Thermodynamics for Biological Systems:
Classical and Statistical Aspects
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Lecture – 68
Ensemble Average, Time, Ergodic, Hypothesis

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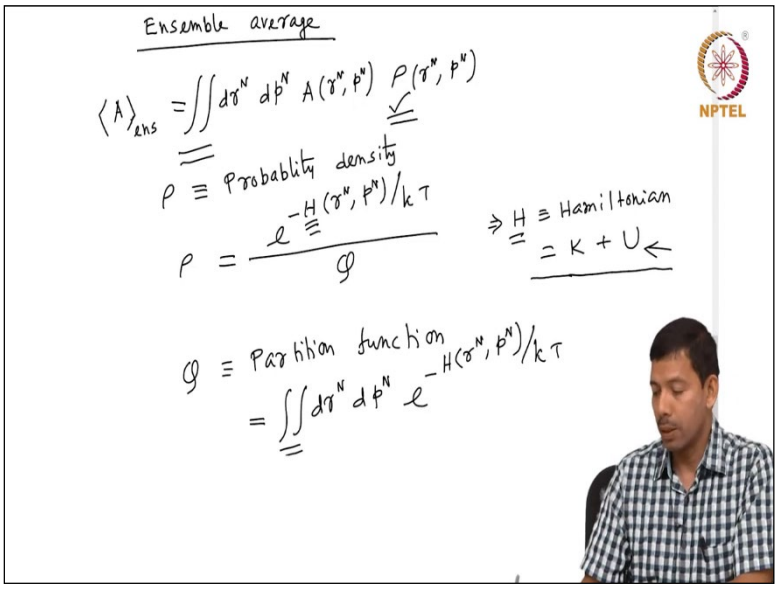

So, therefore we now define something called the ensemble average. So, how do you find ensemble average let us say A is a thermodynamic quantity and we want to get the ensemble average of A.

$$\langle A \rangle_{ens} = \iint dr^N dp^N \, A(r^N p^N) \rho(r^N p^N)$$

So, the ensemble average is usually depicted as this within bracket and ensemble. So, ensemble average of thermodynamic quantity A can be expressed as dr N where r as I said coordinates of each constituent in the system and N is number of particles, so I need to have two integral one for r 1 for p and then A the instantaneous value of A in each microstate.

And then we should have this will have the Rho rN where Rho is called the probability density. So, Rho the probability density and this Rho can be defined as

$$\rho = \frac{e^{-H(r^N p^N)/kT}}{Q}$$

$$Hamiltonian\ (H) = K + U$$

k is the Boltzmann constant and H is that total energy which is the Hamiltonian of the system. Hamiltonian of the system which is the total energy is a group kinetic energy plus the potential energy of the system.

$$Partition\ function\ (Q) = \iint dr^N dp^N\ e^{-H(r^N p^N)/kT}$$

So H is nothing but a total energy of the system. And Q is the partition function Q is a partition function and so basically when you take the ensemble average the concept is very similar what we have seen in the Boltzmann statistics but how we improved on here in ensemble average is that when you take H.

So we have the inter particle interactions as we will see a latter, so inter particle interaction has been introduced in our formalism through the potential energy. So, through this U and then 2H the Hamiltonian we have introduced the inter particle interactions into the system into our into our calculations. So, that is one advantage and number two is now we do not have to look at the 10 to the power N degeneracy that every state in the quantum system will have.

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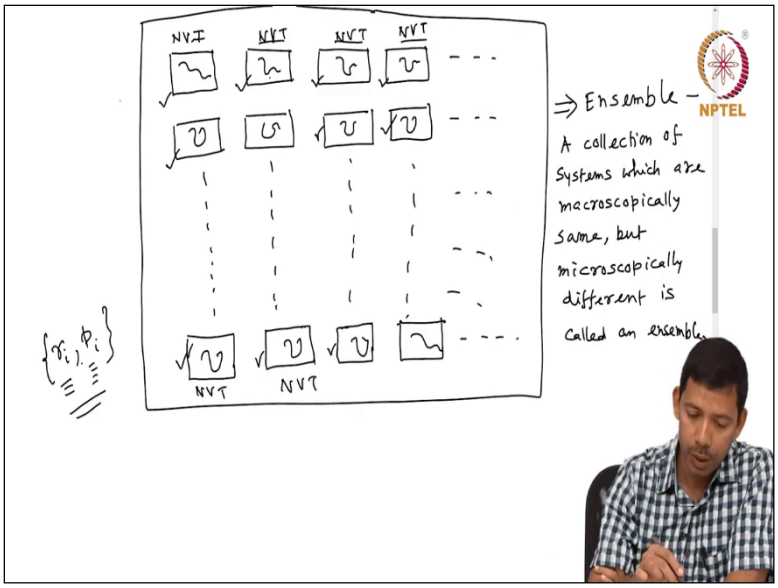

Now instead of looking at the quantum states we are basically looking at each of the microstates as I defined here and each of the microstate is basically defining the different conformation of my molecule of interest on my biomolecule or my lipid molecule of interest. And so basically by ensemble average we are since if you look at it we have this probability density term and this probability density term is basically giving the taking the importance of the confirmations which are occurring more frequently than the others.

For example here out of many confirmations that or that occur here you can see that some of the confirmations like this one they are occurring much more frequently than this particular conformation and therefore when you take the ensemble average you will get the microstate which are more frequently having a greater contribution in the ensemble average and that was again the definition of partition function on Boltzmann statistics provided.

So, basically we have the same concept here it is just that we have now get rid of the; we just now introduced the inter particle interactions and also now here instead of the quantum state you can just look at the microstates in terms of the different distribution or different conformation of my molecule. Now if you look at the definition of ensemble average and we have the integral and it implies that to get down ensemble average we need to generate enormous number of microstates as they appear in the ensemble.

So, when you talk about a one litre of water or when you talk about the confirmation of the biomolecule the biomolecule or the water can have enormous number of microstates because the molecules are always in moving. So, it is actually very difficult rather impossible to capture all possible microstates in an ensemble because the number is just infinite.

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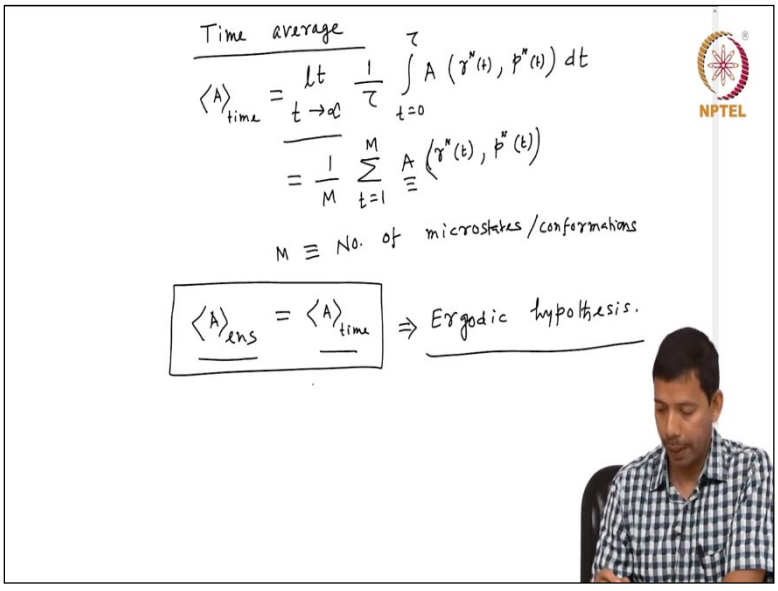

So, instead of going for ensemble average a simpler definition of taking the average is time average. So, in the time average depiction instead of looking at instead of waiting for all possible microstates we basically take the average of average for all those microstates which we can capture within a stipulated time. And so according to this time average we can define a time as

limit t tending to infinity meaning our time should be large enough so that we can cut capture as many possible microstates as we can.

$$\langle A \rangle_{time} = \lim_{t \to \infty} \frac{1}{\tau} \int_{t=0}^{\tau} A\left(r^N(t), p^N(t)\right) dt$$

$$\langle A \rangle_{time} = \frac{1}{M} \sum_{t=1}^{M} A\left(r^N(t), p^N(t)\right)$$

$$M \equiv number\ of\ microstate/conformations$$

So, basically time over is saying that within you within our stipulated time whatever number of confirmations or microstates we have captured.

So confirmations in the context of bio molecules so time emerges basically take the average of the property of interest which is A over the number of confirmations we have captured in that time frame. So, time average is basically a finite quantity. But here that catches this time so long at the time we take more and more number of microstates we will be able to capture and therefore our time average will be very close to the ensemble average.

Another hand if we do not consider many more microstates there is a possibility that we are neglecting the microstates which might occur at a lot of matter time with more probability a proportion. So, when our time is long enough the time averaged an ensemble average should converge. So, a situation where my ensemble average is equal to time average this situation is called **the Ergodic hypothesis**.

$$\boldsymbol{\langle A \rangle_{ens} = \langle A \rangle_{time}}$$

This is all the Ergodic hypothesis where Ergodic the scientists said that explore your system for a long enough time and then your time should be almost equal to the ensemble average because ensemble average is the ultimate target where we should we should explore all possible microstates and then if you take average over all the microstates we get the exact average value of the thermodynamic quantity.