Introduction to Polymer Physics
Dr. Amit Kumar
Department of Chemical Engineering
Indian Institute of Technology Guwahati

Lecture – 22
Unentangled Polymer Dynamics

Hello everyone. In this last week of our course, we will be focusing on the subject of Polymer Dynamics. So, polymer dynamics basically is a study of the motion of polymer chains within polymer solutions as well as in polymer melt. So, the study of polymer dynamics is important to understand the flow behavior of polymer solutions as well as melt and especially for flow of polymer melts. It is important from a practical viewpoint, because molten polymer flow is used extensively in polymer processing operations.

So, now the dynamics of polymers it actually the nature of the dynamics depends on whether the polymer chains are entangled with each other or not. So, in today's lecture we focus on the dynamics of unentangled polymer chains and we will look at a couple of models that describe the dynamics of these unentangled polymer chains in the different kind of scenarios. And in the next lecture we will focus on the dynamics of entangled poly polymer chain. So, the content of today's lecture is somewhat or something like this.

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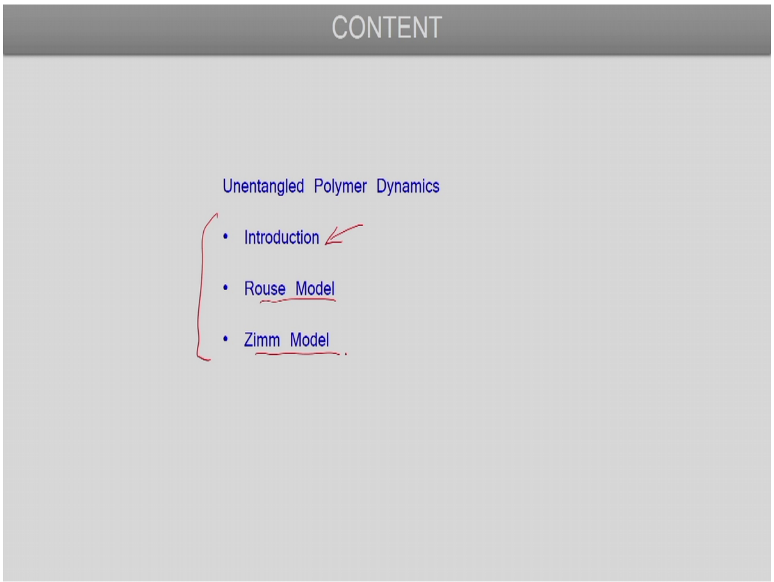

CONTENT

Unentangled Polymer Dynamics

- Introduction
- Rouse Model
- Zimm Model

We will start with an introduction just introduce some common concepts and terms like diffusion coefficient friction coefficient and so on and then we will discuss 2 different models one is the rouse model the other is the Zimm model and these 2 different models are models that describe the dynamics of unentangled polymer chains.

So, we will see that the rouse model is something that is useful for describing the dynamics of polymer melts, provided the chain in the chain length in the polymer melt is short and the chains are not entangled. On the other hand we will see that Zimm model is a good model for describing the dynamics of polymer chains in dilute solutions, again where since the chains are far apart they are not enta entangled with each other.

So, to begin with we will start with some introduction to basic concepts. So instead of focusing on entire polymer chain initial will initially, we will talk about the motion of a particle present inside let us say a liquid. So, if we are considering a particle that is small enough let us say a colloidal particle, then the collision of the liquid molecules with this colloidal particle will lead to motion of this colloidal particle in a random zigzag kind of a fashion.

So, the motion actually might look like a random walk and such motion which was discovered first way the Robert brown is referred to as a Brownian motion. For such kind of motion what is called the mean square displacement of this particle that is observed to be directly proportional to time and the relation between the mean square displacement and time is given by this expression where the quantity D here is referred to as a diffusion coefficient of this particle in that liquid medium.

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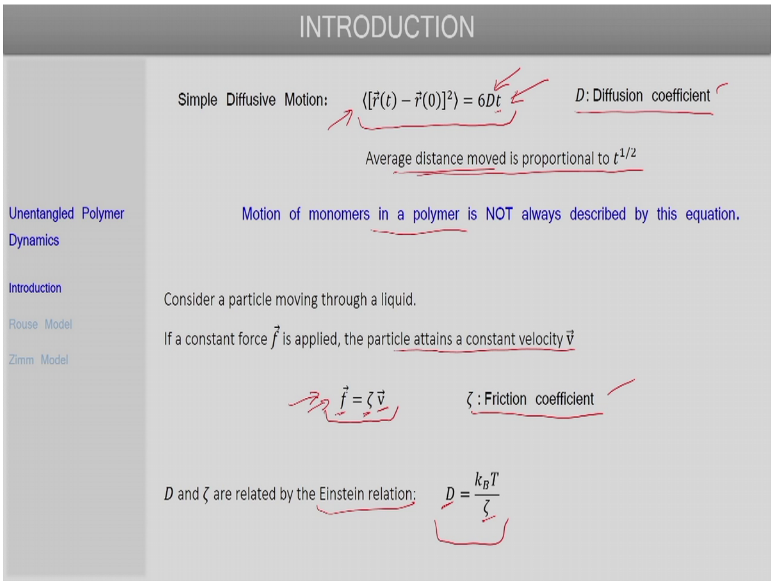

INTRODUCTION

Unentangled Polymer Dynamics

Introduction

Rouse Model

Zimm Model

Simple Diffusive Motion: $\langle[\vec{r}(t)-\vec{r}(0)]^2\rangle = 6Dt$

D: Diffusion coefficient

Average distance moved is proportional to $t^{1/2}$

Motion of monomers in a polymer is NOT always described by this equation.

Consider a particle moving through a liquid.

If a constant force $\vec{f}$ is applied, the particle attains a constant velocity $\vec{v}$

$\vec{f} = \zeta \vec{v}$

ζ : Friction coefficient

D and ζ are related by the Einstein relation: $D = \frac{k_B T}{\zeta}$

This kind of motion is referred to as a simple diffusive motion and it is characterized by the fact that the mean square displacement is directly proportional to time for this particle or on in other words the average this distance at the particle traverses that is proportional to the square root of time, so that is what we have stated here.

So, now this simple diffusive motion that we have what we will see that in the case of polymer chains the motion of the monomeric units on the chain that need not be of the type of simple diffusive motion that we have outlined here. We will see that it will depend on the time scale associated with the observation and under certain time scales the motion might be of the diffusive kind, but at other time scales other kind of response might be observed.

The monomeric unit motion in a polymer is not always of simple diffusive kind, so that is what we are trying to understand here and next we let us continue with our discussion of this motion of particle in a liquid and just try to establish some other common concepts and then we will try to apply that to polymer chains. So, if we consider the motion of this particle and if we say that the certain force f acts in this particle and that leads to the particle moving with a constant velocity V. Then in that case of course if just a constant force is acting on a particle then Newton’s law suggest that we will have a constant acceleration of the particle and not constant velocity.

So, what the particle 2 move around with the constant velocity, whatever force is acting to move the particle there is some other force which would be counteracting and balancing this in this force, so that the particle velocity remains constant. As we discussed that the these particles are moving about due to the random collision of solvent molecules with this particle and the opposing force to this motion is also due to collision of solvent molecules with other liquid molecules with this particle. So, the opposing motion opposing forces what is called the drag force and when the force responsible for moving the particle be is equal to the drag force in this particle will move with a constant velocity.

So, if we have that case where the particle has attained a constant velocity, then what we can say is that this force is related to this velocity through this coefficient which is referred to as the friction coefficient. So, we have defined diffusion coefficient up here as quantity that relates the mean square displacement to the time average displacement happens, here we have the friction coefficient which is a which relates the force acting on the particle and the corresponding velocity which with the particle moves and as we discuss whatever force is moving the particle that will be exactly balanced by the drag force. So, the drag force expression will also be given by the same equation, only thing is that the force drag force will be equal and opposite to this driving force f here.

Next we have a relation which is referred to as the Einstein relation and this relation connects the 2 coefficients that we have identified so far. So, it is a relation between the diffusion coefficient and the friction coefficient. So, what Einstein relation states is at the diffusion coefficient of particle moving in the liquid is equal to KB times T divided by the friction coefficient, where the KB is of course the Boltzmann constant and T is the absolute temperature this equation relates the diffusion and friction coefficient. Next let us try to figure out what are the timescales of motion involved. If you are still sticking with this example of this particle moving in a liquid, what are the kind of time scales involved in the motion of this particle?

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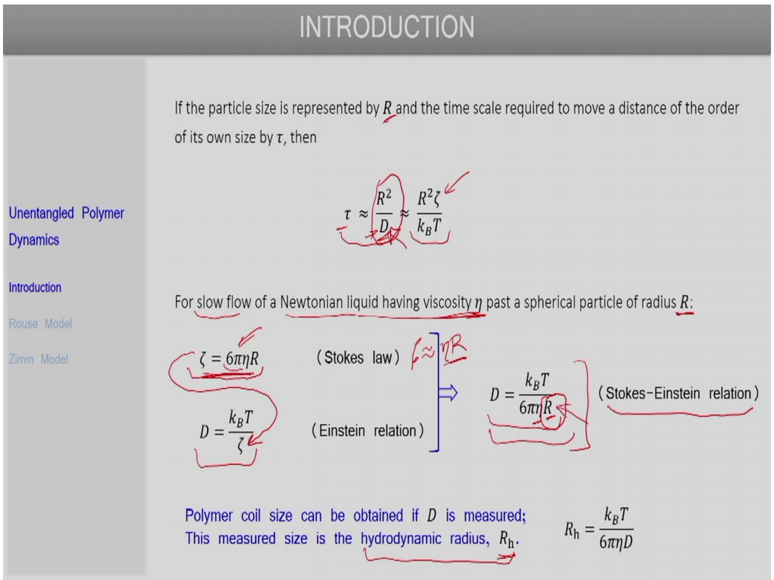

INTRODUCTION

Unentangled Polymer Dynamics

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Rouse Model

Zimm Model

If the particle size is represented by R and the time scale required to move a distance of the order of its own size by τ, then

$$\tau \approx \frac{R^2}{D} \approx \frac{R^2 \zeta}{k_B T}$$

For slow flow of a Newtonian liquid having viscosity η past a spherical particle of radius R:

$\zeta = 6\pi\eta R$ (Stokes law) $\zeta \approx \eta R$

$D = \frac{k_B T}{\zeta}$ (Einstein relation)

$\Rightarrow D = \frac{k_B T}{6\pi\eta R}$ (Stokes-Einstein relation)

Polymer coil size can be obtained if D is measured;
This measured size is the hydrodynamic radius, R_h.

$$R_h = \frac{k_B T}{6\pi\eta D}$$

So, if we represent the size of this particle by this quantity R and let us say we represent the time scale or the amount of time it takes for this particle to move by a distance, which is of the same scale as it is own size we dif if we define this time as tau. Then what we can say is that this tau is of the order of it, of course not equal but it will have similar kind of scale as R square over D, where R square is the square of the size of the particle and D is the diffusion coefficient and since we are talking about a time over which the particle moves a distance equivalent to it is own size.

So, the corresponding time would be of the order of this R square by the diffusion coefficient. So, it is a simple scaling kind of argument and from the Einstein relation the since diffusion coefficient D is just KB times T over zeta that we can substitute here and there which results in this expression for this characteristic time over which the particle moves by a distance equal into it is size. Now let us consider the motion of a spherical particle through a Newtonian liquid and we are considering the flow to win what is called a slow or creeping kind of regime.

So, and if you say that the Newtonian liquid that we are considering has a viscosity eta so the liquid has a Newtonian kind of nature, what that means is that the shear stress is directly proportional to the shear rate and the constant of proportionality is a constant viscosity eta. So, if we have this constant viscosity eta for our Newtonian liquid and if it is flowing fast this spherical particle having size that is corresponds to this R, then stokes derived this stokes law which states that the friction coefficient zeta is simply 6 times pi times eta times R, where eta has the viscosity of the liquid R is the is a measure of the size of our particle.

So, if it is a spherical particle it is just the radius of that particle, so that is the Stokes law and this also suggest that the zeta that we have is again of the order of the product of eta times R. So, if you look at this relation in the Stokes law the friction coefficient is proportional to the product of the viscosity of the liquid and the size of the particle and there is some proportionality constants 6 pi here. So, what we can see is that the friction coefficient is of the order of eta times R, we already have discussed it in Einstein equation relates the diffusion coefficient with the friction coefficient and that relation as discussed in the previous slide is this so if we combine these 2.

So, if we substitute this zeta from stokes law here in Einstein relation then we can get an expression for our diffusion coefficient. So, diffusion coefficient expression by obtained by combining the Stokes law and Einstein equation is the equation is called stokes Einstein relation and it relates the diffusion coefficient to the viscosity of the liquid and the size of our particle ok.

So, the strokes Einstein relation is d is equal to KB times T divided by 6 pi eta R, now the we can measure the diffuse the diffusion coefficient of let us say if now we come to the case of a polymer coil, so if you have a polymer solution in the polymer if it is a dilute polymer solution. Let us say the polymers are in the form of these random coils that is separated by good distance as a solution is dilute.

So, we can measure the diffusion coefficient of such polymer coils using experimental techniques such as dynamic light scattering and that diffusion coefficient measurement will allow us to get a measure of the size of our polymer coils are. So, this R the size measure of size that we get from this relation that is referred to as a hydrodynamic radius. So, the hydrodynamics radius of our polymer coils that we can calculate, if we measure the diffusion coefficient of our polymer chains in a dilute solution using techniques like dynamic light scattering and using the Einstein stokes Einstein relation obtaining the value of R.

So, so just rewriting the stoke Einstein in relation we can get the expression for the hydrodynamic radius which is just KB times T divided by 6 pi eta times the diffusion coefficient. So, now with that this background to the general concepts related to dynamics and flow. Let us move on and focus on case of the dynamics of polymer chains in solutions as well as melt. So, the first and we will consider 2 simple models today for the dynamics of polymer chains which are not entangled.

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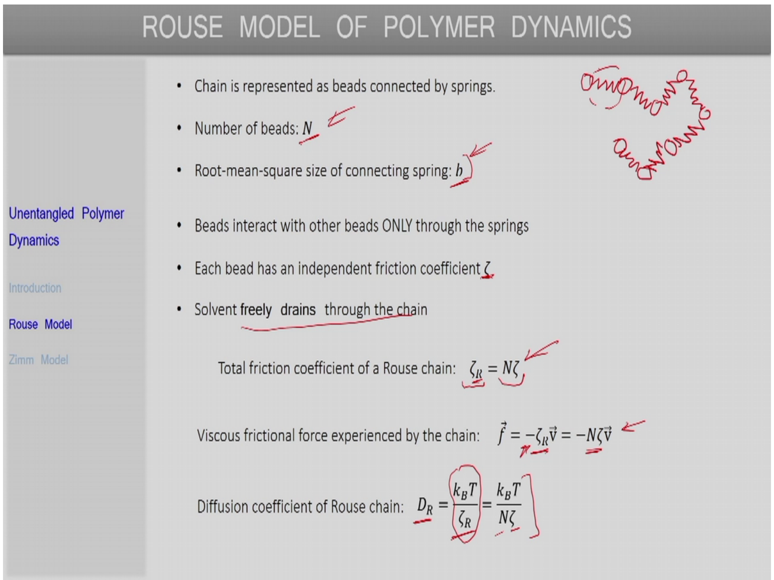

ROUSE MODEL OF POLYMER DYNAMICS

Unentangled Polymer Dynamics

Introduction

Rouse Model

Zimm Model

- Chain is represented as beads connected by springs.
- Number of beads: N
- Root-mean-square size of connecting spring: b
- Beads interact with other beads ONLY through the springs
- Each bead has an independent friction coefficient ζ
- Solvent **freely drains** through the chain

Total friction coefficient of a Rouse chain: $\zeta_R = N\zeta$

Viscous frictional force experienced by the chain: $\vec{f} = -\zeta_R\vec{v} = -N\zeta\vec{v}$

Diffusion coefficient of Rouse chain: $D_R = \frac{k_BT}{\zeta_R} = \frac{k_BT}{N\zeta}$

So, the first model that we will focus on is referred to as the rouse model of polymer dynamics and it was proposed by rouse as the name suggests. So, here in this model the polymer chain is a thought to be come thought to consist of a collection of beads which are connected by strings. So, it is a kind of a bead string model where each we have a bunch of beads which are connected to each other by spring. So, cartoon of this kind of model might look something like this where we have this bead, then we have a spring we have this bead another spring and so on.

So, this is the kind of representation that we have of the polymer chain in this rouse model, the number of beads that is taken to be this quantity N and the size of the spring that is connecting the beads that is taken to be that is denoted by the symbol small b.

So, this kind of nomenclature that we are using the number of beads to be N in the size of spring to be small b, that if you recall is similar to the kind of nomenclature we use when we are talking about the equivalent freely jointed chain model. So, when we talk about the number of Kuhn monomers and the Kuhn lengths so there also be use a similar kind of nomenclature.

So, there the polymer chain was represented by collection of Kuhn monomers and here in this case we are representing the polymer chain as a collection of beads connected by string. So, the size of the spring is a small b number of beads is capital N and some of the other assumptions that are involved is that. In this rouse model the beads that we have they interact with other beads only through the connecting springs, so there is no other way in which the beads interact with each other they only interact with other beads through that strings that connect them.

Another assumption is that each bead is considered to have it is own separate friction coefficient zeta ok. So, each bead is having an independent friction coefficient zeta and the last assumption is that if you are considering this for these polymer chains in a solution let us say, then the solvent molecules freely drain around this polymer chains that is a other assumption.

So, if you go back to the lecture when we talk about the viscosity average molar mass and specifically the different types of viscosities in dilute polymer solutions and the friction properties right dilute polymer solutions, there we introduce the concept of 2 different kinds of models one was freely draining one was non draining. So, rouse model assumes that we are in this freely draining kind of regime, where the solvent molecules can freely flow around all the monomeric units of a polymer chain ok, so solvent freely drains through the chain.

Now, with these assumptions what we can say is that for the entire polymer chain, the friction coefficient for the whole chain is given simply by the number of beads that we have multiplied by the friction coefficient corresponding to each bead. So, that is n times zeta and since the friction coefficient zeta is independent for each bead, we can say that for the entire polymer chain this zeta R and that the overall friction coefficient is just given as a product of these 2 and the R in the subscript of course, denotes the rouse model, so we are talking the rouse model. So, the capital R denotes that.

Now, if we talk about the viscous frictional force that the chain experiences, so as we discussed this force is simply equal to the friction coefficient times this velocity. So, if we talk about the frictional force experience, then we will have this minus sign here because, this will act in a direction opposite to the motion so the frictional force is just minus of zeta times the velocity. So, if the chain is moving with some velocity polymer is moving with some velocity v then this frictional force is minus of zeta R times v and since the overall friction coefficient for the chain is just n times zeta. So, we have this equation as well.

Next we can of course, define the diffusion coefficient of polymer chain in this rouse model, but the Einstein relation states that this diffusion coefficient is just given by K B over T times the friction coefficient. So, the friction coefficient in rouse model is simply the N times the individual friction coefficient of the beads, so the diffusion coefficient for a rouse chain that is given simply by K B T over N zeta. So, now the time that is required for a given polymer chain to diffuse by a distance that is of the order of it is own size or length that time is referred to as a rouse time and it is denoted by the symbol tau R.

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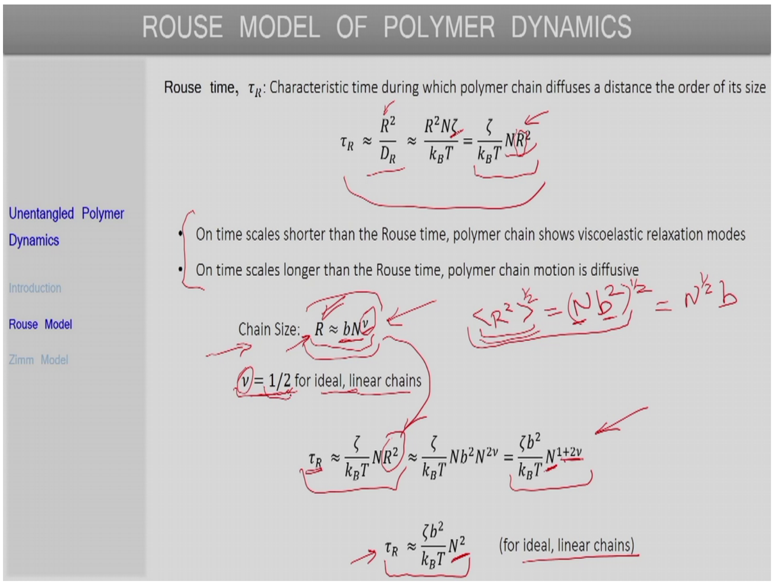

ROUSE MODEL OF POLYMER DYNAMICS

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Rouse time, τ_R: Characteristic time during which polymer chain diffuses a distance the order of its size

$$\tau_R \approx \frac{R^2}{D_R} \approx \frac{R^2 N\zeta}{k_B T} = \frac{\zeta}{k_B T} N R^2$$

- On time scales shorter than the Rouse time, polymer chain shows viscoelastic relaxation modes
- On time scales longer than the Rouse time, polymer chain motion is diffusive

Chain Size: $R \approx bN^{\nu}$

$$\langle R^2 \rangle^{1/2} = (Nb^2)^{1/2} = N^{1/2} b$$

$\nu = 1/2$ for ideal, linear chains

$$\tau_R \approx \frac{\zeta}{k_B T} N R^2 \approx \frac{\zeta}{k_B T} N b^2 N^{2\nu} = \frac{\zeta b^2}{k_B T} N^{1+2\nu}$$

$$\tau_R \approx \frac{\zeta b^2}{k_B T} N^2$$ (for ideal, linear chains)

So, if we want to write a kind of an expression for this rouse time, then we can we will have first have to consider a parameter that specifies the size of our polymer chain and the time required for a given polymer chain to diffuse a distance equivalent to this size that will give us the rouse time. So, the rouse time tau R can be defined as being of the order of R square over D R, where D R as we have discussed is the diffusivity of the polymer chain in the rouse model or the diffusion coefficient, R can be thought of as a of as a measure of the size of the polymer chain. So, it can be related to the um mean square end to end distance, so R square can be the mean square end to end distance. So, next if we express the diffusion coefficient in terms of the friction coefficient zeta; so, DR is K B T over N time zeta as we have established in the previous slide.

So, if we substitute that expression here we will get this expression, for the rouse time where we see that the rouse timescale says [noise] R square here and next what we need to do is express this R the measure of our polymer size in terms of the number of monomeric units present in the polymer as well as the size of a given monomer unit. The rouse time that we have it is significance is can be thought of as in this way, that if we are observing the polymer chain dynamics on scales that a timescales at a smaller than rouse time, then the polymer will show viscoelastic kind of response viscoelastic modes of relaxation. Whereas, if we are observing the polymer chain motion on time scales that are larger than the rouse time, then the polymer will show a simple diffusive kind of motion.

So, with that next let us again go back to how we can express this polymer chain size R in terms of other quantities. So, the chain size R we can what we can say is that it is related to this order of the order of b times N to the power nu, where this nu is an exponent whose values half for an ideal linear chains and it is value will be different if we have non-ideal chains. Now the relation that we have here for an ideal chain the relation of this kind we have already established in the very first week of this course, where we discussed that any ideal chain can be thought of as an equivalent freely jointed chain. So, there what we saw is that the mean square in twelve and distance R square that was expressed at that time as n times b square ok.

Where N was the number of Kuhn monomers b was the Kuhn length ok, this R square that we had discussed at that time this the measure of chain size R is related to the this expression here and if we consider the square root on both sides here then we get N to the power half times b and that is the same expression that we have written for the chain size here, where nu being half will be the case for an ideal chain. But this expression is more general in the sense that the exponent nu it is if it is value is something different then it can describe also the behavior of non ideal real kind of chains as well.

Now let us try to substitute this expression for the chain size R in the expression for rouse time, so that expression for rouse stream is written here and if we write down or substitute this expression here. Then upon simplification we get this kind of an expression and this expression relates how the rouse time scales with the number of monomers in our polymer chain. So, the exponent that we have is 1 plus 2 nu and we have already discussed that nu is half in the case of ideal linear chains. So, in the in that case if nu is half the relation between tau R and N will be of this kind, so tau R will is seen to scale as N square for ideal linear chains.

If we have a non ideal real chains then depending on what kind of environment our real chain is in the value of the exponent will vary. So, if the chain is in a highly expanded set in for example in a good solvent, then it is been shown that the value of nu is close to 0.6 it is approximately 0.588 or that we can roughly take that to be around 3 by 3 by 5 or 0.6. So, for a real chain in good solvent the value of nu will be around 0.6 and for ideal chains it is 0.5 or half.

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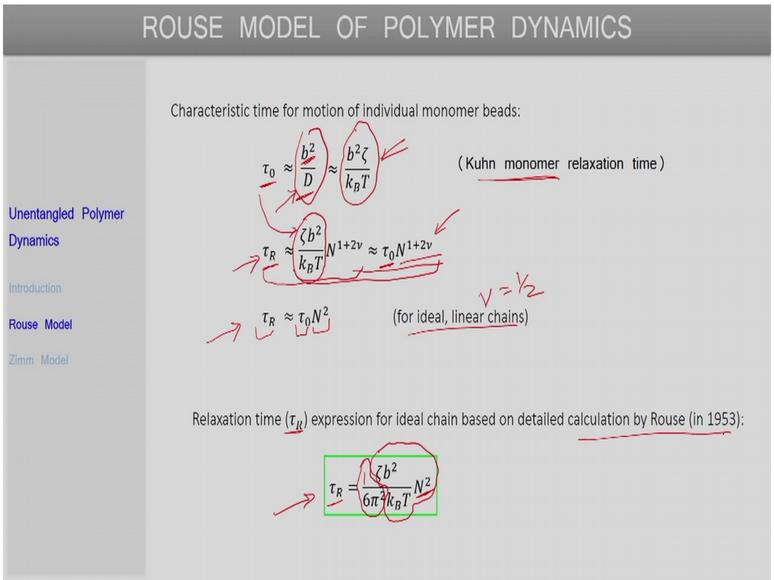

ROUSE MODEL OF POLYMER DYNAMICS

Unentangled Polymer Dynamics

Introduction

Rouse Model

Zimm Model

Characteristic time for motion of individual monomer beads:

$$\tau_0 \approx \frac{b^2}{D} \approx \frac{b^2\zeta}{k_B T}$$ (Kuhn monomer relaxation time)

$$\tau_R \approx \frac{\zeta b^2}{k_B T} N^{1+2\nu} \approx \tau_0 N^{1+2\nu}$$

$\nu = 1/2$

$$\tau_R \approx \tau_0 N^2$$ (for ideal, linear chains)

Relaxation time (τ_R) expression for ideal chain based on detailed calculation by Rouse (in 1953):

$$\boxed{\tau_R = \frac{\zeta b^2}{6\pi^2 k_B T} N^2}$$

Next let us try to define another characteristic time which is which is at the other extreme. So, the rouse time that we have just discussed it can be thought of as a characteristic relaxation time for our entire polymer chain, on the other hand if we consider the smallest unit of a polymer chain that will be the corresponding Kuhn monomer and if we want to talk about a characteristic time of relaxation of the Kuhn monomer. Then again that we can define as that time required for that Kuhn monomer to move by a distance as equal to it is or of the order of it is own size.

So, with that definition the that relaxation time for the Kuhn monomer that we can write as tau naught is equal to b square by D, where b is the size of our Kuhn monomer the Kuhn length and D is the diffusion coefficient of the individual monomer unit and in the rouse model we have already discussed that the individual for each individual monomer the there is an independent friction coefficient zeta. So, this D one can write it as just KB times T divided by zeta and if you do that the expression for tau naught or the Kuhn monomer relaxation time becomes this. So, this is the other extreme this is the relaxation time of the smallest subunit of our polymer chain and rouse relaxation time is the relaxation time for the entire polymer chain.

So, rouse relaxation time now or the rouse time that we can we have already written in the previous slide an expression for that and the general expression in terms of this exponent nu that is given by this relation. So, we see that in this part of this equation or relation this portion of this term is just the tau naught of the Kuhn monomer relaxation time. So, we can write the rouse time in terms of the Kuhn monomer relaxation time and N to the power one plus 2 nu and for ideal linear change the value of nu here will be half, so in that case rouse time is related to the monomer relaxation time tau naught through this N square term. So, in this case for the ideal chains the ratio of the rouse time to the Kuhn monomer relaxation time that will scale as N square. So, the longer the chain becomes the larger the ratio tau R by tau naught becomes and it scales by 10 to the power 2.

Now, the relaxation time or the rouse time that we have discussed we based on some simple arguments we came up with an expression which was not an exact expression, but which gave a relation between rouse time and other quantities. So, the relation that we have developed that is a kind of order of magnitude relation which relates to rouse time to the R to be of the same order of magnitude of as certain terms rouse. In fact, did a detailed calculation for this rouse model and came up with a more precise expression for rouse time which is shown here and we see here that compared to the approximate expression that we had developed in the previous slide, here the only difference is this constant pre factor 1 over 6 pi square.

Otherwise the all the parameters and other things like the N square dependence on rouse time they remain the same, so this is based on a detailed calculation by rouse rep as about in 1953.

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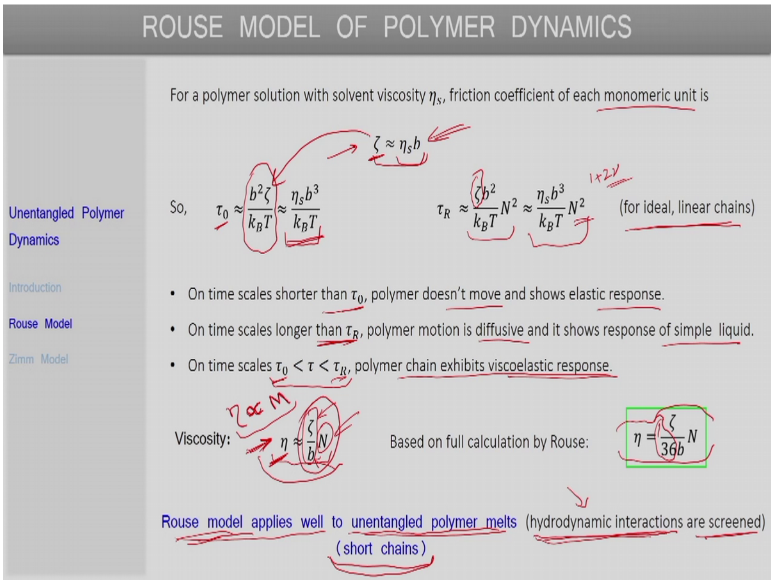

ROUSE MODEL OF POLYMER DYNAMICS

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For a polymer solution with solvent viscosity η_s, friction coefficient of each monomeric unit is

$$\zeta \approx \eta_s b$$

So, $\tau_0 \approx \frac{b^2\zeta}{k_BT} \approx \frac{\eta_s b^3}{k_BT}$ $\qquad$ $\tau_R \approx \frac{\zeta b^2}{k_BT}N^2 \approx \frac{\eta_s b^3}{k_BT}N^2$ (for ideal, linear chains)

$1+2\nu$

- On time scales shorter than τ_0, polymer doesn't move and shows elastic response.
- On time scales longer than τ_R, polymer motion is diffusive and it shows response of simple liquid.
- On time scales $\tau_0 < \tau < \tau_R$, polymer chain exhibits viscoelastic response.

$\eta \propto M$

Viscosity: $\eta \approx \frac{\zeta}{b}N$ $\qquad$ Based on full calculation by Rouse: $\boxed{\eta = \frac{\zeta}{36b}N}$

Rouse model applies well to unentangled polymer melts (hydrodynamic interactions are screened)

(short chains)

And next let us try to relate this concept of relaxation times and all those things to the viscosity of the solvent in constituting the solution. By stokes law which we have already discussed at the very beginning of this lecture, what we can say is that the friction coefficient is related to the solvent viscosity and the size of the particle that is moving through the solvent ok.

So, if we are talking about the friction coefficient of a single Kuhn monomer unit or a single monomer bead in our rouse model of the polymer chain. In the friction coefficient can be defined as the solvent viscosity multiplied by the size of our monomer which is given by v and what we can see is that the friction coefficient will be of the order of this product according to stokes law. So, that is what we have written here for individual monomer beads this is the friction coefficient that we have in the rouse model. Of course, for the entire polymer chain the friction coefficient is just the number of monomeric units times the friction coefficient of individual monomer unit.

So, the zeta R which is the friction coefficient of the entire polymer chain that is just N times zeta. So, now with this definition of the friction coefficient of the monomer units each monomer unit, we can write our Kuhn monomer relaxation time was expression we had developed to be of this kind. We can write that expression to be of this form where what we have done is just substituted eta as times b in place of zeta here and eta s of course is the solvent viscosity.

Next if we talk about the rouse time, then the rouse time expression also we had already developed in the previous slides and if you substitute the expression for the friction coefficient of each monomer unit by eta s time b this is the expression that we get. Again these this is valid for an ideal linear chain if it is a non ideal chain then instead of this n square will have one plus 2 nu as the exponent, but for ideal chains nu is half so we get N square. So, we have these 2 times and both of the both these times associated with the relaxation of either a single monomeric unit or the entire polymer chain these times also give us information about the kind of dynamics that will be observed on different time scales so I given polymer chain.

So, if the time of observation is smaller than tau naught or the Kuhn monomer relaxation time, then pretty much no polymer motion will be observed because, this is the characteristic time for relaxation of a single monomeric unit. If we are talking about time scales of observation between tau naught and tau R, so between the Kuhn monomer relaxation time and the rouse time of a polymer chain. Then the viscoelastic kind of response will be observed as we have discussed previously and if we are observing at a time scale that is larger than the rouse time of the polymer chain, then simple diffusive kind of motion will be observed and the behavior of polymer might be similar to that of a liquid.

On timescales below down art we have elastic response no moment of polymer above rouse time we have diffusive motion and similar to that of a simple liquid and in between these 2 time limits we have for the polymer chain exhibiting viscoelastic response as we discussed. Next we will also like to discuss how the polymer solution viscosity or the viscosity of the polymeric system that the rouse model is describing how that is related to let us say the polymer molar mass or the size of the polymer chain.

So, according to a rouse model without going to any detailed derivation, what we will see is that this viscosity of the our polymeric system that we are that the rouse model is describing that viscosity is of the order of zeta over b times N. So, zeta is a friction coefficient again b is the size of our monomeric unit N is the number of monomer units present in the polymer chain.

So, this is the expression for viscosity that we obtain from this rouse model and what we can say is that the n that we have here capital N the which is a number of monomeric units present, that will also be proportional to the molar mass of the polymer. Because, the more the number of monomeric units the larger the molar mass will be and this will be a linear relation between the number of monomeric units present and the molar mass of the polymer chain.

So, on the basis of this expression what we can say is that the eta that we have the viscosity that will also be proportional to proportionality sign here to the molar mass of the polymer chain and the proportionality will be a direct so that eta varies as M to the power 1. So, this kind of behavior is observed experimentally, if we are talking about the behavior of polymer melts where the polymer molar mass of the polymer chain size is smaller than a certain critical size and if the polymer chains are long molar mass is high then what is observed is the viscosity actually scales in a much stronger way with molar mass. So, it is typically observed that be above a critical molar mass of polymers chains, the viscosity actually starts scaling as molar mass to the power 3.4 whereas, below that critical molar mass the scaling of viscosity with M will be just eta being proportional to M to the power 1.

So, that the power or exponent of the molar mass that changes from 1 to 3.4 as the polymer size, increases beyond a certain critical size and the polymer molar mass also goes up beyond a certain critical molar mass. So, this kind of behavior is observed experimentally and of course the rouse model only captures the behavior for the small molar mass polymer melt systems. Above the critical molar mass due to the presence of what is called entanglement, so we have longer polymer chains now and they can get entangled. So, this entanglement effects lead to a much stronger variation of viscosity with power molar mass which rouse model cannot capture.

So, for this more advanced models for entangled polymer dynamics need to be used to get predictions which match with the experimental observations for such systems. But for a rouse model again the proportionality is direct the prediction of rouse model is that the viscosity is directly proportional to M. Now it is valid if we are talking at a polymer melt where the polymer chains are unentangled, so that the polymer chain size is not too large. Again the viscosity the expression that we have given is kind of an order of magnitude kind of expression, so the viscosity is of the same order of magnitude as this quantity as rouse made a detailed calculation. The prediction of from rouse model is or the calculation of rouse is this where we have this one over 36 as a extra constant factor coming in and finally as we discussed.

Just now this rouse model applies well if we have unentangled polymer melts because, as we will see in the next slide the this interactions called hydrodynamic interactions with which are typically of importance in dilute polymer solutions. But these interactions are screened in polymer melts and since rouse model does not incorporate these interactions it is not a good model for dilute polymer solutions. However, since in the melt these interactions are screened so for the description of dynamics of polymer melts, especially the unentangled polymer melts rouse model is a reasonably good model to apply.

So, when we say an entangled polymer melts again the polymer chains will be short and there will not be any entanglements between the polymer chains. So, what we are just discussed is that rouse model is not a good model for describing dynamics of polymer chains in dilute solutions ok. So, now let us see what kind of model is a reasonably good model for description of such systems.

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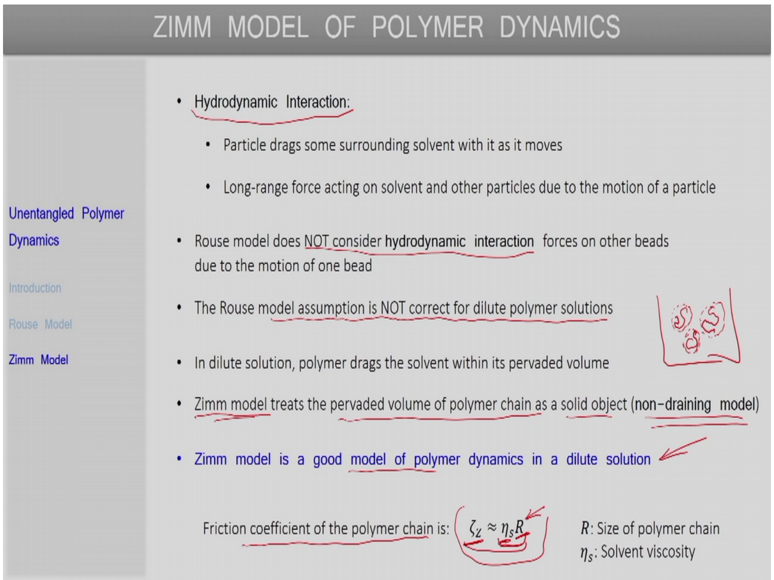

ZIMM MODEL OF POLYMER DYNAMICS

Unentangled Polymer Dynamics

Introduction

Rouse Model

Zimm Model

- Hydrodynamic Interaction:
  - Particle drags some surrounding solvent with it as it moves
  - Long-range force acting on solvent and other particles due to the motion of a particle
- Rouse model does NOT consider **hydrodynamic interaction** forces on other beads due to the motion of one bead
- The Rouse model assumption is NOT correct for dilute polymer solutions
- In dilute solution, polymer drags the solvent within its pervaded volume
- Zimm model treats the pervaded volume of polymer chain as a solid object (**non-draining model**)
- Zimm model is a good model of polymer dynamics in a dilute solution

Friction coefficient of the polymer chain is: $\zeta_Z \approx \eta_s R$

R: Size of polymer chain

η_s: Solvent viscosity

So, so before we move on to this the description of this model which is which applies well to dilute solutions, let us first talk about this concept of hydrodynamic interactions. So, we just mentioned that hydrodynamic interaction is something that are not captured by the rouse model and that is why it is not a good model for dilute solutions. When a particle is moving in a liquid medium, so through a solution or solvent then the particle drags some molecules of the solvent along with it as it moves

So, due to this the there is a long range force on the solvent surrounding solvent due to the motion of the particles through it and if you are talking with a polymer chain which can be thought of as consisting of several be beads of particles connected by some kind of strings that is a bead spring model. Then in that case, the motion of one bead that will lead to a force a long range force in the surrounding solvent as well as on the other beads of the polymer chain. So rouse model states that the interaction between different beads in a polymer chain is only through the connecting springs.

Whereas, if hydrodynamic interactions are present then apart from interacting through the presence of the connecting springs the beads will also experience force due to the hydrodynamic interaction, that is a movement of one bead will lead to a long range force not just in the surrounding solvent but all also on the other beads of the polymer chain.

So, that is the concept of hydrodynamic interaction which is absent in rouse model, so rouse is rouse model does not consider these hydrodynamic interactions at all here in that model the beads interact just by the connecting springs. So, that is why this rouse model the assumptions involved are not correct for dilute polymer solutions, instead in the model that is of choice for describing dynamics of to dilute solutions is the Zimm model. Here what is assumed is that as a polymer moves through the solvent it drags the solvent that is present in it is pervaded volume. So, what is pervaded volume now imagine a polymer chain in a in a given solvent; so, the volume of the solvent or the volume of solution that is spanned by a given polymer chain that would be referred to as a pervaded volume of a given polymer chain.

So, if we let us say consider a system where we have these polymer chains and we have surrounding solvent molecules. So, roughly the volume that is spanned by this entire chain that will the volume of these kind of spheres will constitute the pervaded volume of the polymer chain. So, this pervaded volume of course will be much larger in general than the actual occupied volume of the polymer chain that is a volume occupied by individual monomers of the polymer chain.

So, that occupied volume will be smaller than the pervaded volume and in the pervaded volume of a given polymer chain typically much of that volume will be occupied by solvent molecules. If we have a dilute polymer solution or the pervade volume of a given chain can also be occupied by not just a solid molecules, but other chains if we chain overlap and if the polymers is let us say it concentrated.

What is in the Zimm model what is assumed is that as a polymer chain moves it drags the solvent present in it is pervaded volume and if we if you recall our discussion in the lecture where we are talking of friction properties of polymer solution, then we talked about how the viscosity average molar mass can be measured or determined. So, there we talked about 2 different extremes one was a free draining model which corresponds to the rouse model here, otherwise an was the non draining model and that is what this Zimm model can be thought of as corresponding to.

So, here the pervaded volume of the polymer chain is treated like a solid object in this Zimm model. So, it requires once closer to the non draining model that we had discussed previously and because the Zimm model incorporates the hydrodynamic interactions it is a good model for describing dynamics of dilute polymer solutions. So, here to start with the friction coefficient of a polymer chain in a Zimm, in the Zimm model is defined like this here zeta z is the friction coefficient of the entire polymer chain in the Zimm model and using the fact that the entire polymer chain that pervaded volume acts as a kind of a impermeable sphere.

What one can say is that the friction coefficient is just solvent viscosity eta s times the size of the entire polymer chain given by R here. So, this expression again comes from the stokes law that we have discussed previously and here the entire polymer chain is treated as a particle, in the case of rouse model we say we saw that the individual monomeric units were treated as particles and stokes law was applied there. Here for the entire polymer chain we are applying the stokes law to obtain an expression for the a friction coefficient of the polymer chain.

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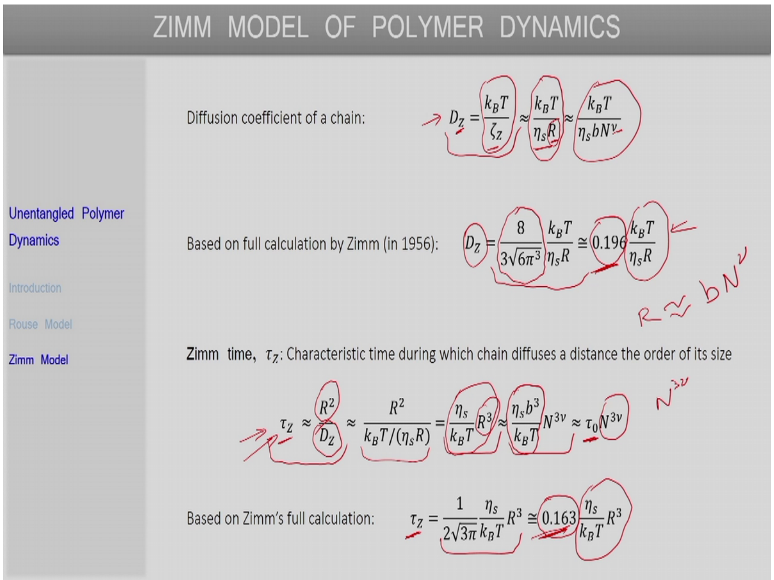

ZIMM MODEL OF POLYMER DYNAMICS

Unentangled Polymer Dynamics

Introduction

Rouse Model

Zimm Model

Diffusion coefficient of a chain: $D_Z = \frac{k_B T}{\zeta_Z} \approx \frac{k_B T}{\eta_s R} \approx \frac{k_B T}{\eta_s b N^{\nu}}$

Based on full calculation by Zimm (in 1956): $D_Z = \frac{8}{3\sqrt{6\pi^3}} \frac{k_B T}{\eta_s R} \cong 0.196 \frac{k_B T}{\eta_s R}$

$R \simeq bN^{\nu}$

Zimm time, τ_Z: Characteristic time during which chain diffuses a distance the order of its size

$$\tau_Z \approx \frac{R^2}{D_Z} \approx \frac{R^2}{k_B T/(\eta_s R)} = \frac{\eta_s}{k_B T} R^3 \approx \frac{\eta_s b^3}{k_B T} N^{3\nu} \approx \tau_0 N^{3\nu}$$

$N^{3\nu}$

Based on Zimm's full calculation: $\tau_Z = \frac{1}{2\sqrt{3\pi}} \frac{\eta_s}{k_B T} R^3 \cong 0.163 \frac{\eta_s}{k_B T} R^3$

So, now that we have an expression for the friction coefficient, the diffusion kind of polymer chain can be defined using the Einstein relation in this way. Here Dz the subscript z denotes that we are talking of the Ximm model and that by Einstein relation the diffusion coefficient of the entire polymer chain is given just by KB T over zeta Z and if we substitute the expression for zeta Z which is this then we and also for the an expression for the size of our polymer chain R as b times N to the power nu, then we get this expression for the diffusion coefficient of a polymer chain in the Zimm model and this expression that we have derived.

It is approximate the exact expression based on detailed calculations by Zimm is given here which shows that again there is an only an extra pre factor constant pre factor present here or here, otherwise the relation between Dz and other terms here are is of the same type as we have discussed here only difference is it this constant pre factor.

So, now that we have an expression for the diffusion coefficient in the of the entire chain in the Zimm model, again we can introduce the concept of a kind of a characteristic time of this Zimm model and that is called the Zimm time and this is again defined as the characteristic time that is taken by a given polymer chain to diffuse by a distance, that is equivalent to the or after order of the it is own size. So, as before as we did for the rouse model for the Zimm model also, the Zimm time of this characteris characteristic relaxation time of the entire polymer chain that will be given by just square of the a measure of the polymer size R square divided by the diffusion coefficient Dz and again if we substitute the expression of diffusion coefficient from above then we get this kind of relation between our Zimm time and the size of our polymer chain R cube um.

So, on the dependences of R cube type and again this R the size of the polymer chain R we can again write as of the order of b times N to the power nu again as before and if we do that we get this expression here. Where we see that the this quantity of this term is nothing but tau naught the Kuhn monomer relaxation time that we have already defined previously in today's lecture.

So, the Zimm time tau z is related to the Kuhn monomer relaxation time tau naught through this factor N to the power 3 nu. So the ratio of tau z to tau naught is n to the power 3 nu and if we consider the full calculation by Zimm as reported by zimm. So, in that case the expression for tau z comes out to be this or we just have this approximate pre factor 0.163 otherwise the terms that appear here, in the detail calculation are also the same terms that we have here only this extra pre factor constant pre factor is present.

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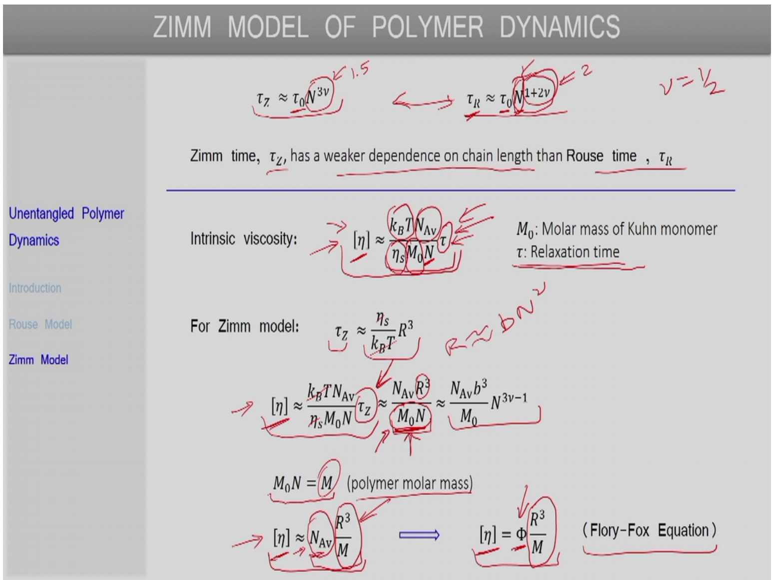

ZIMM MODEL OF POLYMER DYNAMICS

$\tau_Z \approx \tau_0 N^{3\nu}$ ↙1.5 ⟷ $\tau_R \approx \tau_0 N^{1+2\nu}$ ↙2 $\nu = 1/2$

Zimm time, τ_Z, has a weaker dependence on chain length than Rouse time, τ_R

Unentangled Polymer Dynamics

Introduction

Rouse Model

Zimm Model

Intrinsic viscosity: $[\eta] \approx \frac{k_B T N_{Av}}{\eta_s M_0 N}\tau$

M_0: Molar mass of Kuhn monomer

τ: Relaxation time

For Zimm model: $\tau_Z \approx \frac{\eta_s}{k_B T} R^3$ $R \approx b N^{\nu}$

$$[\eta] \approx \frac{k_B T N_{Av}}{\eta_s M_0 N}\tau_Z \approx \frac{N_{Av} R^3}{M_0 N} \approx \frac{N_{Av} b^3}{M_0} N^{3\nu-1}$$

$M_0 N = M$ (polymer molar mass)

$[\eta] \approx N_{Av}\frac{R^3}{M} \Longrightarrow [\eta] = \Phi\frac{R^3}{M}$ (Flory-Fox Equation)

Now, for the Zimm time we have seen that it is related to the monomer relaxation time tau naught by this N to the power 3 nu, rouse time is related to the monomer relaxation time may this factor N to the power 1 plus 2 nu. So, from here from these 2 relations what we can comment is that the Zimm time actually or the ratio of Zimm time to the monomer relaxation time that scales less strongly, than the ratio of rouse time to the monomer relaxation time with respect to the size of the polymer chain which is quantified by this N here.

So, Zimm time has a weaker dependence on chain length the than the rouse time and the reason why we are making this statement is that if we consider. Let us say for example ideal chain where nu is half, so in that case this exponent becomes 1 plus 2 into half which is 2. So, so in that case the rouse time will scale as N square, whereas for an ideal chain sin since we have 3 nu kind of scaling here we will get a exponent 1.5, so the Zimm time will scale as N to the power 1.5.

So, clearly the scaling of Zimm time is weaker and for other cases also let us say for a real chain in a good solvent in even in that case the exponent nu is around 0.6, so it is still less than 1. So, even if we use such values of nu we will see that the scaling of the rouse time with respect to N is much stronger or stronger than the scaling of Zimm time with respect to the chain length or N.

Now, last thing that we want to discuss with respect to this Zimm model is the concept of intrinsic viscosity. So, intrinsic viscosity is something that we have already discussed previously when we talked in the friction properties of polymer solutions and the measurement of viscosity average molar mass. It can be shown will not go into details where it can be shown that intrinsic viscosity is of the order of this quantity where we have this KB T as the Boltzmann constant times absolute temperature Avogadro constant, the solution viscosity test the M naught is a Kuhn monomer molar mass. So, if we considering the chain to be composed of Kuhn monomers then the molar mass of a given Kuhn monomer that is M naught and this N is just the number of Kuhn monomers present in our given chain model.

This tau here is the relaxation time there that we are talking about, so this expression is general it is not specific to the Zimm model, we can try to find out the expression for our intrinsic viscosity in the, for the rouse model as well. So, in that case instead of tau we will replace tau by tau R the characteristic relaxation time of the polymer chain in the rouse model. But since we know that rouse model is not a good model for polymer solutions especially dilute polymer solutions. So, that is why if we do that then the expression for the intrinsic velocity that we will get and the kind of scaling the behavior that it will describe that will be incorrect.

Zimm model on the other hand incorporates hydrodynamic interaction, so it is expected to be a good description of even the friction properties of dilute polymer solution. So, what we will do is in this expression for the intrinsic viscosity will in place of the relaxation time that that time that we will have here, we will use the relaxation time has developed in the Zimm model and we will see what kind of expression we get for the intrinsic viscosity.

So, for Zimm model the characteristic relaxation time of the entire polymer chain that is given by this expression as we have already discussed and if you substitute the that this first this tau z in place of the relaxation time here. So, the expression for intrinsic viscosity in the Zimm model becomes this and in place of tau z we can replace or substitute this expression and if you substitute this expression of course this eta s here will cancel this eta as the KB T here will cancel this KB T. So, we will be left with this term upon simplification and instead of again R we can write Rs to be of the order of b N to the power nu, so if we do that we get this kind of an expression.

Now finally, what we can do is that we can take this M times N M naught times N and say that this is the molar mass of our for entire polymer chain, M naught is a molar mass of a given Kuhn monomer N is a number of Kuhn monomers their product should be the molar mass of the polymer chain. So, this M naught N and we can write as M the polymer molar mass and if we do that here in this expression, then we can write that this intrinsic viscosity is of the order of Avogadro number times R cube over M where we have replaced this M naught times N by M here.

So, what we see here is a kind of relation which is already familiar to us, which we have already discussed when we are talking about the frictional properties of polymer solutions and that expression is a Flory fox equation. That we have discussed previously is the Flory fox equation states that the intrinsic viscosity is some proportionality constant or some universal constant times R cube over M and this kind of a ratio and the same kind of ratio we are getting here as well starting from the Zimm model and we get an Avogadro number. So, of course this is a not an exact equality we are saying that this intrinsic velocity is of the order of these terms. So, it is equivalent to the Flory fox equation that we have already discussed and what we see is that as a Zimm model it is application leads to the Flory fox equation for polymer solutions, which is something with an in agreement with the experimental findings as well.

What we have done in today's lecture is describe 2 different models of polymer dynamics one is rouse model which applies well to a unentangled polymer melt dynamics. But it which is something that is not applicable to, so there are dynamics of dilute polymer solutions because it does not capture the hydrodynamic interactions. On the other hand we have the Zimm model which is a good model for the description of dynamics of dilute polymer solution. Of course these are 2 extremes we have polymer we have dilute polymer solutions, we can also have polymer solutions that are a bit more concentrated. So, we will end by a quick dis with a quick discussion on the dynamics of semi dilute polymer solutions a very qualitative kind of discussion, a semi dilute solution is a solution which cannot be considered as a fully concentrated solution, but which is not also a highly dilute solution as well.

In a semi dilute solution what happens is that it is a solution where the polymer chains present in the solution have just started to overlap with each other. So, the pervaded volume of the polymer chains in the solution they add at this point where we describe the solution as a semi dilute solution. So, at this point the pervaded volumes fill the entire space of our solution and the polymer chains just start to overlap. So, if we have a solution or the polymer concentration below this overlap concentration, then we can say that our solution is a dilute solution and if the polymer concentration is above this overlap concentration then we say that the solution is a semi dilute solution.

So, in general even for semi dilute solutions if we look at the absolute value of the polymer it is a volume fraction in the entire solution, the volume fraction still will be quite small much smaller than one. But since the polymer chains have started overlapping the properties of the solution now will be strongly determined by this overlap of polymer chains and the behavior will be much different from what we see in a typical dilute solution.

So, in semi dilute solutions again the kind of model that we can apply to describe it is dynamics depends on the kind of length scales that we are talking about. So, in semi dilute solutions we can define a kind of an screening length and this characteristic screening length. if we are talking of length scales below this kind of a hydrodynamic screening length, then on that those length scales the Zimm model can be applied because hydrodynamics interactions might be important. But beyond a certain length scales and because now the polymer chain concentration is higher and they have started to overlap, so beyond a certain length scale the hydrodynamics interactions will get screened. So, beyond that length scale one can describe the dynamics using the rouse model where the hydrodynamic interactions are not considered.

So, a semi dilute solution depending on the length scale that we are at either Zimm model or the rouse model can be applicable. So, at small enough length scales where the hydrodynamic interactions are important one should use the Zimm model and at then scales larger than a certain screening length where the hydrodynamics interactions are screened then rouse model can also be applied, that is the description for a semi dilute solution.

If we are talking about polymer melts then if the chain is unentangled then we can use the rouse model, if you have entangled polymer chains if the polymer molar mass is high and the chains are long and we have entanglements then the dynamics is of a completely different kind and it is not captured by rouse model. We have to resort to other models like reputation which will be discussed in the next lecture, so for today we will conclude this lecture on the polymer dynamics of unentangled polymer solutions and melts at this point.

Thank you.