Bio-Physical Chemistry
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Lecture - 11
Electrostatics (Contd.)

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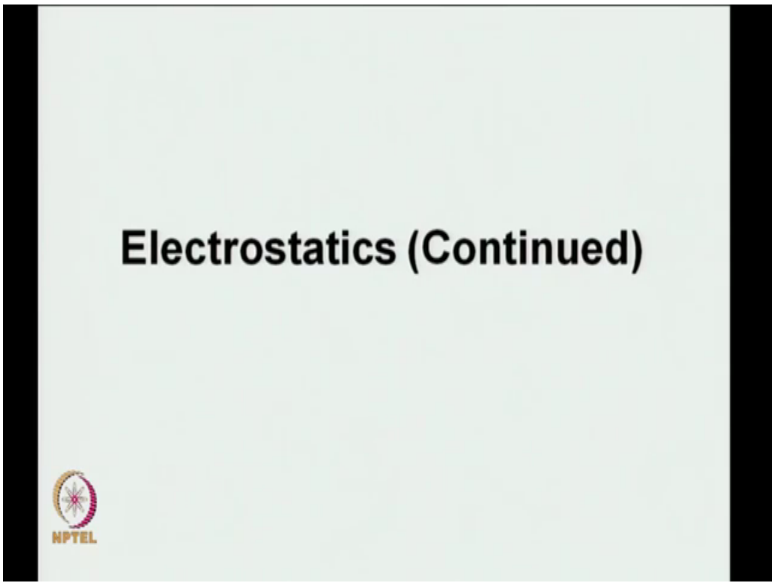

Electrostatics (Continued)

So, will today will finish off with Electrostatics; right essentially the ion dipole, dipole-dipole that is what we were looking at, right, for the last couple of classes.

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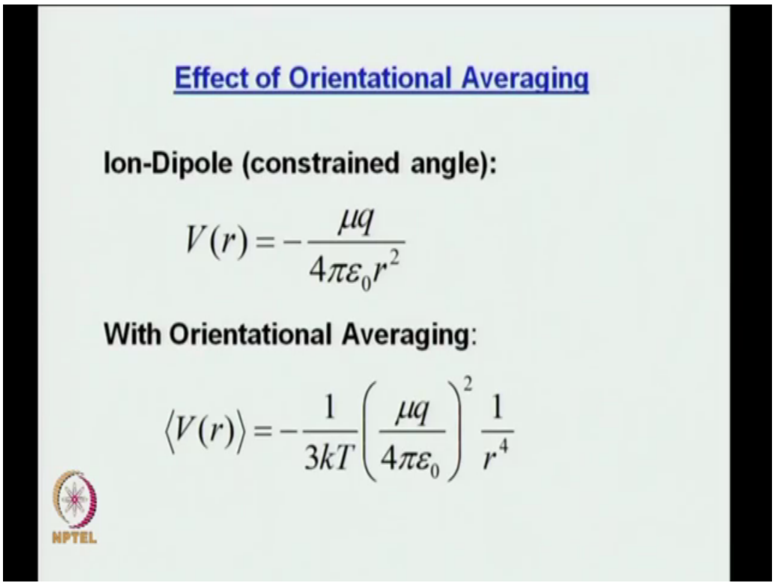

Effect of Orientational Averaging

Ion-Dipole (constrained angle):

$$V(r) = -\frac{\mu q}{4\pi\varepsilon_0 r^2}$$

With Orientational Averaging:

$$\langle V(r)\rangle = -\frac{1}{3kT}\left(\frac{\mu q}{4\pi\varepsilon_0}\right)^2 \frac{1}{r^4}$$

Now, so this is what we looked at in the last class. So, for example, you have your ion dipole interaction, right. And this read as 1 by r square with the negative sign for attractive potential. Now, if you have orientational averaging that means, one is moving with respect to the other but different angles, then essentially it becomes 1 by r to the power 4, that is what we have seen last class.

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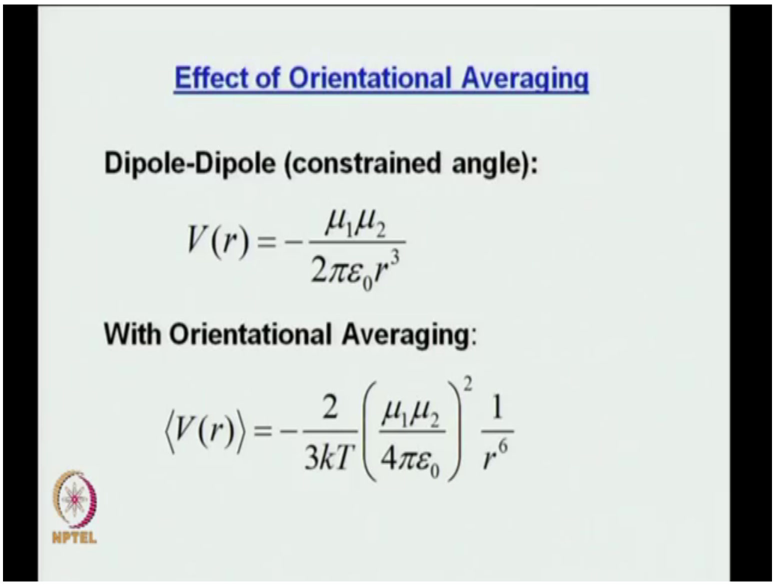

Effect of Orientational Averaging

Dipole-Dipole (constrained angle):

$$V(r) = -\frac{\mu_1 \mu_2}{2\pi\varepsilon_0 r^3}$$

With Orientational Averaging:

$$\langle V(r) \rangle = -\frac{2}{3kT}\left(\frac{\mu_1 \mu_2}{4\pi\varepsilon_0}\right)^2 \frac{1}{r^6}$$

Now, the same thing happens in case of a dipole-dipole interaction. So, when you have a dipole-dipole interaction then V of r, right goes as you can see its 1 by r cubed negative sign for attractive potential, but look at the difference. The difference is for an ion dipole you had the charge q of the ion and the corresponding dipole moment of the dipole.

Now, because it is a dipole-dipole, that charge is been replaced by the dipole moment. So, essentially that is what it is and this is about 1 by r cubed, not 1 by r squared. And how is if its orientational averaging you know what happen last time to, right, by 1 by r square by squared to 1 by r 4. So, this the same thing happens here, right, goes to 1 by r to the power 6. And this resembles something which we know, right. This is your attractive potential we need to talk about dispersion forces, right.

So, see here also you have r to the power 6 dependence, but right now we have not even gone into the dispersion forces as such, ok.

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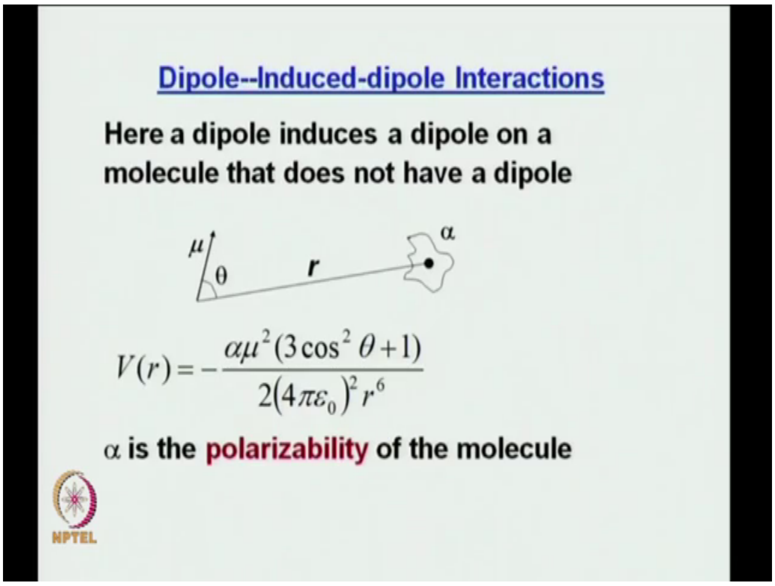

Dipole--Induced-dipole Interactions

Here a dipole induces a dipole on a molecule that does not have a dipole

$$V(r) = -\frac{\alpha\mu^2(3\cos^2\theta + 1)}{2(4\pi\varepsilon_0)^2 r^6}$$

α is the **polarizability** of the molecule

So, you can after that you can have, it is all these you know whatever you have talked up till now there is no induced dipole that means, everything has either a charge or a permanent dipole in a molecule. It is always something like that. But now let us talk about you know something inducing a charge separation or dipole in a molecule which might not be having a permanent dipole to start with.

So, what you can see out here is if you look at the term; if you look at the term V of r is equal to minus alpha mu square well do not worry about the rest of the terms there is a certain term which comes over which is alpha. Now, what is this alpha? This alpha is the polarizability, right. So, let us quickly discuss about polarizability.

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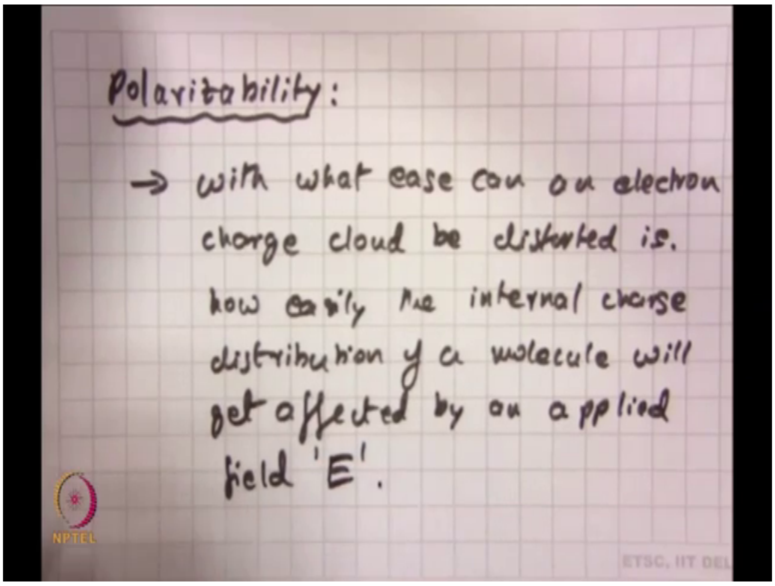

Polarizability:

→ with what ease can an electron charge cloud be distorted i.e. how easily the internal charge distribution of a molecule will get affected by an applied field 'E'.

So, when we talk about polarizability what do we actually mean? When we talk about polarizability what do we actually mean? Can anyone say? I mean just kind of very brief definition of polarizability.

Student: Distortion of the charge.

Distortion of the charge, right. So, well, precisely that is what it is. So, this ensures, so this tells us with what ease with what ease that means, how easily can an electron charge cloud be distorted. That is you can also write this one as or frame it differently. How easily the internal charge distribution of a molecule will get affected by an applied field E, right. That means, you apply a field E and then this polarized unit tells you how easily or to what extent this charge is distorted how easily it can be distorted, right.

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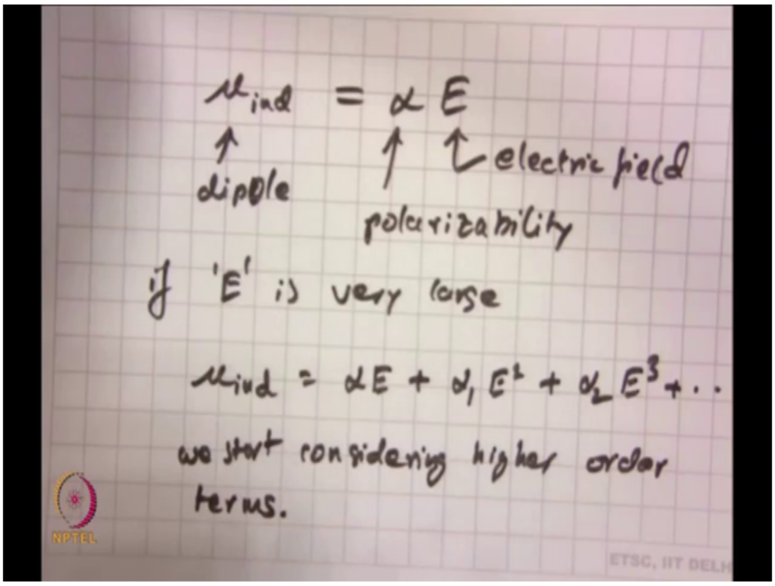

$$\mu_{ind} = \alpha E$$

dipole

polarizability

electric field

if 'E' is very large

$$\mu_{ind} = \alpha E + \alpha_1 E^2 + \alpha_2 E^3 + ..$$

we start considering higher order terms.

So, because it is an induced one because it is we are talking about induced dipole what we can write now is mu induced, is an induced dipole, right mu induced is equal to alpha times E, right where E is the obviously, electric field, where E is electric field and alpha is our polarizability. That we all know, ok.

You know, but there is one thing to it. Look at this is a linear term; linear term in the sense this is a linear expression that means, mu induced is directly proportional to E, right E. Now, what happens if the applied field E is very large? If the applied field E is very large then I cannot just represent this mu induced like this. So, what I can rather do is then mu induced becomes alpha E say plus alpha 1 E squared plus alpha 2 E cubed and so on. That means, if electric field is very large we start considering higher order terms.

Now, this is something you know which you have to keep in mind will not be discussing that much in this class, but this is very important. You know this is very important, specially when you know people are talking about I do not know you are whether you heard of a non-linear optics, right, fair. Non-linear means see this mu induced is equal to alpha times E it is a linear equation the moment you go to this it because a non-linear equation, right because of the higher order terms.

And non-linear optics and non-linear polarizability you know place it is a very huge role in present day or present situation, right .

So, you know keeping this in mind if we go back to what we are looking at in the slide, so for a dipole induced dipole this V of r is equal to minus alpha mu squared 3 cos square theta plus 1 over you know whatever is given. Now, it varies as again r to the power 6. So, it has a 6 dependence or the distance between the dipole and the molecules. So, the molecule is this. It is represented by a polarizability alpha and obviously, this one is the center of the molecule, the center of mass and the mu is a dipole.

So, what this one does is the dipole induces another dipole in this molecule and that is how you get this potential of interaction. So, what you can do now further is, so this is at a specific angle theta, right, but we have done this before, we are not going to have a specific angle we can have a range of angles.

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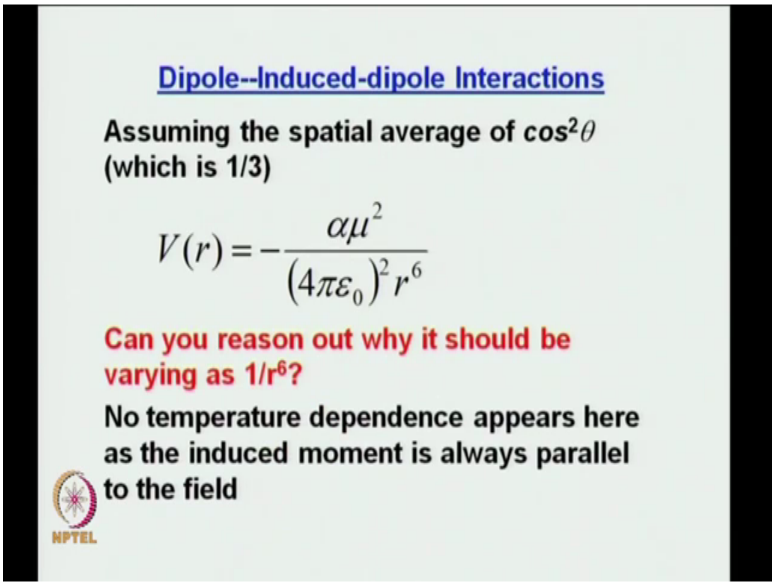

Dipole--Induced-dipole Interactions

Assuming the spatial average of $\cos^2\theta$ (which is 1/3)

$$V(r) = -\frac{\alpha\mu^2}{(4\pi\varepsilon_0)^2 r^6}$$

Can you reason out why it should be varying as $1/r^6$?

No temperature dependence appears here as the induced moment is always parallel to the field

So, in that case what you can do is you can take the average value of cosine square theta. And the average value of cosine square theta turns out to be 1 by 3. And if we take the average value of cosine square theta to 1 by 3, now this is what V of r comes finally, right, you know, the simplest expression.

So, this is an exercise for you can you just one physical principles and based on a very simple equation like mu is equal to alpha E reason out why it should be having a one to the power or 1 by r to the power 6 dependence or r to the power minus 6 dependence. You know that is for you, that is a homework problem for you, right.

Now, look at the last sentence. See no temperature dependence appears here as induced moment is always parallel to the field. Now, please keep this in mind your inducing moment, right, inducing moment means if I have an ion or a dipole which is inducing the one which is induced is an response to the one which is the permanent one.

So, this one is always correlated or always in response to the first one. That means, if this one say this is one dipole where I have a positive and negative charge and if it is inducing a dipole, then this one also induces in such a way that the opposite ends are closer because the potential is always attractive, right because it is an induced dipole we cannot have a repulsive interaction in this case because it is induced.

For dipoles which are permanent dipoles you can always have repulsive interaction because this is not induced. But here you are inducing the dipole. And the dipole induction is such that it is always essentially attractive is that clear.

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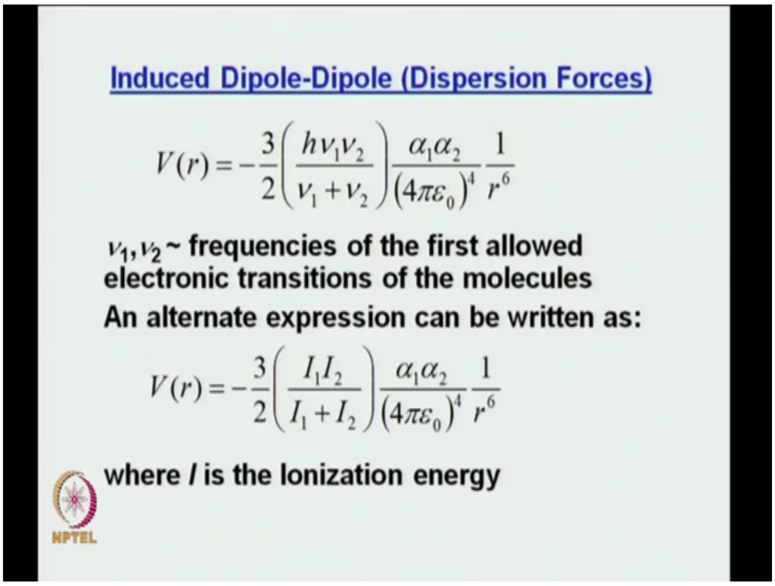

Induced Dipole-Dipole (Dispersion Forces)

$$V(r) = -\frac{3}{2}\left(\frac{h\nu_1\nu_2}{\nu_1+\nu_2}\right)\frac{\alpha_1\alpha_2}{(4\pi\varepsilon_0)^4}\frac{1}{r^6}$$

ν_1, ν_2 ~ frequencies of the first allowed electronic transitions of the molecules

An alternate expression can be written as:

$$V(r) = -\frac{3}{2}\left(\frac{I_1 I_2}{I_1+I_2}\right)\frac{\alpha_1\alpha_2}{(4\pi\varepsilon_0)^4}\frac{1}{r^6}$$

where *I* is the Ionization energy

Now, let us talk about dispersion forces. So, this is essentially the last topic of electrostatics. And if we just you know think about dispersion force a little bit, so what do we really mean by dispersion forces?

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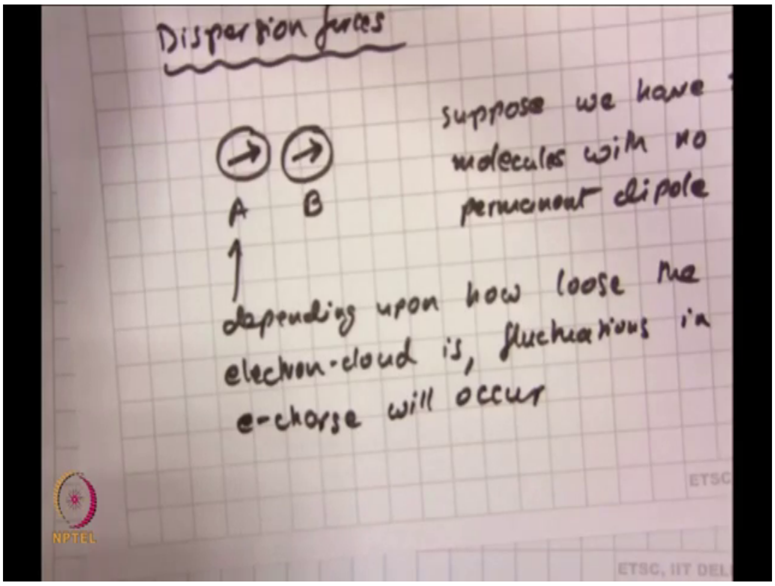

Dispersion forces

suppose we have
molecules with no
permanent dipole

depending upon how loose the
electron-cloud is, fluctuations in
e-charge will occur

So, think about this. I have see a molecule which has a certain dipole, right. Now, this is what I was talking about before. If I have a molecule which has a dipole it will induce on another molecule a certain dipole, right. So, if this is the respective ends, so also be having the say oppositely charged ends out here. Does not matter whatever intention, just keeping it very simple.

Now, suppose we have two molecules with no permanent dipole that means essentially neutral molecules. So, now these have permanent dipoles, so say this is molecule A, this is molecule B. So, that means, A, think about this let us look at A first. A also does not have a permanent dipole and B obviously, will not talking about B right now. But we know about something referred to as what instantaneous dipole, right.

So, what will happen is and say if I am talking about A depending upon how loose the electron cloud is fluctuations in electron charge will occur. So, again depending upon how loose the electron cloud is fluctuations in electron charge will occur. What does it mean? What it means is suppose I have almost you know I have an bunch of electrons and I have my nucleus in the center.

So, nucleus obviously, always has an attractive potential with electrons. But think about the electrons which are far away from the nucleus, right. There essentially screened by the inner electrons, right, so there feel less of the nuclear charge. Now, what this means is if your molecule is not having a permanent dipole moment. What this means is because these electrons are far away from the nucleus, these electrons always undergo fluctuations because see they are not under such a high attractive potential from the nucleus. Now, because of this fluctuations because electrons moving in and out, because of fluctuating of these charge cloud what you can do is you can give rise to what? Instantaneous dipoles, right.

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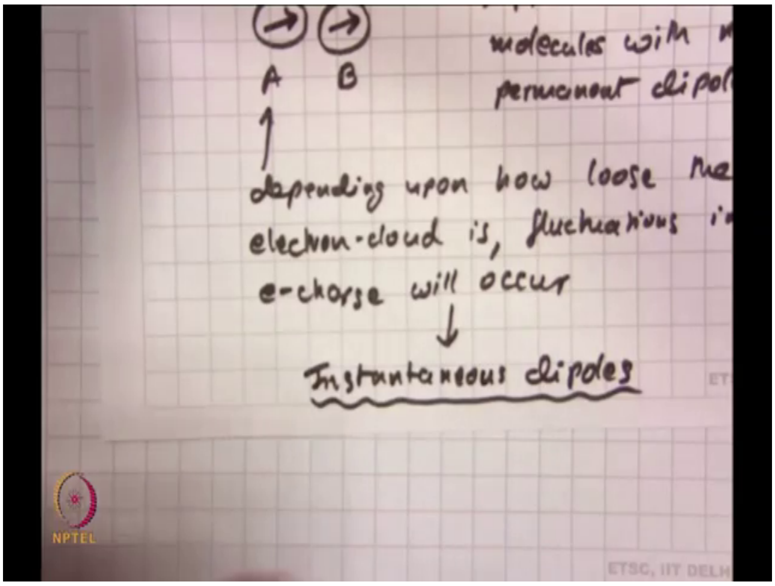

A B

molecules with

permanent dipol

depending upon how loose the electron-cloud is, fluctuations i

e-charge will occur

↓

Instantaneous dipoles

So that means, this will give rise to something known as instantaneous dipoles. So, that is for only one molecule now A, right; that is for only one molecule A.

Now, to have the dispersion force between the other molecules, the other molecule will also have to respond to this, right. So that means, to keep this dispersion force alive B has to respond to molecule A's charge fluctuation; molecule A's charge fluctuation and it has to respond. But, how can you respond?

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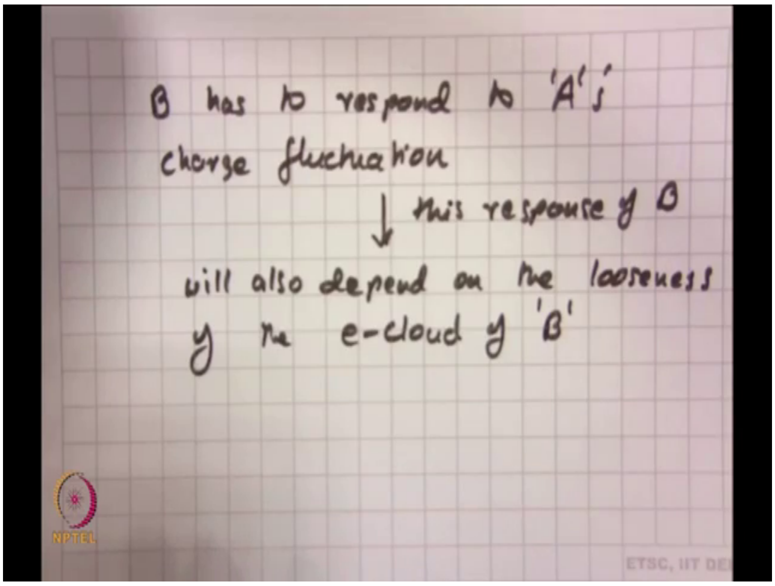

B has to respond to 'A's' charge fluctuation

↓ this response of B

will also depend on the looseness of the e-cloud of 'B'

So, this response of B, we also depend upon what? We will also depend on the looseness of the electron cloud of B, right. See, in one case we have an instantaneous dipole or instantaneous dipole we have for A and to what extent B would you know react or orient itself to this instantaneous dipole will also depend upon the looseness with which you can deform B's electron charge cloud or electron cloud.

Hence, what you can guess; hence what you can guess is that my potential energy of interaction V would be proportional to at least not talking about the resistance dependence now.

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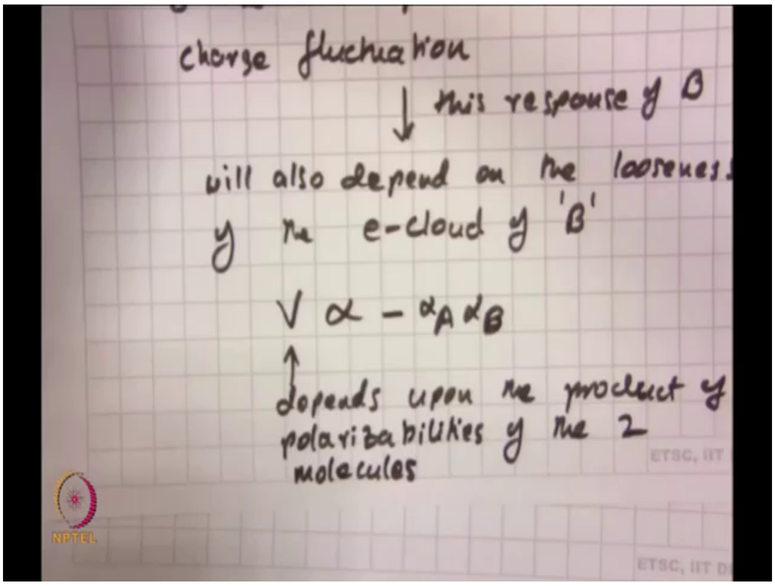

charge fluctuation

↓ this response of B

will also depend on the looseness of the e-cloud of 'B'

$V \propto - \alpha_A \alpha_B$

↑

depends upon the product of polarizabilities of the 2 molecules

Proportional to what tell me? One was the looseness of A, the electron cloud of A that was represented by the polarizability of A. So, I can write alpha A, then once I have once I have the electron cloud which is already in a instantaneous dipole for A, then I will be have the polarizability of B coming in, right. So, it will be having a B term, right. So, this is polarizability of B.

And remember when we talked about this because this is instantaneous dipolar induced dipole, this is induced dipole, if I have a dipole like this the other dipole as induce such that it is always attractive because I am inducing a dipole again. And hence I can straightaway write that my potential energy of interaction is attractive. Is it clear? So, we actually develop in the dispersion with, I am sure you know, but it is kind of you know trying to look at it again from a little different view point. You know keeping it in context of what electrostatics we have been discussing.

So, for this you know this is direct, this is I mean this is directly. It has to depend upon the respective polarizability straight. So, essentially this depends upon the product of polarizabilities of the two molecules.

Now, that is I have done that is clear and you know that is very logical. But, what about the distance dependence? Now, this distance dependence, its the derivation of this is a little bit involved, but you know people have derived it for us, for you, for me, applying principles of quantum mechanics it can be done.

So, what will happen is if you go back to the slides. So, here V of r is equal to minus 3 by 2 h nu 1 nu 2, you see by over nu 1 plus nu 2, then look at this term we have alpha 1, alpha 2 its essentially like alpha a and alpha b, right that is what we have. And then you see the distance dependence it is r to the power 6, right. This is something we had also noticed for what?

Remember dipole-dipole interactions, right, when they were orientational averaged. But here this is induced dipole-dipole. But remember it is still dipole, right whether it is induced or not it does not matter. That was the dipole; this is also dipole only the only factor is its induced dipole. And the difference is in those cases instead of polarizabilities what did we have? Any how do not worry about this nu 1 and nu 2 right now. Instead of polarizability we had the respective dipole moments.

Student: (Refer Time: 17:39).

But here we cannot have a dipole moment instead that dipole moment is being replaced by polarizability is alpha 1 and alpha 2, ok. So, what a nu 1 and nu 2? Not that you have to worry about this too much, but it says that these are the frequencies of the first allowed electronic transitions of the molecules, right.

And an alternate expression for this V of r is given at the bottom, where V of r is equal to you know minus 3 by 2 not this; now, the nu 1 by nu 2 or nu 1 nu 2 has not replaced by the respective ionization energies I 1, I 2. So that means, I 1 is the ionization energy of say molecule A, right or molecule 1. I 2 is the respective ionization energy of molecule 2, ok.

So, anyway the derivation of this is involved. But, and will not be going to that, this class, ok. So, this was about the dispersion forces.

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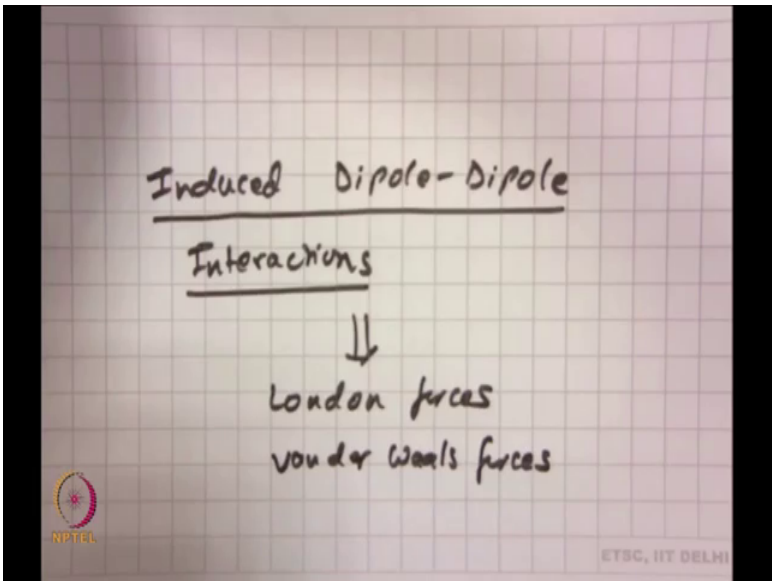

Induced Dipole-Dipole Interactions

⇓

London forces

van der Waals forces

And because this is a induced dispersion forces, so we can write induced dipole interactions, induced dipole-dipole interactions or you can even write instantaneous induced dipole-dipole interactions. It does not matter. But at least the message is out there. So, these are what you know your dispersion forces these are also referred to as something known as your London forces, right and people call this interchangeably as van der Waals forces, right. So, you know all this things you know already, ok.

So, what we have done in electrostatics is that we have started with again you know the Columbic charge, right. Then what did we do? We went for a charge and a dipole, then we for dipole-dipole, but all these are permanent charges.

Then, we take took into consideration orientational averaging because obviously, they are not going to be constraint, thermo motion would always be move them around. After that we came to induced dipole-dipole interactions and saw that this is depend upon essentially the polarizability of the molecule.

So, you think about this, starting from the charged charge to this dipole or in a induced dipole or there is polarizability you have typically covered almost every aspect of this electrostatic interaction, except possibly one more thing which is hydrogen bonding which we have not at talked about. But that is you know a separate topic. We will deal with it later.

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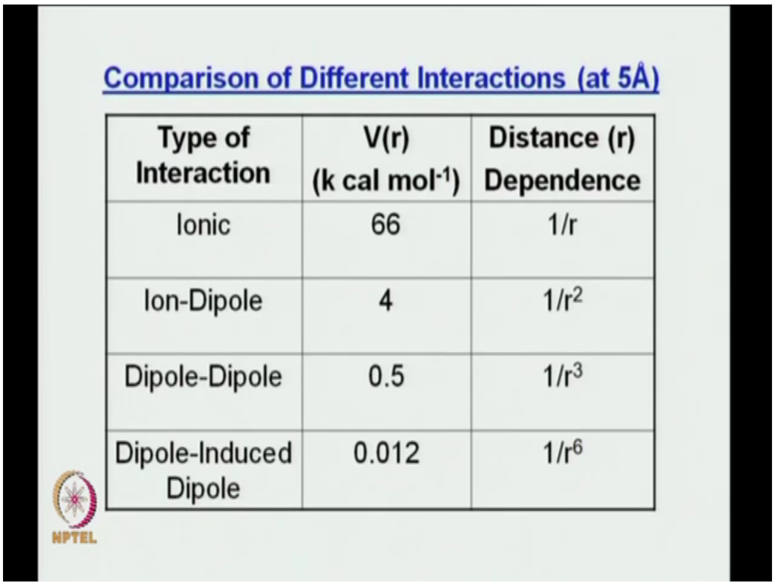

Comparison of Different Interactions (at 5Å)

Type of Interaction	V(r) (k cal mol^{-1})	Distance (r) Dependence
Ionic	66	$1/r$
Ion-Dipole	4	$1/r^2$
Dipole-Dipole	0.5	$1/r^3$
Dipole-Induced Dipole	0.012	$1/r^6$

Now, let us look at some comparisons. Here, the question that comes to your mind is sure I have this different dependences, right, for this you know different interactions. How the how do the energy is compared? So, look at this. So, this is the comparison of different interactions at a set distance of 5 Angstroms. We have to keep the distance fixed.

Now, see you are given a certain dipole moment mu. See for ionic it is a V of r is this, ok, for ion dipole its 4, dipole-dipole point 5 and dipole induced dipole its 0.012. I did not make sense, right. As we are going down not only what happens is that your interactions is decreasing, but you see the distance dependence, the distance dependence it is 1 by r was literally long range.

Remember we had two terms long range and short range, 1 by r is long range. And then you come to 1 by r squared then 1 by r cubed. Beyond 1 by r cubed it essentially becomes short range, right. So, this is how you distinguish between or differentiate between your long range and short range interactions. And that is how the energies also fall in place, right, ok.

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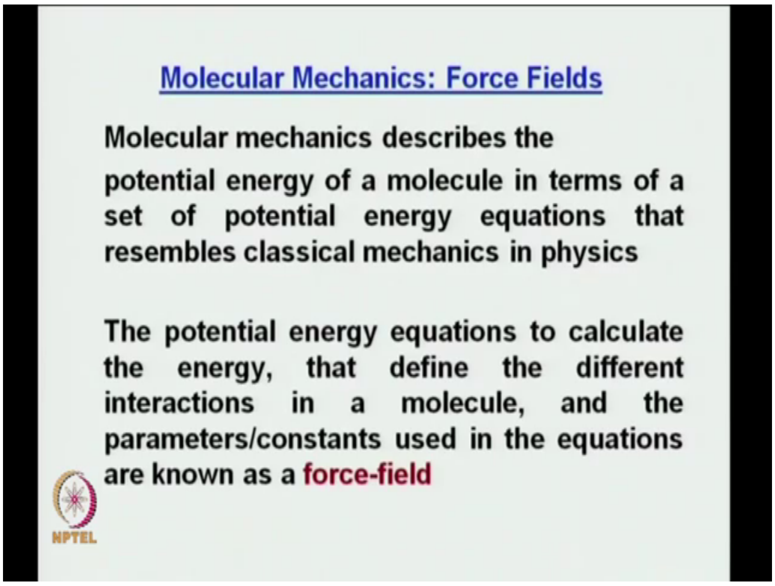

Molecular Mechanics: Force Fields

Molecular mechanics describes the potential energy of a molecule in terms of a set of potential energy equations that resembles classical mechanics in physics

The potential energy equations to calculate the energy, that define the different interactions in a molecule, and the parameters/constants used in the equations are known as a **force-field**

So, having you know look at this another question comes to our mind. I will tell you what the question is the question is, ok. We are talking about different potentials V of r, right, we are talking of these potentials V of r, now if I am talking about these potentials V of r then what is a form of a potential that means, what are some empirical potentials used, some empirical potentials used.

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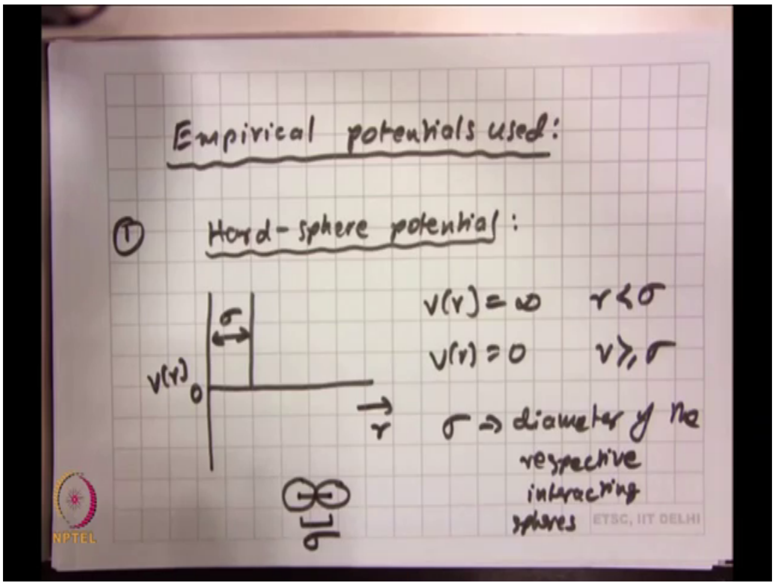

Empirical potentials used:

① Hard-sphere potential:

$V(r) = \infty \quad r < \sigma$

$V(r) = 0 \quad r \geq \sigma$

$\sigma \Rightarrow$ diameter of the respective interacting spheres

Now, these you know or will just again go through it. So, let us look at the first one and the most simplest one, most simple one or rather the simplest one. So, this is referred to as a hard sphere potential. This is referred to as a hard phase potential. Now, what do we mean by hard sphere potential? Say suppose we draw potential energy diagram, say this I have V of r and this line is arbitrary taken as 0 potential energy of interaction.

So, now, let me draw another line here, ok. So, this is your r and this is distance is known as sigma. So, what it means is, so look at this, what it means is if I am going to; so, this is my V of r and this is r, right and if I am going to write V of r what I can write is V of r is equal to infinity if r is less than sigma, right. And V of r is equal to 0 if r is greater than equal to sigma or greater than sigma. And what is sigma? I will tell you what sigma is.

But again look at this plot V of r which is the distance, right between the interacting dipoles or whatever law in the interacting species. This is the potential, how it looks like? You can see from here it just there is no curve or anything it just takes off and goes to infinity. This is something which we have come across in when you in quantum mechanics when you are doing particle in a 1D box, remember like V is equal to infinity outside the walls and hence you could not go there. You know the same thing is happening here. That means, if this guy is coming here then V is infinite.

Now, what is sigma? Sigma is the diameter of the respective interacting spheres. It is diameter of the respective interacting spheres, all right. So that means, if I have two spheres like this is referred to as hard spheres, right, so that means, these are two spheres and I can take this distance to be sigma in touched with each other.

Again, what is the significance of hard spheres can someone tell me? Hard spheres is you look at these, when these two spheres are colliding with each other if they are not hard then what might happen is this one might induce a deformation in this one and hence in that case your distance is going to change, right.

But if it is the hard sphere what does it mean? Hard sphere means, these two collide with each other and then elastically bounce off at this distance sigma that is what you mean by hard sphere. Hard sphere means you just cannot squeeze them further. The moment you they are in contact and they come bounce off elastically and then go away, right. And hence this sigma refers to this that means, because the potential is very high at r less than sigma they can never encroach that sigma length. That is why the potential is short up to infinity, clear.

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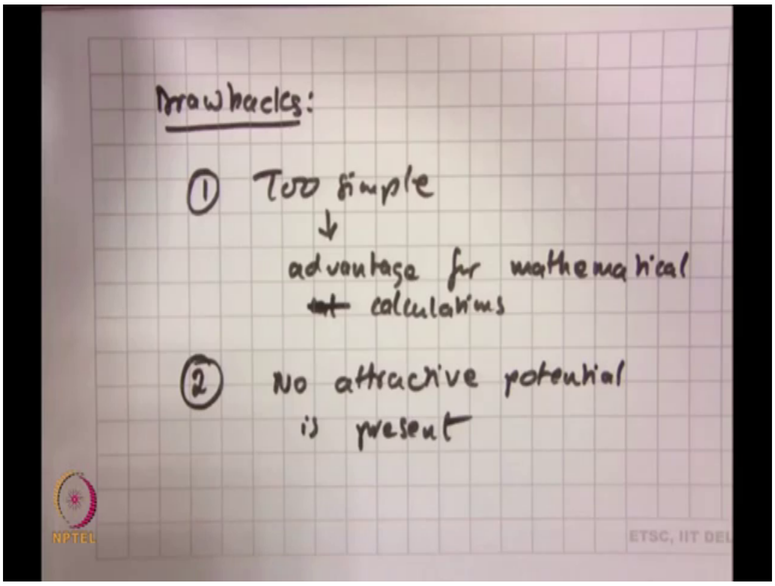

Drawbacks:

① Too simple

↓

advantage for mathematical calculations

② No attractive potential is present

So, there is a hard sphere potential, but see the drawbacks of this hard sphere potential. Drawbacks, well, it is too simple, it is too simple obviously for this the advantage is it is an advantage for mathematical calculations. And number 2, is think about this guys. When we talked about this empirical potential is used see your potential is not only repulsive, right. It also has to have some, what? Attractive potential, otherwise they will never come together.

Hence, what we can say is no attractive potential is present, no attractive potential is present. That is the other drawback of this. Your one is obviously too simple it is an advantage in one sense because you can easily employ you know mathematical calculations or mathematical treatment with it or to it, and number 2 is these molecules will never face any forces of attraction between each other. Now, that is definitely draw back.

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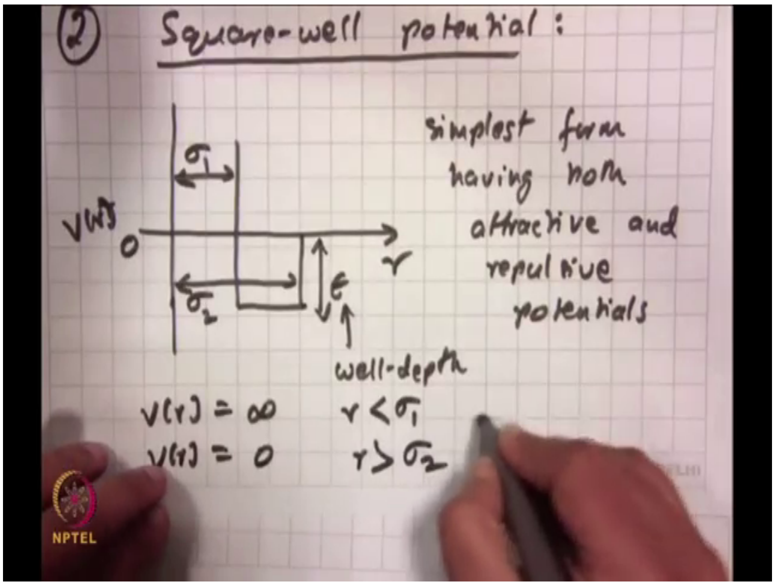
② Square-well potential :

simplest form having both attractive and repulsive potentials

$V(r) = \infty \quad r < \sigma_1$

$V(r) = 0 \quad r > \sigma_2$

What is the next one? The next one is something referred to as a square well potential. Now, this is also a term square well potential which you know from quantum mechanics. When, you remember you did potentials of finite width V naught instead of V is equal to infinity or V is equal to V naught and then we talked about tunneling, right.

So, it is very similar. You see I mean try to think about the priority here. So, if I draw the potential energy curve like this the square well means I will be having a square well something like this. So, let us draw it here, ok.

So, this is again V of r, this is 0, right, this is your r, this is sigma 1, and this is sigma 2, ok. The depth is epsilon. So, epsilon is the well-depth. So, now, look at the difference. When you are talking about the hard sphere potential this term was not there the only term we had was on the positive side that means, V of r was repulsive, right.

Now, we have got in a attractive term, because of the attractive term you see this one is going down that means, it is a negative; it is a negative potential, right. But then the negative potential is just like a square well between this region it is fine, it is negative. Then the moment your r is greater than sigma 2 what happens V of r goes to 0.

So, here that again the drawback is obviously here, it rises to potential rises to infinity very fast and here also it drops to 0 very fast, ok. The first case it was rising to infinity very fast no attractive potential in this case you have an attractive potential, you have a repulsive potential, but both of these are very steep, both of these are very steep. So, here I can say this is the simplest form having both attractive and repulsive potentials. This is the simplest form, right.

So, here what we can write is V of r would be infinity. Now, what should the limit be now? r is less than sigma 1, right. Now, V of r would be 0 for, what should I say now r greater than.

Student: Sigma 2.

Sigma 2. And then, I can also write, and then I can also write. Let me write it here. V of r is equal to my well-depth epsilon which is my attractive potential energy, if what? r sigma 2, sigma 1.

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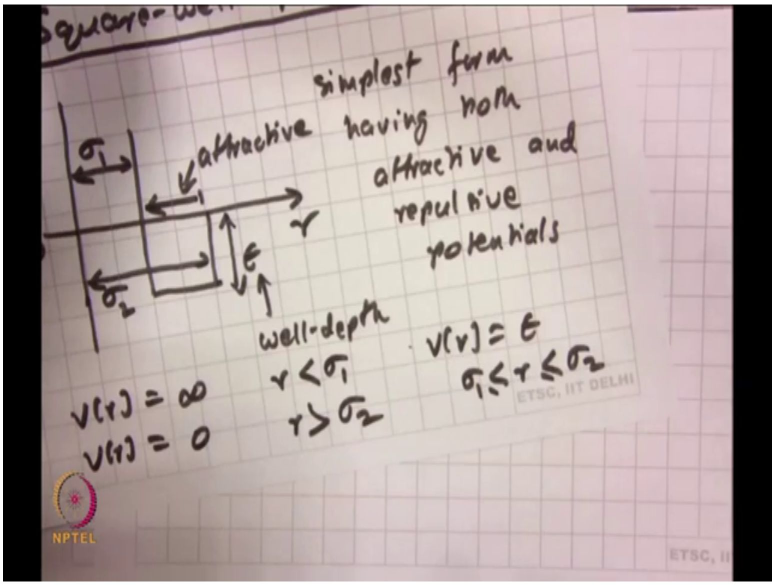

simplest form having both attractive and repulsive potentials

$V(r) = \infty \quad r < \sigma_1$

$V(r) = 0 \quad r > \sigma_2$

$V(r) = \epsilon \quad \sigma_1 \leq r \leq \sigma_2$

Student: (Refer Time: 31:15).

So, only within sigma 1 and sigma 2, do I have; well it is essentially sigma 2 minus sigma 1 essentially you can say because it is it is just this guy, right. It is only this part where it is attractive, ok. So, that is why it says it is greater than sigma 1, but less than sigma 2. It is essentially sigma 2 minus sigma 1, ok. So, this is one form again. But as I said it is not that realistic. It is a simplistic form, but it is not realistic at all.

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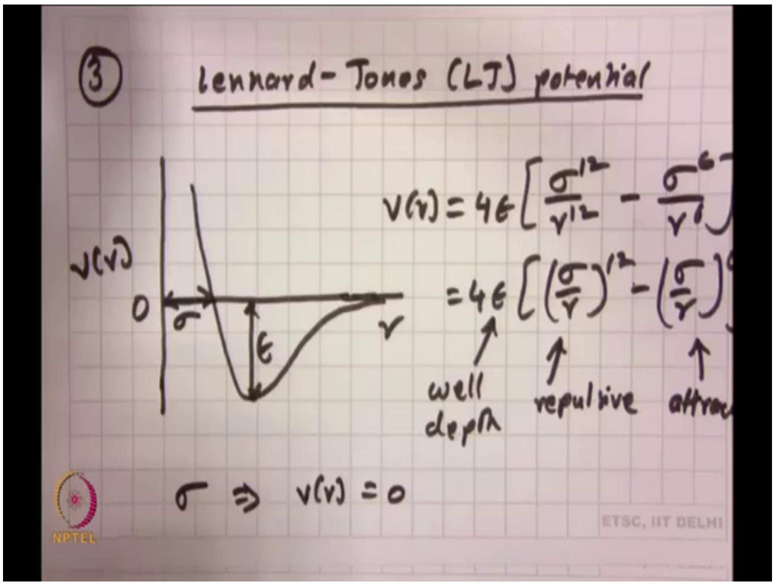

③ Lennard-Jones (LJ) potential

$V(r) = 4\epsilon\left[\frac{\sigma^{12}}{r^{12}} - \frac{\sigma^{6}}{r^{6}}\right.$

$= 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)\right.$

well depth

repulsive

attrac

$\sigma \Rightarrow V(r) = 0$

So, that is why the one people use and the most common one is can someone say what it is referred to as the.

Student: Lennard-Jones.

Lennard-Jones, LJ potential. And how does it go? This, you guys have seen many many times. It goes something like this. I have V of r, right, this well-depth again is epsilon, right. And this one from here to here, this one is sigma, and obviously, this is r. And this Lennard-Jones potential V of r is equal to 4 epsilon, right, then sigma by r to the power 12; sorry, well r minus sigma this or I can write it a little better sigma by r 12 minus sigma by r power 6. So, this is the Lennard-Jones potential.

What it does is this is your repulsive term, this is the attractive term, ok, repulsive attractive. This is your well-depth as it has been defined here. Now, what is sigma? Sigma is that distance, you see this distance sigma, where V of r is equal to 0. So, look at this is my 0 line, right, this is my 0 line, see this is my 0 line, this line is my 0 line. V of r is equal to 0, my x axis is essentially. So, when this V of r crosses this line what happens? It goes to 0 and that is the distance which is essentially your sigma that is how sigma is defined. So, here sigma is that one, where V of r is equal to 0.

Now, do not consider the fact where I mean if you come on this side where r is very high your V of r is also 0, right because there is no interaction. But do not consider that point, I mean there is no use. The weight is defined is if you come here then V of r is equal to 0, this is a point where V of r is equal to 0, ok.

See, immediately one thing you can realize this r to the power 6 dependence we have seen already, right from induced dipole-dipole, dipole-dipole and all those things. This one is repulsive term and it can be derived, but this is you know one of the ways that people have found a very convenient to represent repulsive term. The good point is; the good point is that unlike the previous ones; unlike the previous ones whether this one or the hard sphere potential, where if you r would be less than sigma it would immediately go to infinity this one does not.

It goes to infinity, but with the dependence of r to the power 12 or 1 by r to the power 12. And this is the one which is most commonly used nowadays in many many different forms. And I will tell you what form I am talking about, ok.

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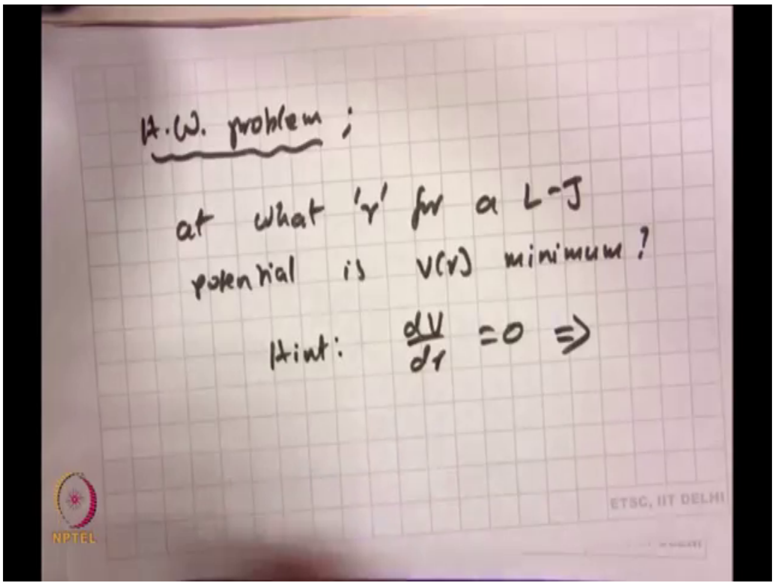

H.W. problem;

at what 'r' for a L-J potential is V(r) minimum?

Hint: $\frac{dV}{dr} = 0 \Rightarrow$

So, from here this is the homework problem, what you should be able to figure out, this is the homework problem at what r for a Lennard-Jones potential is V of r minimum. At what r for a L-J potential is V of r minimum? That means, your potential is minimum, right. So, essentially the hint is you do d V of d of r is equal to 0 and then express r in terms of sigma, ok. That is what you will have to do, ok.

So, that essentially brings us to a discussion about electrostatics. But there was a question that was asked, you know how do we actually do it in molecules.

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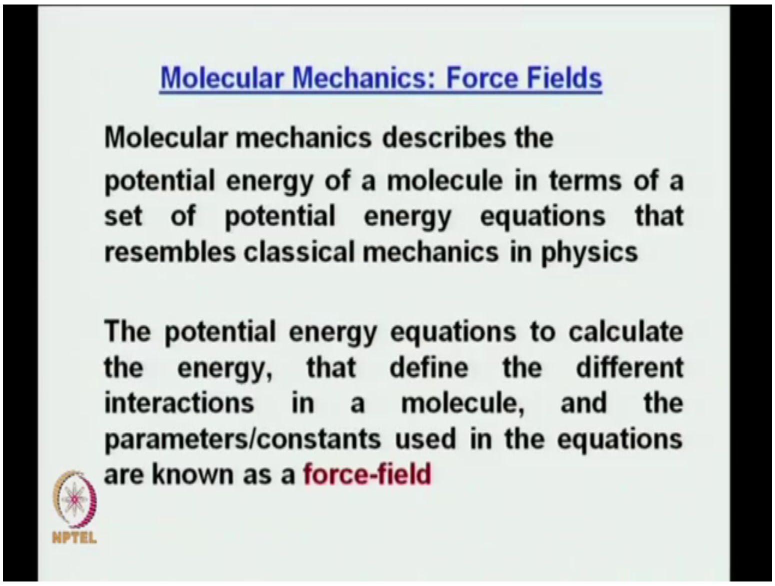

Molecular Mechanics: Force Fields

Molecular mechanics describes the potential energy of a molecule in terms of a set of potential energy equations that resembles classical mechanics in physics

The potential energy equations to calculate the energy, that define the different interactions in a molecule, and the parameters/constants used in the equations are known as a **force-field**

So, if we go to the slides. So, let me go to the slides now. Now, there is something known as molecular mechanics. What is molecular mechanics? So, for example you know, think about the situation: I have given you a protein because this is biophysical chemistry let us talk about a protein. In proteins you will be having different amino acids; you will be having different charge interactions say different dipole-dipole interactions, right. Whatever we have looked at up till now it is essential between two species, but there would be many.

And this potential energy of interaction: what are the different things you should consider, and how do you consider how do you actually calculate it? So, this is done by something known as molecular mechanics. So, as I said molecular mechanics describes the potential energy for molecule in terms of a set of potential energy equations.

Now, these potential energy equations we have already seen, right: V of r for many different systems this you have already seen, not although, but at least you have looked at the looked at it from the electrostatic point of view. That resemble classical mechanics in physics. So, that is why it is called molecular mechanics.

So, see quantum mechanics is all about molecules, right and classical mechanics has all these you know Newton's Laws of Motion and all these things. When you merge these two essentially you get molecular mechanics. That means, you are applying classical mechanics to a molecular description; that is what molecular mechanics is all about, right.

So, the next is if people would be working on molecular mechanics they would be using something known as force fields. Now, remember all these potential energy of interactions is essentially forces of interaction, right. So, the potential energy equations you know to calculate the energy that define the different interactions in a molecule and the parameters you know whichever you can vary to define this interactions together constitute the force field. That means, you are creating a field in which you are taking into account all possible interactions giving rise to certain potential energy. Is it clear what a force field is?

So, force field means, you are talking about you take a molecule and you talking about all possible interaction energies potential I am talking about in a molecule, right. And the field tells you that in this field I better make sure that I take into account all possible sets of potential energy interactions, right. That is what the field is. The field involves everything it is a field that is it has all the typical interactions that can ever occur or suppose to occur in a given molecule. Now, it will become more clear once we go to the next slide. So, look at this.

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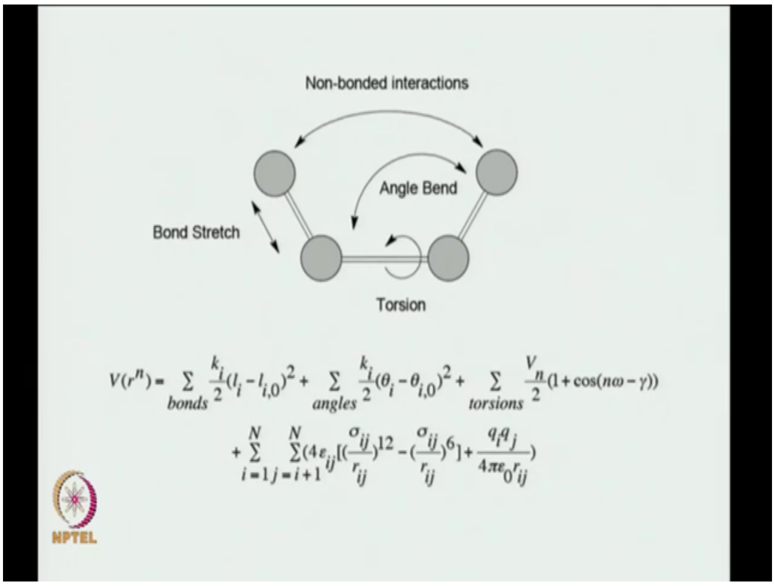

Non-bonded interactions

Angle Bend

Bond Stretch

Torsion

$$V(r^n) = \sum_{bonds} \frac{k_i}{2}(l_i - l_{i,0})^2 + \sum_{angles} \frac{k_i}{2}(\theta_i - \theta_{i,0})^2 + \sum_{torsions} \frac{V_n}{2}(1 + \cos(n\omega - \gamma))$$
$$+ \sum_{i=1}^{N} \sum_{j=i+1}^{N} (4\varepsilon_{ij}[(\frac{\sigma_{ij}}{r_{ij}})^{12} - (\frac{\sigma_{ij}}{r_{ij}})^{6}] + \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}})$$

What are the different interactions that can happen? Now, this is very simple, right. This is the typical see a peptide bond or whatever we are looking at. See, you can have one is a bond stretching and if you remember harmonic oscillator what was the potential it was half k x squared; was not it? So, but that is the potential energy of interaction, it is not obviously electrostatic in that sense, but it is the potential energy of interaction. Is not it?

Then we can have bending motion, right. Like we have stretching, symmetric, anti symmetric we can also have bending that is also potential energy of interaction, ok. Then we can have torsion that means, you are moving it with respect to a bond you are doing a torsion application.

That is also a potential energy of interaction. And last, but not the least you can also have non-body interactions. This is the interactions we have talked about in at length in electrostatics; specially the dispersion force is van der Waals force and all those things, even the Lennard-Jones potential

Now, what is missing from here obviously, what we can point out is a hydrogen bond situation, right. Hydrogen bonds are typically not very easy to model, but people have come up with certain components in force field which can take into account the hydrogen bonding situation, but let us not worry about the specifics. The idea is that if you would want to calculate the potential energy of interaction how the energy of interaction in terms of force field for a given molecule; these are all the different terms you have to look at you see. The first one what is it? The first one is: so this is V of r, right the first one is?

Student: Essentially.

Essentially a stretching, right half k x squared, right. Now, this is bond stretching we are talking about. In the next slide I will tell you what l 0 means. The next one is the same for bending if you can have a stretch you can have a bond bend. The same thing will happen at different force constant though. Next you have a torsion. The torsion is given by this equation, this we have not talked about at length will just keep it at that. But look at the last term, the last term is something we are familiar with by now, right. The first one is what?

Student: Lennard.

Your Lennard-Jones potential. And the last one is what?

Student: Columbic.

Your columbic, right that is what you know. Obviously, will be having many ion dipole and all those things, but this typically as a very broad thing. It covers almost everything except the hydrogen bond we have talked about. Now, just looking at this individually real quick.

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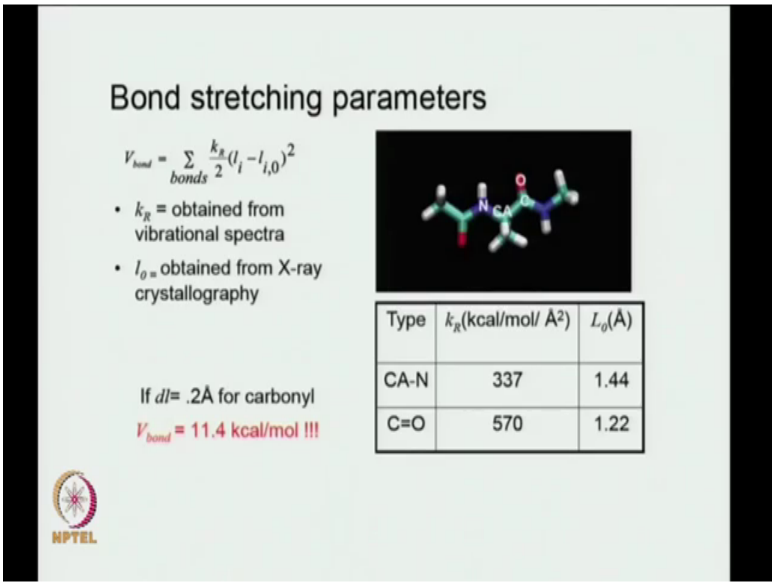

Bond stretching parameters

$$V_{bond} = \sum_{bonds} \frac{k_R}{2}(l_i - l_{i,0})^2$$

- k_R = obtained from vibrational spectra
- l_0 = obtained from X-ray crystallography

Type	k_R(kcal/mol/ Å^2)	L_0(Å)
CA-N	337	1.44
C=O	570	1.22

If dl= .2Å for carbonyl

V_{bond} = 11.4 kcal/mol !!!

If we are talking about the first term which is the bond stretching, right. This you know this force constant is typically the curvature of a potential energy, the force constant k is your if you remember its d 2 V over d x squared let us not go there now, it is the curvature of a potential energy surface. This k you can get easily from vibrational spectra and this you know.

What is l 0; l 0 is equilibrium distance we obtained from x ray crystallography. That means, if you are going to take a protein molecule and if you are going to find out this force field potential energy of interaction you better have the crystallographic coordinates or at least the bond length of the respective bonds I am looking at. This you can only get if you have the respective crystal structure of the proteins or.

That is why if you see people working with molecular mechanics. Most of the times or almost all of the time they would be working on proteins which have crystal structures already deposited in the protein data bank, because they have the coordinates. And if people have coordinates they immediately have what, the bond lengths, bond angles and everything. That it is parameters essentially, right

So, this is now you know what l 0 stands for and l minus l 0 is what it is essentially a force of extension or rather length of extension or length of compression whichever you are looking at, ok. Now, this is just for information.

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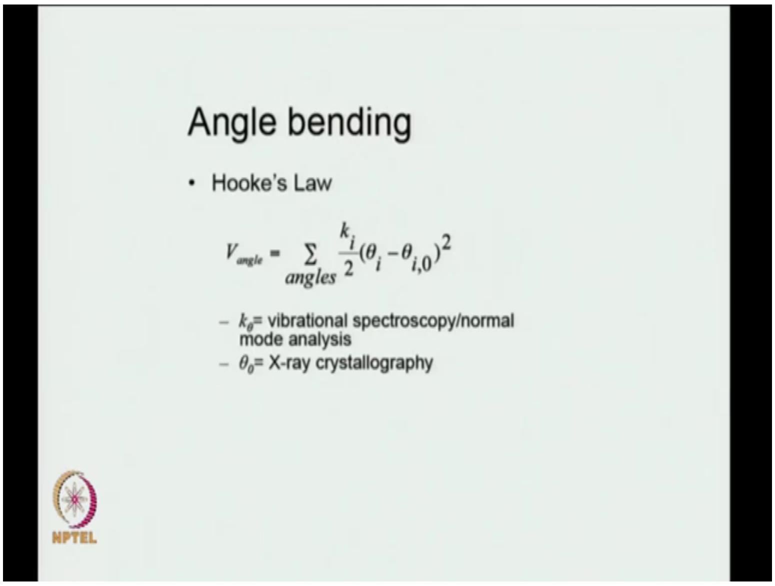

Angle bending

- Hooke's Law

$$V_{angle} = \sum_{angles} \frac{k_i}{2}(\theta_i - \theta_{i,0})^2$$

  - k_θ= vibrational spectroscopy/normal mode analysis
  - θ_0= X-ray crystallography

Now, this angle bending. The same thing again, from crystal structure you will be having theta and all those things.

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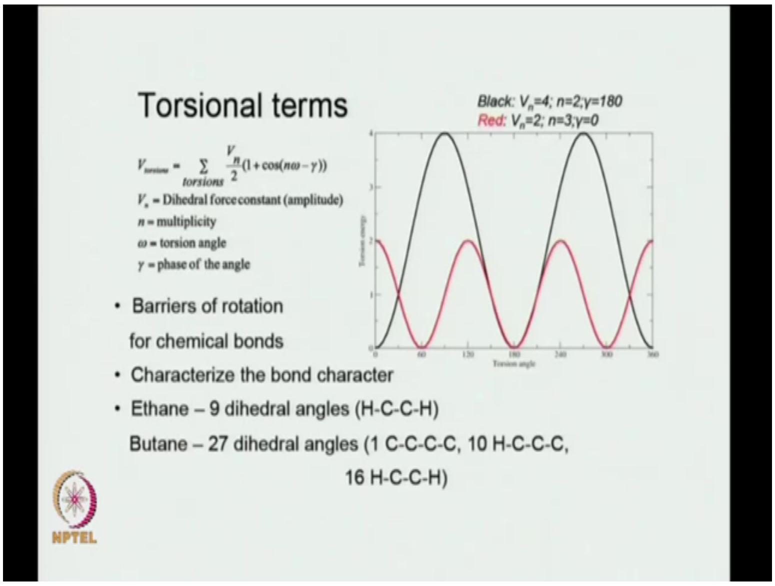

Torsional terms

$$V_{torsion} = \sum_{torsions} \frac{V_n}{2}(1+\cos(n\omega-\gamma))$$

V_n = Dihedral force constant (amplitude)
n = multiplicity
ω = torsion angle
γ = phase of the angle

- Barriers of rotation for chemical bonds
- Characterize the bond character
- Ethane – 9 dihedral angles (H-C-C-H)
  Butane – 27 dihedral angles (1 C-C-C-C, 10 H-C-C-C, 16 H-C-C-H)

This is the torsion term. Now, the torsion term as it goes you look at n; n is the multiplicity essential is a periodicity of a vibration or the periodicity of the distortion, ok. Say n is equal to 1 2 3 4 it can go and like that. Omega is a torsion angle at the angle around which we are doing this torsion application. And gamma is referred to as a phase angle and you know this is these are different I mean this is for radius for V n is equal to 2 n is equal to 3 where periodicity is 3 and this one is for n is equal to 2 gamma is equal to 180.

So, these are different things people look at. And obviously the last term which we had if you remember the last term was something we just looked at some time. So, this is again the importance of this is people when doing or looking at force fields would typically include these. And, say these are the basic minimum or the bare minimum we have to include in the force field.

Now, if you start talking about very specific interactions like hydrogen bonding or some other types of interactions you start refining this potential by adding extra terms or adding extra parameters, that is what you do. But this guys in a nut shell is what people do when they do molecular mechanics forceful calculations, right.

And you can understand depending upon the size of a protein you will be having so many atoms you can understand how many atoms they will have to do it, right. And it competition it becomes very time consuming; because if you are doing it through computer obviously, you have to do it through computer you cannot do it by hand. The computer has to look at each and every such interaction for each and every atom in a protein and when the computer tries to do this calculations it obviously, is going to involve time.

This is also another reason why it involves time, but we do not go there. But this is essentially what a computer does or how a program is built in by people. There are force field programs I do not know whether you have heard of programs like I will tell this to you may be in next class like amber something known as amber force field, there is something known as a CHARMM force field so, yeah. So, the CHARMM is from Harvard. So, its Harvard molecular mechanics that is why C H A R M M: C is obviously chemistry, right.

So, yeah, it is actually if you kind of spend some time with force understand that it is not that something you do not know. You go into the forces you look at these things all this things you know means, at least you can vision you honest on what it is. It is just a mere application of this mere to taking this things and putting them together that is what it is all about, nothing is new to you know that is what the point is, ok.

So, you have that is what about. That is pretty much what I need to tell you about electrostatics and I just thought I make this connection, so that you understand how electrostatics is being used by people to look at different proteins.

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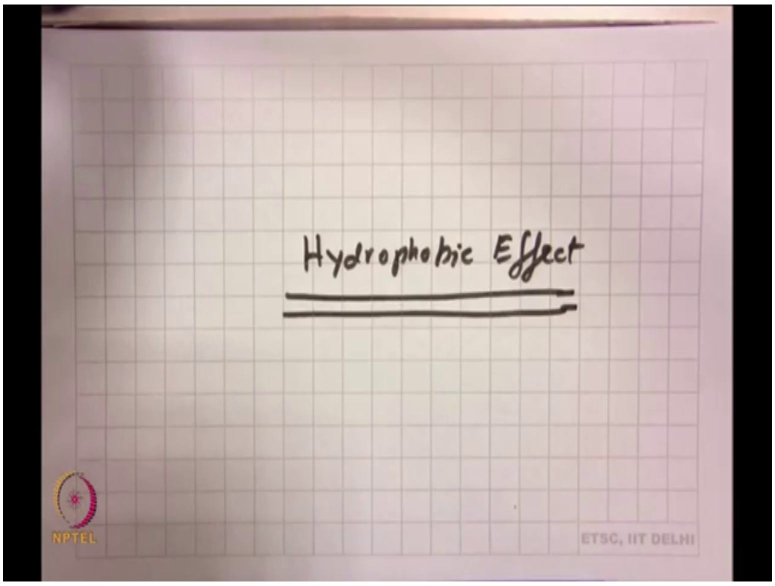

Hydrophobic Effect

Rather, next topic I will just touch it briefly and I will start the next day is hydrophobic effect. Now, hydrophobic effect is of huge importance, ok.

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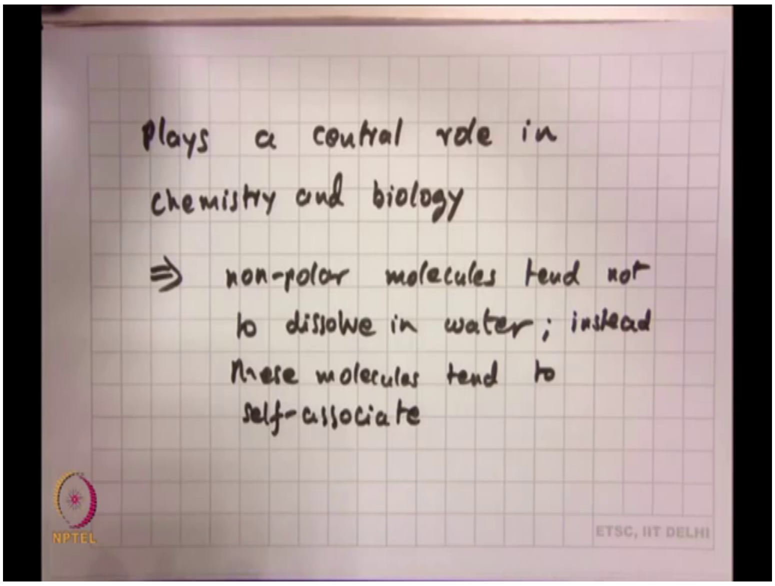

Plays a central role in chemistry and biology

⇒ non-polar molecules tend not to dissolve in water; instead these molecules tend to self-associate

So, this effect plays a central role in chemistry and biology, it is very important. And we will try to understand hydrophobic effect from the very basics. What does hydrophobic effect start from? It essentially starts from the fact; where do I start from that non-polar molecules tend not to dissolve in water. Instead, these molecules tend to self-associate; instead these molecules tend to self-associate. This you all know, right.

Now, think about this in terms of the perspective of a protein folding. Remember we talked about some length you know at some length about a nascent proteins and peptides, and we said that the tunnel ribosomal tunnel does not give it enough space for the full protein to fold. So, depending upon what protein you have a part of it has to fold outside the tunnel.

And when the protein is folding your essentially what you are having is you taking your hydrophobic amino acids and putting them in the interior. The simple reason being that hydrophobic amino acids do not like water, right. But how would you model this? You cannot just take a protein and try to model hydrophobic effect, because the protein has so many amino acids, right; which one would you take, which one would you do not take.

So, then this is where we will start from tomorrow. Now, I just remember this there is there is a scientist called Walter Kauzmann. Walter Kauzmann in 1958-59, he came up with his theory of hydrophobic effect and he said if I have to model this boreal of hydrophobic a non-polar amino acid side chain when it goes from say; when it goes into water it is going inside the interior, how can I do it best?

What I can do? What I can do is; I look at the amino acid and I take a model compound I take a model compound and they look at that model compounds energetics when it is getting dissolved in water. If I can do that and if I can compare this one and that one then possibly I should be having an idea of the energetics involved in this hydrophobicity. That means, when a protein is getting buried or when a proteins interior has all this buried hydrophobic residues.

So, essentially you model a proteins interior or you model this transfer of hydrophobic amino acids from water to the protein interior by doing just a reverse or essentially if you look at the other direction. That means, if you are opening a protein you are taking the hydrophobic amino acids and exposing them to water. What you can now do is try to model that by taking an organic molecule put in an organic liquid you take it out and now put it in water; does the same thing you are doing for a protein and then you compare the energetics and try to model that.

So, that is what Kauzmann, you know that was a brilliant idea that Kauzmann came up with ok, and that is what hydrophobicity is all about. But I hope I can stress upon you the importance of hydrophobicity and you will see how hydrophobicity can be developed, it is actually very nice, and will do that tomorrow, ok.

Thank you.