Rheology of Complex Materials

Prof. Abhijit P Deshpande
Department of Chemical Engineering
Indian Institute of Technology, Madras

Lecture –25
Rheometers

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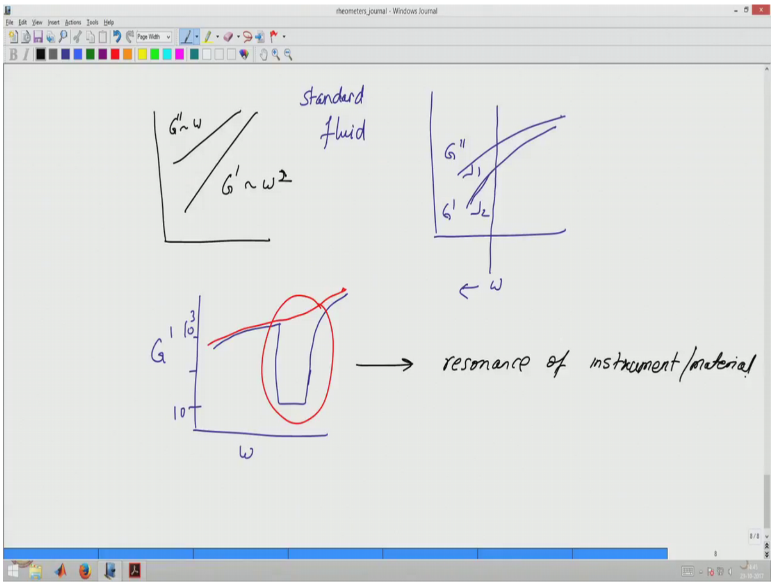

In the last segment we saw how one has to be aware about the Rheometer type and it is capability for examining the results obtained, generally at the extremes of instrument usage; which could be due to operating conditions or due to material properties, proper care has to be taken to understand the results for example; some of the samples when you do measurement and let us say, they are low viscosity measurements it so happens that if you measure G prime as a function of frequency you will see that you will get G prime which seems to be more like a gel like sample that we have seen right, that G prime is relatively independent of frequency and then suddenly there is a response like this and this we are talking about 2, 3 orders of magnitude. So, let us say this is about 10 to the power 3 and this is 10.

So, now the question in such data is at this frequency is something happening to my sample some structure is there which collapses and therefore, I get and then again if you see it again comes back up, so is these kinds of things what is the reason?

So, this is the real analysis that one has to do if we are doing experiments with unknown samples. So, is this real for my sample? Is this an instrument artifact? Is it due to maybe the sample slipping itself? The interaction between the sample and the geometry for example; I have the geometry rotate sample also rotates along with it, but beyond this there is a sudden slip and therefore, now the geometry rotates but the sample does not rotate and therefore I get very low values of G prime, so that is also plausible it is a possibility.

So, therefore, in such cases we really have to look at lot more. So, for example; if I put a standard fluid and I do not see this dip, then maybe I can conclude that motor I mean the instrument may not be responsible maybe something related to sample, but even if it is something related to sample I still do not know whether it is due to slip which is not really a material property or is it due to material structure giving away. So, therefore in all the rheological analysis we need to be careful about noting down what are the limits of the instrument itself? And what kind of instrument is being used?

Student: Sir now.

By the way all the instruments that are available today will also allow you to do your own measurement of raw signals, because in the end it is an electromagnetic device right? Motor and the optical decoder will also in the end everything is done through current and voltage.

So, therefore, you can attach in fact, an oscilloscope to any of the Rheometer and you can look at the torque or position through those sensors themselves. So, that is also another level of examination that you can do, to see if things are going ah not according to expectation because you can look at raw signal and then you can say that look I will not look at the way the sample data is being processed by the software of the instrument.

Remember when the instrument is giving us G prime and G double prime what is it assuming? There are several steps it is assuming right it is assuming that the flow is one dimensional whatever all the assumptions that we have seen is are valid for a flow that we have done, then it is also assuming that whatever is torque that motor is applying is the actual torque that is felt by the sample, then if it is rotating at some given frequency it is also assuming that sample is rotate oscillating at the same frequency as whatever is being imposed.

And further on we will see that it since the response is in the linear domain it is also being assumed that the frequency of oscillation of sample is the same as whatever is the input that is being given, so if input stress is at omega input stray output strain is also at omega. In the non-linear case the outputs will be at different higher harmonics will also be there, so with all these assumptions our software does the calculation and gives you this, so therefore you could always go and look at ross data to try to figure out if things are different, but I still do not understand what your question is about digitization.

Student: We cannot get (Refer Time: 04:39).

Of course you can.

Student: (Refer Time: 04:41).

Any oh yeah, so if you get the data that is well and good because you can do the plot yourself right.

Student: When (Refer Time: 04:47) materialism level in my aim.

Huh.

Student: Even giving only reading.

No, so see there are some quality control kinds of instruments which may not, but most of them will come with R S 32 or some ports like that. So, you can attach a computer and take the readings.

Student: (Refer Time: 05:05).

So, or you have to sit in record the reading yourself and then do the analysis further. In fact, most of the Rheometers today belong to the other class where they are directly interfaced with computers, only very limited set of instruments which are let us say; use for quality control may just come with a digital reading itself and you are not recording them because the analysis is not the purpose, but most of the viscometers and Rheometers are used in lab for analysis.

So, therefore, they will come with all sorts of measurements possible.

And as I said they will also come with; ability for you to actually plug in an oscilloscope and then measure the overall raw signals itself from the motor or the any other sensor that is being used in the instrument ok.

So, this is as far as the controlled strain Rheometers are concerned. Yeah?

Student: Sir (Refer Time: 06:05) if thus 7 decrease of (Refer Time: 06:09).

Hmm.

Student: Then which increasing omega how can increase (Refer Time: 06:11).

Yeah exactly, so this is the nature of the analysis that we will have to do, so I just post that so the other thing you can do for example; is also you can say that I did this experiment at 2 percent strain let me now change to 4 percent strain and then see right. So, there are all the possibilities are there yes, so the fact that the other thing you could also do is you can go to high frequency and then you can reverse, you can say now let me go the other way and then see what the instrument gives if while coming back I get some data like this; then oops, there is something related to instrument operation maybe sample is not doing it is possible right, but then you could also argue that given this was subjected to high strain rate therefore now it has a different trajectory.

So, it is always going back and forth between some of these, but this is how we proceed with the analysis. So, all these arguments you have to bring to the fore to try to then finally conclude, because for this sample you are the only one would be your few of the people who is trying to do measurements for these samples, either in an engineering ah application scenario or in a research scenario.

So, yes! the data this kind of data does ask us to look at different facets and argue back and forth and maybe carry out several trials before we can finally reach to one conclusion, in facts this kind of dip that has that I talked about is generally observed for low viscosity samples and high inertia and at least one plausible explanation of a such dip is based on basically resonance of the instrument material and material combination.

So, the fact that what we talked about before that there is instrument inertia and the overall the governing equation depends on how the overall sample response and material response so this determines actually.

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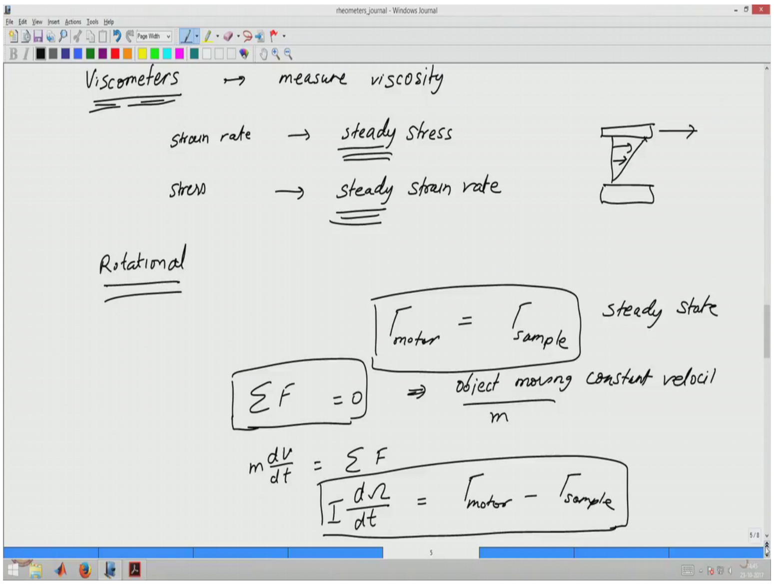

Viscometers → measure viscosity

strain rate → steady stress

stress → steady strain rate

Rotational

$\boxed{\Gamma_{motor} = \Gamma_{sample}}$ steady state

$\boxed{\Sigma F = 0}$ ⇒ object moving constant velocil

m

$m \frac{dv}{dt} = \Sigma F$

$\boxed{I \frac{d\Omega}{dt} = \Gamma_{motor} - \Gamma_{sample}}$

So, you could show that for some instruments and for some samples you may observe this kind of a dip, but that does not mean that any dip you see is because of this reason. So, therefore what we need to do is? For specific set of samples for the specific set of instrument you can do quite a bit of analysis to come up with such an understanding.

So, therefore the rotational Rheometer and the control stress and control strain Rheometers are really the bulk for their workhorses for the rheological industry and for most of the instruments are these; of these the control strain Rheometers are more rare, control strain complain contain of different motors the stress control is not that effective and so earlier when lot of work on polymer melts what was done in 80’s and 90’s they were all done with controlled strain measurements with very precise measurements, but lately when we are looking at rheology we are generally interested in looking at soft matter as we saw earlier where we are looking at multi phase systems combinations of polymers and multiphase and so on.

So, we are looking at a variety of materials and therefore, the controlled stress Rheometer does a better job of managing a widely ranging parameters and it is also much less expensive. So, more often than not therefore you will see that both industrial R N D groups as well as research groups tend to pick up a stress controlled Rheometer because it does a reasonable job for wide ranging conditions, but for some very precise measurements strain control will all is always good and preferred.

Quite often when we end up confronting the anomalies such as what I discuss here; it is also helpful to then change the type of the instrument and then do the measurement. So, if you are observing this on a controlled stress where instrument inertia may play a role then you can just go over to a control strain instrument and then see whether this kind of features are there or not and so these are the basically guidelines which can be used.

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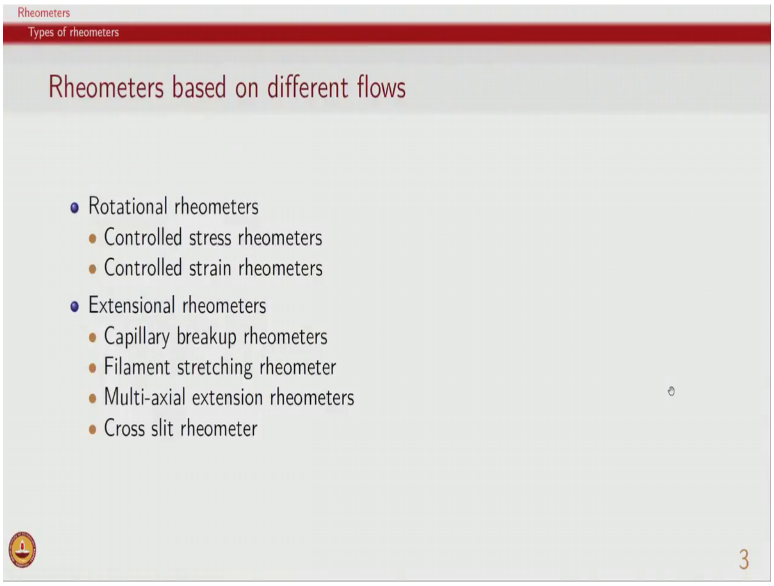

Rheometers

Types of rheometers

Rheometers based on different flows

- Rotational rheometers
  - Controlled stress rheometers
  - Controlled strain rheometers
- Extensional rheometers
  - Capillary breakup rheometers
  - Filament stretching rheometer
  - Multi-axial extension rheometers
  - Cross slit rheometer

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So the; but all of this is in the shear mode. So, therefore, again generally when rheology is being done quite often we are using the shear rheology, but as we have seen in our earlier lectures that extensional rheology is quite important for variety of applications also. So, there are different set of extensional Rheometers which are available, again these are more difficult to operate more difficult to interpret and but still over the last 10 15 years the popularity of extensional measurements has increased.

In fact, there were earlier stories of how no two labs could report same set of extensional performance, in the sense that if I take a melt polymer melt and measure viscosity shear viscosity in two different labs using two different instruments of two different companies I would get the same value, but if I try to do same extensional viscosity measurement using two different instrument in two different labs people were not getting repeatable measurements, because to maintain the just the way we saw that how using feedback and all you can maintain.

So, how to maintain a constant strain rate or a constant whatever are the assumptions that are required for analyzing the extensional flow how well you can reproduce that flow using a given instrument and depending on the type of instruments all of the reliability and all of those were in question in let us say; up to mid-90's, from there on of course the instruments have become better and better, because our control systems have also improved electronics and control systems have improved over years.

So now therefore, the extensional Rheometers are more common compared to earlier, but still it is still a far more experts domain then compared to let us say rheology shear rheology which is used by even not so expert; not so keen experts of Rheology.

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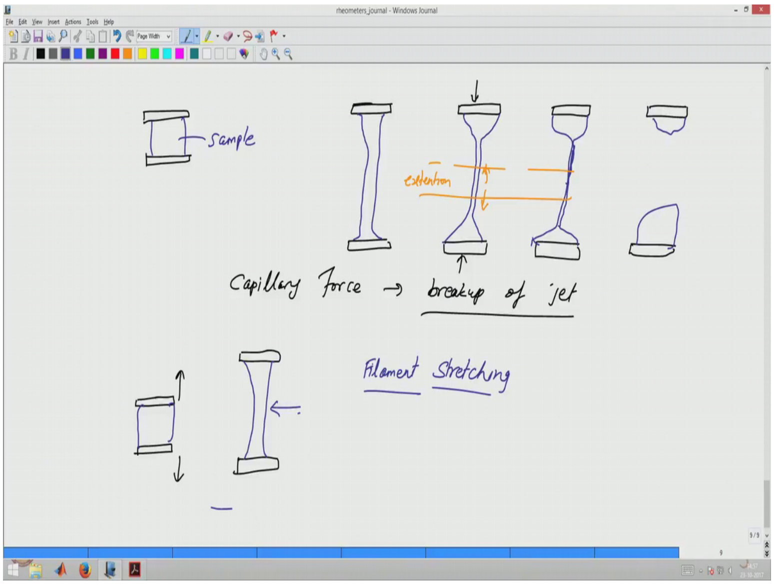

So, in this also there are different methods the first method for example; is a capillary breakup Rheometer. So, what is done in this kind of an instrument? Is you take let us say a material between two plates, so you take fluid between two plates sample and in a quick succession or in a quick motion you put the two plates apart and you hold them at that location.

So, what happens is? When you take these two plates and suddenly move them apart and move them at different location what happens is? You will get basically the overall fluid will also get stretched and with time because of what do you expect would happen to this kind of a cylindrical fluid.

So, with the time what would you expect might happen to a viscoelastic fluid that is now suddenly stretched and left there?

Student: (Refer Time: 14:25).

Ha yeah. So, the after sometime the final thing as he says will be that in the end maybe some fluid may remain stuck here and some fluid will be here, so but so in between this is what happens is there is a capillary and the thinning will happen.

Student: (Refer Time: 14:44).

So, and then even more right at next instant of time it may be even more so.

Student: if gravity them to more (Refer Time: 14:46).

Surface tension ha yeah know. So, gravity will of course, force the whole sample to only come down.

Student: Yes.

And, but there is also surface tension forces. So, that is why this is called a capillary break up experiment. Capillary forces or surface tension forces are important break up of a jet, but what you are doing in this case is; basically you in the central region here is where you have extensional flow, because fluid is basically moving out right, so it is like an extensional flow being achieved and the diameter of the capillary or the thread which is being formed or the fiber which is being formed will continue to decrease.

And then you can also try to do measurement of how much force is required to keep the plate in a given separation. So, you can do force measurement the I take the fluid between two plates; separate them apart and now measure how much is the force required to keep them under this way and then I measure the diameter of how this rate is changing, so I know what is the velocity of fluid which is moving up and down in extensional flow. So, then by analysis of these two I can then back calculate an extensional viscosity. So, this is one measurement which is possible.

So, in this case what you are doing is controlling the position of course, the fluids have to form a nice capillary surface tension forces and the overall viscoelasticity of the fluid have to permit this, in the sense what will happen is sometimes with Newtonian fluid let us say what are if you try to do this experiment the jet will break in no time. In fact, you will not be able to make any measurement because it will break immediately, but with viscoelastic fluids the jet formation is there and then it thins slowly, so therefore you can do and it is for viscoelastic fluid we need to do make such measurements.

So, therefore, this is one way of doing measurements and these are called capillary break up Rheometers, the other one is filaments stretching Rheometer. So, in this case what you say is I am going to stretch a filament between two plates at a controlled rate. So, I take fluid between two plates right then what I do is? I move them apart using some motors, as I move them apart I will have the fluid actually again thinning I will make a measurement of how it is thinning and based on this measurement I will again do control and then try to change the rate of how the two plates are being moved apart.

So, that there is a control on so if I if you remember when we looked at the overall extensional flow problem, the position varied exponentially for us to achieve constant strain rate. So, if I do an exponential motion of the plates I will get basically a constant strain rate in the center, but it is not it is easy to say that I will move exponentially but it may not be easy for us to do that using motor and control systems so, but with lately this has become somewhat more manageable.

So, to get true extensional flow in the center region you can have the reduction in the sense velocity can be there in the radial direction, but in general velocity in the z direction should be 0.

Student: 0.

But of course, when you do actual experiments you will see that you may not be that. So, therefore, you need to do measurements and you need to improve your kind because remember you are doing this for a sample whose behavior you do not know and so the instrument has to do something and then try to figure out whether it is doing it correctly through your inputs, then you have to try to change the conditions at which you are doing it and measure the appropriately and then maybe change the rates at which the plates are being pulled apart and so on and of course, the jet which is being formed or the thread which is being found has to remain stable over the measurement period.

But again the force which is required to pull in this direction and the strain rate which is achieved could be used to again do the measurements in this case also, so these are called the filament stretching. So, in this case you are continuously stretching filament stretching because you are continuously stretching the filament, earlier during introduction I had talked about looking at sugar solution right so that is an example of a filament stretching basically we are taking and then stretching like this.

If we do this and then hold there and then look at how the sugar in fact, that will also so that is called the capillary break up that if I pull suddenly like this and keep it that way and then look at what happens to the diameter of the then I am doing a capillary break up, if I do at different rates then I am doing the filaments stretching Rheometer and of course, this is uniaxial stretching it is possible also to do multi axial stretching where you stretch in more than one direction.

Ah one example of course, of multi axial stretching we saw or can be done using rotational Rheometer by doing lubricated squeezed flow.

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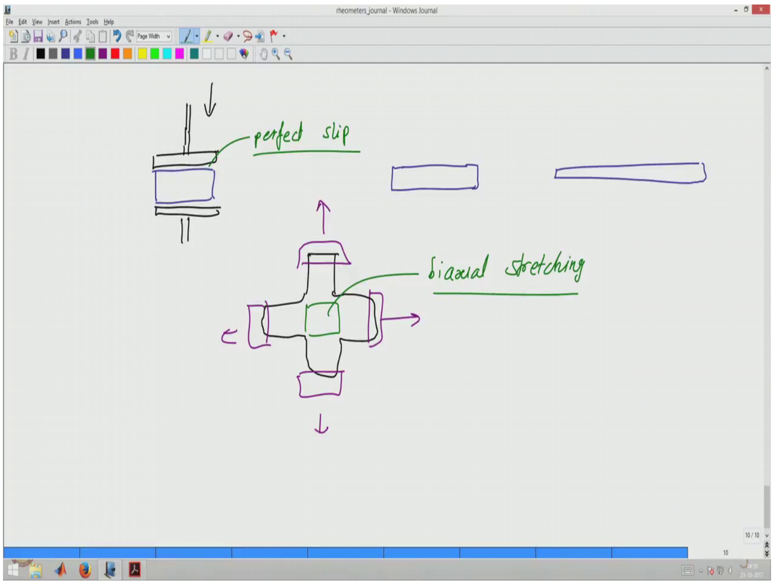

If you recall what we had said was; if you take let us say a parallel plate, so if you take let us say parallel plate and if you ah fluid here and then if you squeeze right if you force the plate to come down and you ensure that there is slip here perfect slip, right in that case what happens is you if you recall what happens to this sample with time is it will become stretched or even at a larger time it will become even further stretched.

So, basically the sample is betting getting squeezed or in other words it is getting stretched in the radial direction. So, this is an example of a biaxial stretching being done through a rotational Rheometer, but you can also have clamps and actually do the biaxial stretching you can take a sample for example; you can take a sample like this and you can have clamps at each and every end so you can clamp this side and then pull and clamp this side and pull clamp this side and pull and clamp the side and pull, so the central region will have biaxial stretching.

So, therefore multiple direction multi axial stretching is also possible of course, this can be done for more a film like sample, if you have melt then this may not be easier to do. So, depending on the types of samples and depending on what materials we are interested in; different types of setups can be used for the multi axial stretching approach. And it is also possible these days we are interested in bio macromolecules or several polymers which are involved in biological systems and we are interested in their behavior in extensional rheology, but we would like to see let us say for example; a D N A how what happens to it in an extensional flow? Or a protein molecule what happens to it in an extensional flow.

So, this is done using cross slit Rheometer where what you do is; you have a fluid coming in through one set of capillaries and you have a cross and then it will go out through other set of, so if you look at this point here there will be extensional flow. In fact, this is an example of irrotational flow and extensional flow.

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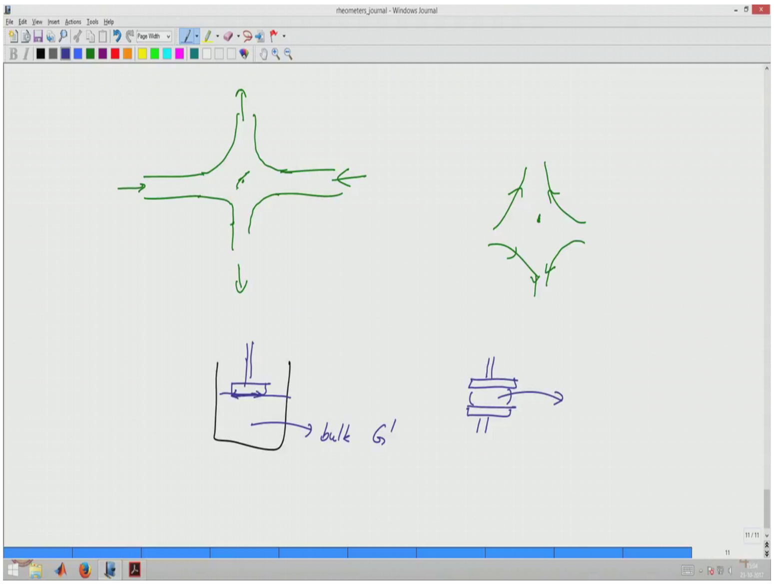

So, the if you keep the molecule here and then by manipulating flow rates you can actually manipulate what is the amount of strain rate that is being felt by the whatever is at the center and so you can do microscopy you can do some observation you can do spectroscopy and then try to examine what is happening to the molecules or particles which are being examined under extensional flow. So, therefore this is a cross slit example of achieving extensional flow. So, if you look at the streamlines they would look like this; that this is a stagnation point and the fluid will go like this right and so using fluid mechanics equations we will be able to show that in fact, it is an extensional stress or strain which the molecules are particle at the center will experience.

So, this is as far as the overall set of Rheometers which are very useful and which are broadly used, control stress is the most commonly used control strain many times and off let extensional Rheometers are also being used for various applications and so the next is whether we can do something more with the Rheometers and so that is why I have I just called it rheometer plus.

So can we add on some features and then try to do measurements with along with rheology and so for example; a there is possibility of doing rheology at the interface, because quite often let us say if I am working with foam or if I am working a with the emulsions or if I am interested in knowing what happens to the interface of a paint film, i am not interested in the viscosity of the paint because that will be important when I am applying, but the weather wrinkling happens on the paint and so on may be more related to the interface property of the paint.

So, I am interested in knowing what is the viscosity at the interface? And viscosity at the interface may differ compared to bulk because some of the particles or some of the molecules may preferentially go to the interface for example; surfactant we know will always go to interference, so similarly there may be ah an aggregation of particles or molecules at the interface which is different compared to bulk and so not just viscosity, but even the storage modulus or loss modulus of an interface may be different compared to what is of the bulk.

So, you do bulk measurement you get one set of properties, but what is more interest of interest will be the interfacial property. So, then can we do a rheology of at the interface? So, basically what we are asking is the fact that if I let us say; take the material, form an interface right so if I take the fluid in a beaker let us say and then form the interface, so in here if I measure then this is the bulk variable let us say viscosity or bulk G prime, but instead I want to know what is the G prime here right? So, what I need to do is the geometry that I use what I was doing earlier was I take this let us say; parallel plate geometry and I say that everywhere in the fluid we have the strain or strain rate or stress being controlled.

Now, instead I need to only do measurement at the interface. So, what I need to do is? Let us say get the geometry in this case what I can do is? I can let us say get the geometry and do the measurement only at the interface and see whether I get different torque, if I lower this I may get more bulk properties but at the interface if I do will I get a property which is slightly different.

And again in this case we will have to go back and forth to again see whether we are getting reasonable measurements, because these are all going to be very sensitive measurements given that we have very sensitivity the interface is definitely not going to be not as the talks generated are not going to be like a bulk sample and so all the issues related to surface tension and the effect of interfaces will have to be borne when you try to do such measurements. So, interfacial rheology is also an important class of rheological response, with this we will now in the next segment we will look at the remaining special purpose, Rheometers which are used for examining the material properties.