Rheology of Complex Materials

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Lecture – 01
Flow phenomena in complex materials and microstructure

As part of the course on Rheology and the introduction module of it, in this particular lecture, we will look at some of the unusual flow phenomena which take place in complex materials and also equally important is; how do we visualize those phenomena to be caused due to microstructure.

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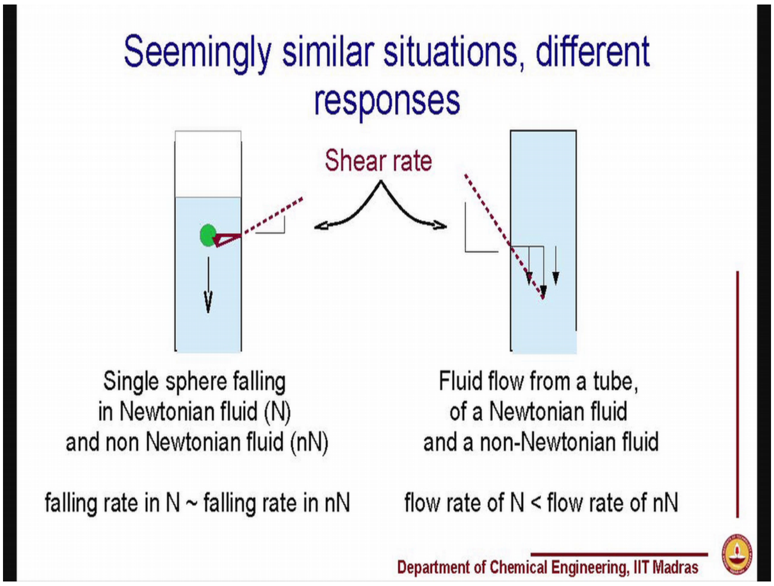

So, let us start with a situation which seem to be similar in respect; for example, we have a single sphere which is falling through a pool of liquid and of course, we learn about this problem whenever we look at a terminal velocity of a sphere falling in liquid and we learn about stokes law.

And let us consider that this single sphere there are 2 cases; one in which the sphere is falling in a Newtonian fluid and then compare the response with the Non-Newtonian fluid. And what we can see is if the viscosities of the Newtonian and Non-Newtonian fluids are similar then the falling rate in a Newtonian fluid will be similar to the falling rate in Non-Newtonian fluid. This is because we know that the settling velocity related directly to the viscosity of the fluid and if the 2 velocities are similar then in this case the falling rates will also be similar.

Now, if the same 2 fluids basically the Non-Newtonian fluid as well as a Newtonian fluid rather than let us say having a sphere falling through the pipe. Now if we just remove the bottom of the if we remove the let us say bottom and allow fluid to flow through the bottom of the pipe then what happens is overall fluid flows through and in this case again the Newtonian fluid as well as Non-Newtonian fluid will flow through, but what is more likely then we will observe that the flow rate of the Newtonian fluid will be much lower than the flow rate of Non-Newtonian fluids.

In other words flow rate of Non-Newtonian fluid will be higher or it would seem as if the viscosity of Non-Newtonian fluid would be lower. So, therefore, what we are seeing here are predominant examples of shear flow. So, in both the cases it is predominantly shear which is involved and just to characterize and quantify the intensity of the shear flow we can think of shear rate. For example, here the velocity would be whatever is the velocity of terminal velocity of the sphere and then it would go to 0 near the wall and therefore, you have a velocity gradient or shear rate, which is very small because in general the terminal velocity of a small sphere is expected to be very low.

On the other side we have a basically tubular flow of the fluid and in general the velocity here will be very high in the center and overall flow rate will be very high and therefore, towards the tube where the velocity is 0 to and that velocity which is maximum basically what you will have is a shear rate which is very high. So, what we can again summarize in this situation shear rate is low while in this situation shear rate is very high. So, the 2 situations that we have seen and where the similar fluids give completely different responses because in one case they give a falling rate of the sphere which is similar, in the other case the flow rates of the fluid are very different and those are caused because of the difference in the shear rates.

So, effectively what we have is high shear rate viscosity is lower and low shear rate viscosity is higher.

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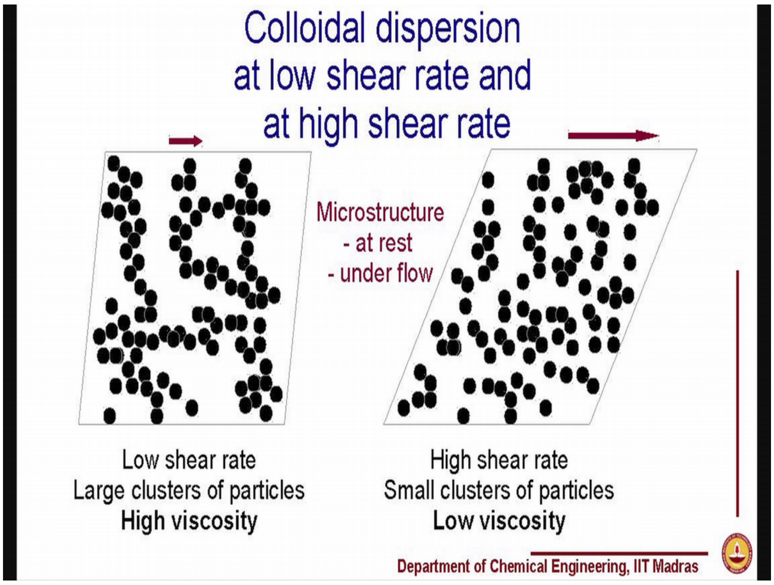

And just to understand why in a complex material such behavior can be observed what we can do is look at an example of colloidal dispersion. Now colloidal dispersions are nothing, but collection of particles and these particles are agglomerated in a network form with each other at reasonably high amount of colloidal particles and then surrounded by a liquid.

So, therefore, you can see in this how there is a network of these colloidal particles. And so this would be the situation at a low shear rates also at rest and so when a sphere is falling through this kind of a very high network of a colloidal particles, then the sphere is likely to experience a higher viscosity and there because of the larger clusters which these colloidal particles make. On the other hand if we now let us say apply a very high shear rate to this colloidal dispersion what ends up happening is these large colloidal clusters actually start breaking up and now what we see is large number of smaller isolated clusters.

So, in because of the smaller clusters at this higher shear rate the fluid viscosity would appear to be lower and therefore, what we have is low shear rate would correspond to large clusters of particles while high shear rate would correspond to small clusters of particles and in turn large clusters would imply high viscosity and small clusters would imply low viscosity. Now looking back at our 2 examples that we saw earlier what we can see is the microstructure is very important to explain the results in both the cases, in one case we have microstructure of the material at rest when there was no shear rate at all, when we apply very small or low shear rate there is a small disturbance of that equilibrium structure retaining large clusters of colloidal particles; however, when we have it under flow and with large shear rate those clusters break down.

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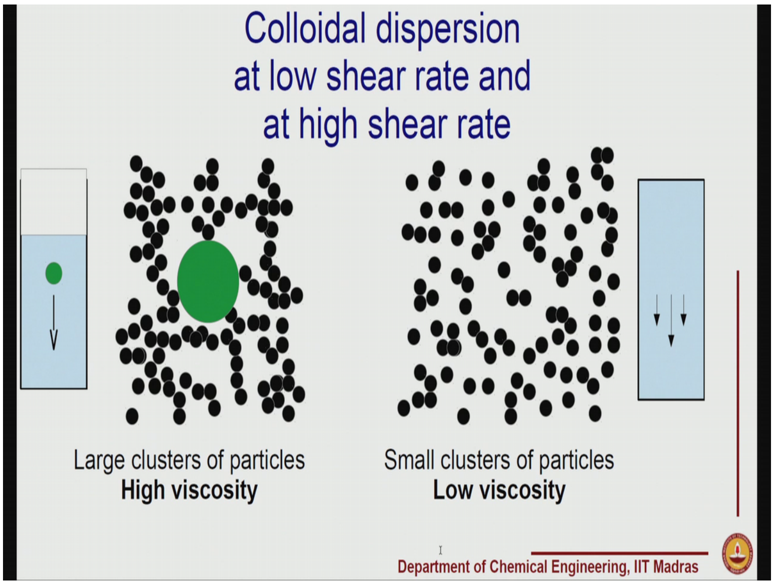

So, therefore, when we visualize the 2 cases that we discuss, in one case we have a sphere which is falling through basically a strong network of colloidal particles and therefore, this particle experiences high viscosity and therefore, the if Newtonian and Non-Newtonian fluids are of same viscosity we would see that the particle falls at the same rate.

Now, when the same fluid the colloidal particle system is subjected to high shear rate it ends up being in small clusters and low viscosity therefore, the flow rate is very high. Newtonian fluid on the other hand in both the cases has same microstructure same molecular structure and therefore, would have the same high viscosity in both cases. So, it would have a small falling rate for sphere, in this case and correspondingly it would also have a very small flow rate.

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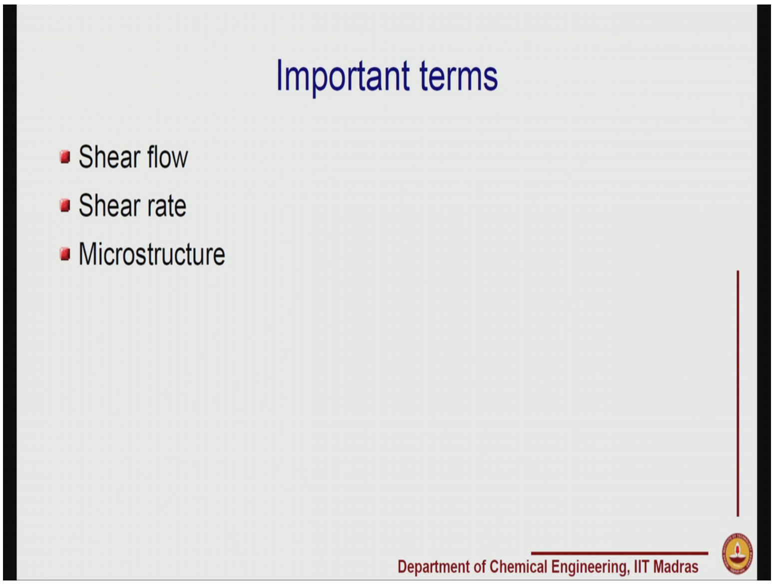

So, what we have seen in this discussion so far is that when fluids the complex materials are subjected to shear flow, we can quantify the deformation that the fluid is experiencing during flowing with shear rates and properties of fluid seem to be dependent on the shear rate very strongly.

And the example that we saw was that of a shear thinning fluid because the viscosity was lower at higher shear rate and more importantly we also saw that the response of the material could be correlated back to the microstructure that the material has.

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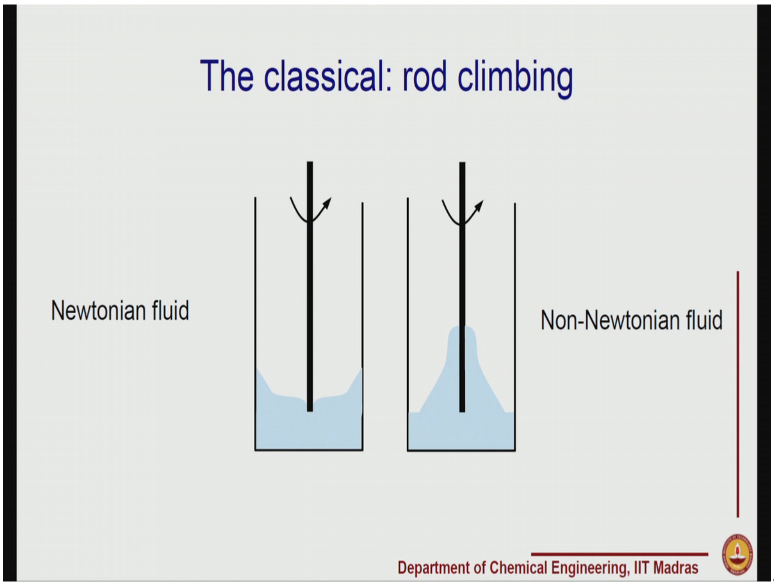

Now, let us move on and look at another example again now these flow phenomena that we are seeing for complex materials one of the most important things to remember is that they are in fact qualitatively very different. For example, if we take a beaker in which there is a fluid and then I put a rod and then I have the rod stirred with a motor if I rotate this rod with a motor then what we would expect is at the center the fluid to go down and we would see that the fluid air interface takes a shape which is concave upwards. And this is what we would observe in when we let us say are stirring tea or milk using very high rates in in day to day life.

On the other hand if we take a Non-Newtonian fluid and do a similar exercise what happens is the fluid actually starts climbing onto the rod which is being used to stir and therefore, this phenomena is called rod climbing. So, in this case even though the 2 fluids are being subjected to same situation their response is qualitatively different and the importance of rheology in general is that if you know small amount no amount of modification of Newtonian flow behavior is going to lead to this kind of qualitatively very different response.

So, clearly a different class of a fluid behavior is required for us to explain and observe such phenomenon.

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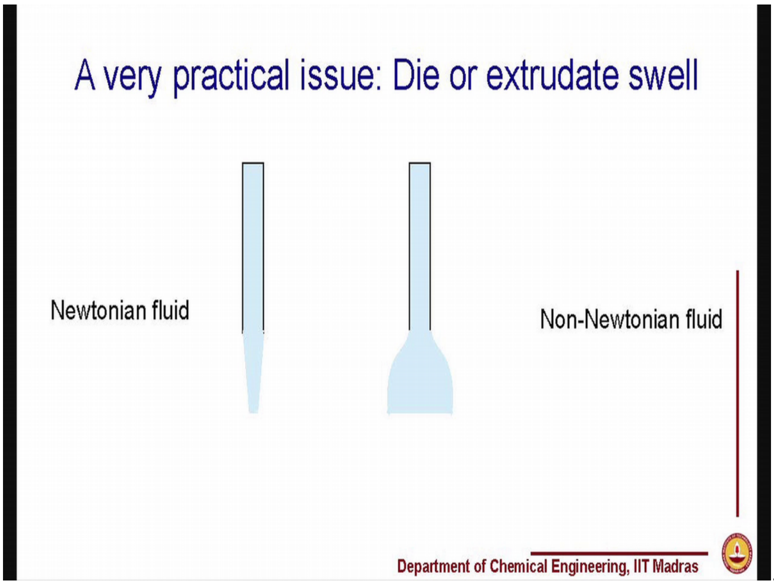

Another example which is a very practical issue and when we are making a objects out of polymer and these could be fibers for example, polyester fiber which are used in clothing or upholstery or it could be a grocery bag films thin films, in all of these cases what is done is we take a small capillary in which through which fluid is forced out. So, generally we apply a very high pressure at this end and then through pressure we push the fluid out and this is what happens. In fact, when we open a tap at home and then we have a Newtonian fluid water flowing out of the tap.

Because the other end of the pipe line there is higher pressure quite often due to gravity because the tank is located somewhere upstairs and due to that pressure difference the fluid flows through, and we generally observe that the jet of the fluid is smaller than the diameter of the tap and of course, this is as long as we maintain a flow rate which is lower and such that the jet does not breakup and forms a spray in which case of course, it start spraying everywhere.

So, we are still looking at a jet nicely following and usually the diameter of the jet would be same or so similar order of magnitude and slightly smaller. In fact, it is about eighty to ninety percent of a depending on the conditions of the diameter of the tube on the other hand if we take a Non-Newtonian fluid and again carryout the same exercise and this is what is done when a fiber is made or a sheet is made, we basically have a what is called a die and there is a die opening through which a fluid is extruded.

And therefore, this material which is extruded is called extrudate and the device through which this extrusion happens is called a die and given that the fluid when it comes out it is diameter is much larger than the diameter of the tube this phenomenon is referred to as die swell or extruded swell. So, again this is an example of an unusual flow phenomena in the sense that the qualitative response itself is diametrically it is opposite to what you would see in case of Newtonian fluid. In case of Newtonian fluid we see the extrudate being smaller than the diameter of the tube or the die in the case of a Non-Newtonian fluid we see that the diameter is higher.

And again we can try to understand; what is the origin of this phenomena by looking at the microstructure.

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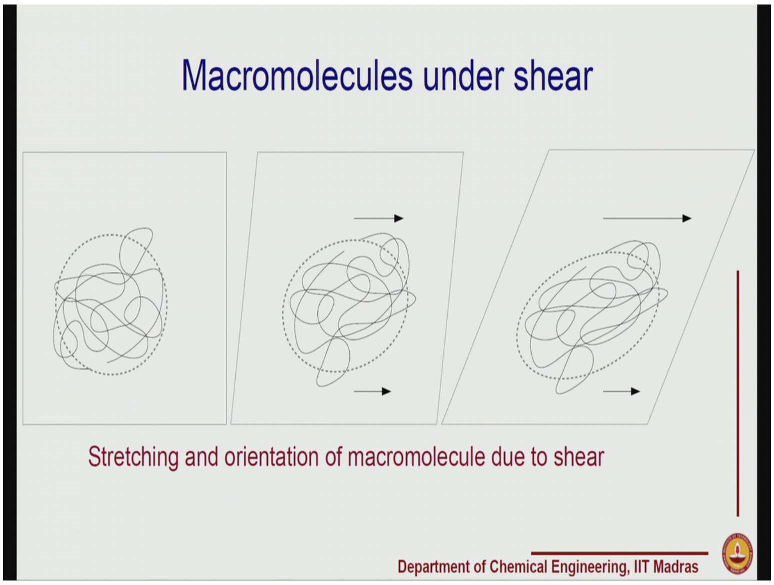

And. So, let us now look at a let us say macromolecular solution. So, what we have here is a micro molecule which is a very long molecule and generally it will adopt the conformation which is coil like and therefore, we can encase the overall macro molecule in a hypothetical sphere and of course, the radius of this sphere would be called the radius of gyration of this particular macromolecule and we are talking about a macromolecular solution.

So, therefore, surrounding fluid is the solvent. So, we have a situation where we have a polymer solution or a macromolecular solution being sheared and we can look at 2 different cases let us say where there is a high shear rate and there is a low shear rate. So, in case of a shear shearing the material what we can do visualizes the let us say the top surface of this domain is moving; faster than the bottom surface we can think for example, that the top surface is moving with a velocity and while the bottom surface let us say stationary, what that does is basically as you go higher and higher the velocity would be higher and higher.

So, if you look at the macromolecule zoom in this is of course, a considerably zoomed in version in which we are able to see the macromolecule, what we will see is the macromolecule which is closer to the top surface will have a higher velocity and the macromolecular portions which are in the lower part will have lower velocity. So, therefore, there is a velocity gradient on the scale of the macromolecule and what we would end up seeing is the solvent will drag these portions of macromolecular little faster while the molecules macromolecular portions here will actually be dragged with a lower rate.

And if the same situation can be seen at the higher shear rate what we would see is the difference between the velocity at this end of the macromolecule and will be very different compared to the velocity here and in general the upper part of the macromolecule may get dragged little a higher. So, in effect what we are seeing is this macromolecule, which in general could be described as a random a coil object seems to have stretched a bit as well as oriented a bit. So, we can see that it is stretched and as well as oriented. So, therefore, what is happening is whenever we are subjecting these macromolecules to shear what we have is stretching as well as orientation?

So, stretching and orientation are inherent phenomena which take place at the macro at the molecular scale when we have macromolecules under shear. Of course, the result of this stretching and orientation is also an inherent elasticity which is built into these macromolecular systems.

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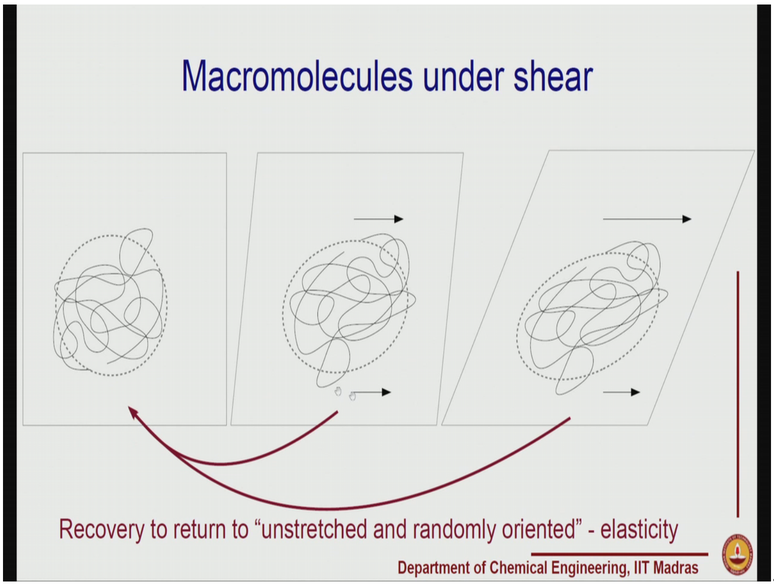

Because as soon as we let us say we stop the shear here there is a tendency of this macromolecule to go back to the spherical conformation a random conformation that it had when there was no flow. So, therefore, whenever we stop the flow there is a tendency to return to “unstretched and randomly oriented” macromolecule and which is anyway what is a predominant mechanism for elasticity in these systems.

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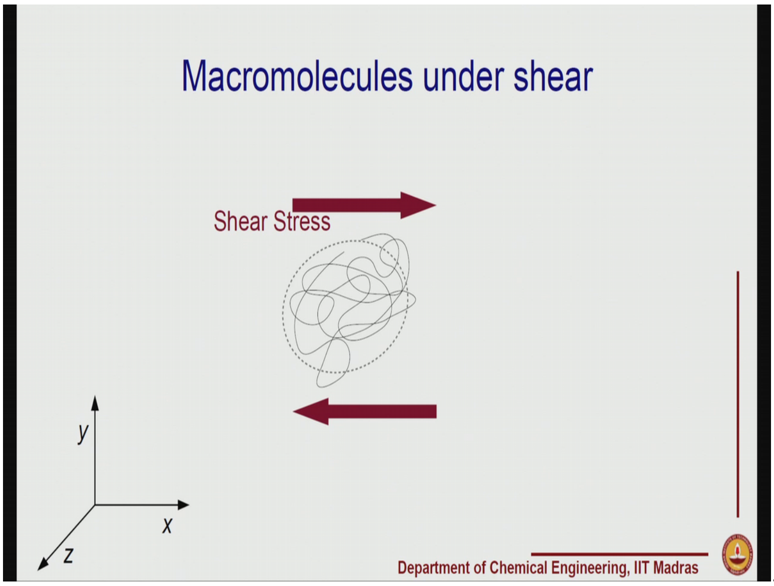

So, now let us look at a given that we have understood that how a macromolecule stretches, when it is put in a shear flow, what we can see here is that a macromolecule is there in shear flow and clearly there are shear stresses involved. Because we are sharing the molecule in along these planes we have Shear stresses which act on this macromolecule, but because of the stretching that this macromolecule experiences as we saw, what we end up also having in these materials is the presence of Normal stresses.

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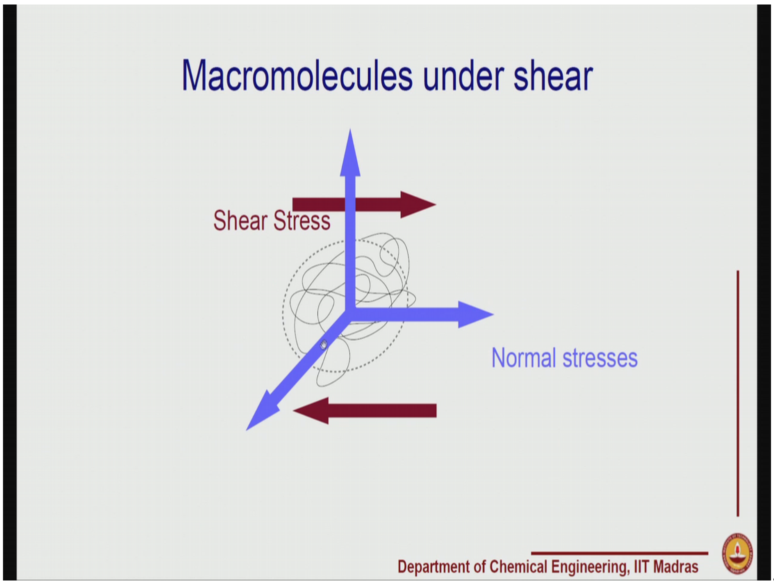

So, even though at the boundaries we are only applying a shear stress, because of the normal stress present in the material at the boundaries we can again measure what is called a normal force? So, due to this we can see that the fluid response is again qualitatively very different compared to what a Newtonian fluid would be. In case of Newtonian fluid since we are applying a shear stress we will only observe a shear stress in the material. In case of macromolecular solution even though we are applying shear stress we observe normal stresses also and just to go back and look that this is the coordinate system that we can use where X is the direction of the flow and Y is the direction of the shear and Z is the third direction.

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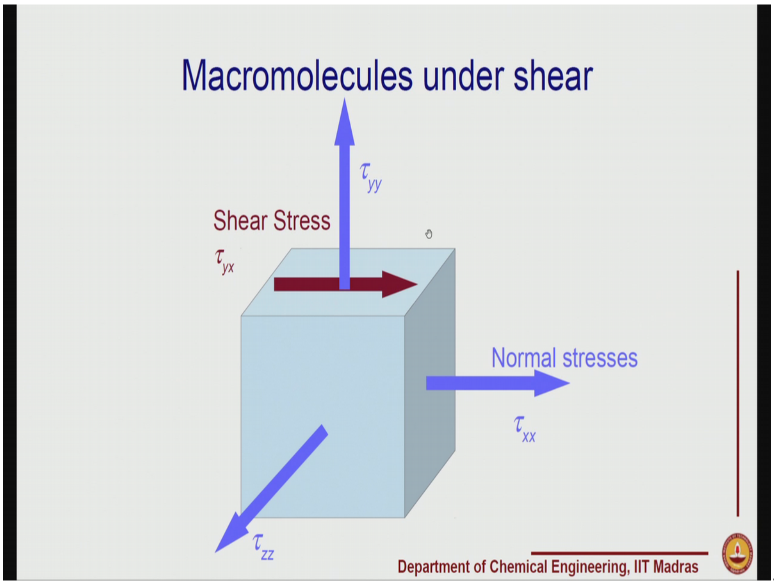

So, therefore, in this situation when we are looking at these normal stresses, we could denote them as tau XX which is a normal stress in X direction on X plane. Here by X plane we mean this surface whose unit normal is in the same direction as X direction. And therefore, in the macromolecular under shear in this case we have the stress components which are not only shear stress, but also these normal stresses. So, the normal stresses that arise which are due to the stretching of the macromolecule and due to it is orientation they are very important in explaining the unusual flow phenomena that we saw earlier namely extruded swell or die swell as well as rod climbing effect.

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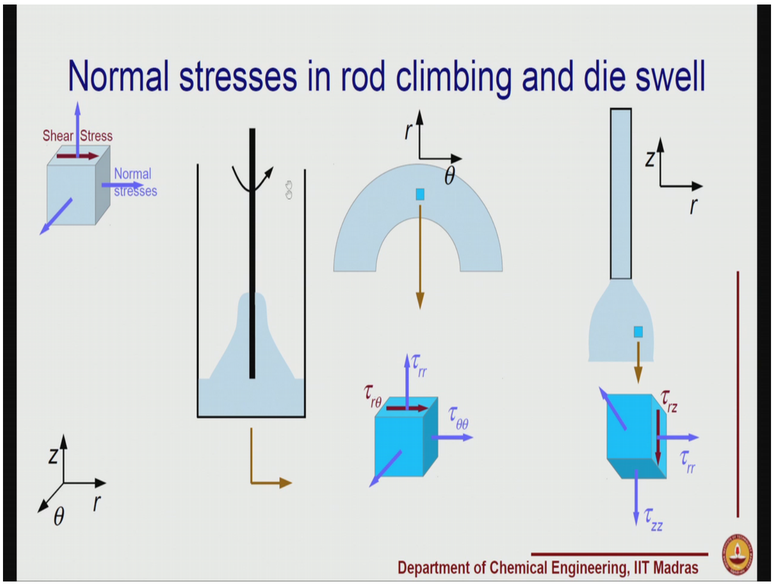

So, let us now try to see; how do these stresses actually explain at least qualitatively how the rod climbing and die swell phenomena are observed. Later on in the course we will actually solve the governing equations related to such situations and observe the response to be conforming to what are experimental observations or what are qualitative differences between a Non-Newtonian fluid, which has elasticity in it when we compare it is response to Newtonian fluid.

So, now, let us look at the first example of rod climbing that we saw where the fluid actually climbed up on the rod and we can use the cylindrical coordinate system where r is this direction and Z is of course, the vertical direction, if we look at it from this side from the what we see is basically spheric the circular a polar coordinates and what we have is fluid moving like this because of the rotation of the rod and we can look it let us say one small element here and then look at what may be the presence of stresses in that fluid element. Similarly in the other example of die swell we had the tube from which the fluid was being forced out and again in this case, we can look at the zr plane r being this direction and the velocity being in the Z direction, we can try to see what are the stresses which are present.

So, for example, what we will do is try to look at a small element fluid element here and then try to see; what are the stresses which are present. So, as I mentioned earlier because of the shearing that is there due to the rod rotating this component of stress which is tau r theta will always be present. In case of a Newtonian fluid this is the only stress component which would be there, but given that with the shearing here the macromolecules are getting stretched and oriented what will happen is they will also get the normal stresses.

So, therefore, both tau theta theta and tau rr both the normal stresses in theta direction as well as r directions will also be there and it is the normal stress difference which is defined based on these quantities which leads the fluid to actually go in the Z direction. And similarly in this case also we have again the shear stress which is a tau rz and when we have the fluid flowing whether it is Newtonian or Non-Newtonian because of shear this component will always be present, but because of the normal stress differences between tau rr and tau ZZ we actually have the normal stress difference being present and therefore, a tendency for fluid to dilate.

Now, one difference we can see in these 2 cases is this difference between tau rr and tau theta theta; in this case is in this direction and, but we have confined the fluid based on this wall and the result of this will end up this fluid rising here, while in this case the result of this normal stress difference is in terms of having the fluid x 2 a swell in the a radial direction. While in this case the fluid actually ends up climbing in the Z direction, but later on in the course we will actually see the governing equations which show how some of these normal stresses arise in the material and therefore, we will be able to quantitatively and qualitatively describe such phenomena.

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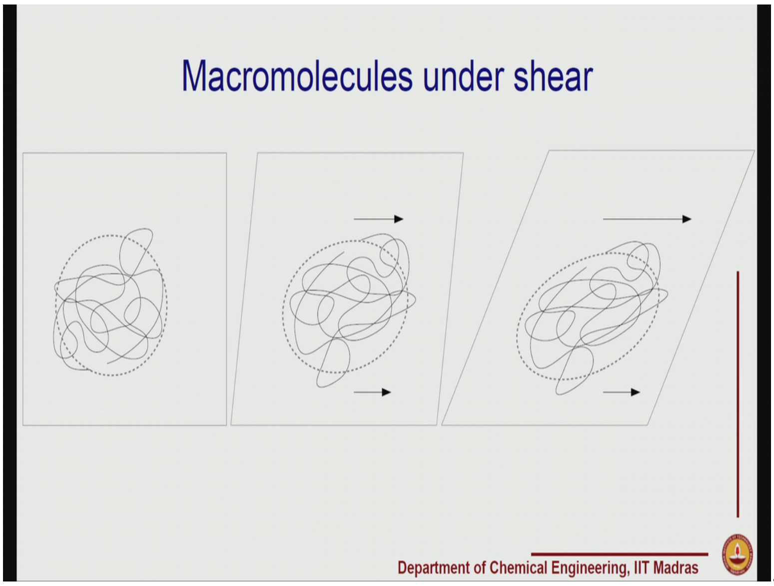

In summary what we have looked at are basically macromolecules under shear and we have understood the basic need for looking at the material and it is microscopic mechanisms.

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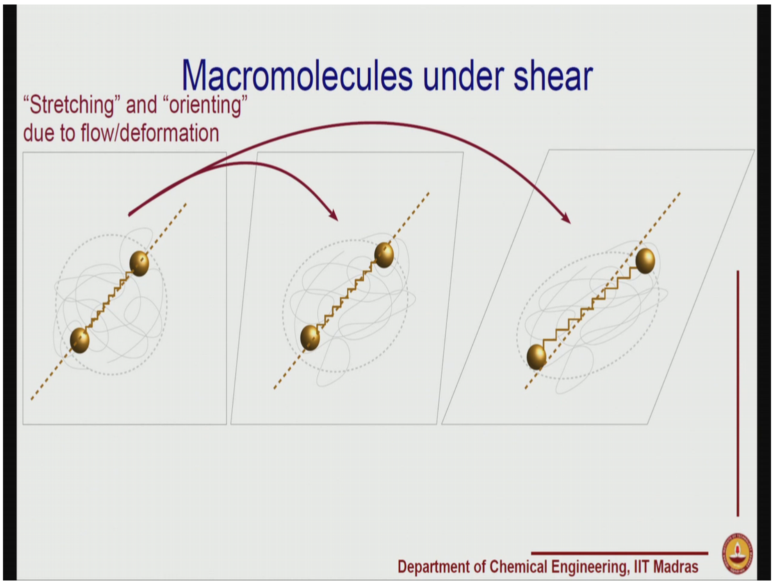

So, in Macromolecules under shear we can think of these macromolecules as if they are made up of a beads which are connected by a spring. So, this particular mechanical analog can actually orient when the shear is applied because this bead which exchange exchanges friction with the surrounding will move little faster compared to this bead and therefore, this particular dumbbell will have a tendency to orient itself as well as it will stretch.

So, you can see that at higher and higher shear rates the stretching as well as orientation will be higher one other issue that we should always remember is that this picture of macromolecule the way we have drawn here is only one snapshot of it. In general because of the thermal energy being sufficient the macromolecular segments are undergoing thermal motion and similarly the solvent molecule is also undergoing thermal motion. So, there are random collisions of solvent molecules and the macromolecules and there is segmental motion.

So, when we look at this bead and spring picture what we have is actually these beads and springs by themselves will also be vibrating. So, the between these 2 there will be vibration going on as well as the orientation of the dumbbell will keep on changing even under when there is no flow, but when we have flow what will happens is these beads on an average are get oriented along the flow direction on an average they gets stretched in the flow direction. So, therefore, we should remember the overall fluctuating picture at the microscopic scale, but the on average feature is what is important to describe the bulk properties such as viscosity or normal stress differences.

And again just to restate what we had seen earlier that stretching and orientation happens because of the shear rate being imposed on the material and conversely.

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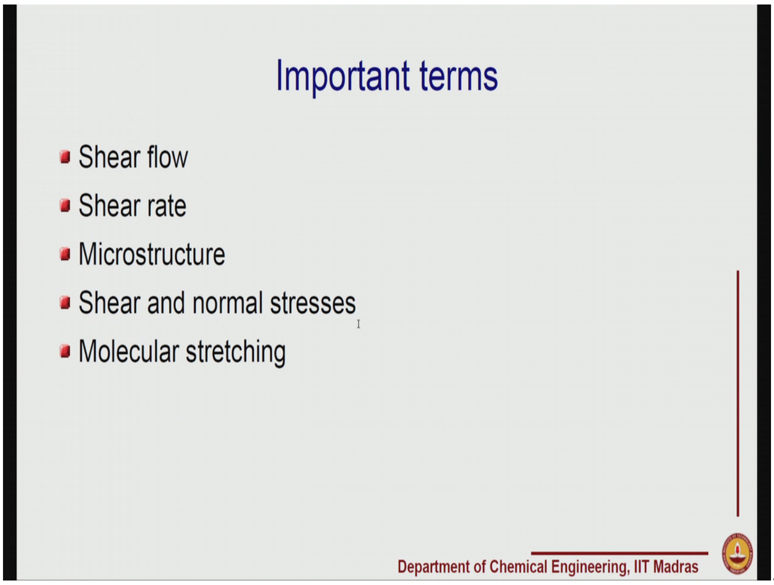

Because of this stretching and orientation we can have elastic recovery also. So, what we have seen. So, far are aspects of shear flow which is characterized using shear rate and microstructure of a colloidal system as well as molecular stretching in macromolecular systems are very important to understand what were the unusual flow phenomena and of course, we can quantify and the characterize the overall phenomena using the shear and normal stresses during the flow.

So, in the next part of the lecture what we will see is additional examples of these flow phenomena and how they are related again to the microstructure and if there are what we will also see is an addition to shear flow additional types of flows may also be encountered.