Thermodynamics for Biological Systems:
Classical and Statistical Aspects
Prof. Sanjib Senapati
Department of Biotechnology
Indian institute of Technology - Madras

Lecture – 67
Ensemble Approach

Till now we have made the link between partition function and various thermodynamic quantity of a N particle quantum system. And the approach was mainly led by Boltzmann and that approach is called the Boltzmann statistics.

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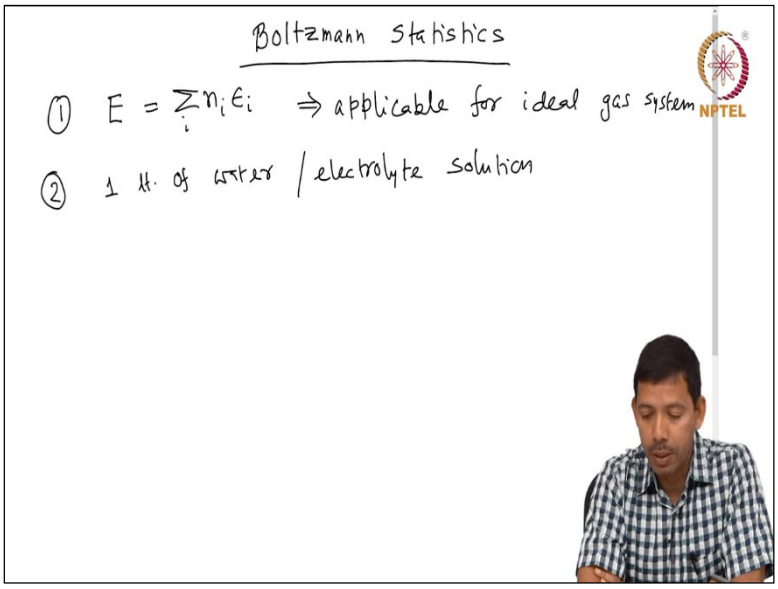

So, what we have seen so far is also called Boltzmann statistics were Boltzmann based on the distribution of the particles across the energy states in a quantum system, defined the partition function and from the partition function we made link of various thermodynamic quantities. Now one of the problems one of the drawbacks of the Boltzmann statistics number one drawback is Boltzmann considered that particles are non interacting.

And therefore total energy of the system he could write as sum over ni epsilon i that is total energy of the system is sum of the energy of the of the particles of the individual particles and these particles are non interacting. And therefore Boltzmann statistics is applicable only for ideal gas systems were the inter particle interactions are very few. But if you consider system let us say one litre of water or an electrolyte solution.

So here not only we have inter particle interactions but also the fact that the degeneracy of the lowest energy state alone is 10 to the power N where N is total number of particles. So, when you have a liquid system or when you come to a more complex biological system so there number of energy states to be consider is enormous 10 to the power N it is just a degeneracy of the lowest energy state. And therefore the Boltzmann statistics will not be appropriate to apply.

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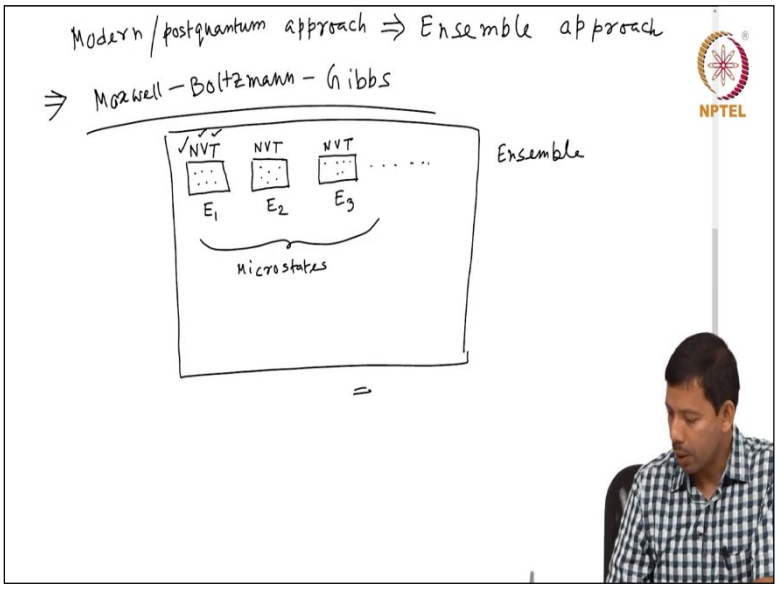

So at that point we follow another approach which is called the modern or post quantum approach which is called the ensemble approach. And this ensemble approach was proposed by Maxwell-Boltzmann and particularly by Gibbs. So, post quantum approach of statistical thermodynamics is called the ensemble approach proposed by Maxwell Boltzmann and Gibbs.

So, according to the ensemble approach now we need not look at the quantum states for our liquid system or for biomolecule system there are so many quantum states that instead of looking at them we can look at the distribution of the particles at different time point. So, let us see what is in ensemble? So, let us say that this is my box and I have N number of particles in that and this box is having a volume of V and the temperature of the system is T. So, here my particles in number of particles are distributed in certain ways.

And this gives me the energy of the system is E1 I can have the same system with same number of particles same volume same temperature but now the particles distributed little differently. Here energy of the system would be E2 here could be another instance where number of particles are same volume is the same the temperature is same with the particles are distributed again

differently. Here energy could be E3 so here numbers of particles are fixed but the heat con flow and since it can throw the energy of the system can vary.

And why the energy of the system is varying is because the inter particle interactions are different because the particles are distributed differently. So, you can have different such states and the collection of these microstates. So, here each of them are microstates so these are the different microstates where they differ microscopically. Here the microscopic difference is the particle arrangements are the arrangement of the particles are different.

So this is ensemble where we have lot many microstates which are different microscopically in the distribution of particles are different but macroscopically they are same. So, when it is microscopically so all the microspheres have same number of particles all of them do have same number same volume all of them do have same temperature. So, in this ensemble all the microstates have same NVT same thermodynamic quantities but microscopically they are different from that distribution of the particles.

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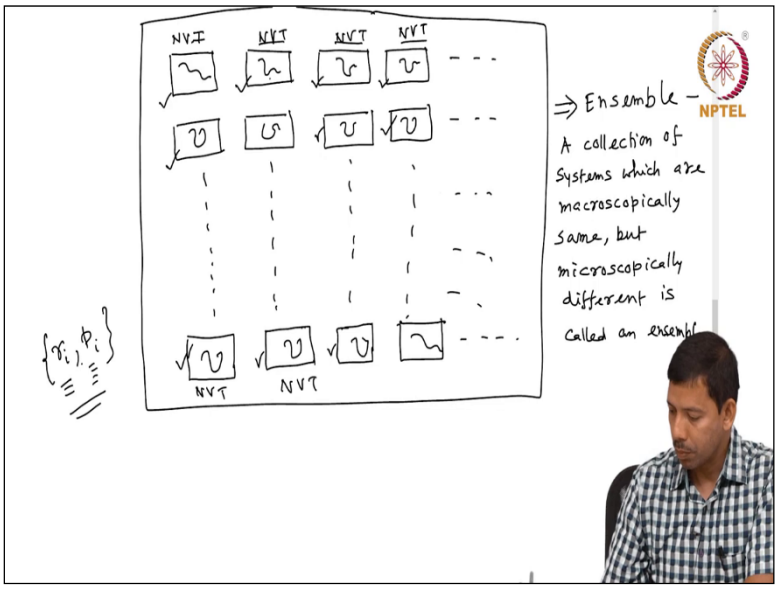

So the definition of ensemble I will make clearer by taking a more relevant example of this course which is reaches to a biomolecule. Let us say I have a protein and I am putting that protein in a box and I say the protein a small polypeptide. Let us say the polypeptide was you know unfolded straight here and I see the protein in our different time instant and I see the evolution of the peptide is like this. So, so everywhere my total number of particles in the box volume and temperature all I am keeping fixed.

All so all boxes do you have them NVT so here particulars like this never mind my drawing the boxes may not look the same but assume that all my boxes are of exactly the same dimension and I had the same NVT it is just that .just a polypeptide is changing its conformation. So, this goes on so I can have many such states I can have many such states, many of them and each of this drawing is basically signifying a microstate of this polypeptide.

So, I can have many such microstates and, this collection of system is called the ensemble. So, what is ensemble? So, I can define ensemble is it is a collection of systems which are macroscopically same. So here are all of them do have same microscopic contraries. So, all of them have the same NVT number of particles volume and temperature fixed.

So a collection of systems which are microscopically same but microscopically different is called an ensemble. A collection of systems which are microscopically same but microscopically different is called an ensemble. So, here microscopically did they differ in the conformation of the protein. So, you see here the polypeptide was unfolded here it is you know half folded and so here it is it is kind of going through some various metastable states.

So, the polypeptide is basically under going through different conformations and from unfolded to fold it and from fold it can go back again to the unfolded states. So, if you look at it so they are differing not in their quantum energy states but they are differing in their conformation.

So, this conformation we can represent by ri and pi, so require ri is basically the coordinates of each atom constituting the polypeptide and pi is the momentum mass into velocity of each atom are in the polypeptide. So, basically this set of our ri and pi they define the different conformation in the whole. So, what we need to get is basically if you want to; now if you want to compare our statistical thermodynamic quantities with the classical thermodynamic quantity.

What you have to do we have to basically take an average over all these ensembles we have to take an average over all these microstates and then the average quantity of that of all the microstates will give us the thermodynamic property.