Polymer Physics

Dr. Amit Kumar
Department of Chemical Engineering
Indian Institute of Technology, Guwahati

Lecture – 02
Ideal Chain Models

So, in the previous lecture we discussed some introductory concepts of polymers. So, what are polymers, what are different types of polymers, how polymers can be classified into different categories and how the molar mass of polymer is defined in different ways, these are some of the things that we discussed in the previous lecture. Today, we will be starting at different topic and that topic is basically the ideal models of polymer chains. So, before we go ahead I will just briefly discuss the content of this lecture.

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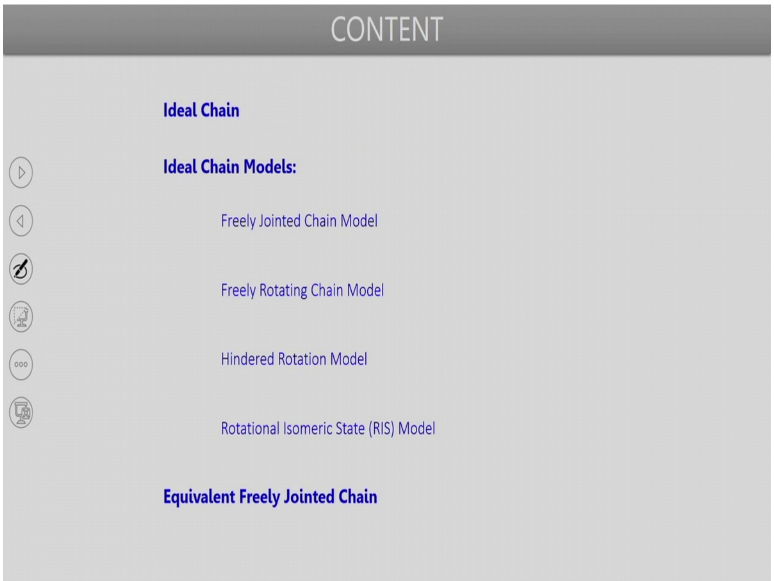

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Ideal Chain

Ideal Chain Models:

- Freely Jointed Chain Model
- Freely Rotating Chain Model
- Hindered Rotation Model
- Rotational Isomeric State (RIS) Model

Equivalent Freely Jointed Chain

So, in this lecture we will be starting off by discussing what ideal chains are and how they are different from real polymer chains, and then we will be talking about different the models that are available for ideal polymer chains. So, specifically we will be focusing on four different models. The first model is the freely jointed chain model, the second model will be the freely rotating chain model, the third one is the hindered rotation model and the last one that we will discuss very briefly is the rotational isomeric state model.

So, as we go from top to bottom these models actually increase in complexity more and more constraints are added. So, the top most model is actually the simplest one, but it is the least realistic one and as we go down the bottom one, which is rotational isomeric state model that is the one which is more realistic and it is actually used to predict the conformation of polymer chains to good degree of accuracy in many cases.

And finally, we will also be discussing the concept of what is an equivalent freely jointed chain. So, any of the chain models that ideal chain models that we have listed here; they actually all of them can be represented by an equivalent freely jointed chain. So, how that can be done that we will discuss towards the end of this lecture. So, what is an ideal chain?

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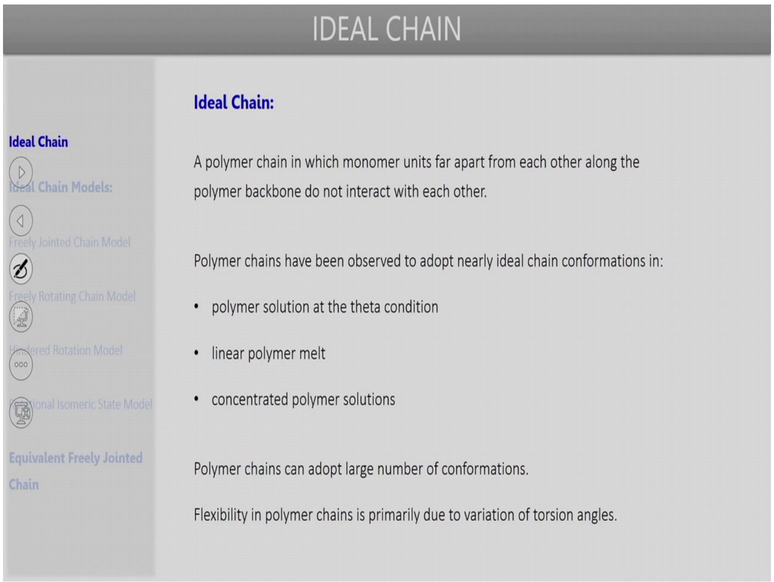

IDEAL CHAIN

Ideal Chain

Ideal Chain Models:

Freely Jointed Chain Model

Freely Rotating Chain Model

Hindered Rotation Model

Rotational Isomeric State Model

Equivalent Freely Jointed Chain

Ideal Chain:

A polymer chain in which monomer units far apart from each other along the polymer backbone do not interact with each other.

Polymer chains have been observed to adopt nearly ideal chain conformations in:

- polymer solution at the theta condition
- linear polymer melt
- concentrated polymer solutions

Polymer chains can adopt large number of conformations.

Flexibility in polymer chains is primarily due to variation of torsion angles.

So, by an ideal chain what we mean is polymer chain, in which monomers which are far apart along the polymer backbone they do not interact with each other. So, monomers which are very close to each other monomers, which are close along the polymer chain they will in fact, interact, but those which are sufficiently far apart they do not interact in the case of ideal chain models.

So, this kind of model might seem quite unrealistic, in the sense that any actual polymer chain in any actual polymer chain the monomers no matter how far apart they are when they come to close together they will actually interact, but it turns out that these kind of models they serve to two purpose. One is that using these models as a base one can actually build upon them to develop more realistic models for real polymer chains and the other thing is that many in many cases actually real polymers systems or polymer chains are known to adopt ideal chain conformations.

So, if we look at some of the cases here polymer chains have actually been observed to adopt chain conformation, which are very nearly ideal in certain cases. So, some of the cases are listed here one is the case of a dilute polymer solution at what is called the theta condition. So, we will not going the details here because when we come to the topic of polymer thermodynamic few after a few lectures, then we will discuss this concept of theta conditioning in detail and we will see that at certain special condition the polymer chains in a dilute polymer solution actually start to behave or tend to adopt the conformation of an ideal chain.

Similarly, if we have polymer in molten state or even concentrated polymer solution they have also been shown to exhibit nearly ideal chain conformations. So, before we move move ahead it is important to emphasize that polymers actually can adopt many different conformations. So, single polymer molecule, it is a long chain molecule and molecules are usually quite flexible. So, due to the inherent flexibility of the backbone the polymer molecule conformation keeps on changing with time and due to this the long chain nature and the flexibility of the backbone the then numerous conformations, then that a given polymer chain can adopt.

So, this flexibility of the backbone which is responsible for the various number of conformations that are possible so, this flexibility arises not because of the flexibility in terms of bond angles, but it the flexibilities because the different torsion angles are allowed for a given polymer chain or given group of atoms in a polymer chain, they can adopt different torsion angles and this flexibility in adopting multiple torsion angle actually leads to flexibility of the polymer chain itself.

So, before we move ahead it is important to describe what a torsion angle is because in some of the models that will be discussing later on in this lecture the concept of torsion angle will actually arise.

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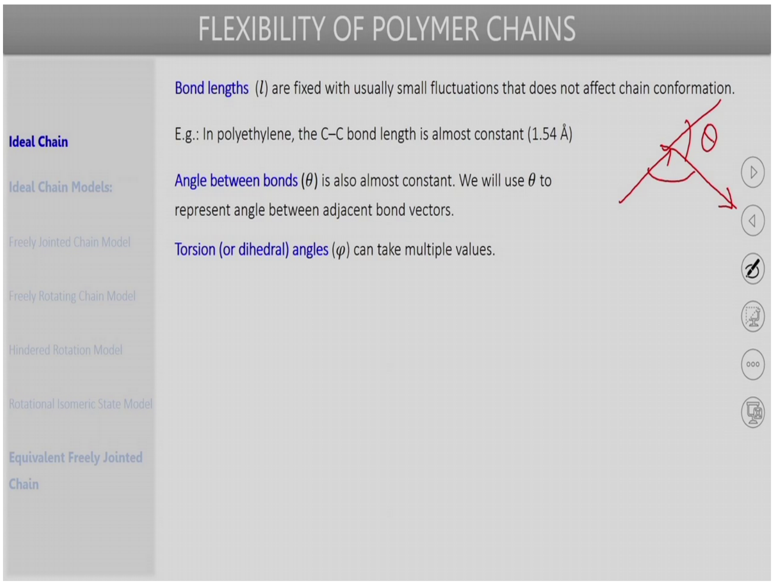

FLEXIBILITY OF POLYMER CHAINS

Bond lengths (l) are fixed with usually small fluctuations that does not affect chain conformation.

E.g.: In polyethylene, the C–C bond length is almost constant (1.54 Å)

Angle between bonds (θ) is also almost constant. We will use θ to represent angle between adjacent bond vectors.

Torsion (or dihedral) angles (φ) can take multiple values.

So, when we talk about a polymer long polymer chain polymer chain will be constituted by atoms which are bonded to each other forming a long sequence. So, the bond lengths in a polymer chain are typically fixed. So, if we take the example of polyethylene then the C-C single bond along the backbone that bond length is pretty much fixed at around 1.54 Armstrong they might be some small fluctuations due to thermal vibrations, but that the fluctuation is not large enough to impart any flexibility to the polymer chain itself.

So, bond lengths are pretty much fixed. The bond angles also in the case in the case most of the polymer the bond angles are also fixed. So, if we again talk about the case of simple case of polyethylene in that case the bond angles the carbon carbons are basically tetrahedrally arranged. So, the bond angle is typically close to the tetrahedral angel which is around 109 degrees.

So, there also the bond angles are pretty much fixed they might be against some variation in the bond angle, but that is not enough to impart enough flexibility to the overall polymer chain. So, before we move on it is important to mention that in this course the symbol theta, that we have here this symbol theta will primarily be used for angle between bond vectors and this angle between bond vectors is actually some more different from the convention definition of a bond angle.

So, if we let say consider a bond like this two bonds like this which form an angle. So, so, let us say the first bond is defined by this vector in the second bond by another vector, the angle that we drew here. So, the angle that we draw here this angle here that is conventionally referred to bond angles in many text.

So, in this course we will be using a slightly different angle for our purposes. So, if we extend the first bond like this then the angle that the extension of first bond the angle that it forms with the second bond vector which we can show like this here, this angle this is the one that way call as theta in this course. So, the conventionally defined bond angle actually will be 180 minus theta. So, so any time we are talking about the angle theta between bonds it is actually the angle between the adjacent bond vectors.

Next let us move on to torsion angle which is also referred to as dihedral angle. So, just like we have bond angle defined by the presence of two bonds, a torsion or a dihedral angle is actually defined by three consecutive bonds in a polymer chain next let us look at a schematic of a typical polymer chain and let us focus on three consecutive bonds of this polymer chain and let us see how using this three bonds torsion angle is defined.

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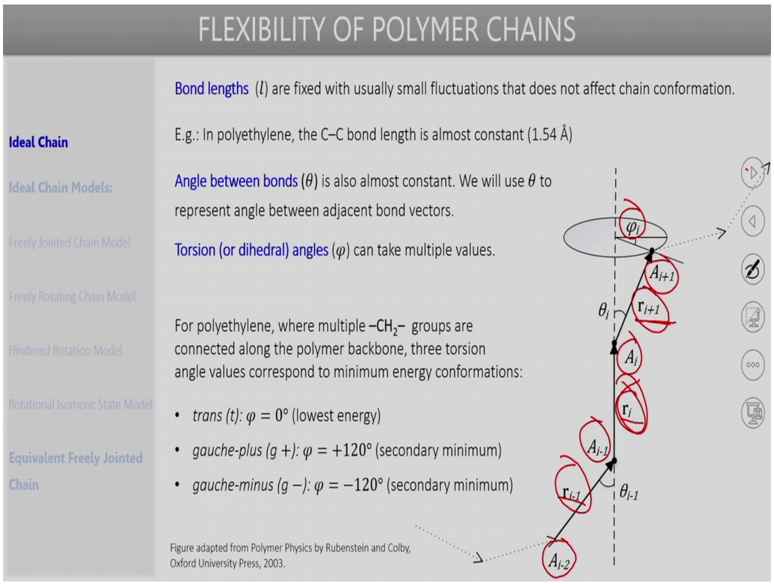

FLEXIBILITY OF POLYMER CHAINS

Ideal Chain

Ideal Chain Models:

Freely Jointed Chain Model

Freely Rotating Chain Model

Hindered Rotation Model

Rotational Isomeric State Model

Equivalent Freely Jointed Chain

Bond lengths (l) are fixed with usually small fluctuations that does not affect chain conformation.

E.g.: In polyethylene, the C–C bond length is almost constant (1.54 Å)

Angle between bonds (θ) is also almost constant. We will use θ to represent angle between adjacent bond vectors.

Torsion (or dihedral) angles (φ) can take multiple values.

For polyethylene, where multiple $-CH_2-$ groups are connected along the polymer backbone, three torsion angle values correspond to minimum energy conformations:

- *trans (t):* $\varphi = 0°$ (lowest energy)
- *gauche-plus (g +):* $\varphi = +120°$ (secondary minimum)
- *gauche-minus (g −):* $\varphi = -120°$ (secondary minimum)

Figure adapted from Polymer Physics by Rubenstein and Colby, Oxford University Press, 2003.

So, if we look at this chain it is it the part which is shown in bold consist of four atoms A i minus 2, A i minus 1, A i and A i plus 1 and the bonds connecting these four atoms we have three bonds one is r i minus 1, one is r i, one is r i plus 1. So, with these three bonds connecting these four atoms and of course, the polymer chain is much longer. So, it continues in either direction which is shown through dotted lines. So, in the torsion angle is defined as the angle formed between two planes; so, the first plane is the plane containing the bond vectors r i minus 1 and r i. So, these two bond vectors basically form a plane the other plane can be defined using bond vectors r i and r i plus 1.

Now, the angle between these two planes basically that is the torsion angle. So, now, if we look at the schematic here then the if we consider the bond vector r i plus 1 again and if we consider it is rotation about fixed standard A i and if we consider that it is free to rotate in space only maintaining a constant bond angle theta i then the angle pi i that is shown here that is the torsion angle. So, that is how torsion angle or dihedral angle is defined and for polymer chain these torsion angles actually can take multiple values.

And, the that is the origin of the flexibility of polymer backbone. So, again if we consider the example of polyethylene then in that case the backbone basically consist of groups of CH 2 CH 2 groups bonded together in a long sequence.

So, for polyethylene basically if we consider torsion angles for polyethylene then there are three torsion angle values which correspond to a potential energy minimum. So, these three torsion angle values actually are 0 degree plus 120 degrees and minus 120 degrees and that torsional states associated with these angles are referred to as trans state for the 0 degree torsion angle and gauche plus state for plus 120 degree state and gauche minus state for the minus 120 degree states.

So, these are the three torsion angle values if we consider any three consecutive bonds along the polyethylene chain. So, these are the three torsion angle values where the potential energies shows a minimum or shows minima and specifically the minimum energy at the trans state is actually lower than those for the gauche state. So, the gauche plus gauche minus states basically represents secondary minimum whereas, a trans state is the lowest energy state, with that introduction to torsion angle and the fact that the variation in torsion angle is responsible for the flexibility of polymer chains.

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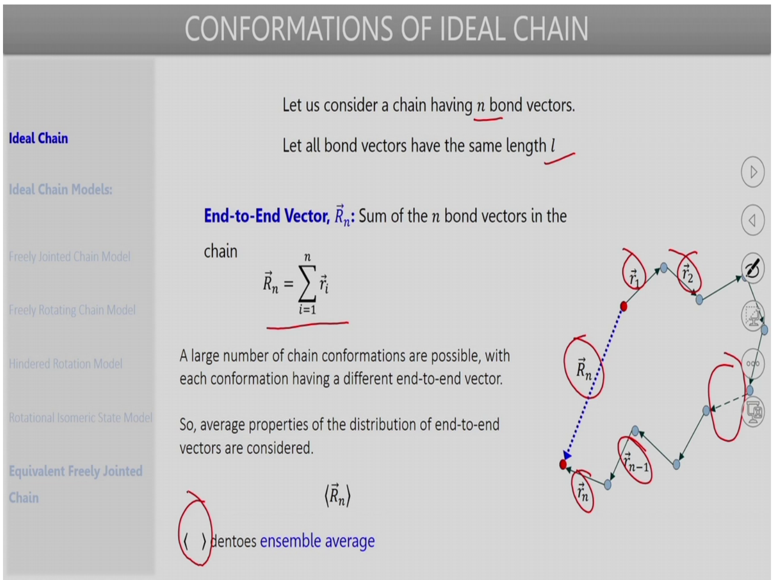

CONFORMATIONS OF IDEAL CHAIN

Ideal Chain

Ideal Chain Models:

Freely Jointed Chain Model

Freely Rotating Chain Model

Hindered Rotation Model

Rotational Isomeric State Model

Equivalent Freely Jointed Chain

Let us consider a chain having n bond vectors.

Let all bond vectors have the same length l

End-to-End Vector, $\vec{R}_n$: Sum of the n bond vectors in the chain

$$\vec{R}_n = \sum_{i=1}^{n} \vec{r}_i$$

A large number of chain conformations are possible, with each conformation having a different end-to-end vector.

So, average properties of the distribution of end-to-end vectors are considered.

$$\langle \vec{R}_n \rangle$$

$\langle \ \rangle$ dentoes ensemble average

Let us move ahead and discuss different conformations that an ideal chain can possibly adopt.

So, in our discussion let us say that the we are considering a polymer chain which has n number of bonds. So, the number of bonds represent that by small n and let say that the all the bond vectors have the same length represented by small l. So, in the model that we are using or to describe polymer chain conformation, we will consider only linear polymers having fixed bond length l and having a number of bonds equal to small l. So, if we consider now this quantity which is referred to as a end to end vector. So, this end to end vector it is represented by the symbol R n it is a vector and it is basically the sum of all the bond vectors in the polymer chain. So, it is vector sum of all the bond vectors in the polymer chain and it is so, in that sense it can be defined in this way.

Now, if we look at the schematic of this typical polymer chain conformation, here the polymer chain or the bond vectors in the polymer chain are shown as arrows and the dots basically correspond to the atoms which these bond vectors are connecting. So, the small r r i which shown as r 1, r 2 or r n minus 1 and r n here, these correspond to the individual bond vectors and the end to end vector is basically this R n capital R n which connects the two ends of the polymer chain. So, if we construct a vector staring from one polymer chain and ending at the other chain end then that vector is referred to as a end to end vector as a name suggests and as we see here as we see in the schematic here, it basically can be just represented as a vector sum of all the bond vectors present in the chain.

So, here in this case this is very representative drawing of a typical polymer chain where the polymer chain has been shown through only a few bonds and this dash bond here basically represents the that, they are polymer chain is actually long and we have broken it and shown only the initial and the final parts of this chain because that is what is relevant to the discussion of this end to end vector.

Now, as we know because of the flexibility of the adopting different torsion angles the polymer chain can display many different conformations. Number of conformations that typical polymer chain can display is very large and each of the conformation actually will have a different end to end vector. So, for a even single polymer chain if the conformation changes the end to end vector will change both in direction and magnitude and since a number of conformation is very large and number of possible end to end vectors that is also very large.

So, inst ahead of defining a single end to end vector, what we can do as we did for the case of polymer molar mass is that we define a kind of average measure of this end to end vector. So, one way to define that average is through what is called an ensemble average. So, in this case what is done in an ensemble averages you consider large collection of same polymer chain in different conformations and you basically add up the all the different end to end vectors that this polymer chains have and finally, take the average. So, this kind of ensemble average basically is typically represented by this angular brackets that are shown here. So, anything within these angular brackets is basically denotes the ensemble average of that quantity.

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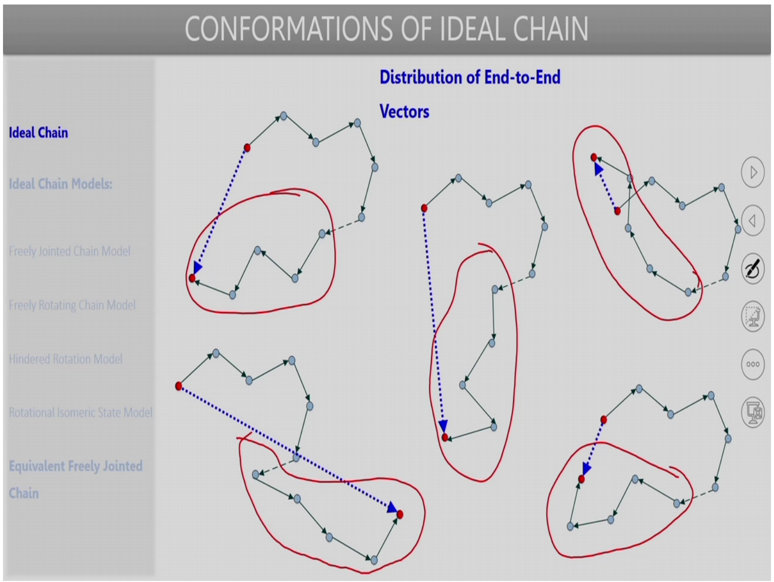

CONFORMATIONS OF IDEAL CHAIN

Ideal Chain

Ideal Chain Models:

Freely Jointed Chain Model

Freely Rotating Chain Model

Hindered Rotation Model

Rotational Isomeric State Model

Equivalent Freely Jointed Chain

Distribution of End-to-End Vectors

So, next if we look at the typical some of the typical conformation that polymer chain can adopt then here only five conformation of representative polymer machine are shown. So, if we look at all these five chains. So, if we look at all these five chains then in all of them the initial the first few atoms are basically exactly the same arrangement. So, these different conformations have result just by changing the changing the arrangement of the atoms towards the very other end of the polymer chain.

So, if we look at the first case here then the last five atoms or the last 4 bonds are arranged in a certain fashion in the second case the last five bonds are arranged in a different fashion the first last four bonds, the first few bonds are arranged identically to the first case. Similarly, in the third case also it is only the last few bonds whose arrangement has been changed in all these cases.

So, in all these cases we see that just by changing the arrangement of few bonds the overall end to end distance actually changes. So, next if we just draw the end to end distances for all these different polymer chains one by one, we see that there is a large variation in not just length of the end to end vectors, but also in the direction of these end to end vectors. So, what this suggest is that just by looking at very small sample of the different conformations that are possible, what we can say is that there is a wide variation in the end to end individual end to end vectors for different polymer chain conformations.

So, if we just for clarity if we just remove the polymer chain and leave the end to end vectors then it will be clear as to the wide distribution of the length and direction of these end to end vectors. So, just by these five representative cases what we have been able to show is that the end to end vectors basically they can vary in length or magnitude as well as in direction significantly and for a typical polymer sample, which will have a large number of polymer chains. The chains will typically will be in different conformational states and will be having different end to end vectors.

So, ultimately what that suggests is that if we have very large collection of such chains and the end to end vectors can assume different lengths and different directions then if we just take the direct average ensemble average of these end to end vectors, then it turns out that that average is actually 0 provided the collection is quite random and isotropic.

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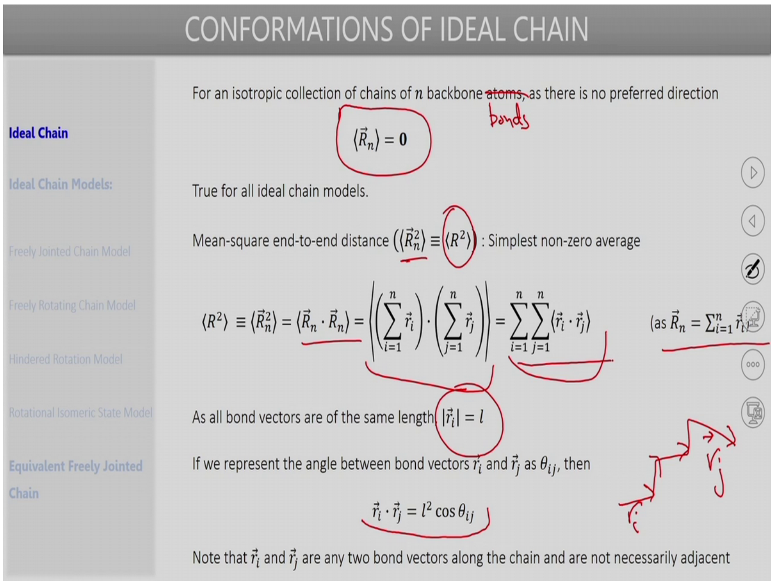

CONFORMATIONS OF IDEAL CHAIN

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Equivalent Freely Jointed Chain

For an isotropic collection of chains of n backbone ~~atoms,~~ bonds as there is no preferred direction

$$\boxed{\langle \vec{R}_n \rangle = \mathbf{0}}$$

True for all ideal chain models.

Mean-square end-to-end distance $(\langle \vec{R}_n^2 \rangle \equiv \langle R^2 \rangle)$: Simplest non-zero average

$$\langle R^2 \rangle \equiv \langle \vec{R}_n^2 \rangle = \langle \vec{R}_n \cdot \vec{R}_n \rangle = \left\langle \left(\sum_{i=1}^{n} \vec{r}_i \right) \cdot \left(\sum_{j=1}^{n} \vec{r}_j \right) \right\rangle = \sum_{i=1}^{n} \sum_{j=1}^{n} \langle \vec{r}_i \cdot \vec{r}_j \rangle \qquad (\text{as } \vec{R}_n = \sum_{i=1}^{n} \vec{r}_i$$

As all bond vectors are of the same length $|\vec{r}_i| = l$

If we represent the angle between bond vectors $\vec{r}_i$ and $\vec{r}_j$ as θ_{ij}, then

$$\vec{r}_i \cdot \vec{r}_j = l^2 \cos \theta_{ij}$$

Note that $\vec{r}_i$ and $\vec{r}_j$ are any two bond vectors along the chain and are not necessarily adjacent

So, as we just discussed for an isotropic collection of chains multiple chains each having n backbone bonds. So, inst ahead of atoms it should be let say bonds. So, for a isotropic collection of chains having n backbone bonds as the collection of isotropic that is no preferred directions. So, the end to end vector the direct ensemble average of the end to end vector actually comes out to be 0, because in a large enough collection the different vectors will have different directions and different magnitudes and the overall vectors sum it is not the scalar sum it is a vector sum. So, overall vector sum actually will turn out to be 0.

So, and this is the true for any general ideal chain models that will consider. So, what they suggest is that this measure of the polymer size which is the end to end vector this is not a very effective measure simply because and we cannot many end to end vectors and the average value for a large enough collection of polymer chains will be 0. So, in essence it does not tell us anything about the size of the polymer chain. So instead of just considering the average of the end to end vector what we can do is consider the mean square end to end distance. So, the instead of just the average on a direct vector, we can consider the average of its square.

So, it turns out that is the simplest non zero average that we can define for the end to end vector. So, the mean square end to end distance which is just the mean of the square of this end to end vector. So, we will represent this mean square end to end distance by this kind of a notation here just R square inside again angular brackets. So, denotes that it is also an ensemble average which means that, it is the average mean square mean square end to end distance for all the different polymer chains present in a given polymer sample.

Next, if we consider mean square end to end distances just square of the end to end vector then that can again be represented as a dot product of the end to end vector. So, R n dot R n that is just R n square and that is what the mean square n to n distance that is what the mean square n to n distance which we are discussing. So, now, if we represent this R n, so, the capital R n basically the end to end vector as we discussed earlier that the end to end vector is nothing, but the sum vector sum of all the bond vectors present in your chain.

So, if we replace the end to end vector by the corresponding sum of all the bond vectors in the in the equation that we have here like this and so, in that case the mean square end to end distance basically becomes equal to a double summation of the dot product of the bond vector and again we are considering the an ensemble average of dot product. So, whatever dot products we are considering it, we are averaging it over all the different possible polymer chain conformation that are there.

So, next as we discussed earlier in our treatment of this conformations of polymer chains as we discussed all the bond lengths are assume to have the same length small l. So, the bond length is nothing, but the magnitude of this bond vector. So, essentially all the bond vectors their magnitude magnitudes are also equal to the small l. Next, if we let say represent the angle between the two bond vectors r i and r j small r i and small r j, if we consider these two bond vectors and if we define the angel between them as the theta i j, in that case the dot product can simply be written by the definition dot value we can simply write it as l square times cos theta i j.

So, one thing to note here is that is that the r i and r j. So, the r i and r j that we have in the expression here these are not bond vectors corresponding to adjacent bonds, and therefore, the theta a j is also not something related to bond angle. So, r i and r j can actually be two bond vectors in different locations along the polymer chain and theta a j just the angle between these two. So, let us say if we consider small part of a polymer chain and we have these five bond vectors as shown here the first bond vector is represented by r i and the fourth one by r j.

So, whatever the angle there is between these two vectors that is the theta i j and as we have a double summation here then as i and j change basically the bond corresponding bond vectors also change. So, the point that I am trying to impress upon here is that r i and r j are not adjacent bond vectors, they can be one vectors some distances apart along the polymer chain and theta i j is also not related to a bond angle it is just the angle between any two bond vectors r i and r j in the polymer chain.

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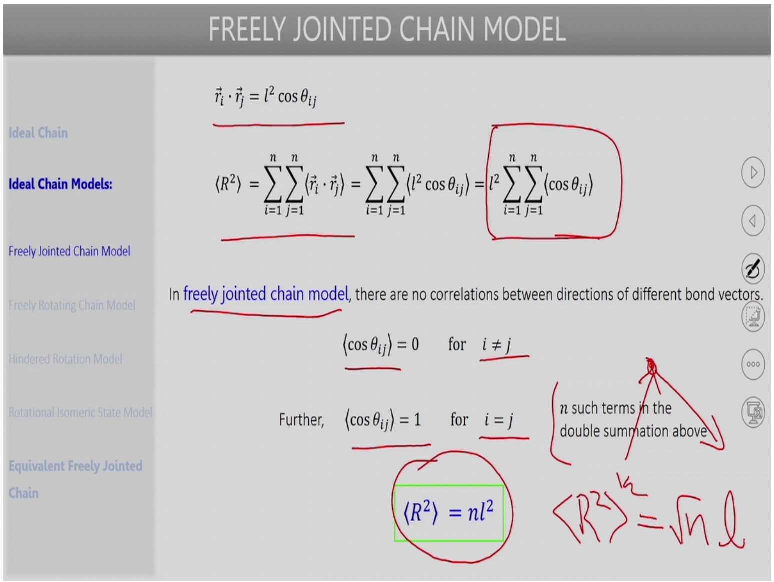

FREELY JOINTED CHAIN MODEL

Ideal Chain

Ideal Chain Models:

Freely Jointed Chain Model

Freely Rotating Chain Model

Hindered Rotation Model

Rotational Isomeric State Model

Equivalent Freely Jointed Chain

$$\vec{r}_i \cdot \vec{r}_j = l^2 \cos\theta_{ij}$$

$$\langle R^2 \rangle = \sum_{i=1}^{n}\sum_{j=1}^{n}\langle \vec{r}_i \cdot \vec{r}_j \rangle = \sum_{i=1}^{n}\sum_{j=1}^{n}\langle l^2 \cos\theta_{ij} \rangle = l^2 \sum_{i=1}^{n}\sum_{j=1}^{n}\langle \cos\theta_{ij} \rangle$$

In freely jointed chain model, there are no correlations between directions of different bond vectors.

$$\langle \cos\theta_{ij} \rangle = 0 \quad \text{for} \quad i \neq j$$

Further, $\langle \cos\theta_{ij} \rangle = 1$ for $i = j$

n such terms in the double summation above

$$\boxed{\langle R^2 \rangle = nl^2}$$

$$\langle R^2 \rangle^{1/2} = \sqrt{n}\, l$$

So, now that we have these two expressions the dot product is just one square cos theta by j and the mean square end to end distance, that is a double summation of the sum on average of the dot product of bond vectors. So, if we combine these two if we combine these two expressions we end up with a relation between the mean square end to end distance and the sum or average of angle between different bond vectors as shown here. So, this is how we have simplified our expression for mean square end to end distances.

Now, all the discussion that we had till now is valid for any ideal polymer chain model. Now, next we will make a certain assumptions so as to develop what is called the freely jointed chain model. So, the assumption that we make next basically defines ideal this ideal chain model has a freely jointed chain model and the assumption is that the directions of different bond vectors are not correlated with each other. So, if the we have different bond vectors in a polymer chain and if their directions are completely correlated, there is no there is no connection or no relation between the direction of given bond vector and direction of some other bond vector in the same polymer chain.

So, if they are completely uncorrelated then the model that we get is called the freely jointed chain model and because the bond vector directions are completely uncorrelated there is no actually fixed bond angle as well. The reason for this is if we just consider two bond vectors adjacent bond vectors. Now, since the direction of these two bond vectors are completely uncorrelated so, the whatever direction of the first vector we have the second vector can take any direction. So, since the second vector can take any direction independent of the direction of the first vector, there is no fixed bond angle and bond angle also you can take any value.

So, in this freely jointed chain model basically at the joints at these joints the bonds have been basically connected freely. So, they can have any orientation irrespective of the orientation of the adjacent bonds. So, now, since this no correlation between the direction of different bond vectors what mathematical that what that implies is that the ensemble average of this quantity cost theta i j this ensemble average actually becomes 0 if i is not equal to j.

So, if we are considering two vectors where r i and r j are not equal it is two different bond vectors distinct bond vectors. Since in this model they are directions are completely correlated. So, cos theta is actually can have any value between minus 1 and plus 1. So, since the cos theta i j can have any value minus 1 and plus 1, for if we average over a large enough collection of conformations then in general this summation will come out to be 0 if i is not equal to j.

On the other hand when i is equal to j this means that we have we are talking about the same bond. So, when i and j are equal r i and r i r j are the same and we are talking about the dot product of a bond vector with itself. So, when i is equal to j when we are talking about same bond then of course, the cos theta i j will be one and ensemble average. So, all the cos theta i j values of such kind will be 1 and hence the ensemble average will also be 1.

So, for i equal to j cos theta i j will be 1. Now, we need to determine how many terms are present in this summation here. So, in this summation that we have shown how many different terms are present where i equal to j. So, just by looking at this double summation we can what we can claim is that actually n such cases where i is equal to j. So, when i and j both are equal to 1 or when i and j both are equal to 2 or when i and j both are equal to 3 and so on up to when i and j both are equal to n. So, all these different cases are the only cases when i and j will be equal.

So, we have basically n terms where i is equal to j in that double summation and the cos theta i j value is one for all the other terms i will not be equal to j and the ensemble average of cos theta i j will be 0. So, they will not be contributing anything to the summation that we have.

So, we these observation we can simplify the relation for mean (Refer Time: 30:51) and distance further and the final expression that we get for a freely jointed chain is that the mean square end to end distance is equal to n l square. So, here the what is important note here is that if you let us say consider a polymer chain, which it can be described freely jointed module which is of course, not very realistic, but let us hypothetically consider polymer chain which as side by the free freely jointed chain model.

So, the maximum length that this polymer chain can have is when the chain is completely stretched and all the bond angles are 180 degree. So, in that case when the chain is completely stretched all bond angles are 180 then the in that particular conformation the end to end distance be just n times l because n number of bonds and each bond has a length l and all are aligned next to each other. So, the overall length will be n l. So, that is the maximum length that this polymer can attain if we stretch it completely.

On the other hand typically on an average what the, this expression tells us is that the mean square end to end distance is n l square. So, so, the square root of this quantity which will be a measure of average measure of the end to end distance that we just be square root of n times l.

So, we see that the average size of this polymer is much smaller than the fully extended size and the difference will be the larger the value of n or number of bonds present the larger this difference will be between the dimension of fully extended chain and the average dimension that the polymer chain adopts.

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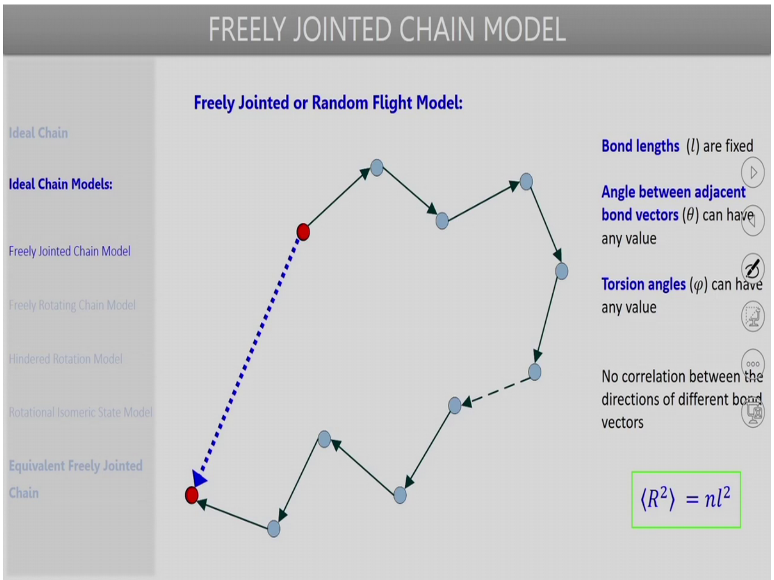

FREELY JOINTED CHAIN MODEL

Ideal Chain

Ideal Chain Models:

Freely Jointed Chain Model

Freely Rotating Chain Model

Hindered Rotation Model

Rotational Isomeric State Model

Equivalent Freely Jointed Chain

Freely Jointed or Random Flight Model:

Bond lengths (l) are fixed

Angle between adjacent bond vectors (θ) can have any value

Torsion angles (φ) can have any value

No correlation between the directions of different bond vectors

$$\langle R^2 \rangle = nl^2$$

So, before moving let just summarize what we have discussed for freely jointed chain model. So, freely jointed chain model just as an additional information it is also referred to as random fight model simply because from as we go from one bond vector to the next the orientations are pretty much random. It is the orientation of a given bond vector is completely in independent of what the orientation of the previous bond vector was and so on.

So, it is also called a random fight model and in this model the bond length is fixed let us add the value small l the bond angle is free to have any value and the torsion angle is also free to have any value. So, in this in the simplest ideal chain model that we have which is a freely jointed chain model we have fixed bond length, but free bond angles in torsion angles and it is most flexible case that one can have. So, you have flexibility basically at every bond linkage or connection and also there is no correlation between the direction of the bonds as discussed earlier.

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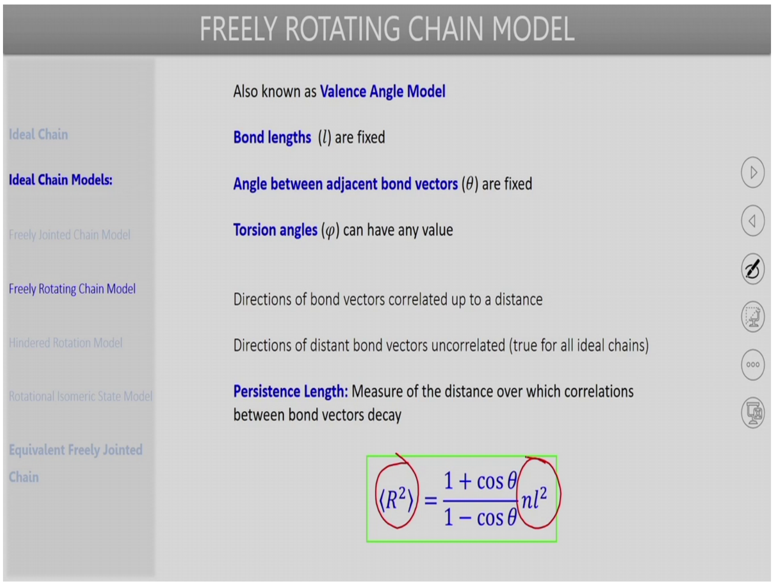

FREELY ROTATING CHAIN MODEL

Ideal Chain

Ideal Chain Models:

Freely Jointed Chain Model

Freely Rotating Chain Model

Hindered Rotation Model

Rotational Isomeric State Model

Equivalent Freely Jointed Chain

Also known as **Valence Angle Model**

Bond lengths (l) are fixed

Angle between adjacent bond vectors (θ) are fixed

Torsion angles (φ) can have any value

Directions of bond vectors correlated up to a distance

Directions of distant bond vectors uncorrelated (true for all ideal chains)

Persistence Length: Measure of the distance over which correlations between bond vectors decay

$$\boxed{\langle R^2 \rangle = \frac{1+\cos\theta}{1-\cos\theta} n l^2}$$

Next let us talk about freely another model which is called freely rotating chain model. So, when we discuss freely jointed chain model there we said that the bond angles are not fixed they can take any value, ok. So, that is not very of course, not realistic kind of assumption because in most of the typical polymers bond angles also have some certain fixed values.

So, that restriction is basically relaxed in this freely rotating chain model this model is also referred to as the valence angle model and in this model apart from the bond length which is again fixed at value of l. The bond angle or the angle between the bond vectors theta that is also fixed.

So, these two quantities are fixed in this model, but this again no restriction on the values that are torsion angle can take. So, torsion angle is free to take any allowable value in this model again. So, the due to the fact that the bond angles are fixed in this case at certain value theta due to that the direction of bonds actually in this model are correlated up to certain distance.

So, in a freely jointed model there is no direction correlation in bonds bond direction, but because the bond angles are fixed in this freely rotating model. So, the bond direction are correlated up to a certain distance. So, a measure of the distance over which these correlations decay out. So, that kind of measure is provided by what is called a persistence length. So, we will not going to the, into the rigorous definition of what persistence strength is, but it this quantity can be thought of measure of lengths scale or length or distance over which the correlations in the direction of bond vectors decay.

So, again for this model also the mean square end to end distance and expression can be derived starting from basics, but we will not going to those details we. So, the expression for the mean square end to end distance for freely rotating chain model is shown here directly without any derivation and we see that the mean square end to end distance R square that is again proportional to n l square.

So, for the freely jointed chain model R square was equal to n l square here it is proportional to n l square, but there is another factor that comes in here which is which is related to the fixed bond angle in this model. The previous model the freely rotating chain model actually as fixed bond angles were torsion angles are free to have any value, but again in realistic polymer cases the torsion angle is not free to have any value. So, this restriction on the values torsion angles can take also due to static hindrance in similar effects.

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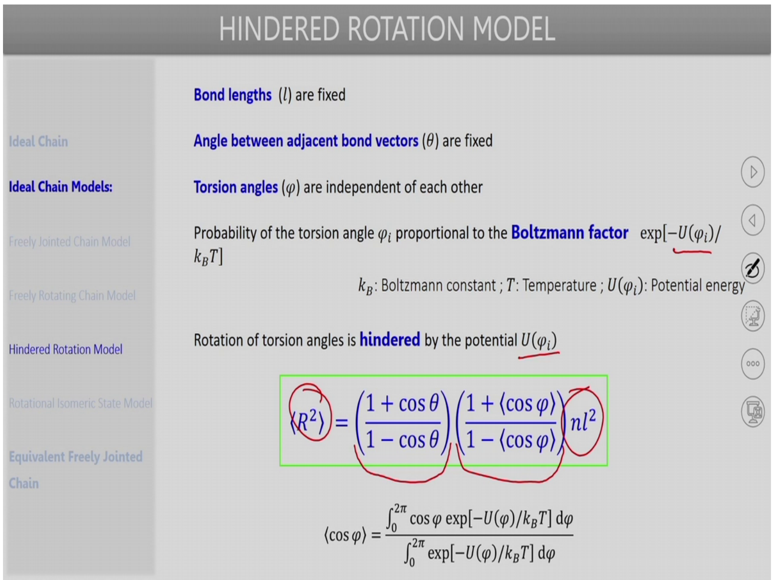

HINDERED ROTATION MODEL

Ideal Chain

Ideal Chain Models:

Freely Jointed Chain Model

Freely Rotating Chain Model

Hindered Rotation Model

Rotational Isomeric State Model

Equivalent Freely Jointed Chain

Bond lengths (l) are fixed

Angle between adjacent bond vectors (θ) are fixed

Torsion angles (φ) are independent of each other

Probability of the torsion angle φ_i proportional to the **Boltzmann factor** $\exp[-U(\varphi_i)/k_BT]$

k_B: Boltzmann constant ; T: Temperature ; $U(\varphi_i)$: Potential energy

Rotation of torsion angles is **hindered** by the potential $U(\varphi_i)$

$$\boxed{\langle R^2\rangle = \left(\frac{1+\cos\theta}{1-\cos\theta}\right)\left(\frac{1+\langle\cos\varphi\rangle}{1-\langle\cos\varphi\rangle}\right) nl^2}$$

$$\langle\cos\varphi\rangle = \frac{\int_0^{2\pi}\cos\varphi\,\exp[-U(\varphi)/k_BT]\,d\varphi}{\int_0^{2\pi}\exp[-U(\varphi)/k_BT]\,d\varphi}$$

So, to account for such effects the next model, that we discuss which is called the hindered rotation model. In this model what is done is again the bond length and bond angle are kept fixed, but the torsion angle is not allowed to have any free torsion angle is not allowed to have any value that is possible. So, torsion angle actually can have values, which is related which is given by a certain kind of probability in this model, but the torsion angles are still independent. So, what the torsion angle define by a given set of three bonds will be is independent of what the previous torsion angle was along the chain or what the next neighboring torsion angles are.

So, torsion angles in this model are also independent, but they are not free to have any value and the probability with which a torsion angle can occur along the chain that is related to what is called the Boltzmann factor. So, that Boltzmann factor is given by exponential of negative of kind of potential energy which dependents on the torsion angle divided by k B T where k B is a Boltzmann constant and T is a temperature.

So, in this model the rotation of torsion angles is not free, it is actually hindered by the presence of the potential given by U here and only when for a certain torsion angle phi i only when the value U are the potential energy is small only then in that case such torsion angles will have high probability of occurrence as the value of this energy U goes high. So, the probability of occurring of such torsion angles goes down significantly.

So, again the mean square end to end distance without going to the derivation for such models, the mean square end to end distance is related to n l square through this equation that shown here. So, again we see that the R square and n l square are proportional, but we have two terms which relate the mean square end to end distance to n l square one term contains the bond angle and another term contains an average of the cosine of the torsion angle.

So, how is this average defined? So, the average is can be defined the average of the this cosine of the torsion angle can be defined by multiplying it by the Boltzmann factor and integrating from 0 to 2 pi and then again normalizing scaling with the integral of that Boltzmann factor itself. So, this is the hindered rotation model.

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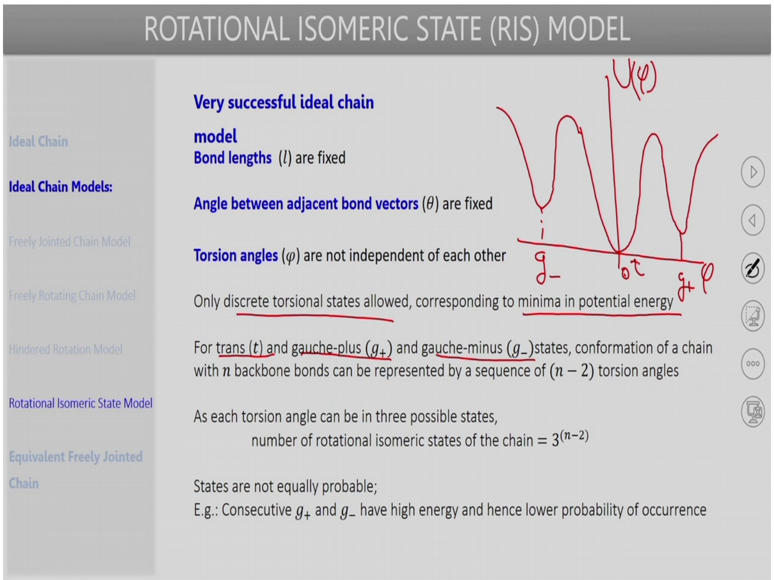

ROTATIONAL ISOMERIC STATE (RIS) MODEL

Ideal Chain

Ideal Chain Models:

Freely Jointed Chain Model

Freely Rotating Chain Model

Hindered Rotation Model

Rotational Isomeric State Model

Equivalent Freely Jointed Chain

Very successful ideal chain model

Bond lengths (l) are fixed

Angle between adjacent bond vectors (θ) are fixed

Torsion angles (φ) are not independent of each other

Only discrete torsional states allowed, corresponding to minima in potential energy

For trans (t) and gauche-plus (g_+) and gauche-minus (g_-)states, conformation of a chain with n backbone bonds can be represented by a sequence of ($n-2$) torsion angles

As each torsion angle can be in three possible states, number of rotational isomeric states of the chain = $3^{(n-2)}$

States are not equally probable;
E.g.: Consecutive g_+ and g_- have high energy and hence lower probability of occurrence

The next model which is the most sophisticated, but the most complex of all the models that we have discussed is what is called the rotational isomeric state model. So, this model is quite successful in naturally describing the conformation of polymer chains and it is widely used as well, but the model itself is quite complex. So, will not going to into the details of this model or will just briefly discuss some of the important points related to this model.

So, here the bond angle and bond length again are kept fixed in this model. The torsion angle is not free against. So, just like hindered rotation model torsion angle is not free to take any value, but the difference between the hindered rotation model in this model is that the successive torsion angles in this model are also to independent. So, given torsion angle values will depend on what the torsion angle value of the, what the previous torsion angle values along the chain. So, torsion angles are not independent. So, the torsion angles are allowed to only take certain discrete values. So, if we look at it so, only discrete torsional states are allowed as just mentioned and these discrete torsion angles basically correspond to minima in the potential energy.

So, for the case that we discussed earlier also when we are talking about example of polyethylene chain let us say if we have three torsion angles states defined by trans state t and gauche plus state and gauche minus state g plus and g minus which (Refer Time: 41:44) corresponds to torsion angles are 0, plus 120 and minus 120 degrees.

So, for each torsion angle each torsion angle can be one of these three states according to this model. So, if we have a chain which contains n bond vectors. So, if a chain contains n bond vectors and again we are talking about linear chain. So, all the discussion that we are having apply is only to linear chains. So, if we it has n bond vectors, then it will have n minus 2 successive torsion angles, n minus 2 successive torsion angles can be defined. Now, each of these n minus 2 torsion angles can have one of these three discrete values trans gauche plus or gauche minus.

So, so, the total number of possible torsion states in for such a chain is actuated 3 to the power n minus 2 because for each torsion angle three possible values are defined and if we have n minus 2 torsion angles in a given chain then 3 to the power minus 2 such states are possible. But, this is actually not the total number of states that this model will predict because that torsion angles are not independent of each other and all the states are not equally probable.

So, if we have a let us say sequence of torsion angles where a gauche plus and gauche minus or gauche minus and gauche plus occur consecutively then in that case the probability of such sequence occurring is very low, because such arrangement actually leads to steric overlap and high energies. So, the torsion angles are not free to have any value and the there the value of it given torsion angle depends on the value of torsion angles in the value of neighboring torsion angles.

So, if we talk about a trans and gauche plus gauche minus state states here it might be useful to just illustrate that through simple plot or graph. So, let us say in the y axis we are plotting potential energy which is the function of torsion angle and x axis we are just plotting the torsion angle. So, for a typical case of let us say polyethylene the graph might look something like this. So, let us say this is 0, this correspond to the gauche plus and this will correspond to the gauche minus state and this 0 torsion angle will correspond to the trans state.

So, we see that the potential energy actually shows minimum values that these three states that is those minimum value potential energy torsion, torsion states are only considered in this model.

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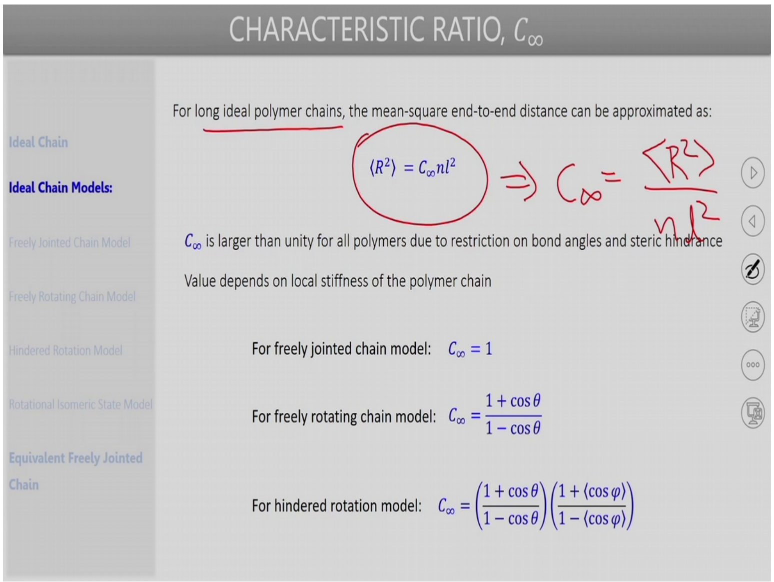

CHARACTERISTIC RATIO, C_∞

For long ideal polymer chains, the mean-square end-to-end distance can be approximated as:

$$\boxed{\langle R^2\rangle = C_\infty n l^2} \Rightarrow C_\infty = \frac{\langle R^2\rangle}{n l^2}$$

C_∞ is larger than unity for all polymers due to restriction on bond angles and steric hindrance

Value depends on local stiffness of the polymer chain

For freely jointed chain model: $C_\infty = 1$

For freely rotating chain model: $C_\infty = \frac{1+\cos\theta}{1-\cos\theta}$

For hindered rotation model: $C_\infty = \left(\frac{1+\cos\theta}{1-\cos\theta}\right)\left(\frac{1+\langle\cos\varphi\rangle}{1-\langle\cos\varphi\rangle}\right)$

So, we have talked about various different models, now, let us also discuss quantity or a parameter that is important in describing how stiff given polymer chain is. So, this characteristic ratio which is, which gives indications about the stiffness of the polymer chain that is defined for long ideal polymer chains this characteristic ratio is defined through this equation.

So, for any long ideal polymer chain the mean square end to end distance is equal to the characteristic ratio multiplied by n times l square. So, one can also think of characteristic ratio, as the ratio of the mean square end to end distance for a given ideal polymer chain divided by the mean square end to end distance for freely jointed polymer chain. So, this what this implies is that C infinity is equal to mean square end to end distance by n l square and this n l square is nothing, but the mean square end to end distance for a freely jointed chain.

So, as discussed so, this c infinity the value actually depend depends on local stiffness of the polymer chain and the stiffer the polymer chain typically the higher the value of this C in quantity C infinity will be or the characteristic ratio will be and the value of characteristic ratio for all the polymers is always greater than 1, for highly flexible polymers value can be in the range of 4 to 5 whereas, for rigid polymers it can be actually the value can be very high. So, for let say polystyrene, which has a bulky side group and makes the polymer chains stiff. So, for such case such a polymer the values actually close to 10.

Now, if we look at the different chain models that we have discussed and try to find out what the expression for this characteristic ratio will be for a freely jointed chain C infinity actually will be will have a value of just one for a freely rotating chain model the C infinity value will be 1 plus cos theta by 1 minus cos theta where theta is again the bond angle between the successive bond vectors. And, finally, for the hindered rotation model the C infinity is given by the expression that is shown here.

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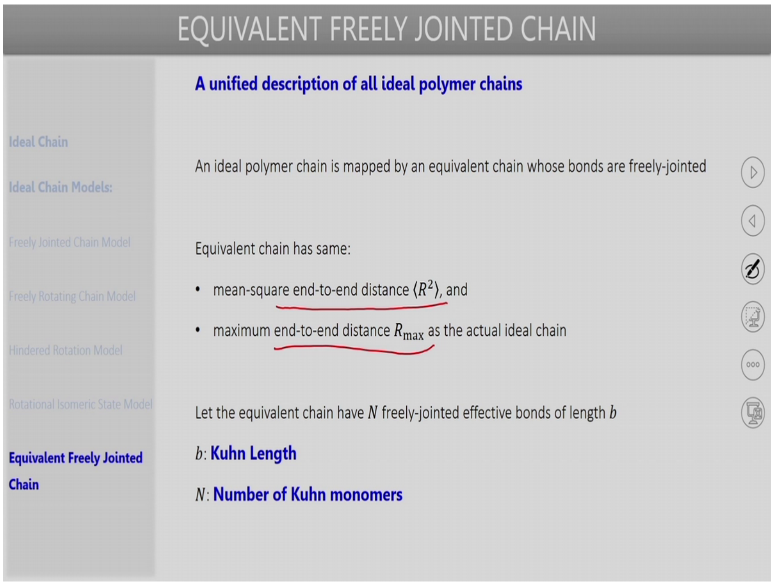

EQUIVALENT FREELY JOINTED CHAIN

Ideal Chain

Ideal Chain Models:

Freely Jointed Chain Model

Freely Rotating Chain Model

Hindered Rotation Model

Rotational Isomeric State Model

Equivalent Freely Jointed Chain

A unified description of all ideal polymer chains

An ideal polymer chain is mapped by an equivalent chain whose bonds are freely-jointed

Equivalent chain has same:

- mean-square end-to-end distance $\langle R^2 \rangle$, and
- maximum end-to-end distance R_{max} as the actual ideal chain

Let the equivalent chain have N freely-jointed effective bonds of length b

b: **Kuhn Length**

N: **Number of Kuhn monomers**

So, the last topic that will cover today before concluding is the concept of an equivalent free freely jointed chain. So, we discussed different chain models today, the first one and simplest one is freely jointed chain, but that model if directly applied is quiet unrealistic because actual real polymer chains have fixed bond angles and have some restrictions on the torsion angles as well.

So, for ideal polymer chains which are not freely jointed so, let us say polymer chain that is described by the freely rotating model or rotation isomeric state model, for such polymer chains the one can actually define or map an equivalent chain whose bonds are freely jointed. So, this equivalent freely jointed chain is an equivalent chain which can be mapped on to any ideal chain and this equivalent freely jointed chain has a property that the bonds are the equivalent bonds that we get are freely jointed.

So, this equivalent freely jointed for any chain for any ideal chain the equivalence is to establish by these two conditions; one is that the mean square end to end distance of the equivalent freely jointed chain that we are defining that should be equal to the actual ideal chain on which we are mapping this equivalent chain and the other is the maximum end to end distance. For this equivalent freely jointed chain that should also be equal to the maximum end to end distance of the actual ideal chain, which we are trying to map with this equivalent freely jointed chain.

So, let us say that the equivalent freely jointed chain has number of bonds capital N and let us say the bond length is represented by b. So, these quantities actually have. So, the bond length of effective bond length of an equivalent freely jointed chain is referred to as a Kuhn length and the N which is capital N, which is the number of freely jointed effective bonds in this chain that is referred to as an number of Kuhn monomers present.

So, now using these two conditions that we have here let see how we can come up with expression for Kuhn length and the number of Kuhn monomers present.

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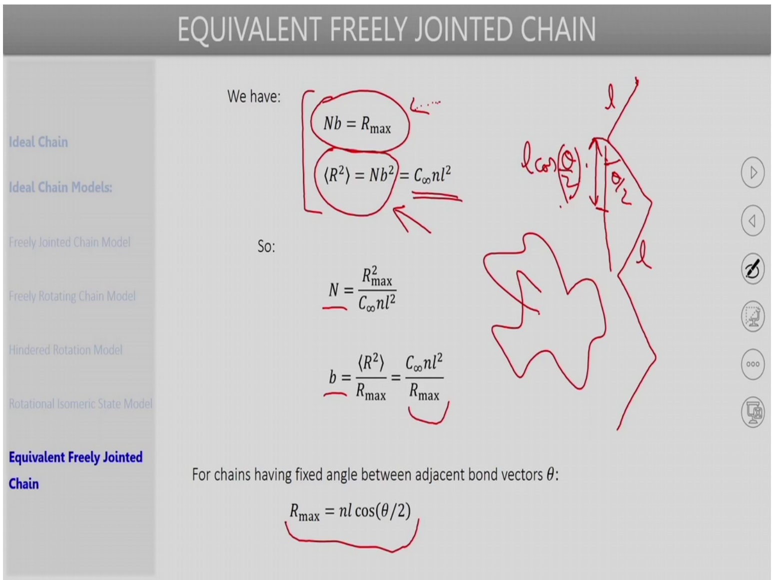

EQUIVALENT FREELY JOINTED CHAIN

We have:

$$Nb = R_{\max}$$

$$\langle R^2 \rangle = Nb^2 = C_\infty n l^2$$

So:

$$N = \frac{R_{\max}^2}{C_\infty n l^2}$$

$$b = \frac{\langle R^2 \rangle}{R_{\max}} = \frac{C_\infty n l^2}{R_{\max}}$$

For chains having fixed angle between adjacent bond vectors θ:

$$R_{\max} = nl\cos(\theta/2)$$

So, we have for a equivalent freely jointed chain the maximum chain length is simply given by the number of bonds multiplied by the bond length because if the chain is freely jointed, then it is one can completely stretch it and the maximum length possible is just the number of bonds multiplied by the length of each bond.

So, that is R max and the mean square end to end distance that for a freely jointed chain equivalent freely jointed chain that we will simply be given by capital N b square by capital N is number of equivalent bonds and b is the length of our equivalent bond for this freely jointed chain and we also know that for any ideal chain this R square is also equal to C infinity n l square. So, using these two equations one can basically derive expressions for capital N which is a number of Kuhn monomers and also small b, which is a Kuhn length.

So, these two quantities are basically characterized the equivalence freely jointed chain and capital N is by using these two equations here we can basically take the square of this first equation and divide that by this second equation. So, doing that will basically give us an expression for N is R max square by C infinity n l square and similarly the expression for b is small b also can be found out by using the above equations and finally, this r max that we have here the R max is actually the maximum chain length maximum chain length for the actual polymer chain on which we are trying to map this equivalent chain.

So, so, as we discuss is a chain is freely jointed then the maximum chain length is just n times l, but if the chain has a fixed bond angles or the angle between the adjacent bond vectors if they are fixed then in that case R max basically is given by in expression like this it is given by n l cos theta by 2 and we can basically visualize this in this fashion. So, let us say we have. So, the for a any polymer chain having constant bond angle the maximum possible length is possible when all the torsion angle are in the trans state and the entire polymer chain actually lies in the single plane in zigzag kind of conformation.

So, if we consider that conformation then the length of individual bonds is l and we want to find out the R max which is the end to end distance in this conformation, ok. So, if we consider this part here. So, this distance from here to here this distance since this the angle that we have here this will be theta by 2. So, this the distance shown by these arrows here that distance from standard trigonometry, that will just be l cos theta by 2. So, each bond basically contribute a length l cos theta by 2 to R max and if we add up the contribution of all the bonds present along the polymer chain then we will get n times l cos theta by 2 as the value of R max.

So, with that we will conclude today's lecture on ideal polymer chains. So, all these ideal polymer chain models are characterized by the fact that the monomers that are next to each other monomer units are atoms which are next to each other they interact in some way to different levels, but a monomers which are far the apart along the chain they do not show any interaction with each other. So, basically if we have a polymer chain like this such a conformation is allowed where distant monomers basically overlap with each other. So, in ideal polymer chains such overlap is allowed because distant monomers are not interacting with each other.

So, in the next class we will discuss some other concepts related to ideal polymer chains and then we will move on to the discussion of real some real polymer chain models or typical real polymer chain model, which is actually built upon these ideal polymer chain models which, but which incorporate what is called excluded volume repulsion. So, so, what that means, is that two monomer units basically cannot occupy by the same space same regional space. So, due to this polymers segment, segment repulsions inside the chain the overall size of the polymer chain in many case gets expanded from what the ideal chain sizes are.

So, in the next lecture we will be discussing a real chains behavior and conformations in slight more detail.