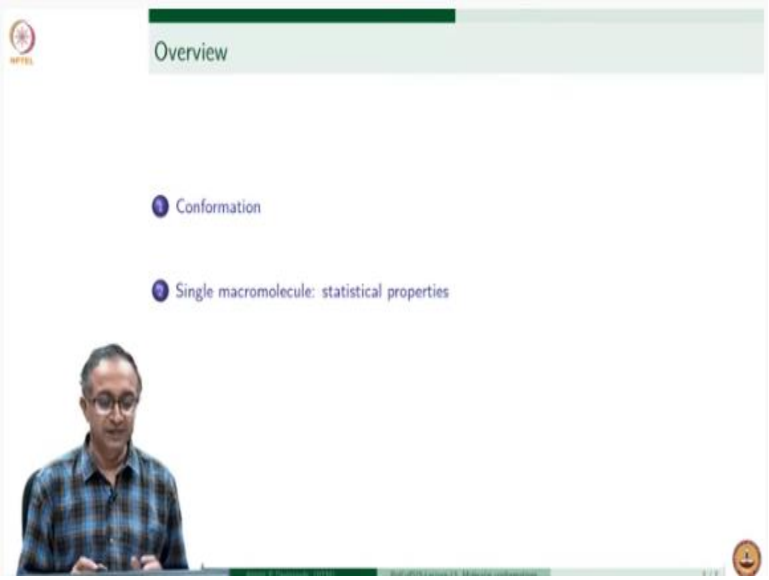
Simple Concepts Related to Single Macromolecule
Prof. Abhijit P Deshpande
Department of Chemical Engineering
Indian Institute of Technology – Madras

Lecture - 13
Molecular Conformations

Hello. Single macromolecule - that's what we're going to focus on. For the next three-four lectures. You will see that it's very fascinating that a single macro molecule can explain so many phenomena associated with polymers.

And an important idea behind why single macromolecule behaviour is important is related to conformation. So, in this lecture, we will focus on molecular conformations and then in the next three sets of three-four lectures, this set of lectures, we will look at the aspects associated with single macromolecules behaviour and concepts related to the behaviour of single macromolecule will prove us to be very important while describing phenomena such as visco elasticity phenomenon such as why how can protein and DNA molecules back themselves the way they do in cell How do they recognise things. So, variety of things are related to single macro molecular phenomena.

(Refer Slide Time: 01:27)

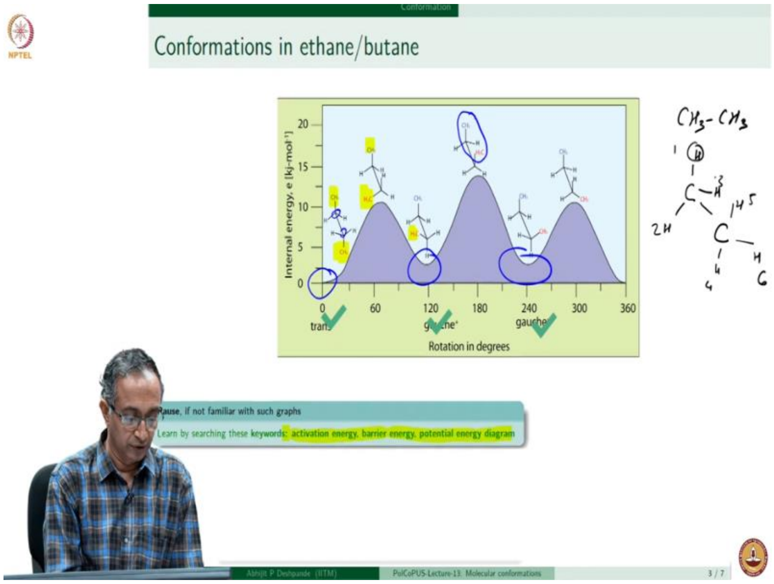


Overview

1. Conformation
2. Single macromolecule: statistical properties

And so, we will begin by first looking at what do we mean by conformation. And, we will see that because of the changes in conformation that a single macro molecule can do a single macro molecule becomes a statistical object. It has a randomness associated with it. So, we will try to understand concepts related to randomness and statistical properties of a macro molecule.

(Refer Slide Time: 01:57)



Conformation

Conformations in ethane/butane

Pause, if not familiar with such graphs

Learn by searching these keywords: activation energy, barrier energy, potential energy diagram

Abhijit P Deshpande (IITM)

PolCoPUS-Lecture-13. Molecular conformations

3 / 7

So, let's first look by what do we mean by conformation. So, here Even simple molecules like Ethane and Butane have conformations. And what we mean by that is just the position of different atoms which are there. So if I were to draw ethane, which is nothing but CH3-CH3. And so when I say the positions of different atoms, what we mean is there is 1 carbon atom and another carbon atom, and on each of these I have 3 hydrogens. And so now if I look at the positions of the hydrogen atoms on the other carbon, and if I number these, so let's say if I say this is 1, this is 2, this is 3, 4, 5, 6.

So the question that I'm asking is, how is the relationship in terms of where is position one 1 hydrogen located and where is five 5 located and things like that. In fact, if you can think of if these three are the three hydrogens on one carbon and these are three hydrogens on the other, we are basically saying that look carbon carbon bond rotation is possible and therefore, this 1 and 5 are they located like this or is it like this or so. Therefore, because of the carbon carbon bond rotation, this ethane molecule can have lots of conformations - infinite basically.

So, the angle that way I am showing, so, if this I call zero then 90, 180 and all kinds of angles are possible. And how we can represent this is depicted here, for example, for butane molecule. So, in case of butane molecule now what we have is 2 of the hydrogens are replaced with CH3. And so, what I have highlighted here is, for example, the position of CH3 with respect to another CH3.

And if you look at the energy associated with this molecule, when this carbon-carbon bond rotation keeps on changing, what you can notice is there are some energy maxima and minima. And we know that whenever energy is minimum, those are the conformational states, which will be preferred. So, if you look at this butane molecule, we have one conformational state, second conformational state and third. These are where there is the minimum.

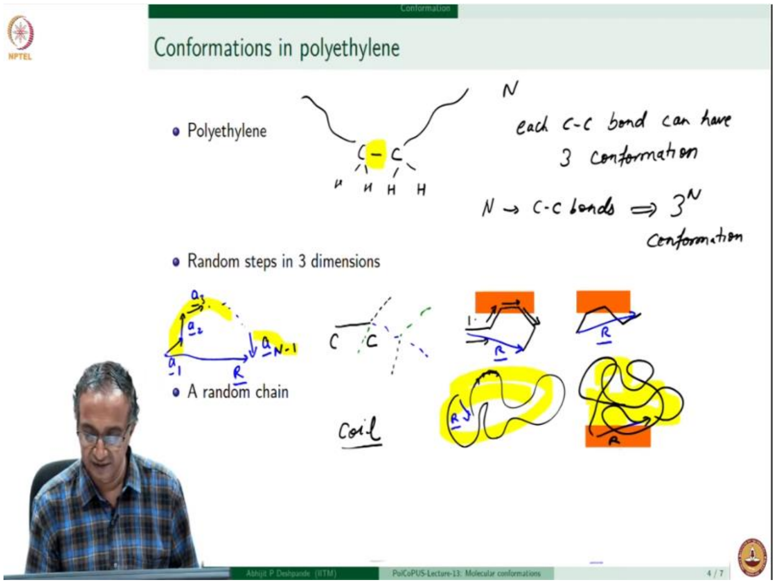
So, we have this minimum, this minimum and this minimum. So, you can pause here and look at how the positions of 2 methyl groups are on 1 carbon, this carbon and this carbon. And of course, when both the methyl groups are closest to each other the energy is maximum and therefore, that state is unlikely to be obtained. So, therefore, the idea behind such an energy diagram, so, if you look at the methyl groups on carbon atoms in this conformation, both of them are close to each other and that's energetically not favorable at all.

Because the energy of this conformation is very high. So, therefore, based on this such kind of energy diagram, we can say that which are the 3 states which are going to be most probable. And what that leads us is in terms of, if I take a snapshot of a butane sample, I will find some of the molecules in conformation state each of these 3.

So, some molecules will be in one conformation states and others in another and in the third one, or if I am able to pick just 1 butane molecule, then that butane molecule can flip back and forth between these 3. And so, a conformational change can happen where a butane molecule is just doing this. Or if I take a random snapshot of several butane molecules, I will see approximately one third in each of the conformational states.

So this is the basic idea behind conformational change and C-C bond rotation. And if you're not familiar with this diagram, I suggest that you please look at these phrases carefully. What's a potential energy diagram? What do we mean by barrier energy? Because in this case, when conformation has to change, if conformation is this and it has to flip like this, then a barrier energy has to be crossed and whenever temperature is higher, it will become easier for this flipping back and forth to happen. So therefore, all of these things, please rush up in terms of activation barrier and potential energy diagrams.

(Refer Slide Time: 06:55)



Conformation

Conformations in polyethylene

- Polyethylene
- Random steps in 3 dimensions
- A random chain

N

each C-C bond can have 3 conformation

$N \rightarrow$ C-C bonds $\Rightarrow 3^N$ conformation

Abhijit P Deshpande (IITM)

PolCoPUS-Lecture-13: Molecular conformations

4 / 7

So these potential energy diagrams are crucial in terms of explaining why conformational changes happen in Polymer. So, if you look at polyethylene, we can again just think in terms of a single carbon-carbon bond and there will be 2 hydrogen which are there, but then of course, this polymer chain continues. So, what I have drawn is a single ethylene unit and then chains which are going on and of course, rotation is possible around this carbon-carbon bond.

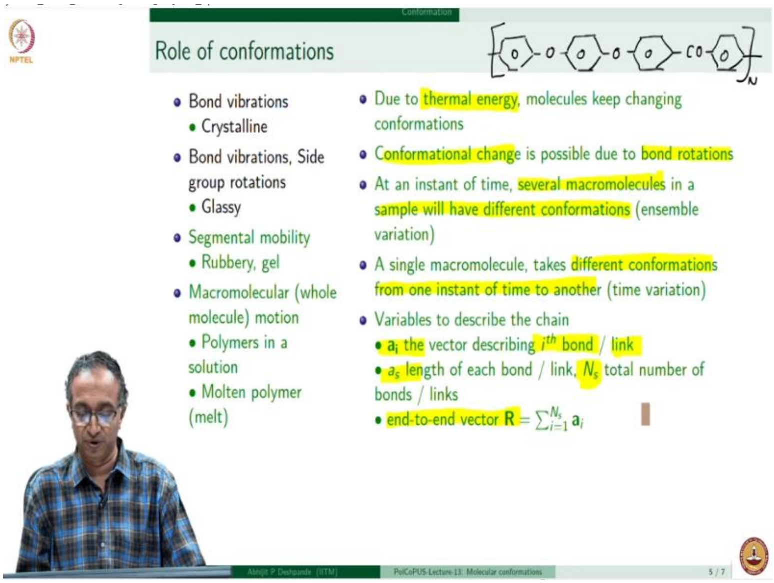
So, effectively if we have N bonds and each C-C bond can have 3 conformations, polyethylene molecule with N C-C bonds will have 3 to the power N conformations. Now, just think what capital N is for Polymer. And you will realise how large this 3 to the power in numbers. So, single macro molecule, when conformational changes are possible is an extremely dynamic object where all the different conformations can take place.

And if you start thinking of this in terms of each and every C-C bond as a single step. So, for example, if I say let's say draw the first C-C bond. Now, the next question is the next C-C bond can occupy three different states and I'm just going to use three different colours to indicate where the 3 different positions are, and then the next bond again, so if I let's say, take the let's say the blue bond was what is the conformational state.

So, again, I will have three options from this blue bond also. So, effectively when I start drawing, I may get a single bond, second bond, third born bond, forth bond fifth born bond. And so, what I am drying is a snapshot of a configuration of a polymer chain same polymer in the next instant of time could be first one second born bond, third born bond, fourth one and so on. So, what we will show is the fact that therefore, polymer will be like a random chain.

Where each and every step because there are thousands and thousands of steps, when I draw the overall polymer chain I it looks like a random chain which keeps on binding over each other keeps on collapsing over each other. At the same time when we look at one instant of time and another instant of time, then polymer chain changes its can formation. So that's why it's called a random chain, we also will use the word coil to describe this kind of a macromolecules system. Now, when is conformational change possible?

(Refer Slide Time: 10:28)



Conformation

Role of conformations

- Bond vibrations
  - Crystalline
- Bond vibrations, Side group rotations
  - Glassy
- Segmental mobility
  - Rubbery, gel
- Macromolecular (whole molecule) motion
  - Polymers in a solution
  - Molten polymer (melt)

- Due to thermal energy, molecules keep changing conformations
- Conformational change is possible due to bond rotations
- At an instant of time, several macromolecules in a sample will have different conformations (ensemble variation)
- A single macromolecule, takes different conformations from one instant of time to another (time variation)
- Variables to describe the chain
  - $\mathbf{a}_i$ the vector describing i^{th} bond / link
  - a_s length of each bond / link, N_s total number of bonds / links
  - end-to-end vector $\mathbf{R} = \sum_{i=1}^{N_s} \mathbf{a}_i$

Abhijit P Deshpande (IITM) PolCoPUS-Lecture-13: Molecular conformations 5 / 7

So, let's look at the role of conformations and when they are possible. So, if we have a crystalline macromolecule or any other crystalline material also then what we only have our bond vibrations. So, in such cases conformational changes will not be there. Similarly, if we go to an amorphous solid state or a glassy state, then again bond vibrations are there and maybe we will see this that in glassy state of macromolecules side groups may be able to rotate we will see that. For example, that if you have polystyrene and then the side group which is this benzyl group can rotate even in glassy state, but the C-C bond rotation which is crucial for the conformational change is not possible in glassy state. So, therefore, as far as conformations are concerned, we don't really have to look at many of these conformational changes as often in glassy glassy or crystalline states.

But, as far as conformational changes are concerned in the rubbery state or in case of melt state or solution state, they are extremely important. And so, clearly you can see that this is associated with temperature. At lower temperature we will have crystalline or amorphous solid states and at higher temperature we will have rubber, even high temperature we will have melt. And of course if we include a solvent then that plays a role very similar to temperature by improving the carbon-carbon bond rotational probabilities or making sure that conformational changes are possible.

So, thermal energy is very crucial to provide energy for crossing the barriers and changing conformations and conformational change is associated with backbone bond rotation of macromolecules. In this case, what we have discussed so far is carbon-carbon bond. So, here you can think what happens if instead of carbon-carbon bond, single bond if I have a double bond in the backbone will that make the chain less flexible? Instead of a single C-C bond, what if I have a benzyl bond?

So, polyether ether ketone is a very strong engineering material which is used for aerospace and it has ether bonds. So, C-O bonds and it also has benzyl groups along its backbone. Polyether ether and then ketone. What do we expect conformational changes in this kind of a polymer, where there are not as many C-C bonds along the backbone and clearly yes, your hunch is correct, that such kind of polymers conformational changes will not be as easy.

And therefore, many of these may not have as quite coil like structure, but they may have more rod like structures. So you can already see that how I'm talking about an engineering material which is very strong and hard and its backbone has a particular degree of flexibility based on conformational change. So, using a single macro molecule, we are already talking about mechanical properties of a polymer, and that's why single micro molecule behaviour is so important.

So, just to summarise again, when we look at a single macro molecule, then it will take different conformations from one instant of time to the other. If we look at several macromolecules then each of the molecule in this ensemble will have a different state and therefore there is a variation in an ensemble. And so the variables which can be used to describe this polymer chain are as follows. We can look at the chain that we had drawn earlier.

So if I start looking at and saying that you each and every link here between C-C bond is a small vector. So basically my polymer chain is a collection of all these vectors. So I have one vector, which I'll call a1, then another vector, which I'll call a2, then another vector a3 and so goes going on and on till a(n-1), a(n-2) and so on. So, what I can see is this is a chain. So in this polymer chain also that I had drawn, I can have these bonds everywhere.

And so, a polymer chain is basically a collection of these links or these bonds. And the collection of all of them is eventually the response of the overall macromolecule. So, the variables to describe the polymer chain are the vector which describes the ith bond or the link. Here I'm also describing bond as well as link, because soon we will see that instead of describing the polymer behaviour, in terms of a single bond and groups like CH2-CH2 in case of polyethylene or CH2-CHCl in terms of PVC and so on.

We will start describing polymers more from a model, which is like a coil like material or a chain like material because the The length of the chain link the how the link is free to rotate may depend from one polymer to the other, but description of the overall chain can be based on what are called coarse graining methods. We disregard the molecular details, but incorporate the interactions of the hydrogens and chlorines and oxygens and carbons into the parameters of our coarse grained model.

So, therefore, ith link or ith bond can be thought of, there is a length associated with each link. And of course, we have Ns total number of bonds. What is the relationship between Ns and the molar mass? They are of course, linearly proportional to each other when molar mass is higher, and this Ns is also higher. And a key characteristic of this chain is the end to end vector. And so, in this case, from the first to the last, this is the end to end vector.

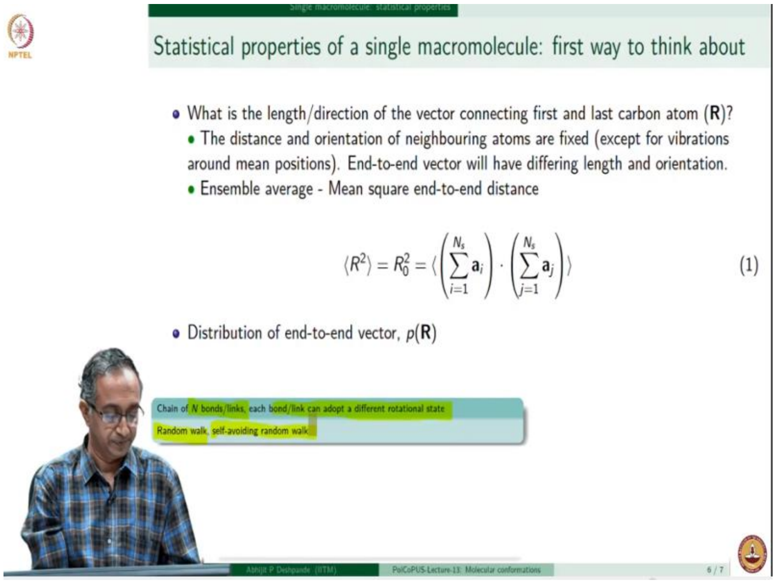
$$R = \sum_{i=1}^{N} a_i$$

And what is crucial is the statistical properties and all these information conformation changes of macromolecule can be described by this, the fact that R keeps on changing. You can also see already in the random drawing that I had drawn earlier, you can see that how not only information is changing each and every position, but R, the end to end vector also captures the change in the conformation.

Other important thing that you can notice is, when I drew the chain, it's extremely long, but the end to end distance is very small. And to end distance, in fact, is much smaller. This is something which is new to the coil like nature of macromolecules because it's a very flexible object, because the conformational change is easy in case of polymers like polyethylene, generally end to end distance will be much smaller than the contour length, or the overall length.

So if I take two ends of this macromolecule and stretch it and open it completely, then that's the overall length called contour length. So, the end to end distance is always going to be much less than the contour length. Of course, you can think what happens for a rod like molecule in which case this conformational changes are not permitted and polymer is generally in an extended state. So think about it, we will come back to this later on during the course also

(refer time: 19:49)



Single macromolecule: statistical properties

Statistical properties of a single macromolecule: first way to think about

- What is the length/direction of the vector connecting first and last carbon atom ($\mathbf{R}$)?
  - The distance and orientation of neighbouring atoms are fixed (except for vibrations around mean positions). End-to-end vector will have differing length and orientation.
  - Ensemble average - Mean square end-to-end distance

$$\langle R^2 \rangle = R_0^2 = \langle \left(\sum_{i=1}^{N_s} \mathbf{a}_i \right) \cdot \left(\sum_{j=1}^{N_s} \mathbf{a}_j \right) \rangle \qquad (1)$$

- Distribution of end-to-end vector, $p(\mathbf{R})$

Chain of N bonds/links, each bond/link can adopt a different rotational state

Random walk, self-avoiding random walk

Abhijit P Deshpande (IITM) PolCoPUS-Lecture-13: Molecular conformations 6 / 7

So this idea of conformational change and therefore a single micro molecule being a statistical object, we can now start talking in terms of quantitatively. So the first way to think about statistical property of a single macro molecule is to ask the question, you know, what is the length and direction of the vector connecting the first and last unit on the polymer chain. And we saw this that this keeps on changing and conformation changes.

And so, in terms of definition, this is nothing but summation of all the so R just a vector sum of all the individual links. And so if I'm interested in knowing the distance or the magnitude of this R, then I have to just look at two different conformations and what is the overall distance between end to end and these brackets here < >, we will use in the course many times. This indicates ensemble average.

$$\left\langle R^2 \right\rangle = R_0^2 = \left\langle \left(\sum_{i=1}^{N_s} a_i \right) . \left(\sum_{j=1}^{N_s} a_j \right) \right\rangle$$

If I take a bulk sample of polymer there are 10 to the power 23 macromolecules and each of them having different conformations.

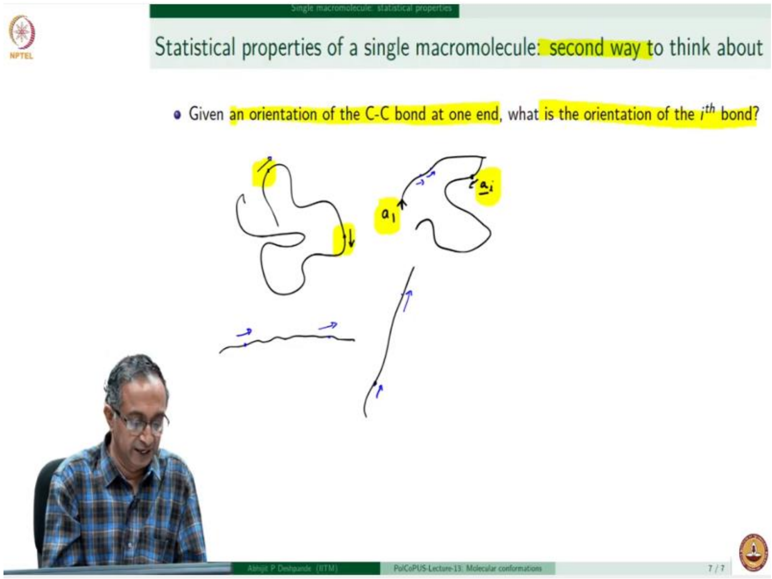
So, when I answer pose this question as to what is the average end to end distance between macromolecules two ends of macromolecules, I need to do an ensemble average. And so, I what I need to do is I need to look at all the possibilities of conformations that I had shown earlier. So,

this is one confirmation This is another confirmation. So, all such confirmations and their averages. And what you can see the way I have drawn as if you look at the first link okay let me just so, this is the first link, this is the first link, this is the second link and this is the second link.
So, this is only 2 conformation. You can already see that the first link orientations are very different in the 2 cases. So if I doing start doing dot products of a1 with a1, a1 with a2. So, all of this eventually algebraically you can show because of the randomness associated with this random chain that this can simplify as long as we say that the chain can have different conformations at a random scale.

So, therefore, we can describe different types of properties, different types of chain by specifying this end to end vector and probability associated with what is a specific instance of conformation of a macro molecule. So, effectively what we have is a polymer chain has N bonds and links and each bond can adopt a different rotational states and it is equivalent to doing a random walk. So it's like first step, then second step, then third step, fourth step.

So therefore, it's like a random walk in three dimensions and this is what is the fundamental model theory based on which we get properties of polymers. Remember that a polymer chain cannot overlap on itself, because if there is one link here, and then there is second bond and third bond and it can come back and after some time again a bond can come close to this, but it cannot overlap. So, therefore, we have random walk but it can be a self-avoiding random walk. So, this is again theoretical framework to describe properties of macromolecules.

(Refer Slide Time: 23:46)



Single macromolecule: statistical properties

Statistical properties of a single macromolecule: second way to think about

- Given an orientation of the C-C bond at one end, what is the orientation of the i^{th} bond?

Abhijit P Deshpande (IITM)

PolCoPUS-Lecture-13: Molecular conformations

7 / 7

Now, the second way we can think of the property of a single macro molecule is in terms of orientation correlation. What we are seeking here is if I draw a random conformation of macromolecule. And if I take any two points on it. So let's say I take this point and this point, the question I'm asking is, how are the orientations related to each other. If I have a rod like molecule, then it will be like this.

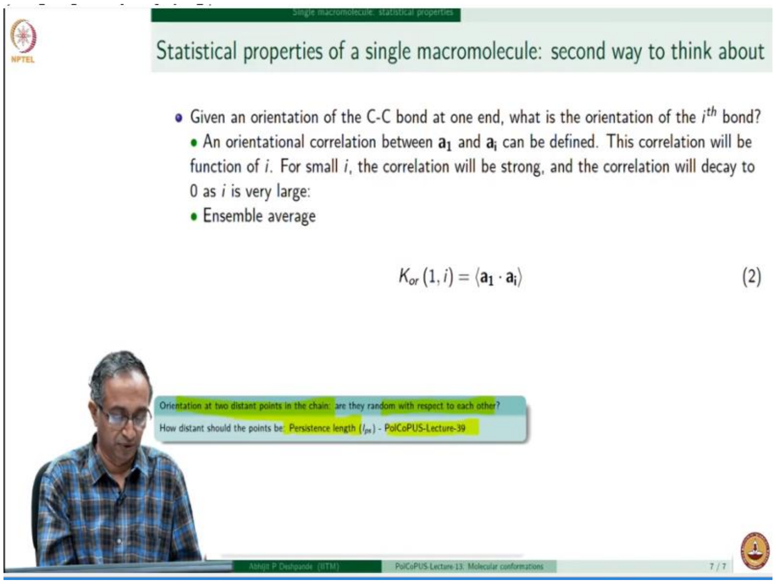
And so if I take any two points on that chain, we can see that the orientations are closely related to each other, because it's a rod like molecule conformational changes are not easy and no bond rotation is possible. So therefore, we find no if I know rotational state of one bond, I know also rotational, the orientation state of another bond. Same macromolecules can adopt move like this, but again, if I take a look at two different points, so in a rod like molecule, there is always correlation between orientation of one point with another point.

But that's not the case in case of a flexible macro molecule. So, by looking at this orientational correlation, we can think in terms of how flexible is this macro molecule, how easy are conformational changes happening in this macro molecule? And what we can notice here is, if I take two points which are close to each other.

Then what happens is their bonds might be correlated with each other, but when we go far apart, then the correlation drops off. So the question that we can pose is given an orientation of C-C bond at one end, what is the orientation of another bond. So basically what we are saying is, if we look at, let's say, if I start by saying that, you know, I know orientation here, which is my firstborn bond , and I take some other point randomly, and then I'm asking this question, what is the relationship between orientation of 1 and orientation of i?

And intuitive answer that we can get is, if even in a_1 and a_i are close to each other, then they will be correlated. If a_1 and a_i are far apart from each other, they will not be correlated. But if we have an odd rod like molecule, then a1 and ai will always be correlated, no matter how far apart they are from each other.

(Refer Slide Time: 26:47)



Single macromolecule: statistical properties

Statistical properties of a single macromolecule: second way to think about

- Given an orientation of the C-C bond at one end, what is the orientation of the i^{th} bond?
  - An orientational correlation between $\mathbf{a_1}$ and $\mathbf{a_i}$ can be defined. This correlation will be function of i. For small i, the correlation will be strong, and the correlation will decay to 0 as i is very large:
  - Ensemble average

$$K_{or}(1, i) = \langle \mathbf{a_1} \cdot \mathbf{a_i} \rangle \quad (2)$$

Orientation at two distant points in the chain: are they random with respect to each other?

How distant should the points be: Persistence length (l_{ps}) - PolCoPUS-Lecture-39

Abhijit P Deshpande (IITM) PolCoPUS-Lecture-13: Molecular conformations 7 / 7

So this is done by defining something called a correlation orientational correlation function, which is again an ensemble average of comparing the orientation of first one with ith bond. And we would expect this function to decrease as you increase i. So, bonds which are closer to each other will are correlated bonds, which are further apart are not correlated. So, in this lecture what we have seen is conceptually how conformations make some macromolecule a dynamic object.

In which case conformations keep on changing and because of this statistical quantities have to be used to describe conformational state of a macro molecule. So, one other important thing that you need to just remember is that, since, orientations at too distance point are more random with respect to each other, we can think of a length scale in the macromolecule - persistence length. Persistence of correlation. So two points closer to each other - correlation persists, if we go farther apart, there is no correlation. So, persistence length is a quantification of this idea that orientational correlation goes down when you go far apart in a polymer chain. And we will look at some of these properties of macromolecules and their flexibility in a lecture later on. Thank you.