Thermodynamics for Biological Systems:
Classical and Statistical Aspects
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Lecture – 70
Pair Potentials for Atomic System

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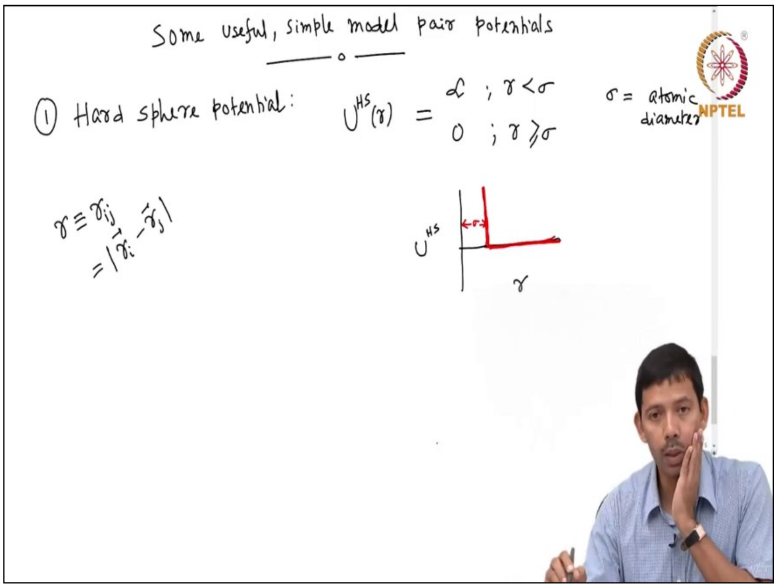

Some useful, simple model pair potentials

① Hard sphere potential: $U^{HS}(r) = \begin{matrix} \infty ; r < \sigma \\ 0 ; r \geq \sigma \end{matrix}$ σ = atomic diameter

$r \equiv r_{ij} = |\vec{r}_i - \vec{r}_j|$

So, some useful simple model the model potentials are following. One such model pair potential is called Hard Sphere Potential, so what is this Hard Sphere Potential?

$$U^{HS}(r) = \begin{matrix} \infty; r < \sigma \\ 0; r \geq \sigma \end{matrix}$$

Hard Sphere Potential is hard sphere let us take this as U since you are using U Hard Sphere Potential is basically is infinity for the inter particle distance less than Sigma. And it is 0 when r is greater than equal to 0 so this is the hard sphere pressure. The hard sphere potential tells that r which is basically r ij and r ij is nothing but the distance between ith particle and the jth particle, so this is my r which is r ij. So, basically what it tells is that if the inter particle interactions in the inter particle distance is less than Sigma where Sigma is the molecular diameter what outside the atomic diameter and when r is greater than 0 then potentially 0.

So if you draw this how from the potential look, so if I have to draw you U hard sphere versus r how will the potential look like? The potential so basically if you can see here, so that, so you are bringing up 2 particles together and then so it is just like this, so, this is our Sigma. It tells that when your r this is r when r is less than Sigma there are the particles repel each other and if r is here this would be this will be Sigma and when r is greater than equal to Sigma then U is 0.

So, this is the nature of hard sphere potential, so it is 0 for any value r greater than Sigma and it is infinity for r less than Sigma. So, this is hard sphere potential, so as you can see in the hard sphere potential we have only the repulsive part.

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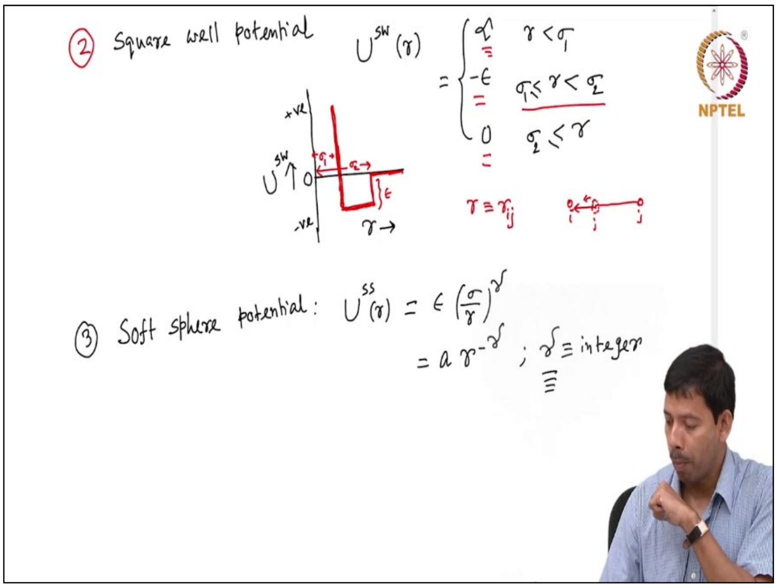

② Square well potential

$$U^{SW}(r) = \begin{cases} \infty & r < \sigma_1 \\ -\epsilon & \sigma_1 \leq r < \sigma_2 \\ 0 & \sigma_2 \leq r \end{cases}$$

$r \equiv r_{ij}$

③ Soft sphere potential: $U^{SS}(r) = \epsilon \left(\frac{\sigma}{r}\right)^{\nu}$

$= a\, r^{-\nu}$; $\nu \equiv$ integer

$$U^{SW}(r) = \begin{cases} \infty ; & r < \sigma_1 \\ -\varepsilon ; & \sigma_1 \leq r \geq \sigma_2 \\ 0 ; & \sigma_2 \leq r \end{cases}$$

The other model potential is called Square Well Potential, so square well potential is U square well it is infinity for r less than Sigma 1 it is - epsilon for r greater than Sigma 2 and it is 0 something like this when r is greater than equal to sigma 2. So, this is the square well potential. So, if you draw the square well potential with r how does look like? So, you see here we have two distances and we have a attractive potential here. So, if I draw so for r greater than Sigma 2 the potential is 0.

So potential basically goes this is my U is equal to 0 this is the negative and this is the positive side of the U. So, for r greater than equal to sigma 2 my potential goes 0 for r less than Sigma so Sigma 2 and between Sigma 1 it is minus Epsilon and when it is less than Sigma 1 it is infinity so this is how my square well potential will look like where is Epsilon. So, this is Epsilon.

This distance is the Sigma 1 this is Sigma 1 and sigma2 is basically this whole distance this is Sigma 2. So, now if you look at it so this is my Sigma 2, so for r greater than Sigma 2 my U is 0 for r between Sigma 1 and Sigma 2 it is minus Epsilon and once the inter particle distance so again as I said r is nothing but r ij and basically bringing ok; so, what it is? So, potential is nothing but I have particle i here, I have particle j here and what I am doing is basically I am bringing this jth particle closer and closer to i.

And in the process how the interactions how the potential is changing so this is exactly what I am showing here that when j is very far away from i they do not sense each other and therefore their interaction is 0. When j is here that is the optimal distance where they sense each other and they attract each other. So, this is a distance which is representing by this one that here when j is here, so i and j they have an attraction and their energy is minus Epsilon.

If I take j further closer to i then they repel each other and therefore the energy shoots up and that is this r less than Sigma 1. So, this is square well potential so the square well potential is also having a attractive term by minus Epsilon. So, square well potential is little more complex and hard square potential in a sense that it has a attractive town, square well; the hard sphere potential have a attractive term.

$$U^{SS}(r) = \varepsilon \left(\frac{\sigma}{r}\right)^{\gamma}$$

$$U^{SS}(r) = ar^{-\gamma}$$

The third popular potential is called soft sphere potential, and the soft sphere potential is equal to Epsilon Sigma which is again the diameter by r to the power gamma which we can write simply as since epsilon is a constant sigma is a constant so I can multiply that those two constants and I can write this simply as r to the power minus gamma where gamma is an integer.

So this is soft sphere a potential, now if I ask you to draw U SS versus r what will it turn out to be? So, so that nature of U SS versus r will be decided by this gamma factor depending on the value of the comma the nature of U SS versus r will be different.

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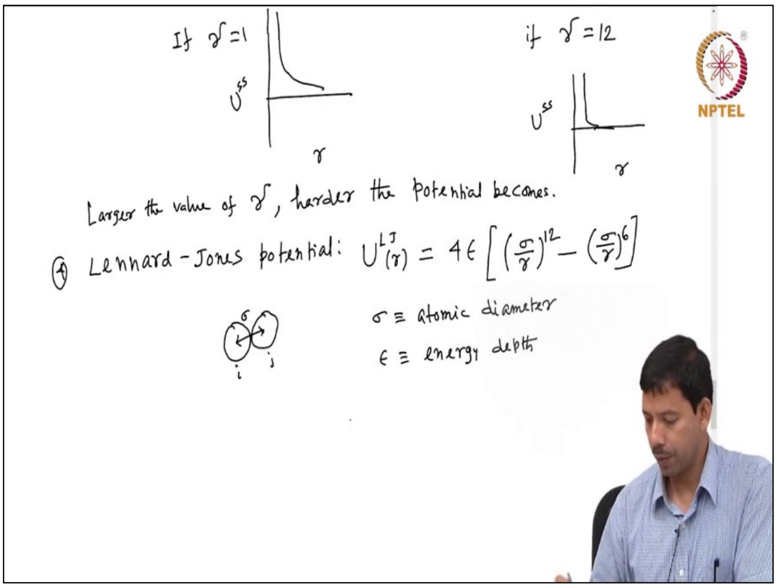

If $\gamma = 1$

if $\gamma = 12$

Larger the value of γ, harder the potential becomes.

④ Lennard-Jones potential: $U^{LJ}_{(r)} = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$

$\sigma \equiv$ atomic diameter

$\epsilon \equiv$ energy depth

So, if gamma is equal to 1 versus if gamma is equal to 12 how U SS versus r will look like? So, this is my square soft sphere potential so how my soft sphere potential will look like if I my gamma is 1 versus my gamma is 12, so you can work it out and what you will see that for gamma is equal to 1 or smaller gamma the potential will die down slowly whereas if gamma is 12 or I can write it I can draw it little better. So, if my gamma value is less so the function will decay very slowly.

Whereas if gamma is large you can easily work out that the decay would be rather quick. So, what it indicates is that larger the value of gamma larger the value of gamma harder the potential becomes that means as you increase the gamma value the soft sphere potential turns out to be a hard sphere potential so at high value of gamma software potential and hard sphere potential we have almost the same nature. So, all the 3 potentials the model potentials what we have seen everyone has some advantage and also have some disadvantages.

Hard sphere and soft sphere potential they do not have any attractive term square well had an attractive term because it has a minus epsilon when r is between Sigma 1 and Sigma 2 but the problem of square well potential is that even though it has an attractive term but the potential is not a continuous potential it is a discrete potential. Same is with the hard spear the square well potential sorry soft sphere potential is more continuous compared to the hard sphere or the square well potential.

But here the problem is the soft sphere does not have an attractive potential. But most of the particles what we see in reality and the biomolecules they do have both an attractive and repulsive interactions. So, they have attractions at the equilibrium distance and then they repel at a distance other than that. And they stay at an equilibrium distance because there is optimal distance where attraction or repulsion is basically balanced out.

So therefore each particle in practice in reality should do have does have an attractive and repulsive potential. And therefore scientists look for other model potentials where we have both attractive and repulsive plus the potential is continuous not the discrete potential like square well and therefore the next potential which is the most popular and widely used is called the Lennard - Jones potential okay.

$$U^{LJ}(r) = 4\varepsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

$$\sigma \equiv atomic\ diameter$$

$$\varepsilon \equiv energy\ depth$$

So, what is the Lennard-Jones potential expression? So, the Lennard-Jones potential is U LJ r 4 epsilon Sigma by r to the power 12 - Sigma by r to the power 6 this is the Lennard-Jones potential where Sigma is again the atomic diameter. So, basically why they repel each other? So, basically you have one particle and you know if you go back to the hard sphere potential so this is one particle, particle i and the other particle is j.

So basically here to here is the Sigma this value is nothing but the Sigma so when the particles basically try to penetrate, penetrate each other the potential source up and epsilon is basically is an energy function.

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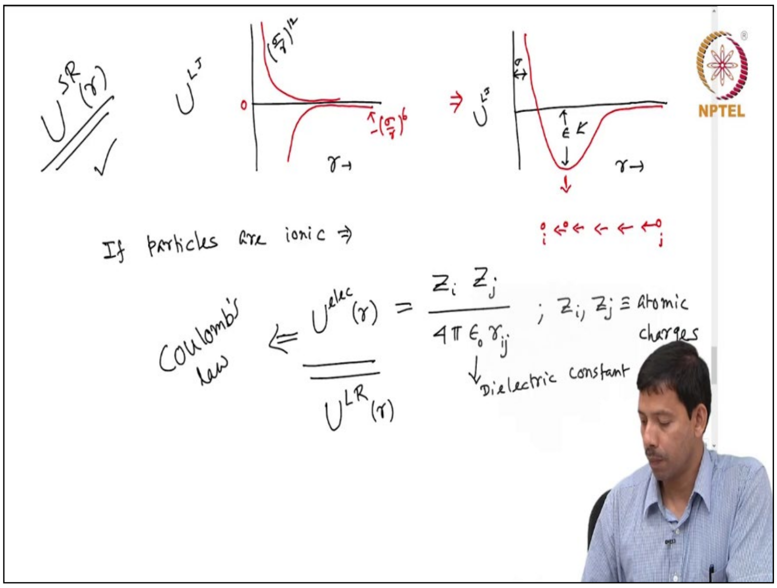

If particles are ionic ⇒

$$\text{Coulomb's law} \Leftarrow U^{elec}(r) = \frac{Z_i Z_j}{4\pi \epsilon_0 r_{ij}} \; ; \; Z_i, Z_j \equiv \text{Atomic charges}$$

ϵ_0 ↓ Dielectric constant

$$U^{elec}(r) = U^{LR}(r)$$

So, if we draw U LJ versus r how would this look like okay, so here you must be you must have noted that this potential has two terms one is this one is this which is attractive which is repulsive among this two so the second term represents the attraction because it has a negative sign and the first term Sigma r to the power 12 is represents the repulsion. So, it has both repulsion and attraction and if you look at the nature of the potential so your Sigma by r to the power 6 if you draw it, it would represent something like this.

This is basically the sigma by r to the power 6 top this is my 0 and if you draw the other one so no party has my drawing is to be better. So, if you draw this one this would be more like this and if you match them together the Lennard-Jones potential we will look like something like this. So, this is Lennard-Jones potential where this depth is the epsilon. So, this is epsilon and this is obviously the Sigma and this is the Sigma by r to the power 12 term the repulsive part.

So, as you see here so the U Lennard-Jones potential over r is r continuous potential so the potential is very continuous. So, when you when you are bringing jth particle to the ith particle and that is how sorry so here is your jth particle and here is your ith particle and when you are bringing j2i this is how your potential is changing. So, this is basically the inter particle distance where the two particles are having the best energy the lowest energy and that is the equilibrium distance.

So, this is the equilibrium distance and if you push them further closer then they try to repel. So, therefore we have seen for use a very useful model potentials which present inter particle interactions they are the hard sphere potential, the square well potential soft sphere potential and finally you saw the Lennard-Jones potential so all these potentials are very useful and depending on the problem you choose your model potential.

As you saw that out of this for potential then Lennard-Jones potential is more accurate because it has attractive repulsive and also it is continuous but it is more difficult to calculate it takes more time and therefore if your system is too big then you better use something simpler. Hard sphere potential even though it is very simple perhaps the simplest of all it is still widely used in physics problem like if you want to look at the Association dissociation of two biomolecules or two polymers.

Then in physics hard sphere potential is still widely used but if you want to look at a biological problem where you want to design for example a small molecule potential drug there you need to look at the atomic level interactions. So, their atomic level in depth interactions will be more useful and they are instead of going for the other potential one should go for the Lennard-Jones potential because it takes care of the interaction between i and jth particle more rigorously than the other potentials.

One thing I should have mentioned before that all these modern potential what we have discussed so far these are these are applicable for atomic systems and so for example liquid argon if you want to use any of these potentials and find out the potential energy or any other common any quantity of liquid argon you can easily use all these model potentials. We talked about it when how it changes to the molecular system.

$$U^{elec}(r) = \frac{Z_i Z_j}{4\pi\varepsilon_0 r_{ij}}$$

So, this potential so you have written r for atomic systems and now we will see if we have a system now where particles are ionic, so if particles are ionic so apart from one of those above interactions one also has to include the electrostatic interactions which is Zi Zj by 4 PI epsilon 0 rij right were Zi Zj they are atomic charges and this epsilon 0 not to be confused with the epsilon here this epsilon 0 is basically the dielectric constant.

Like the dielectric constant of bulk water is 78, so this epsilon 0 is the dielectric constant of the medium who had these two particles is orbited. So, if the particles are solvated in water so epsilon 0 is 78 which is the dielectric constant water. rij is the distance between ith and jth particle and Zi is atomic charge of ith particle Zj is atomic charge on them on the jth particle.

So, one thing you should look at is that out of these 5 potentials what we have looked at the electrostatic is called the long-range interactions U LR is called long-range interactions because this interaction the entire ionic interactions are experienced by the particles even when they are quite apart whereas hard sphere and square well soft sphere and Lenore Jones particles are there the short-range potentials.

So, these are short potentials there is hard range potentials because these potentials die down pretty quickly whereas the long range of the electrostatic interaction it exists or quite long distance. So, when you so when your particles are ionic so you should use one of this short range potential plus you should use are this long range.

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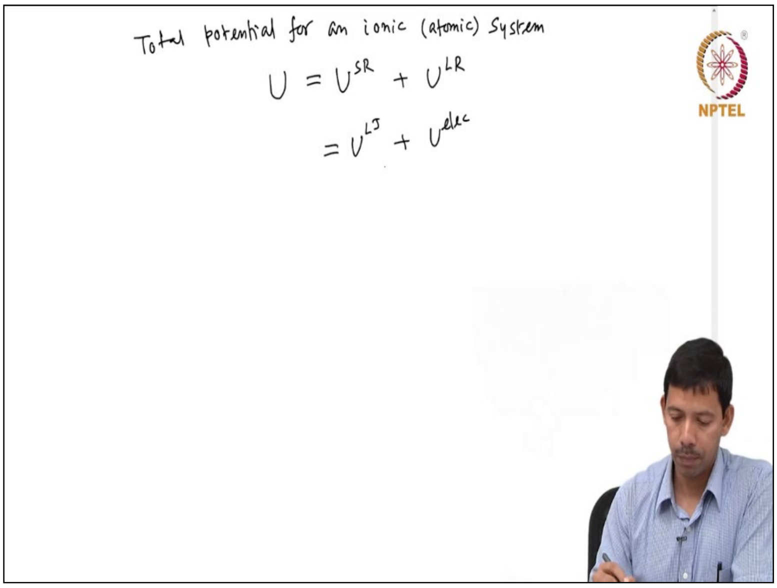

Total potential for an ionic (atomic) system

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

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

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

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

So, your total U, so total potential or an ionic how to make system we will be total U is U short range plus U long-range, so your U short range could be you can take Lennard-Jones plus here you can take U electrostatic which is a Coulomb so the previous this is nothing but the Coulomb's law. This is the Coulomb's law about the electrostatic interactions between the charged particles okay.

So this is what we have discussed so far is for the atomic system but in biological in biology our molecules are not just consists of atoms there are other composed of molecules.