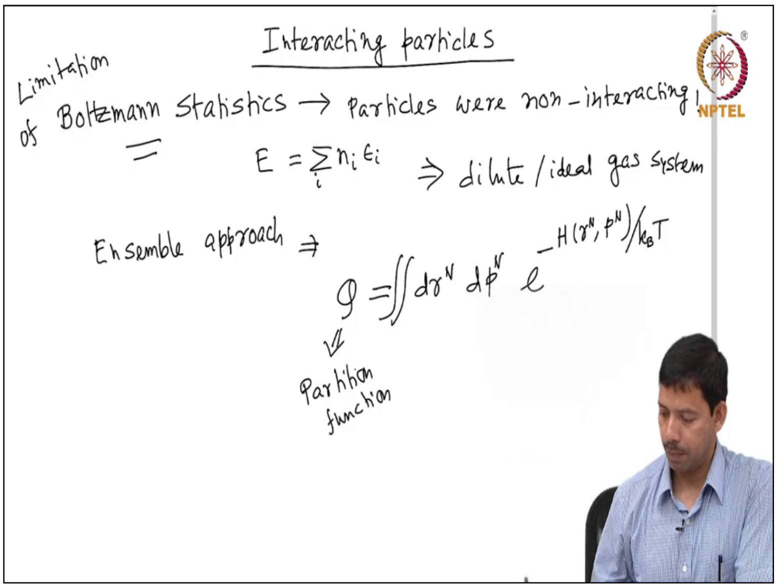
Thermodynamics for Biological Systems:
Classical and Statistical Aspects
Prof. Sanjib Senapati
Department of Biotechnology
Indian institute of Technology - Madras

Lecture – 69
Partition Function for Classical System

(Refer Slide Time: 00:17)



Interacting particles

Limitation of Boltzmann Statistics → Particles were non-interacting!

$E = \sum_i n_i \epsilon_i$ ⇒ dilute / ideal gas system

Ensemble approach ⇒

$$Q = \iint dr^N dp^N e^{-H(r^N, p^N)/k_B T}$$

$\Downarrow$

Partition function

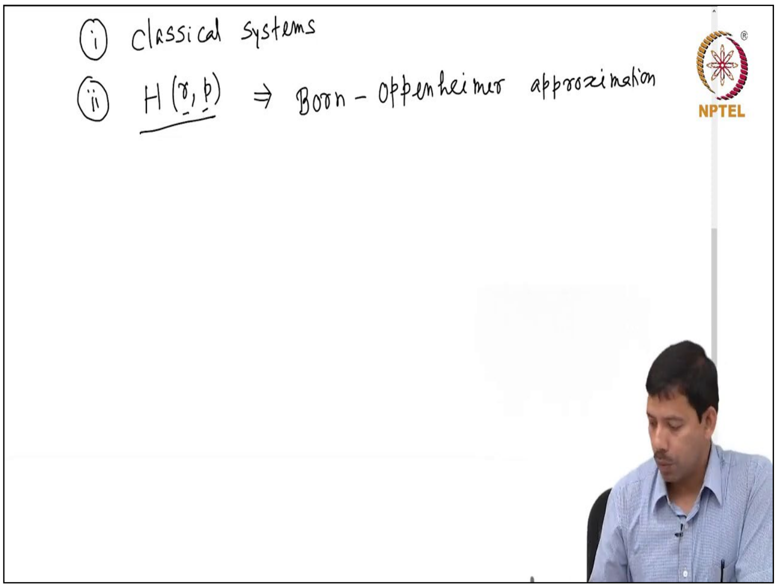
Interacting particles so if you recall we said that the limitation of Boltzmann statistics which we started from we started from Boltzmann statistics and the limitation of Boltzmann statistics was that particles were non-interacting and that is why the total energy of the system we could write as sum over individual particle energy. So, this is good for a dilute or ideal gas system.

But here we are more interested in a biological system or dense liquid system where particles are very much interacting and therefore the Boltzmann statistics will not work well there and therefore we move on to the ensemble approach. And in the ensemble approach we got the partition function Q as

$$Q = \iint dr^N dp^N \; e^{-H(r^N p^N)/k_\beta T}$$

H is the Hamiltonian , Boltzmann constant k.

(Refer Slide Time: 03:08)



(i) Classical systems

(ii) $\underline{H(\underset{-}{r}, \underset{-}{p})} \Rightarrow$ Born - Oppenheimer approximation

So, here are a few things we need to remember is that now we have shifted to the classical regime and we are treating the classical systems here. Because the biomolecules or the liquid state of a system is basically a large systems they are large systems and therefore large systems cannot be tackled quantum mechanically and therefore from now onwards wherever it will be talking about the biological molecules thermodynamics or the statistical thermodynamics of biological system.

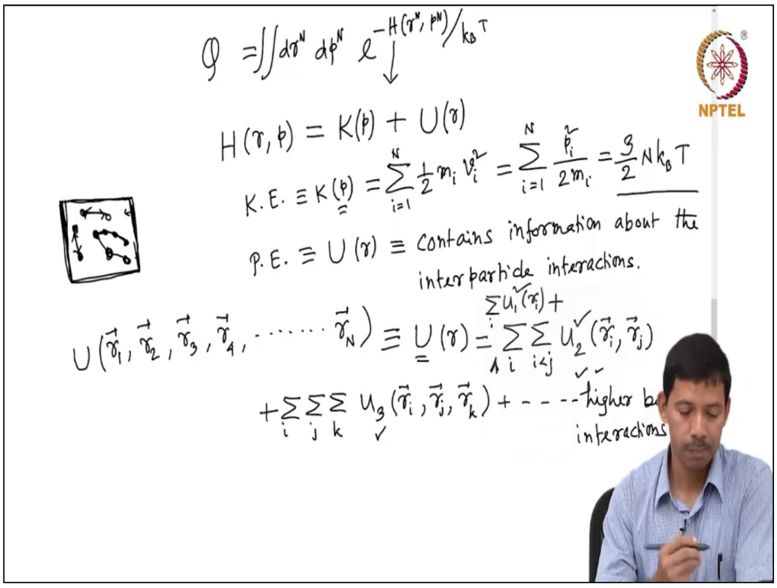
We are basically in the classical regime and we will be talking about classical mechanics not the quantum mechanics. And the other thing we need to remember is that like we retain Hamiltonian which is a function of r and p, for r is a coordinate of a particle and p is a momentum. So, here the r and p they represent the nucleus of the atom and to have this we have introduced or we have taken care a very important approximation called Born Oppenheimer approximation.

So Born-Oppenheimer approximation assumes that you know in an atom the nucleus the motion of the nucleus and the motion of the electrons are independent. And therefore so that is one that the motion of the nucleus and the motion of the electrons are independent and since the electrons they move much faster they basically move so fast they have an electronic cloud around the nucleus and therefore the electronic motion can be erased out.

So in classical mechanics all you have to do is basically look at the motion of the nucleus alone because the motion of the electrons is so fast in that the motion of the electrons can be averaged out and you just look at the motion of the nucleus and thats a Born-Oppenheimer approximation which we have implemented here and therefore the r and p what you see here in the partition function and in the Hamiltonian they are basically the position and the momentum of the nucleus of atoms all right.

So, we have to introduce the interactions among the particles in this regime for the biological systems and how do we do that?

(Refer Slide Time: 06:50)



$$Q = \iint dr^N dp^N e^{-H(r^N,p^N)/k_B T}$$

$$H(r,p) = K(p) + U(r)$$

$$K.E. \equiv K(p) = \sum_{i=1}^{N} \frac{1}{2} m_i v_i^2 = \sum_{i=1}^{N} \frac{p_i^2}{2m_i} = \frac{3}{2} N k_B T$$

P.E. $\equiv U(r) \equiv$ contains information about the interparticle interactions.

$$U(\vec{r}_1, \vec{r}_2, \vec{r}_3, \vec{r}_4, \ldots\ldots \vec{r}_N) \equiv U(r) = \sum u_1(\vec{r}_i) + \sum_i \sum_{i<j} u_2(\vec{r}_i, \vec{r}_j) + \sum_i \sum_j \sum_k u_3(\vec{r}_i, \vec{r}_j, \vec{r}_k) + \text{- - - - higher b}$$

interactions

$$Q = \iint dr^N dp^N \; e^{-H(r^N p^N)/k_B T}$$

$$H(r,p) = K(p) + U(r)$$

$$Kinetic\ energy\ (K.E) \equiv K(p) = \sum_{i=1}^{N} \frac{1}{2} m_i v_i^2 = \sum_{i=1}^{N} \frac{p_i^2}{2m_i} = \frac{3}{2} N k_B T$$

$$Pottential\ enrgy\ (U) \equiv U(r) = U(\overrightarrow{r_{1,}}\, \overrightarrow{r_{2,}}\, \overrightarrow{r_{3,}}\, \overrightarrow{r_{4,}} \ldots \ldots \overrightarrow{r_{N,}})$$

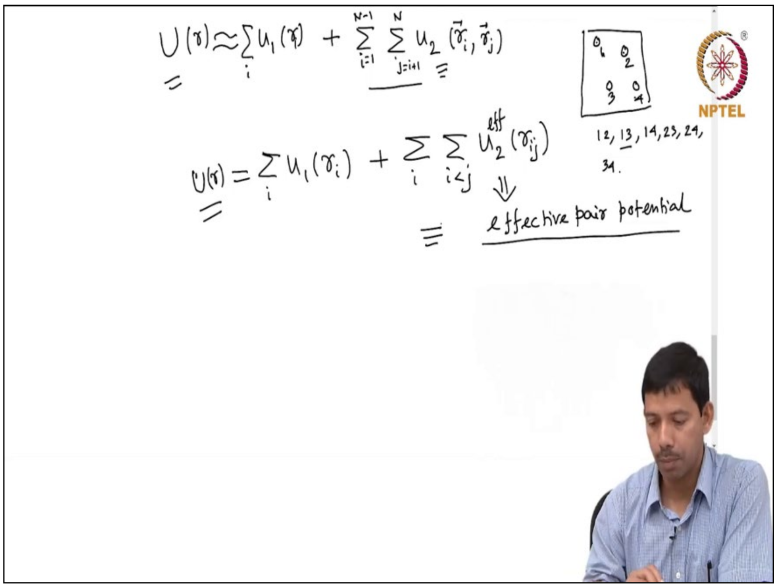
So, you saw that my partition function Q had the partition function is a function of Hamiltonian. What is this Hamiltonian? So, Hamiltonian or which is a function of r and p represent the total energy of the system and total energy of the system is the sum of kinetic energy and the sum of the potential energy. Kinetic energy is a function of p and the potential energy is a function of r.

So, as you see the kinetic energy is constant p is constant Boltzmann constant and till their temperature is fixed for system. So, the kinetic energy is fixed the potential energy U which is a function of r this basically contains the information about the inter particle interactions. So, Ur contents information about inter particle interactions. How? because U your total U the potential energy it basically is a function of particle 1 is a function of particle 2 is a function of particle 3 function of particle 4 and is a function of overall N particle.

If the particles are contained in a container and the part the wall of the box is influencing the particle motion.

Then you also have our term interactions where the wall is influencing the motion of each particle. So, that you can say one body interaction if the box; if the container is influencing the motion of the particles. Apart from this the two body interactions here so total energy total potential energy. Now is the sum of 1 body interactions 2 body interactions 3 body interactions and the higher body interactions.

(Refer Slide Time: 15:58)



$$U(r) \approx \sum_i u_1(r) + \underline{\sum_{i=1}^{N-1} \sum_{j=i+1}^{N}} u_2(\vec{r}_i, \vec{r}_j)$$

$$U(r) = \sum_i u_1(r_i) + \sum_i \sum_{i<j} u_2^{eff}(r_{ij})$$

$$\Downarrow$$

$$\equiv \underline{\text{effective pair potential}}$$

So, what do you mean by this 2 body and 3 body interactions and what is the definition of 3 body interactions. Let us look at here, so this is our box which contains these particles and so two body interaction is the interaction between this and this or this on this, this is a two body interactions. But the particle here and the particle here they also can have interactions through this particle. So, I am talking about interaction of this to this through this.

So, this is the 3 body interactions we can have 4 body interactions if particles are you know line very close so this particle and this particle can have interaction through the intermediate particles and this is called the 4 body interactions. So, in reality we have many kinds of interaction. Interaction of this container wall on the particles which is this 1 body interaction, we can have paired interaction between each pair of particles which is here.

Then we have 3 body interaction between particle 1, 2 and 3 which is 3 body interactions we can have 4 body interactions between 1, 2, 3 and 4 and we can have many higher body interactions but if you look at it carefully the pair interactions will have the largest contribution because pair is basically the particles find to each other more closely than the 3 body or 4 interactions.

So, for practical purposes the total U which is a function of r very often is written–

$$\boldsymbol{U(r) = \sum_{i} U_1(r_i) + \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} U_2(\overrightarrow{r_i}\,\overrightarrow{r_j})}$$

So, that we do not count the same pair interaction twice when we put this in equality we make sure that we do not count the same interaction twice.

For example if I have a system of four particles total number of pair interactions we have 1 2, 1 3, 1 4 then we have 2 3, 2 4 and then we have 3 4 these are the distinct interactions we can also consider 2 1 but 1 2 and 2 1 are the same interactions likewise 1 3 and 3 1 are the same interactions 4 1 and 1 4 are the four interactions. So, if we count 1 2 and 2 1 so that means we are over counting the number of interactions. And therefore we should not over count and because and to overcome that the over counting we have put this inequality where j is more than i, j is exactly i + 1 to N and i is equal to 1 to N -1 okay.

So that is the definition of pair interactions and since pair interactions contribute measurably this is not a bad approximation that my total U is sum over 1 body interaction if the particle wall is influencing the particles plus the pair interactions between the particles we can easily omit the 3 body 4 body and the hybrid interactions. There is also a when we model those pair potentials we also can make this pair potential better by looking at the experimental data.

$$\boldsymbol{U(r) = \sum_{i} U_1(r_i) + \sum_{i} \sum_{i<j} U_2^{eff}(r_{ij})}$$

And by using the experimental data we can improve this pair potential which to some extent or indirectly incorporate the higher body interaction terms and in that case this u2 is called the u effective pair potential where this is called effective pair potential. So, what is the effective potential effective pair potential is something which is better than the regular pair potential. In effective pair potential the interactions of higher body terms have been indirectly incorporated into the u2.

And how we have we can incorporate the higher body influence into u2 that will be clear to you shortly when I write some of the expressions of these u2. So, because of this effective pair potential and the definition of u total u in terms of effective pair potential is not a bad approximation and it gives a pretty good match in this match data okay. So, as you see this effective pair potential basically talks.

And with the inter particle interactions that is what we are talking about here that in Boltzmann statistics. Since we miss the inter particle interactions we need to introduce interpreting interactions in the liquid system or the biological systems and therefore we have introduced inter particle interactions through the potential energy. And my total potential energy of the system is nothing but sum over all the pair interactions.

Now so if you have this effective pair potential known then we have a good hand on u and therefore we have a good hand on H the Hamiltonian because kinetic energy is constant and therefore we have a good hand on the partition function once we have the partition function known, we know everything about the system we know every thermodynamic quantity of the system.