Introduction to Soft Matter
**Professor. Dr. Aloke Kumar**
Department of Mechanical Engineering
Indian Institute of Science, Bengaluru
Lecture 22
Polymer Concentrations

So welcome back to another lecture on Introduction to Soft Matter. Last week we had stepped into the lab and we did experiments in the lab with polymer solutions and we got an intuitive what we had been building an intuitive idea for and theoretical ideas in the class. We were able to actually see it in action. Now, in this particular class, I had like to discuss some of the important issues related to the lab experiments. Now when we went into the lab, we did an experiment with what we call a polymer solution. Is that important to state of existence of the polymer where the polymer exists in a binary solution or as a binary mixture, because we added powder to water and that is why we call it binary, is this a, this a solvent in a sense, the water and there is the polymer.

So this is one mode in which or one state in which you can find polymers. You can obviously also find polymers and there original state, where only polymer molecules and nothing else. So with regards to that, let us clarify some of the things that we saw in the lab and how they might affect experimental results. So once again, as I said we looked at polymer solutions and polymers can exist in different states and the polymer solution is basically a binary mix, liquid mixture.

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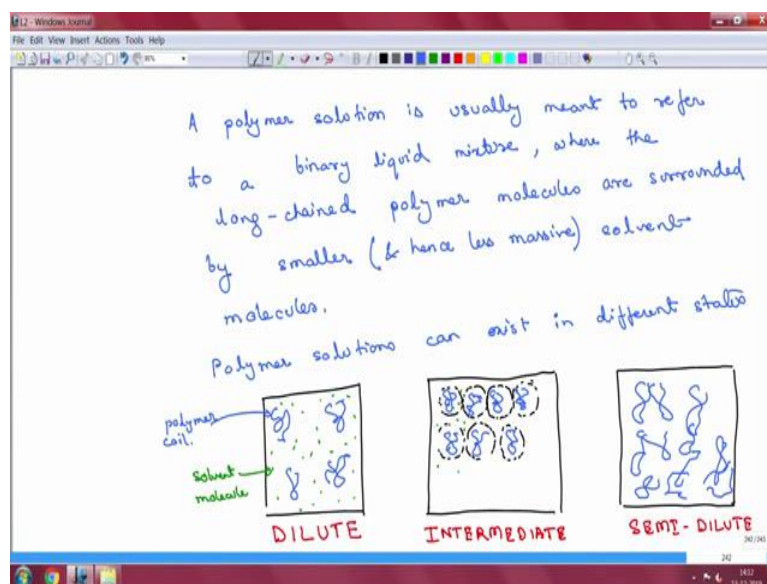
So a polymer solution, it is usually meant to refer to a binary mixture or a binary liquid mixture. Where, the long chained polymer molecules are surrounded by smaller and hence less massive solvent molecules. Now, such polymer solutions can exist in different states. The moment I am saying a binary liquid mixture, so obviously a binary liquid mixture is simplest type of polymer solution, you can have other more complicated forms, but for the sake of simplicity, that is what we did in the lab we looked at a binary liquid mixture.

So let us keep our attention focused to that. So the moment I say a binary liquid mixture, it should come to your mind that you can have. So basically, you have a certain concentration of the polymer in another solvent and that concentration can be varied because in the lab, what would, what did we do? We took a powder and then we dissolve it in water. The amount of powder that we dissolved in a certain amount of volume of liquid or water, that is some, that is a parameter that we can control.

So, we can decide how much polymer we want to mix in the solvent. So depending on this concentration, so in a binary solution, the most, one of the most obvious parameters is the concentration of the solution, or the mixture. So the concentration will start to decide how the polymer solution really behaves. Now depending on the concentration of the polymer in the solvent, there are many different types of states of a polymer solution that are possible. And they differ from each other in important physical respects. So, let us see what they are. So polymer solutions can exist in different states.

So I will make a few boxes and 3. There are five different ones that we will consider today. So I will make two more. So the first and the simplest possible system is where you have, this is let us say a polymer molecule. It exists as a, it is not exactly a globule, but it is neither all straightened out. It is a polymer coil, so the polymerase chain exists in a coil state. So this is a polymer molecule in blue that I have drawn. So let us say there is another polymer molecule somewhere else and we have a few more.

And then interspersed here, another solvent molecules, I am drawing them as dots because they are smaller and has that less massive. So this refers to, this is solvent molecule and this is a polymer coil. Under normal conditions, the polymer has to exist in coil state because of Brownian motion, I mean we have talked about that before.

So this is also what is known as a dilute solution. This is, and it is called dilute and we will write it down in a moment. The reason it is called dilute, this image should give you an idea

of why so sorry. The reason we call this dilute is because the polymer molecules exist by themselves and that so less in number, they do not interact with each other. So there molecules are separated by large distances and they are hardly interact. Obviously, this is not a static picture, Brownian motion will eventually make one interact with the other one. But the idea is that the number of polymer molecules is small enough that the chances of encounter are less, are very small.

So this immediately tells us that there should be another state where they are large, larger in number than the dilute case and where the polymer molecules just about to start interacting. So, if I draw up polymer molecules in a state like this, this is another one. So now you see I am drawing slight larger number of polymer molecules and this is such that this polymer coil has a certain volume and so does the neighbouring one. And so does the neighbouring one.

And this sphere that I am drawing is the effective volume of the coil. And you can see that the effective volume is just such that the coils are not really overlapping but they are just about to do that. So I am not drawing all of them. And obviously the, there are solvent molecules so the solvent molecules are so small that they are just around in the solution space.

So later on I am going to leave out this, the solvent molecules because we know that they are really small, less much less massive than the polymer molecules. So this is also what is known as a intermediate stage or intermediate regime. So the next regime is old semi dilute. Here the polymers chains of large enough in number that different polymer chains start to interact. This is another polymer chain and they are large in number such that the chains are just about to, the concentration is such that the chains are just about started overlapping.
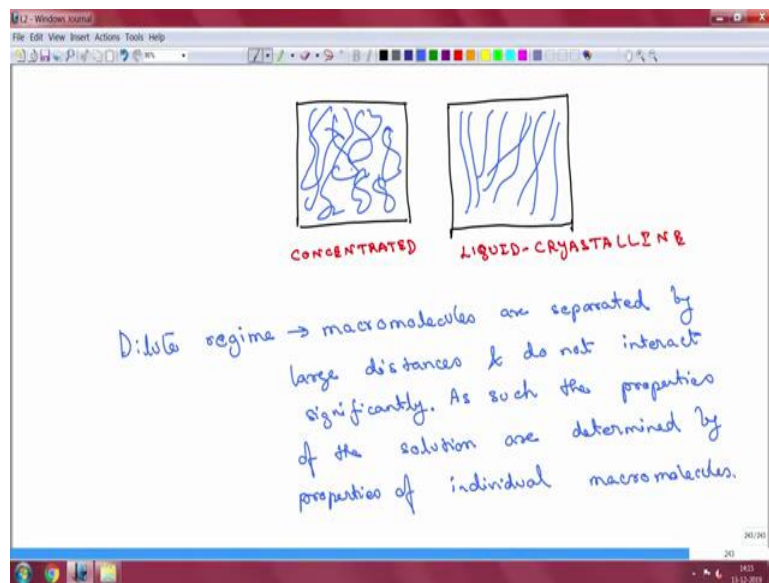
This is a very intuitive description at this moment. We will make it quantitative in a second, but let us first understand it from a intuitive perspective. So obviously, the idea here is to keep on increasing the polymer concentration and decrease the solvent concentration. So you can reach another state, which is called the concentrated state. If you keep on increasing the amount of polymer.

And finally this one mode, which is called liquid crystalline. In this concentrated case, you have a much larger number of polymer molecules, they are still in a situation where they are not really, they are still scattered in isotropic way in the liquid crystalline certain order can start to emerge in the system, the polymer of molecules, they are very large in number, but there is some amount of an isotropic that has started to come about.

So, just write it down, so the first one was the dilute case. So dilute regime in this regime, macromolecules are separated by large distances and do not interact significantly. As such, the properties of the solution are governed by the properties of individual macromolecules, sorry are determined by properties of individual macromolecules. Now, just because the solution is not dilute state does not mean that the polymer does not have an effect.

It can still have a very strong effect, but whatever the effect is essentially because, so let us say you subjected to external stress and the flow starts to occur and the flow properties will be governed by as if the polymer molecules, it is the stresses on the individual polymer molecules, which will be largely responsible for the behaviour of the solution or the response

of the solution. So, in a sense, this is similar to low density gases where they are not interacting with each other.

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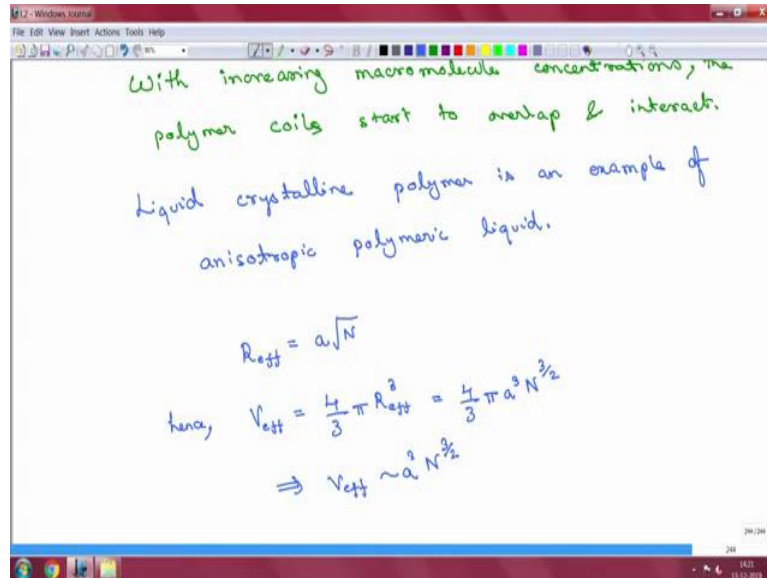
So with increasing concentrations, so increasing macromolecule concentrations. So I am using the word macromolecule and polymer interchangeably here. The polymer chains start to, or the polymer, actually a better word is coils because they exist in a coil state, the polymer coils start to overlap and interact. And it becomes much harder to discern the contribution of the individual macromolecules.

Now when you take a solution like that, let us say a semi dilute solution and you subject that to an external stress, the solution will behave in a way as if the polymer molecules are obviously individually stressed, but the polymer interactions is also start taking place. So it is like information is going to be passed from one polymer to the its neighbour and his friend. It will tell its friend how it is, what stress has it is feeling and then his friend will also end up feeling some stress.

So that is how this interaction now that starts to become important in that case. And one of the final state that we drew is called the liquid crystalline state. In this particular case, obviously the polymer concentration is very very high now, but a liquid crystalline regime. So liquid crystalline polymer is an example of an isotropic polymeric liquid. We are not going to go into how an isotropic develop, but it suffice to say here that this an isotropic and also develop spontaneously under certain conditions.

So till now our discretion discussion has been more or less intuitive and qualitative but we had want to make it quantitative now. So let us discuss some of the important numbers that we can associate with these kinds of systems. Before we do that, I just wanted to recall that we have discussed what the effective radius of a polymer coil is. And I hope you remember.

So we had discussed a few lectures back that the effective radius for, so R effective, the effective radius for a polymer, sorry with N segment where the length of each segment is a is a root over of N. So the volume of such a polymer, the coiled polymer. So the volume or the effective volume, so I just write V for volume.

So hence V effective where V stands for volume is now going to be 4 by 3 by pi R effective cube, which is equal to 4 by 3 pi by a cube N to the power 3 by 2, which implies that V effective. If we drop this number 4 by 3 into pi, then this skill says a cube N to the power 3 by 2. So now let us figure out. Well, so let us define concentration.

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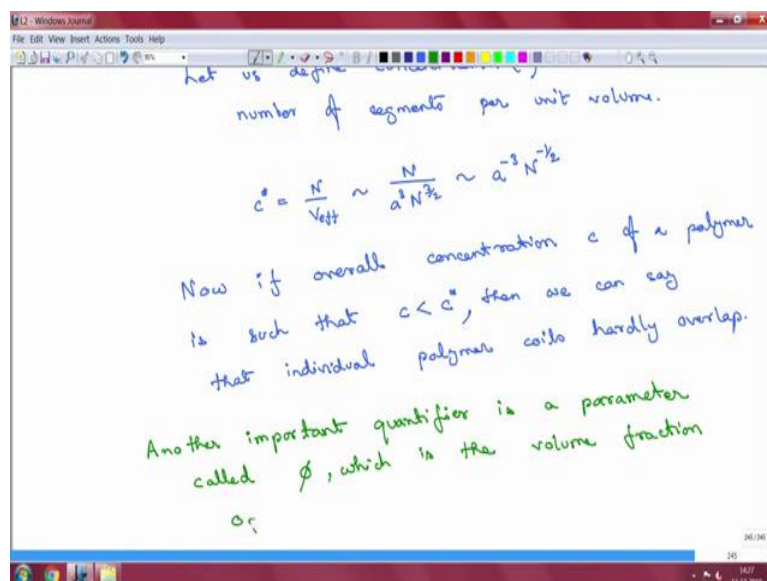
So let us define concentration C as the number of segments per unit volume. I am just going to quickly go back to the 5 states that we discussed. So, in the intermediate regime, you have a situation where the polymer coils are in such a state that each of them is occupying a certain effective volume, but the effective volume of each is such that the volumes are basically touching each other.

So it is almost as if there are N number of, so each polymer has, let us say this is a mono disperse polymer, so each polymer molecule is exactly has N number of segments. So in this case, if this is a state which we would define as the critical state, or where the concentration is

of a critical nature, then this c critical is such that, so c critical is such that there are N segments per volume or for the effective volume of a polymer coil. So, this gives us, this is N we just saw this effective volume scale says we got 3 by 2, so this skills has a to the power minus 3, N to the power minus half.

This is a very important equation because it gives you the dependence of c star on N, usually for polymers, if there are carbon carbon is the backbone of the polymers carbon chain, then you do not have much control over the size of the length segment, but it is N which is usually varied in the polymer.

So this gives you a very nice explicit dependence of c star on an, so now if overall concentration c of a polymer is such that c is less than c star, then we can say that the individual polymer coils hardly overlap that individual polymer coils hardly overlap. What does this mean? This means that in, in the lingual of the previous states that we had discussed, that this will belong to the dilute state or the dilute region.

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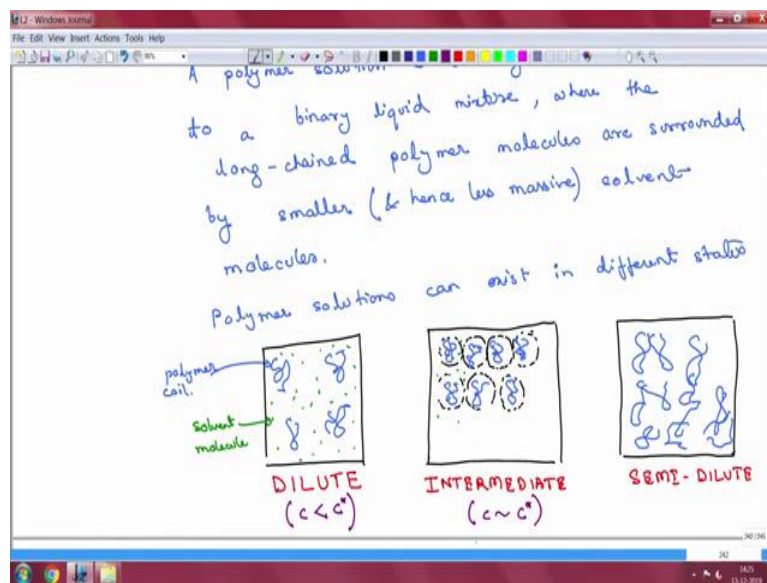
So if I had to write down, I am just going to erase this because I am going to write down some of the expressions of a this particular case, the dilute case, your concentration c is such that c is less than c star. Obviously, here I had to write the overall concentration is such that just a second of overall concentration is such that c is the same order as c star. So c star corresponds to this threshold regime or the intermediate regime. Now, there is a slight problem with using c as a important parameter and that is, it has units.

So it is a, if you see what we have, we have defined it is number of segments per unit volume. So in that in such kind of a case, another important parameter that becomes very useful is a quantity called phi. So phi will define it as the volume fraction of the polymer in the solution. So another important quantifier is a parameter called volume fraction or parameter called just say, let us say phi, which is the volume fraction of the polymer in solution of volume fraction of the polymer in the solution. Now How would, obviously the moment we have, we are associating a number which are associating a quantity. We have to tell how do you calculate it.

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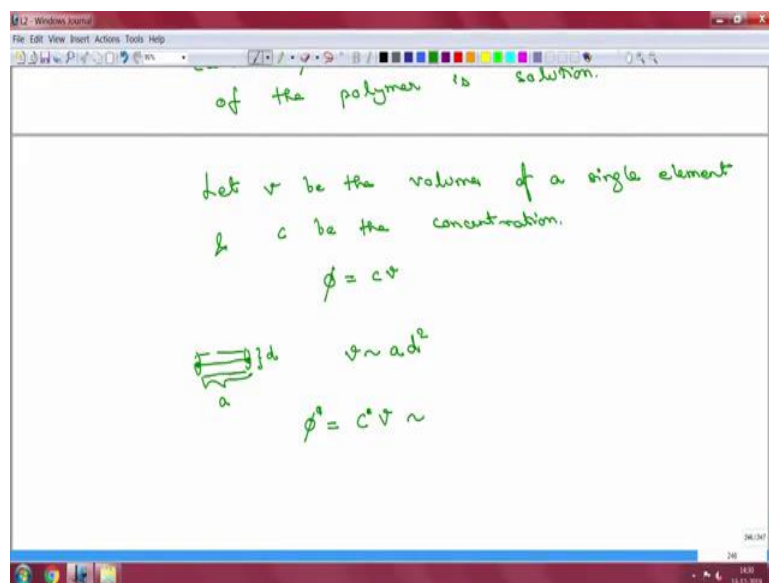
So let small v be the volume of a single element and c be the concentration. Then obviously phi is related to c and v by phi equal to cv. So what does this imply? So when you have phi equal to 1, you will have a situation where there are no solvent molecules. There are only be polymer molecules, so that is also called a polymer melt by the way. So let us try to estimate this number. So let us say that a single, so we have already said that.

So when we are considering a single segment, we said that this distance was a. So it also has some effective diameter and let us call this diameter d. This is a single segment of the polymer. So then your v scales says a times d square, this is the volume of this cylinder without that pi by 4. So I am dropping that same number over here.

So now phi star is a critical volume fraction is a volume fraction such when your concentration is also critical. So phi star should we be equal to c star into v. So we have

already seen how did c star vary c star varied as a to the power minus 3, N to the power minus half.

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So a to the power minus 3, N to the power minus half. And what is v? v is a into d square. So my phi star is varies as d by a square N to the power minus half. Now this d by a is a molecules scale information. This is in some senses looks like almost aspect ratio. So this is an important number, but it is usually sort of fixed in most cases. Now d can range from in practice it can range from anywhere from 1 to 50.

For example, DNA molecules can have d by a of the higher on the higher side, but for the time being, let us just imagine the d by a is equal to 1, then what happens? So if d by a is equal to 1, and let so I am trying to take a very specific scenario and N equal to let us say 10 to the power 4.

So I am taking a polymer such that on a molecular scale, this d by a comes out to be almost 1 on 1 and it has tended to by 4 segments. So what does my phi star come out to, 10 to the power minus 2, what does this mean? This means that polymers, so this is an example. So here, let us say, so just a second. So this an example problem, so here, this implies that in such a situation, the polymer chains will start to interact when the polymer concentration is only 1 percent in this case polymers can start interacting only a at 1 percent concentration or volume fraction

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This is quite interesting because typically we tend to think that phi or a 1 percent is a small number, but for polymers, 1 percent can be very, very large. They can be extremely significant, which is why for the kinds of polymers that we were using at 1 percent you can actually end up getting very significant viscoelasticity. So, we should not bear the notion that for polymers dilute means 1 percent can be dilute, but 1 percent need not to be dilute.

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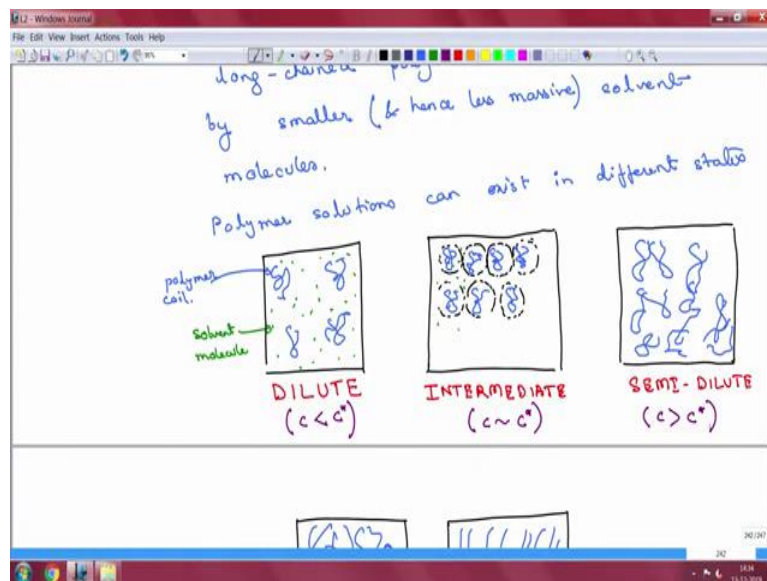
So this is an important issue here, which is why when we had discussed this intuitively or just on a qualitative basis, then it does not really tell us at what a scale or what is the real concentration at which these states are achieved, but now that we have gone through this quantitative process, we know that this kind of a state or these states can be achieved at or the intermediate state for example, can we achieve very low concentrations also.

So obviously the intermediate, sorry, the semi dilute situation will occur when c will be greater than c star and as c starts to tend towards 1, you will start getting the concentrated and you can also get the liquid crystalline under different conditions but here c is just slightly greater than c star and as c tends starts standing to 1, you will end up getting a concentrated regime.

So basically for polymers chains, the takeaway notion or the takeaway lesson is that when N is much greater than 1, there will exist many states where by varying the volume fraction you can achieve all these different states. And this argument will not hold if N is very small. So we must remember that this entire calculation holds only when N is much greater than 1.

And what is the reason for that? Is because in the beginning itself, we took the idea that the polymer exists as a coil.

So that coil structure can only exist if N is much greater than 1. So this I hoped, sort of clarifies to you the exercise that we took in the laboratory where we looked at a binary solution of polymers and that is why we did this entire exercise of going through figuring out c star and phi star.

Now another thing that we did not do much in the lab is when you do experiments there are important conditioning exercises that one has to do. That is something that we did not do. For example for creep compliance tests. It is often that standard conditioning operation is done where the load is applied on a fluid or a material and it is unloaded and this is done repeatedly.

And, usually the maximum possible load is applied and then it is kept unloaded for about even 10 times the time of the loading situation. And this is done repeatedly and the reason it is done is so that the system should not have any long term memory and that it loses long term memory so that the results can be treated as if the system did not have long term memory and it is only the acting to the stresses during the duration of the said experiment.

So those are things that you would learn if you take a very detailed course on Realogy. That is why this is an introductory course as we have already discussed in the very beginning of the course. So, those are things that you would probably encounter and understand and learn much better when you take up advanced courses. So, we will end today's lecture here and I will see you in the next class. Thank you.