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

Lecture – 71
Potentials for Molecular System

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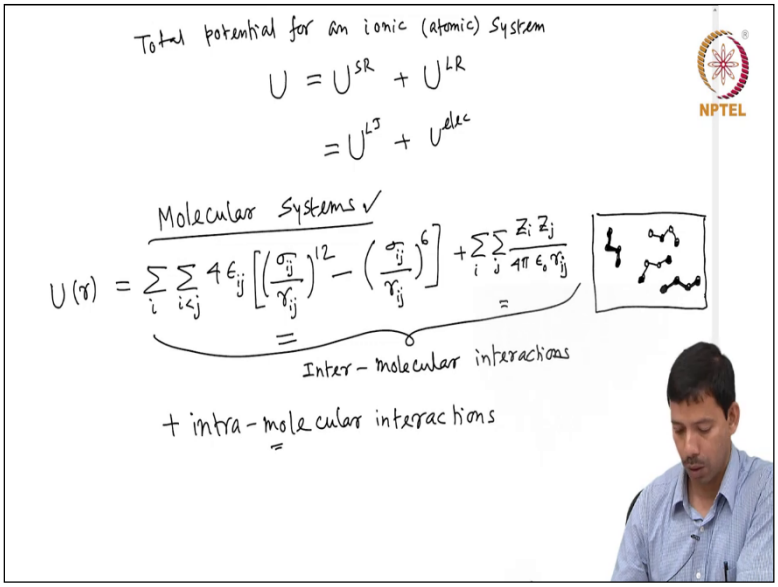

Atomic to molecular systems how are potential chances, so for molecule system what will be our total U so when you are talking about a molecular system, this is what I am talking about so previously our particles were just atoms but here now our particles are our systems are composed of molecules. I have this molecule I have several such molecules floating in the system.

So I am talking about now the total U for this system. So, each molecule is composed of 4 atoms as I have drawn here. So, therefore this atom will interact with this atom this atom will interact with this atom this atom will interact with this atom this atom is interact also this atom this one will also interact with this atom by pair potential. So, we have one of those inter particle pair potentials one of them let us say we say we take the Lennard-Jones.

Total potential for ionic system–

$$U = U^{SR} + U^{LR}$$

$$U = U^{LJ} + U^{elec}$$

For molecular system-

$$U(r) = \sum_i \sum_{i<j} 4\varepsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right] + \sum_i \sum_j \frac{Z_i Z_j}{4\pi\varepsilon_o \, r_{ij}}$$

$$+ intra\ molecular\ interactions$$

If we take the Lennard-Jones so we have i's and j's for epsilon ij Sigma ij divided by r ij to the power 12 minus Sigma ij r ij to the power 6 so we have the short-range potential if the particles you know or biological systems of particles also have their partial charges it correct this one instead of saying atomic charges I would prefer to say partial charges, so, therefore how this plus you also have sum over i sum over j Zi Zj by 4 PI epsilon 0 r ij.

So, these are; these 2 are inter molecular interactions apart from this we also have intra molecular interactions. We also have intra molecular interactions and what are those intermolecular interactions because in the molecule we have bonds this particle is connected to this particle by an bond, this particle is also connected to this particle by an angle and this particle also connected to this particle by dihedral angle.

So here in each of my molecule I do have an angle here I am sorry I do have a bond between here and here here and here another bond here and here on the bond. And each molecule also have angles here is one angle here is another angle and then I do have a dihedral composed of 4 atoms. So, these are the intra molecular interactions. So, for a molecular system apart from the Leonard-Jones or hard sphere plus electrostatic we also have the intra molecular interactions. So, what is the form of the inter intra molecular interactions that we need to incorporate into only here.

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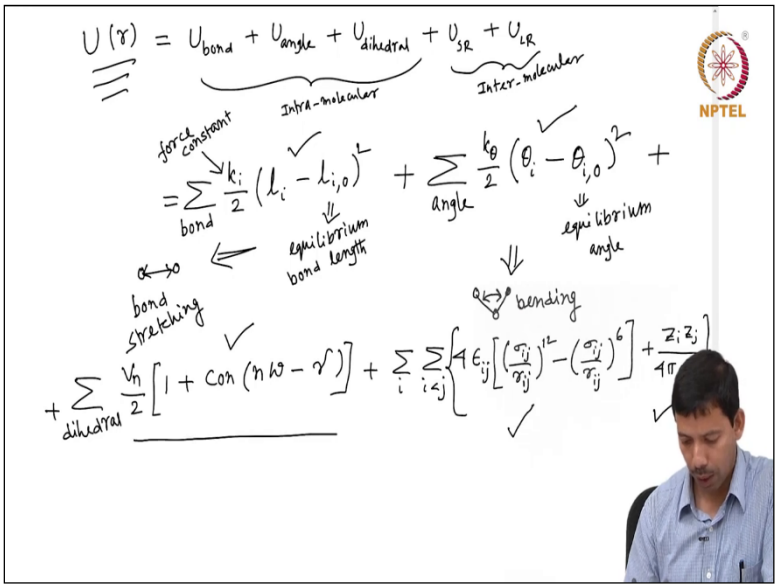

$$U(r) = U_{inter-molecular} + U_{intra-molecular}$$

$$U_{inter-molecular} = \sum_i \sum_{i<j} 4\varepsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right] + \sum_i \sum_j \frac{Z_i Z_j}{4\pi\varepsilon_o \, r_{ij}}$$

$$U_{intra-molecular} = U_{bond} + U_{angle} + U_{dihedral}$$

So, total U r a molecular system will composed of as I said that it will have a bond potential it will have a angle potential it will have a dihedral potential plus it will have a U shot range plus U long-range inter molecular plus intra molecular interactions. So, my total U of a molecule would be something like this which we can expand as you bond we can write as something like this sum over all bonds into the system all bonds.

$$U_{bond} = \sum_{bond} \frac{k_i}{2} \left(l_i - l_{i,0} \right)^2$$

k_i – is the force constant

$l_{i,0}$ – equilibrium bond distance

This can be written as ki by 2 by Hookes law so not to confuse you I would say li - li where this is the equilibrium bond length and ki is the force constant. So, this is overall bonds likewise angle also we can express by Hookes law. So, here I write k theta by 2 and I can express that as theta i - theta - theta i 0 square here again this is the equilibrium angle. So, basically this term represents this term represents the bond stretching.

$$U_{angle} = \sum_{angle} \frac{k_\theta}{2} \left(\theta_i - \theta_{i,0} \right)^2$$

k_θ – is the force constant

$\theta_{i,0}$ – equilibrium angle

How this bond basically stretches and compresses so this is the bond stretching contribution. This term represents the bending the angle bending plus you have the dihedral term from here I come to dihedral which we can write sum over all dihedral so this is one of the different forms for dihedral one can write of course for angle also you have more sophisticated potential. But the potential based on Hook's law also holds good for most of systems.

$$U_{angle} = \sum_{dihedral} \frac{V_n}{2}[1 + \cos(n\omega - \gamma)]$$

So, for dihedral the expression we can use his Vn by 2 1 + cos n Omega - gamma I will explain each of these terms very soon. So, this is dihedral so therefore 1 2 3 they are the intra molecular and then you have intermolecular okay. so this I can put together so this is the total potential of a molecule system where you have the bond contribution due to all bonds in the in the system you have the angle contribution from all the angles you have in the system.

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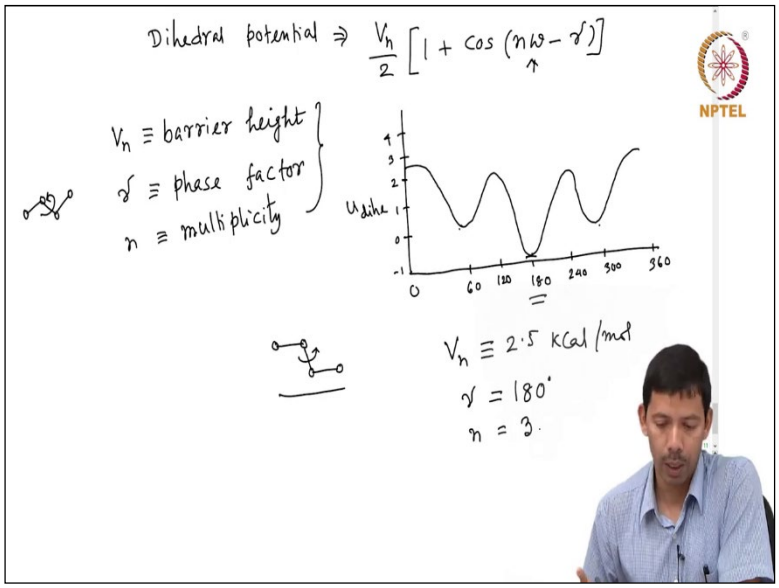

You have the dihedral contribution and then you have intermolecular interactions which can be defined by short range Leonard - Jones or one of the other products lab I have introduced and if you; if your particles are having partial charges then you also have that electrostatic potential. So, this is the total U of a molecular system. Now let us look at what are the different terms we have in this dihedral potential.

$$V_n = barrier\ height$$

$$\gamma = phase\ factor$$

$$n = multiplicity$$

Which we have written as V n by 2 1 + cos n Omega - gamma so what are the terms representing. So, the first term V n is called barrier height we call barrier height gamma is called the phase back phase factor and n is called the multiplicity and here Omega is basically the instantaneous value of the dihedral yes one thing I should have mentioned you hear is that so this li 0 is the equilibrium bond length whereas li is the instantaneous value of the bond which means that the bond is basically stretching and compressing.

So li 0 is an equilibrium bond distance around which it is stretching and coming back stretching and coming back. So, this change in li 0 change in bond length is basically they li. So, li is the instantaneous value of the bond length and li 0 is the equilibrium bond distance likewise your theta i is basically the instantaneous angle between particle i, j and k. Now atom i, j and k and theta i0 is the equilibrium angle between those 3 angles here.

And here also the Omega is basically the instantaneous value of the dihedral. So, what is dihedral? Dihedral is basically you have particle 1, 2, 3 and 4. So, this angle is called the dihedral angle, so which you can basically rotate from 0 to 360 degree and how in the process of this 1, 2, 3 and 4 how the energy is changing from 0 to 180 to 360 now so that is a dihedral potential and that is the definition of the dihedral angle.

So, how well so the definition of these 3 terms will be clear to you if I draw the U dihedral of let us say will draw for a single carbon-carbon bond. So, if I draw this let us say so this is my 180 so it is my 0-60 degree 120, 180, 240, 300 and 360. So, basically I have the single so with respect to this bond. I am basically rotating these 4 atoms and how the energy is changing and in x-axis this is my 0 this is -1 this is 1 this is 2 this is 3 and so on.

So the nature of this rotation dihedral is also called the torsional angle. So, this should look something like this, it is let me draw it little better okay. So, how you just need to change my; so this is 180 this is 60 0 I am sorry it is not exactly this should be 240 this is 300 and this is 360 ok. So, what is Vn so Vn is barrier height so here okay so if this is my 2 and so here Vn is the barrier height which is the maximum energy.

The rotation has to cross so the the the barrier basically the highest energy is here 2.5 so Vn is the barrier height which is 2.5 kcal/mol, gamma is the phase factor which tells the angle at which the energy is least, so here my gamma is 180 degree because this is the angle at which the energy is the least and n is the multiplicity which is basically the number of minima in the whole rotation. So, here I have one minima 2 minima 3 minima so n is 3, so this is the dihedral potential and this is intra molecular property what one has to include to make the model of our molecular systems.