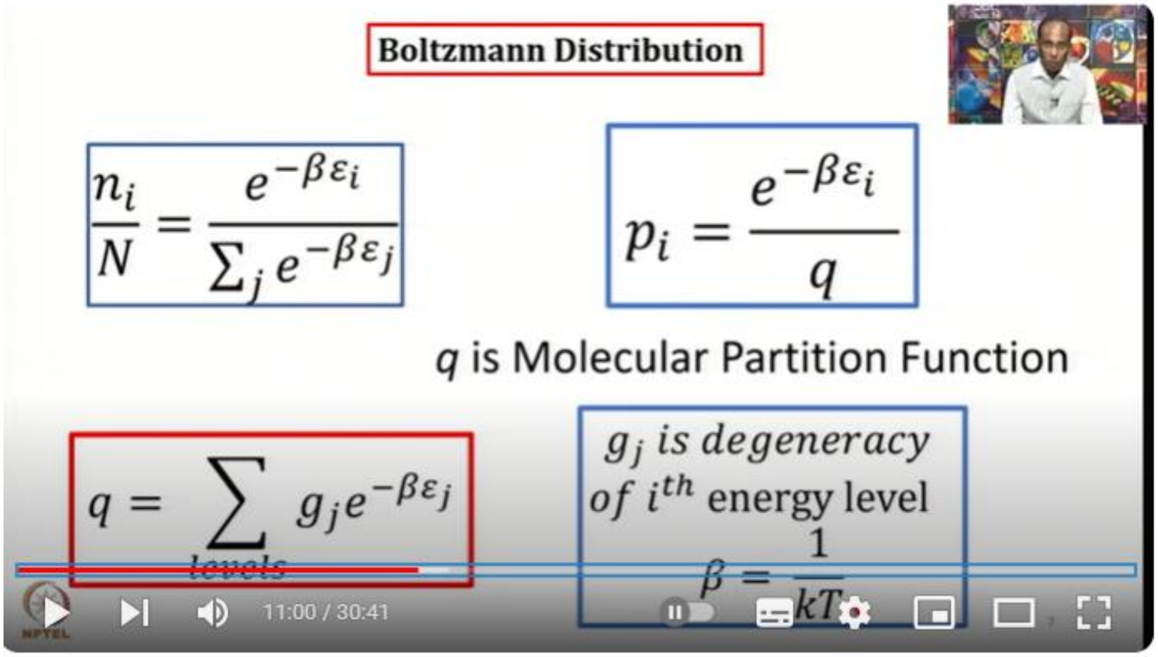

Boltzmann Distribution

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

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

q is Molecular Partition Function

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

g_j is degeneracy of i^{th} energy level

$$\beta = \frac{1}{kT}$$

Then as discussed previously this N_i upon n is equal to π which is the population of i^{th} state which is further equal to exponential minus β_i divided by q. So, once we have the population, we drew another very important conclusion. How did we derive that conclusion? We considered two level system which are separated by E the ground state had an we always took ground state as 0. First excited state is E we started our discussion by considering only two-level system and we found expressions for P_0 and P_1. What we observed that as T approaches infinity both the populations become half half.

Generally one may think that when you keep on heating the system when you apply infinite temperature then all the molecules should go to the upper state. It does not happen. These calculations suggest that as temperatures approaches infinity all the available states energy states energy levels in a molecule are equally likely to be populated. Since here we took example of a system of having only two energy levels ground state and first excited state. So, we observed that as temperature approaches infinity population of the ground state is 0.

5 and population of the first excited state is also 0.5. And this is what I was trying to tell you that 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. But note that since there are only two, they become populations become equal. If there are three then it will be one third one third one third.

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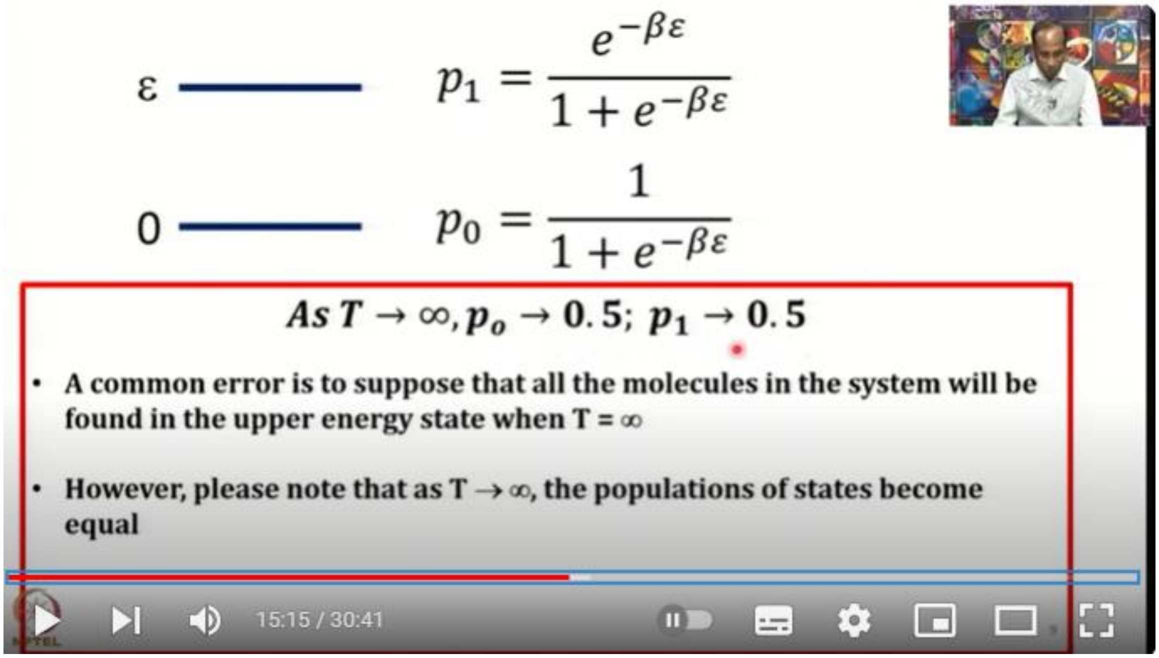
ε

$$p_1 = \frac{e^{-\beta\varepsilon}}{1 + e^{-\beta\varepsilon}}$$

0

$$p_0 = \frac{1}{1 + e^{-\beta\varepsilon}}$$

$$As\ T \rightarrow \infty, p_o \rightarrow 0.5;\ p_1 \rightarrow 0.5$$

- **A common error is to suppose that all the molecules in the system will be found in the upper energy state when T = ∞**
- **However, please note that as T → ∞, the populations of states become equal**

If there are four one fourth one fourth one fourth one third. So, that means this conclusion is also true for multilevel systems as T approaches infinity all states become equally populated. Remember this result a quick result when the temperature approaches infinity all states become equally populated all right. Now, after that the knowledge of molecular partition function the next step was to move more closer to connecting the molecular partition function with thermodynamic quantities. And then we started realizing that let us now discuss different modes of motion.

For a molecule different modes of movements include translational, rotational, vibrational, electronic these are the main contributions. We also discussed at some point that if q_x is the molecular partition for the translational motion of the particle or molecule in x dimension q_y for translational movement in y dimension q_z in z dimension that overall partition function is a product of all. Whereas, for energy it is a sum of all remember always molecular partition function it is always multiplicative of different contributions total energy is always summative. We derived an expression for translational partition function which was v by λ^3 where λ is equal to β h square by 2 π m or h by 2 π m kT. We also found out that this λ has a unit of length and that is why we started calling it as thermal wavelength.

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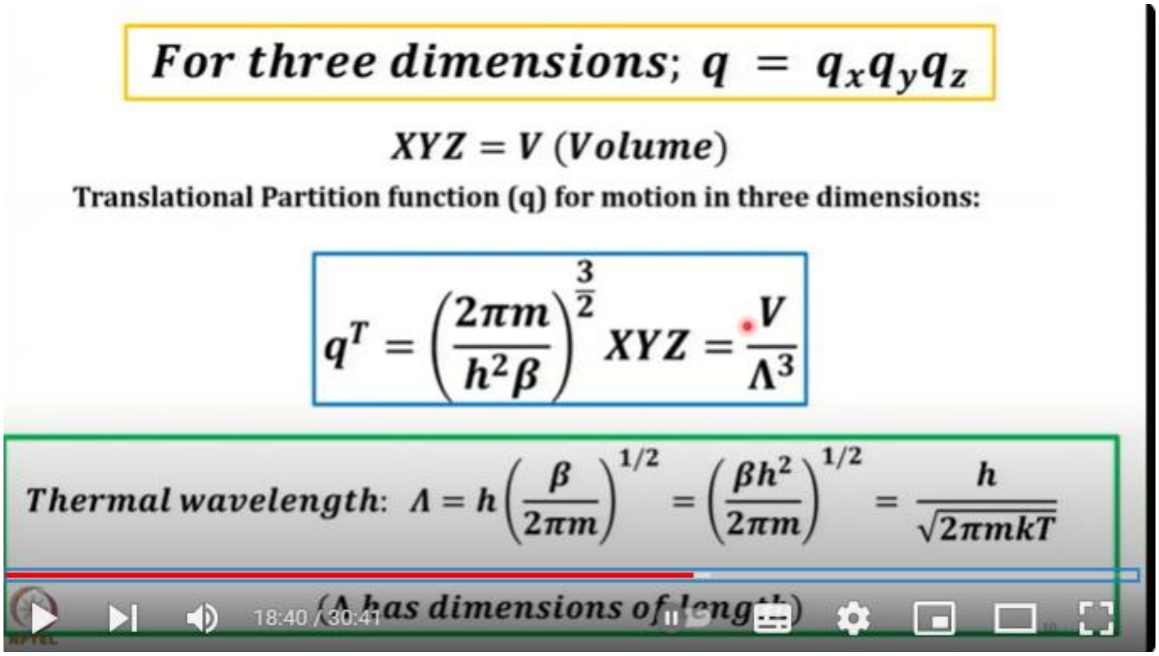

For three dimensions; $q = q_x q_y q_z$

$XYZ = V$ (Volume)

Translational Partition function (q) for motion in three dimensions:

$$q^T = \left(\frac{2\pi m}{h^2\beta}\right)^{\frac{3}{2}} XYZ = \frac{V}{\Lambda^3}$$

Thermal wavelength: $\Lambda = h\left(\frac{\beta}{2\pi m}\right)^{1/2} = \left(\frac{\beta h^2}{2\pi m}\right)^{1/2} = \frac{h}{\sqrt{2\pi mkT}}$

(Λ has dimensions of length)

So, if we know the thermal wavelength if we know the volume of the system, we can easily calculate translational contribution. And the thermal wavelength this depends upon mass and temperature Boltzmann constant and Plax constants are constants. That means, the higher the mass the lower is the thermal wavelength the lower is the thermal wavelength the higher is the translational partition function. So, therefore, from the knowledge of thermal wavelength we can calculate the translational partition function or in other words if I say that if we can determine thermal wavelength, we can always get translational contribution to the partition function provided we know the volume of the system.

Translational contribution specifically we discussed that has a lot more meaning if we are talking for perfect gases.

So, if it is only one atom then what are the different contributions which are possible. If it is only one atom then you have translational contribution. One atom cannot rotate one atom cannot vibrate that means, rotational and vibrational contribution is not there you do not need to worry about that. One important point that I would like to mention over here is that if I write q is equal to summation j. So, this is the expression for the rotational contribution g_j exponential minus β E_j the minimum value of q when you expand it the minimum value is equal to g_0 that is minimum.

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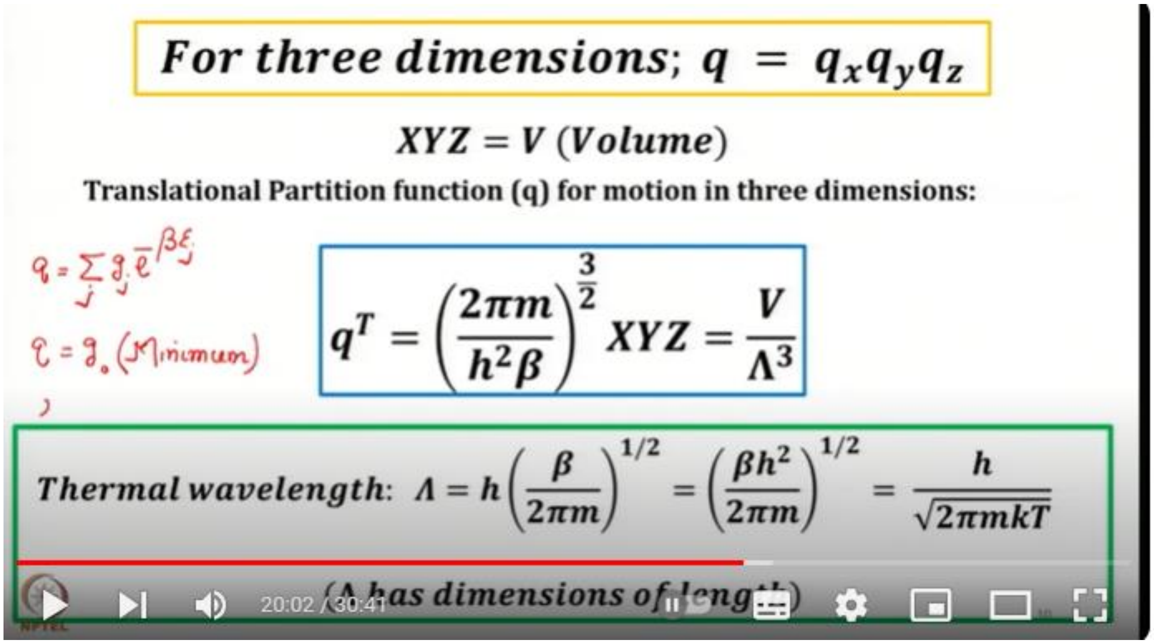

For three dimensions; $q = q_x q_y q_z$

$XYZ = V$ (*Volume*)

Translational Partition function (q) for motion in three dimensions:

$q = \sum_j g_j e^{-\beta \epsilon_j}$

$q = g_0$ (Minimum)

$$q^T = \left(\frac{2\pi m}{h^2\beta}\right)^{\frac{3}{2}} XYZ = \frac{V}{\Lambda^3}$$

Thermal wavelength: $\Lambda = h\left(\frac{\beta}{2\pi m}\right)^{1/2} = \left(\frac{\beta h^2}{2\pi m}\right)^{1/2} = \frac{h}{\sqrt{2\pi m k T}}$

(*Λ has dimensions of length*)

Why I am saying minimum? Suppose if the higher energy levels are not possible to be excited to then only ground state contribution will be there. So, we need the degeneracy of the ground state E_0 E_0 is equal to 0 this exponential factor becomes 1. So, always there is a minimum contribution which is equal to the degeneracy of the ground state. Now, once we had the molecular partition function we started connecting with the various thermodynamic quantities. What are the various thermodynamic quantities that we usually worry about? There are only a few to name internal energy heat capacity Gibbs free energy Helmholtz free energy enthalpy entropy heat capacity.

Then we we can think of you know how heat capacity can be related to any other quantities. For example, if I say C_v C_v is equal to δu by δt at constant volume C p is equal to δH δt at constant pressure. So, if I have information on internal energy, I can have C_v if I have information on enthalpy, I can have C_p by recognizing that the temperature total energy added up in all the form is equal to internal energy we wrote u is equal to U (0) plus E. And we could come up with this expression u is equal to U (0) minus n by q δq by δβ at constant volume which in other words can be written as minus n δq by δβ at constant volume. So, this expression which describes internal energy in terms of molecular partition function is very very important.

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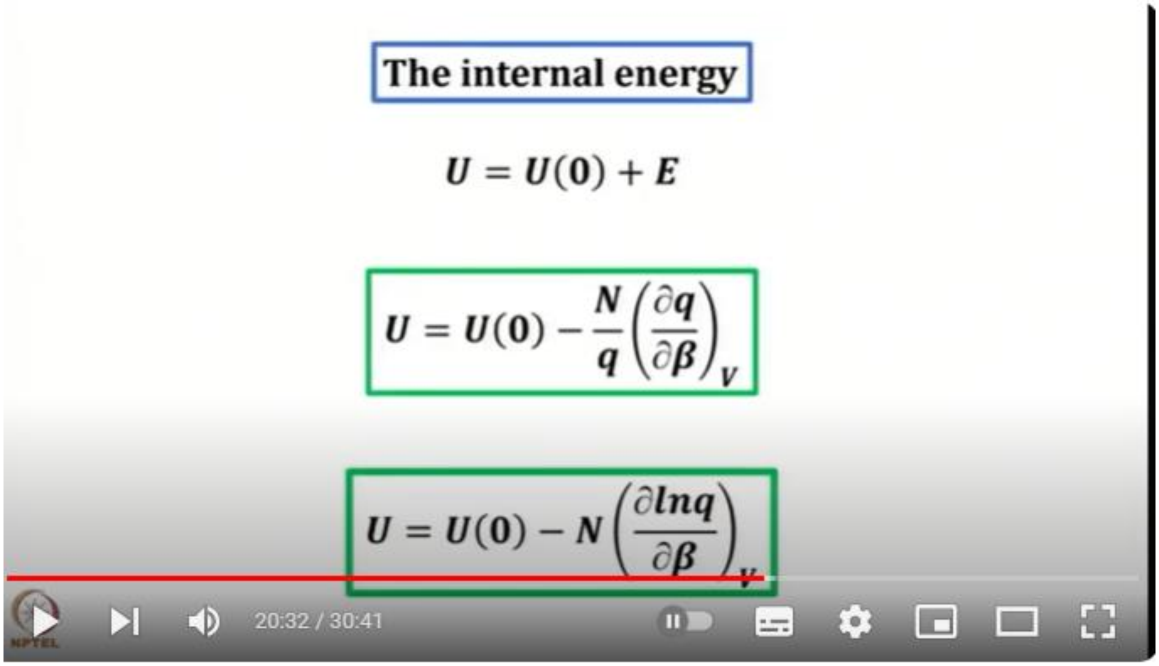

The internal energy

$$U = U(0) + E$$

$$\boxed{U = U(0) - \frac{N}{q}\left(\frac{\partial q}{\partial \beta}\right)_V}$$

$$\boxed{U = U(0) - N\left(\frac{\partial \ln q}{\partial \beta}\right)_V}$$

Now, then very important property which is entropy the statistical definition S is equal to k log W which many students know for a long time we derived that where here k is Boltzmann constant and W is the weight of the configuration which is most probable. And here we started discussing perfectly ordered systems versus not perfectly ordered systems we took the example of HCl that if HCl is arranged like this where all the arrangements are HCl HCl HCl HCl at absolute 0 there is a perfect order. If there is a perfect order that means, this minimum energy confirmation can be achieved only in one way that means, W is equal to 1. If you set W equal to 1 then S is equal to k log 1 that is equal to 0. This is where the third law of thermodynamics becomes important.

What is third law of thermodynamics is the entropy of each element each substance is positive. It may become 0 at absolute 0 and it does become 0 at absolute 0, but for perfectly ordered systems perfect crystals. And we demonstrated here that for such perfect crystals S is equal to 0 and if there is no perfection even at absolute 0 for example, you talk about carbon monoxide. Carbon monoxide the molecular dipole moment of carbon monoxide is very small that means, in the crystal at absolute 0 if the arrangement is like C O O C C O C O Somewhere C O's are overturned as O C then the energy of the crystal does not change. That means, at absolute 0 there can be two possible orientations which leads to same energy.

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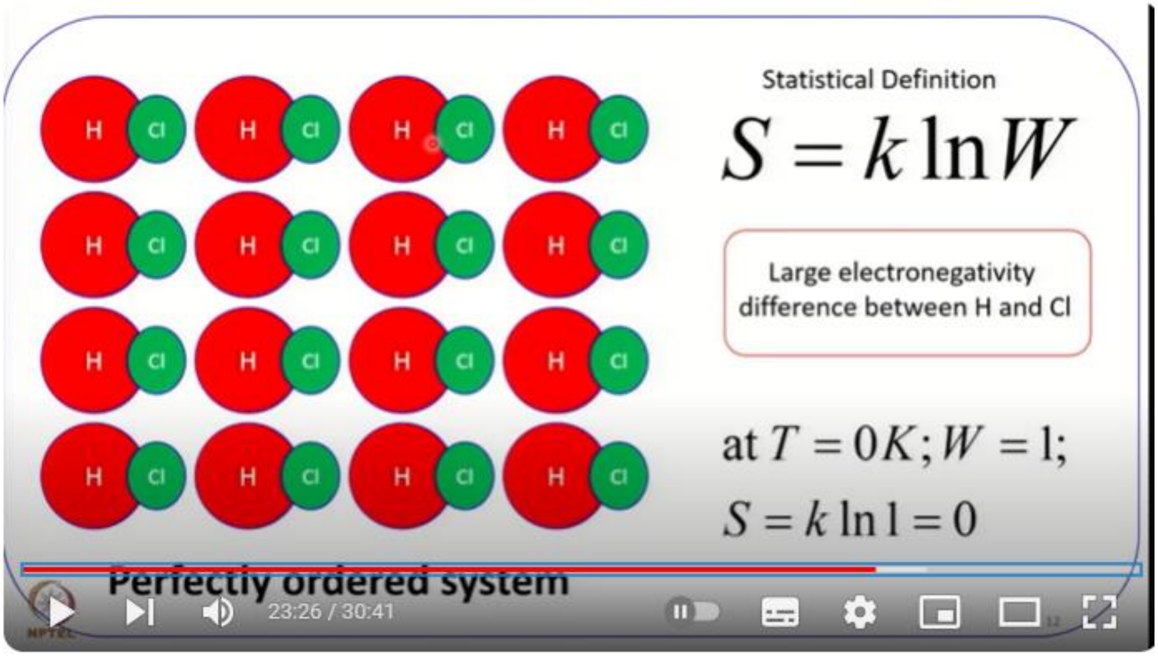

Statistical Definition

$$S = k \ln W$$

Large electronegativity difference between H and Cl

at $T = 0K; W = 1;$

$S = k \ln 1 = 0$

Perfectly ordered system

In this case the weight of a configuration is equal to 2. And just even I look at this arrangement suggest that this is not perfectly ordered system. There is some disorder and this disorder which is still existing at absolute 0 we called it as residual entropy and we had a way of even calculating the residual entropy. Once we have statistical weight then S is equal to K log W you substitute and the value which you get is 5.76 joules per Kelvin per mole this is at absolute 0.

Therefore, the entropy of all substances is not 0 at absolute 0 it is only 0 for perfectly crystalline substances. And if it is not 0 if there is some disorder present at absolute 0 then that value that entropy is called residual entropy alright. So, we had expression for q from q we switched over to U and we had expression for Q. And from U we switched over to S, S is equal to U minus U (0) by T plus n k log k. And in derivation of these equations, we never said that temperature should be positive or negative.

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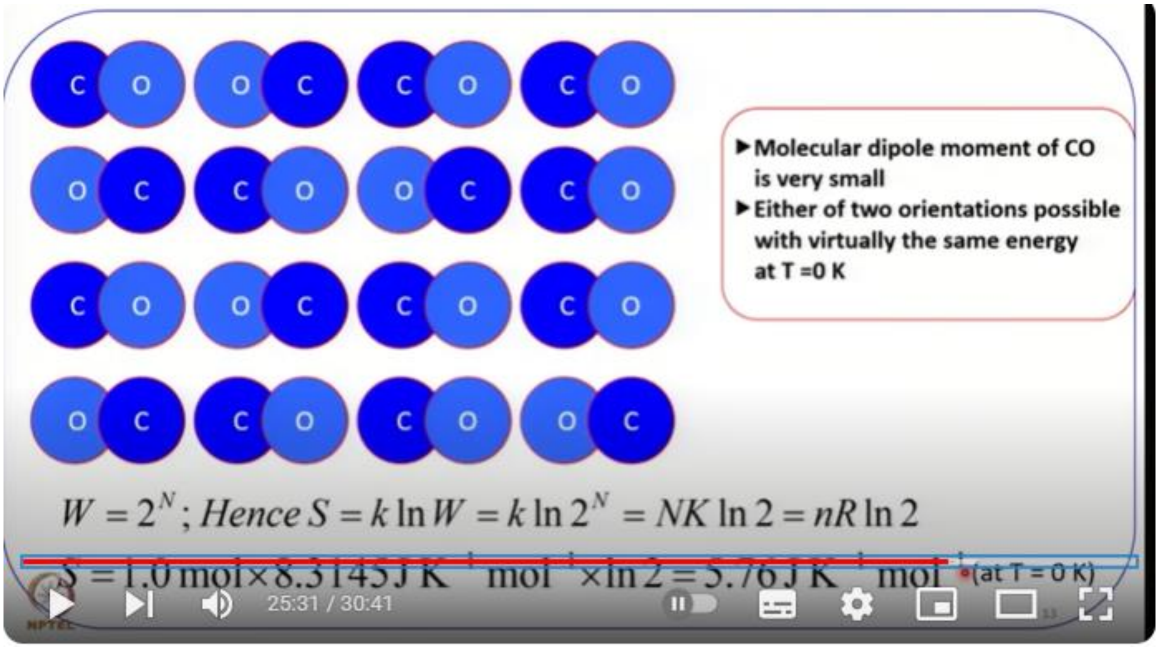

- Molecular dipole moment of CO is very small
- Either of two orientations possible with virtually the same energy at T =0 K

$$W = 2^N ; Hence\, S = k \ln W = k \ln 2^N = NK \ln 2 = nR \ln 2$$

$$S = 1.0\,\mathrm{mol} \times 8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}} \times \ln 2 = 5.76\,\mathrm{J\,K^{-1}\,mol^{-1}} \text{ (at T = 0 K)}$$

That means, the expressions that we derive here they are applicable to positive as well as negative temperature. Positive versus negative temperature is a subject of another discussion. But what we did was we derived q we connected that q with the internal energy we connected that q with entropy of the system alright. So, once we had the molecular partition function remember that we started with independent molecules. We said that let us assume that they are not interacting with each other and if they are not interacting with each other, you can consider NVT which is canonical ensemble.

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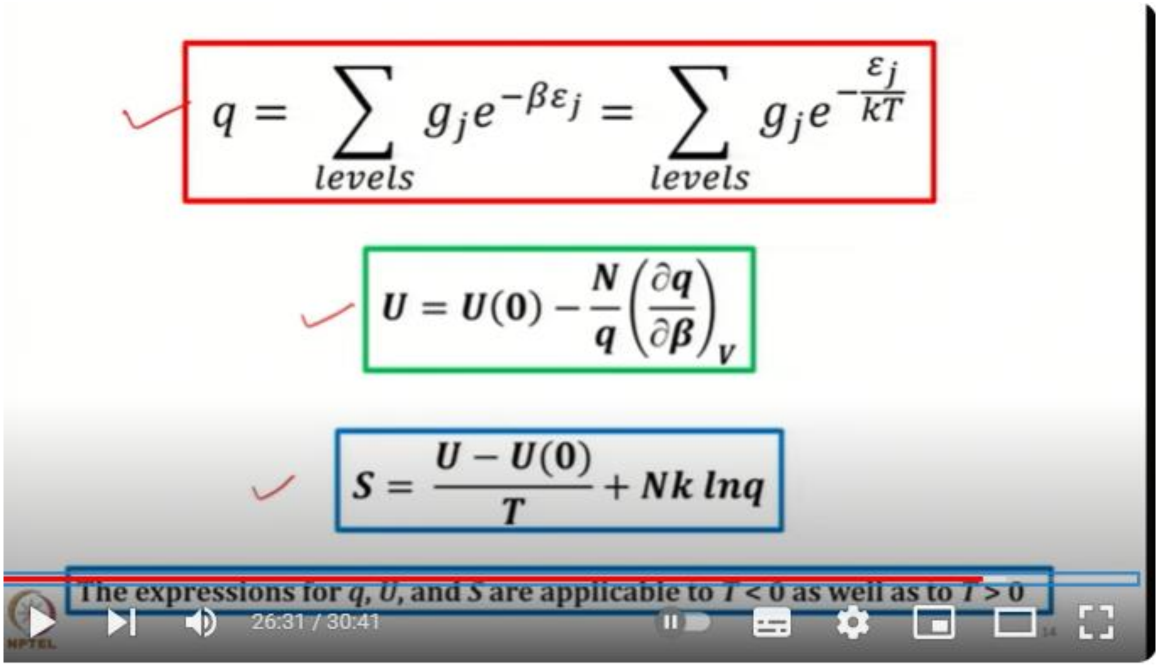

$$q = \sum_{levels} g_j e^{-\beta\varepsilon_j} = \sum_{levels} g_j e^{-\frac{\varepsilon_j}{kT}}$$

$$U = U(0) - \frac{N}{q}\left(\frac{\partial q}{\partial \beta}\right)_V$$

$$S = \frac{U - U(0)}{T} + Nk\,lnq$$

The expressions for q, U, and S are applicable to $T < 0$ as well as to $T > 0$

Therefore, we based our further discussion on canonical ensemble because we did not address the interaction between particles to large extent. We introduced the concept of micro canonical ensemble in which NVE energy is same NVT. NVT means temperature is same energy need not be same molecules can interact let the energy be exchanged between different members. Then that exchanging energies that means exchange of energies we allowed in canonical ensemble where N was constant V was constant and T was held constant. But if you hold E constant then it becomes micro canonical ensemble.

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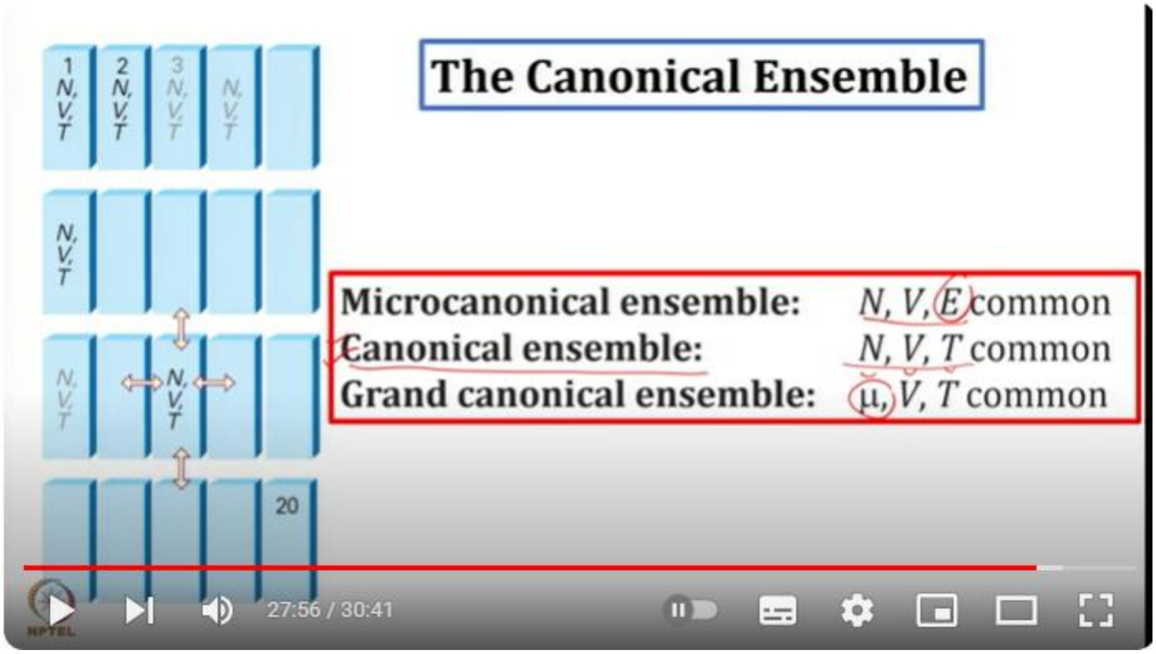
The Canonical Ensemble

Microcanonical ensemble: N, V, E common

Canonical ensemble: N, V, T common

Grand canonical ensemble: μ, V, T common

If you also hold chemical potential constant it becomes grand canonical ensemble. Therefore, you can proceed with an ensemble which is your target the ensemble that you want to consider. Therefore, by bringing in the concept of ensemble we allowed even the interaction between the particles to take place. So, once we define an ensemble, we have canonical partition function and this canonical partition function was to be connected to molecular partition function. We showed that if the particles or molecules are distinguishable then q is equal to small q raise to the power n.

That means, canonical partition function is equal to molecular partition function raise to the power n and for indistinguishable particles we discussed that the canonical partition function is equal to let me correct it this should be molecular partition function raise to the power n divided by n factorial. So, once we had established a connection between canonical partition function and molecular partition function, we were all set to connect the canonical partition function with all the thermodynamic quantities and then discuss the other derivable thermodynamic quantities from the equations that we develop in various lectures of this course. This was a major part of our course where we understood what is canonical partition function and what is molecular partition function. How to recover molecular partition function from canonical partition function is described in this discussion. Next in the next lecture we will see that how these canonical partition function or molecular partition function could be connected to the other thermodynamic quantities and useful information could be derived from those. Thank you very much. Thank you.