Rheology of Complex Materials
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Lecture – 03
Applications of rheology: some example material systems

The lecture today the plan is to look at examples of material systems and also examine at a microscopic scale or a molecular scale what are the key features or key mechanisms, that these material systems have then look at some applications of these material systems and then finally, end up with asking the question given the material system given the microscopic mechanisms given the application, what might be the questions that rheologist may ask what might be questions which are of real logical relevance.

So, again todays this class is also related to setting the stage for what we are going to do and these are the kinds of things that we ought to be able to answer when we learn about rheology and these are the kinds of questions we should be able to ask. So, the example; material systems belong to different classes and so to begin with we will just look at the overall set of materials which are there.

So, for example, what we have are polymer solutions I already mentioned that there are 2 broad class of material systems that we will see macromolecular and multiphase.

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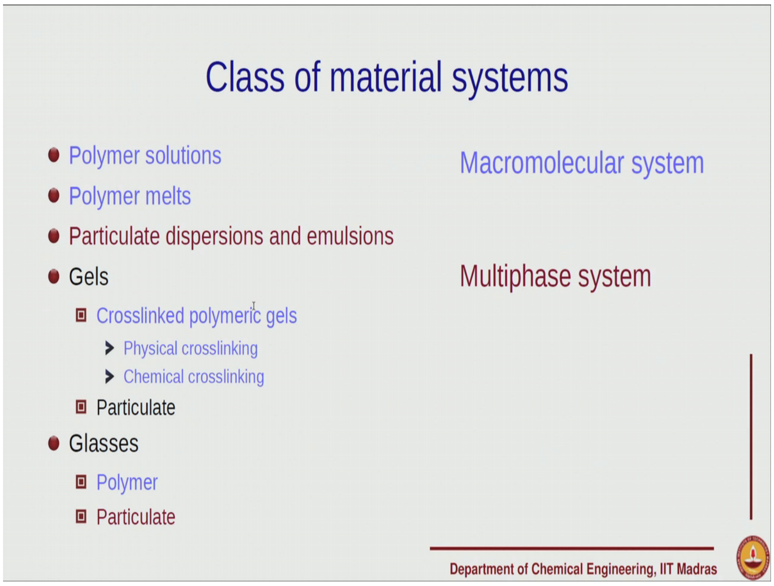

Class of material systems

- Polymer solutions
- Polymer melts
- Particulate dispersions and emulsions
- Gels
  - Crosslinked polymeric gels
    - Physical crosslinking
    - Chemical crosslinking
  - Particulate
- Glasses
  - Polymer
  - Particulate

Macromolecular system

Multiphase system

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So, the classes of material system that we will generally see are polymer solutions. So, Polymer solutions is one example. So, in this case we have polymer mixed with a solvent then we have polymer melts. So, we take plastic material to a very high temperature where it starts flowing. So, therefore, that is another class of material system.

Of course, we have particulate dispersants this could be a colloidal solution where the solid is dispersion in liquid it could be an emulsion where oil is dispersed in water or water and oil. Basically 2 phase systems solid and liquid or liquid in liquid and then we have a large class of material systems which are called gels. The idea of gel is what we see for example, in the kitchen also we have a gelly; it is largely solid like material, but it seems to be very soft. So, it is a soft solid material and gels can be in fact, made from polymers as well as particles. So, soft solid gel like systems are also another class of material systems and then finally, we have glasses as opposed to soft solid gels glasses are usually more harder and brittle more rigid. So, they are not soft and of course, the common glass the silica glass that we know is of course, very hard and brittle material, but using again macromolecules or polymers and using particulate systems again glasses can be formed.

So, largely when we think of rheology first in our minds we should try to picture which of these glasses the material system of interest belongs to and then then we can actually compare the material system of our specific interests with what is out their good models for these kind of material systems and so on. So, that way therefore, this kind of a classification is very helpful.

So, what you can notices the polymer there are the macromolecular systems which are one class and then we also have multiphase systems. So, the overall thing again can be classified in these 2 broad categories. In one case you have very large molecules polymers or micro molecules; in the other case we have 2 phases minimum. So, in a colloidal dispersion there is basically solids dispersed in a liquid and in in case of colloidal glass also you will have particles, which are dispersed in a continuous liquid, but the overall behavior of this material will be almost like a hard solid and it is possible that same kind of colloidal system may also show gel like behavior under certain circumstances glass like behavior under certain other circumstances and so on.

So, these are broadly the categories in which we would want to classify, because what we will see is in each and every case be microscopic and molecular mechanisms would be different. So, how do we understand the microscopic picture and how do we understand rheological response will be related to which of these materials system we are predominately interested in.

So, one last category which we will see towards the end is when both of these are together 2 classes ago we already discussed that food is a very good example, because you will have polysaccharides and starch and variety of these polymers in there, but we also have usually emulsions oil and water will be there. And so they are the a multiphase system they will also be crystals of certain food ingredients like sugar for example. So, therefore, it is a crystal solid which is in liquid and oil and water. So, actually food is a very good example of a system which has combinations of macro molecular multiphase things.

So, at the end of this segment of class what we will also discusses those, which are actually far more interesting somebody such point of view because many of the modern material systems. In fact, belong to this a cement for example, is also we think of it as cement slurry is only solid particles in water, but these days to have good performance of the cement slurry we may add a polymer. So, again that also becomes an example of a macro molecular multiphase system, this what we will do and I will go through now some of the mechanisms which are important at microscopic scale, because before we start analyzing rheology it is important for us to start to know what are the basic features of these material systems actually.

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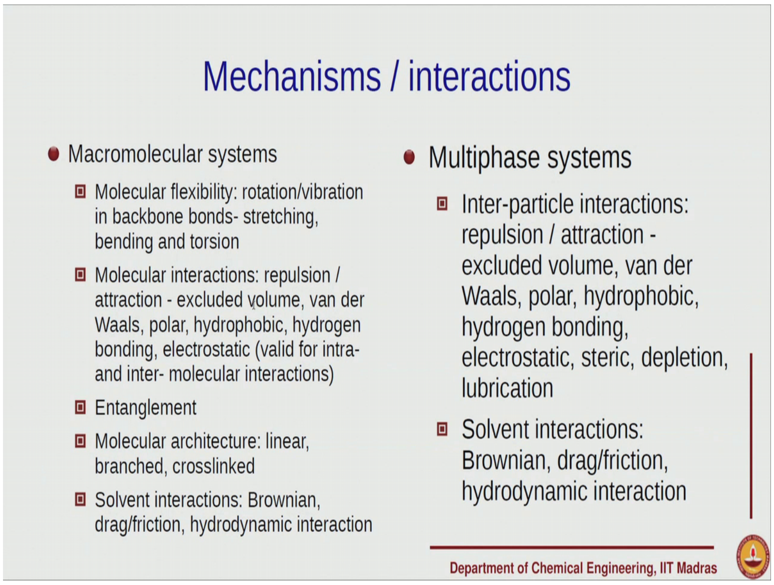

Mechanisms / interactions

- Macromolecular systems
  - Molecular flexibility: rotation/vibration in backbone bonds- stretching, bending and torsion
  - Molecular interactions: repulsion / attraction - excluded volume, van der Waals, polar, hydrophobic, hydrogen bonding, electrostatic (valid for intra- and inter- molecular interactions)
  - Entanglement
  - Molecular architecture: linear, branched, crosslinked
  - Solvent interactions: Brownian, drag/friction, hydrodynamic interaction
- Multiphase systems
  - Inter-particle interactions: repulsion / attraction - excluded volume, van der Waals, polar, hydrophobic, hydrogen bonding, electrostatic, steric, depletion, lubrication
  - Solvent interactions: Brownian, drag/friction, hydrodynamic interaction

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It is just a slide summary of all those mechanisms, but right now let us first go through one each one of them systematically. So, at the end again we will come back to the slide and then see that we have summarized all of them.

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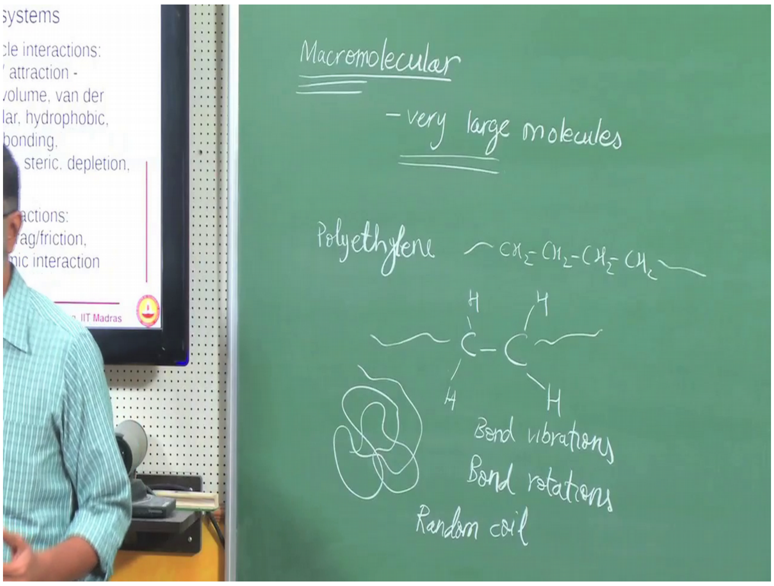

So, let us start with a macro molecular system. So, most of you of course, have heard of polymers and plastics, which are very large molecules and the key feature of macro molecular system lies in the fact that they are micro or they are very large molecules. And what that brings in is the ability of molecule to respond at different length scales and time scales. We will continue to elaborate on benzene have basically the length scales and time scales of interest are limited and therefore, there behave as simple fluids while complex systems such as polymer will have multiple length scales.

So, we naturally will see that the microscopic mechanisms that we are going to discuss also will be of different length scales and different time scales. So, let us begin at the very smallest scale which will be of interest from a rheological response point of view which is bond level. So, for example, for polyethylene we have this CH 2, CH 2, CH 2 and so on right. So, this is polyethylene continuous on it is a chain of ethylene put together and so what is possible in this case is the bond level interactions and so the fact that there is bond rotation possible.

So, if you look at each of these bonds the CC bond actually can rotate and if you recall from so if you just were to draw let us say the one particular bond the one particular bond will have CC bond, it will have 2 hydrogens and then it will have the polymer chain right. So, this is somewhat like tetrahedral 2 tetrahedral and in fact, rotation around this is possible. So, if you see one strand of the polymer molecule can rotate this is let us say one stand of polymer and this. So, this molecule can adopt actually very different conformation due to this bond rotation.

So, because of this bond rotation in general this macromolecule will have basically a call coil like conformation and the idea here is to think off each and every bond as a random step given that there are all these different things. So, angle between this the polymer branch and this polymer branch can be anything and so it is like saying that you are taking if there are n bonds here it is like saying N random steps. So, I can take first random step that is one orientation of the bond then the next one can be then the third and so on. And in the end what happens most often is after 10,000 steps, you are not very far away from your original step because each and every step is random.

In 2 D what I am doing is I can show you I can say I will take some steps to the right and some steps to the left and randomly I keep on doing this. So, even if I take 10,000 steps most likely I will be back here, because with equal probability I will take 5,000 steps roughly 5,000 into the right and roughly to the left.

So, my most likely position at the end will be again at the center. So, basically this is what the random work is what polymer macromolecule is doing. So, therefore, it is a fairly flexible object and add the bond level the bond vibrations. So, bond vibrations and bond rotations are involved and depending on the type of molecule the kind of conformation that this molecule takes will be specified based on the torsional angles and so on. So, therefore, add the bond level we have these information available the fact that cc bond it itself there will be vibration and the fact that there is rotation twisting and rotation and so on. So, this is at the molecular scale.

Because of which this molecule adopts usually what is called the random coil structure. So, one way to describe this coil like structure of macromolecule is to talk about it is flexibility. So, the fact that CC bond rotation is allowed we end up getting the macromolecule which actually coils, but let us say if I have a macromolecule in which single CC bond is not there, but double CC bond is there then in that case rotation around that will not be possible then that molecule on the average will have some conformation like this which is the more rod like conformation.

So, then we can say that this molecule is not flexible this molecule. In fact, the chain flexibilities limited it is. In fact, more often than not rod like conformation and the end to end distance is very high.

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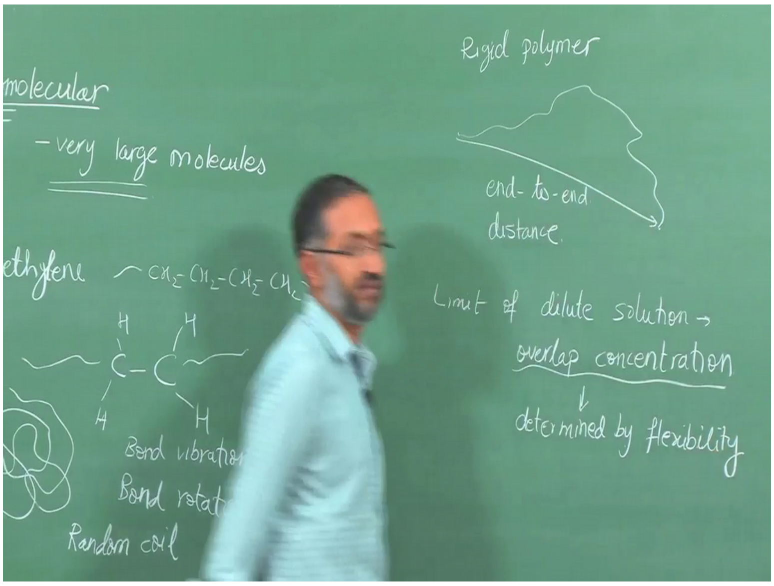

So, generally to characterize the flexibility end to end distance is also useful and this is an example of Rigid Polymer. So, therefore, flexibility of macromolecule is an important concept. So, bond level information leads to related to flexibility of polymer macromolecule and the ability of rotation and how the backbone is this is called the backbone right.

So, how the backbone bonds are will decide whether you have flexible molecule or rigid macro molecule and why is this important for example, let us say if I am making the solution of these kind of macromolecules, in one case I have solution of these and I take the same molecular weight which means the cantor length is the same, but I the polymer is now reject if I make a solution of these 2 what would be the difference why would be expect that this flexibility might play an important role.

The other feature which is important we will discuss that is when we make a solution there will be interactions between the solvent and the polymer and there will be interactions between polymer and polymer, both of these are possible. Now at what concentration does the polymer interaction become important will define whether it is a dilute solution or non-die or concentrated solution in dilute solution the assumption will be that dominant interactions or polymer and solvent. So, this limit of dilution will be very different because in general these will be random coil and therefore, smaller they will occupy less space while these are rod like object. So, they will occupy more space.

So, generally at smaller concentration polymer solvent interaction and intra macromolecular interactions are important. So, in general at the limit of dilute solution this is also generally referred to as overlap concentration the idea being that that concentration of polymer at which they start just about overlapping which means they start interacting with each other. So, this overlap concentration is it depends on flexibility of micro molecule. So, is determined by flexibility.

And clearly in a in a given rheological application we would want to know whether we are in a dilute solution regime or we are in the concentrated solution regime and in fact, the response will be very different also viscosity. In fact, will vary quite a bit if you are in the dilute system we will see the viscosity increases gradually with concentration as soon as we reach polymer polymer interactions the viscosity increase will be much stronger. So, in general to understand rheological response it is important for us to map which regime we are in in terms of dilute or concentrated.

So, clearly molecular flexibility and molecular makeup right what the bonds are important from the point of view of determining the rheological response and they are important microscopic mechanisms and as we said depending on the flexibility the stretching will also be decided. If it is already a rod like molecule then it is not going to stretch much more, but if it is a flexible molecule which is coil. So, that has the ability of stretching quite a bit right so, but this is all molecular ductility usually we use at a microscopic scale here we are talking about flexibility and everything at the molecular scale.

Of course it has consequence in terms of defining the rheological response at a bulk scale also and that is what we are going to learn throughout this course that is to how microscopic mechanisms affect rheological response at the macroscopic scale. So, that is what we have seen are these first set of interactions which are related to flexibility.

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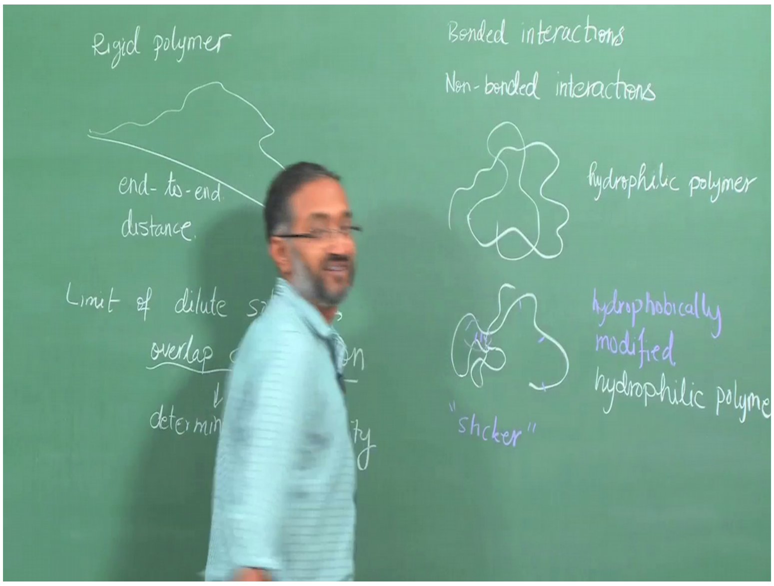

Now, the next set of things are related to interactions get so non-bonded interaction. So, generally we think of what we have talked about that all examples of bonded interactions and now we will talk in terms of Non-bonded interactions. And here basically the solvent and the micro molecule as well as different parts of macromolecules will interact with each other.

So, for example, here this part of macromolecule and this part of macromolecule may have interactions, these interactions could be Vander Waals interactions could be hydrogen bonding could be electrostatic if let us say there is a polymer chain and it has ionic group on it, then there will be electrostatic interactions also. So, all possible modes of molecular interactions will be possible here. We will soon see that quite often it is important to make a polymer system interact more strongly by introducing different type of branch on it.

So, let us say this is a polymer molecule which is coiled on that if I let us say introduce. So, this is let us say a hydrophilic polymer. So, it will generally adopt some basically coil like structure now the same hydrophilic polymer I take and I start adding let us say few hydrophobic branches on it. Now what will happen is these hydrophobic branches will have a tendency to come together. And so in that case what will happen is you; you might get far more titer this thing of the molecule, because all these different sections all want to come together and form such hydrophobic regions.

So, what we are doing is we are inducing hydrophobic interactions in the polymer. So, this is one example of hydrophobically modified. So, this is hydrophobically modified hydrophilic polymer. So, clearly this is all molecular interactions being manipulated. Secondly, if we are in the non-dilute regime then the interaction between 2 different polymer molecules will be much stronger in this case, because we are putting stickers it is almost like as if we have putting stickers all the molecule and they will stick. So, we have put in places where 2 molecules can stick with each other. So, we have specifically put in interactions.

As far as molecular interactions are concern one important molecular interaction is also repulsion or excluded volume.

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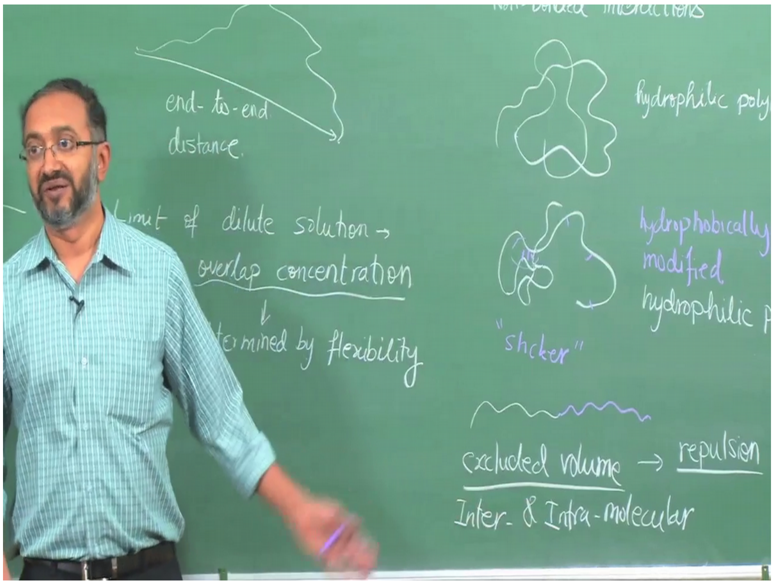

So, when I talked about the steps to the left and right if I had taken a step to the right I could again come to the same place and take a step to the left right. So, actually I was overlapping on the same place where I was earlier, but if you think of these 10,000 steps the tenth step and twentieth step cannot be in the same place, because 10th space there is already a bond the molecule cannot go back and again cross the same path basically the same space cannot be occupied by different parts of the molecule there is what is called excluded volume.

So, once there is a molecule in place the other part of molecule cannot occupy the same place. So, this is an excluded volume and this is generally a repulsion between electronic clouds of macromolecule or any other molecule also. So, we you might have attractive interactions like hydrophobic interactions hydrophobic are attractive and then you also have a repulsive interactions, if you have electrostatic certainly if you have similar charges then you in have a repulsive if you have unlike charges then you may have attractive.

So, in general these molecular interactions can be of attractive and repulsive type depends on what specific material system are there and one key thing is that interactions are both intramolecular as well as intermolecular. I already talked about that in dilute limit you may have this as a more compressed object or a smaller object, but when we have a very high concentration then these stickers will make a more effective job of linking different macromolecules together. So, that is intermolecular yeah. So, it will be what is called cross linking.

So, therefore, you have both the inter and intra molecular interactions and this intra is important, because it is a macromolecule in case of small molecules there is only intermolecular interactions, but because we have micro molecule which is very large we have intra molecular interactions also very important.

Now, the next feature the; that we will look at is valid when we have very high concentrations, what you can see here we have discussed are mechanisms which are important for dilute and maybe somewhat concentrated solutions, but when we go beyond the certain concentration. Basically the idea of bowl of noodles where one noodle is very difficult to extricate is valid. So, those are either melt or concentrated solutions.

So, there the most important interaction that is very relevant is called entanglement.

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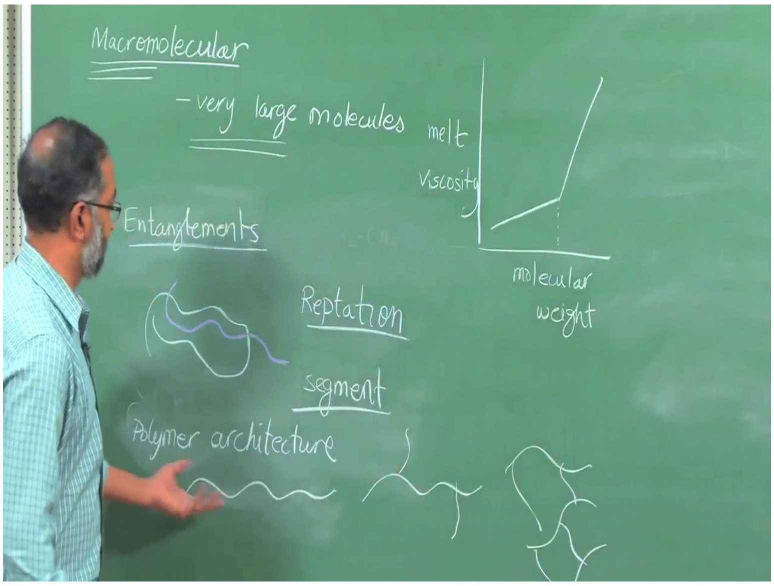

So, Entanglements so basically one molecule is entangled with the other molecule and because of all these entanglements molecules cannot freely move, they are confined basically what you can think is each and every molecule is confined in a tube and that tube is made by all the other surrounding molecule. And so this molecule cannot go beyond the tube because it is there always molecules which are entangled, but what this molecule can do is it can move like a snake.

So, that motion is called Reptation in fact, this is was the key finding during 70es to try to use the models related to Reptation to describe the behavior of polymer melts. And how viscosity or many other properties of polymer melt depend on the microscopic feature mainly the entanglement was described using theories of Reptation. Where molecule predominantly can basically whenever head follows the tail will follow there because in general it is confined by other molecules in a tube. So, it is motion in a tube basically.

So, these entanglements when they are there we will see that the rheological response will be very different, if we have non unentangled solution versus entangled solution there will be a big difference in any of the rheological response and whenever we have an entangled system an important term which we will use is called segment. So, if we look melt viscosity as a function of molecular weight as a function of molecular weight and this is log; log plot what you will see is generally and this is actually for any lots of different types of chemistries.

So, in the sense many different systems where you start adding more and more monomer units so that the polymer molecular weight increases, then of course, viscosity will increase, but beyond a certain point the viscosity increases much more drastic. And so what happens is if you have small molecules and they do not entangle with each other it is like a few cut noodles very small then there would not be any entanglement, but if there is long noodles then it will be easy for them to get entangle. So, therefore, entanglement happens whenever there is critical length beyond which entanglements are possible.

Now, if I freeze this system and melt it of course, there are no entanglements, this system there are entanglements when I freeze it of course, in the glassy state also there will be points at which macromolecules interact very closely. Though in general we would not need to characterize them as entanglement, because in general molecular motion is frozen in glassy state or in the solid state. So, only when we bring to the melt rest of the molecule between entanglement point is more free to move, but due to entanglement there is a;

Student: Restriction.

Restriction. So, that is why in the melt state is where entanglements get more importance. So, in general if I increase the concentration also I would see that entanglement are formed at low concentrations, basically one molecule does not even interact with the other then when concentration of polymer molecules is increase some interaction between them will start and then beyond a concentration they will start getting entangled with each other.

So, entanglements are an important microscopic mechanism and then important to describe the polymer architecture, because that will determine whether what kind of entanglement will happen, what kind of interactions are possible whether it is a linear, whether branched or whether there is cross link network. So, whether you have a linear system or branch system or a cross link system.

So, all of these you are also important in terms of determining the overall response and one last feature of course, remains is now what is the interaction this is all related to the to the micro molecule itself what about between macromolecule and solvent. So, the same set of interactions that we talked about are valid, in case of solvent and micro molecule also and that is what we will you see now in the next lecture.