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

Lecture – 27
Rheometers

So, in this segment we will look at the remaining aspects of rheometry, where we try to use rheometer along with other techniques and the first example is using dielectric spectroscopy.

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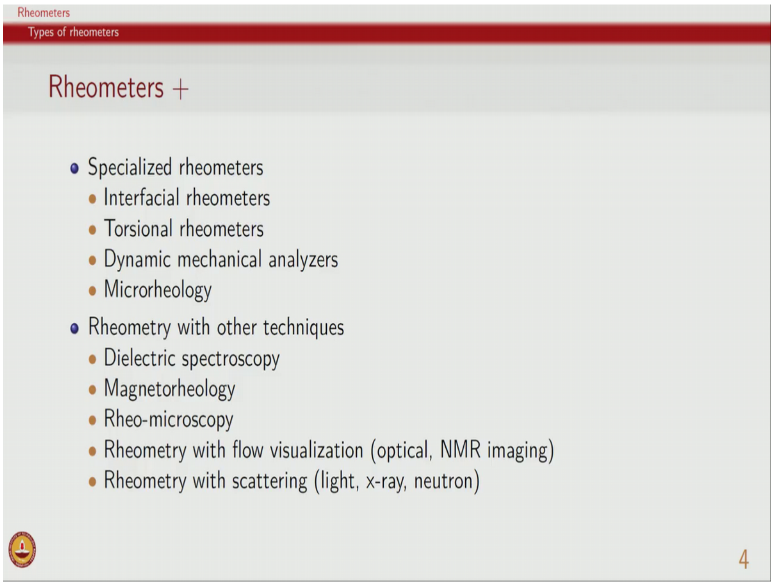

Rheometers
Types of rheometers

Rheometers +

- Specialized rheometers
  - Interfacial rheometers
  - Torsional rheometers
  - Dynamic mechanical analyzers
  - Microrheology
- Rheometry with other techniques
  - Dielectric spectroscopy
  - Magnetorheology
  - Rheo-microscopy
  - Rheometry with flow visualization (optical, NMR imaging)
  - Rheometry with scattering (light, x-ray, neutron)

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So, dielectric spectroscopy is very similar to the mechanical spectroscopy, which we have discussed in the course so far, where we apply a stress or strain sinusoidally and when we apply the stress, the strain or strain rate is the output.

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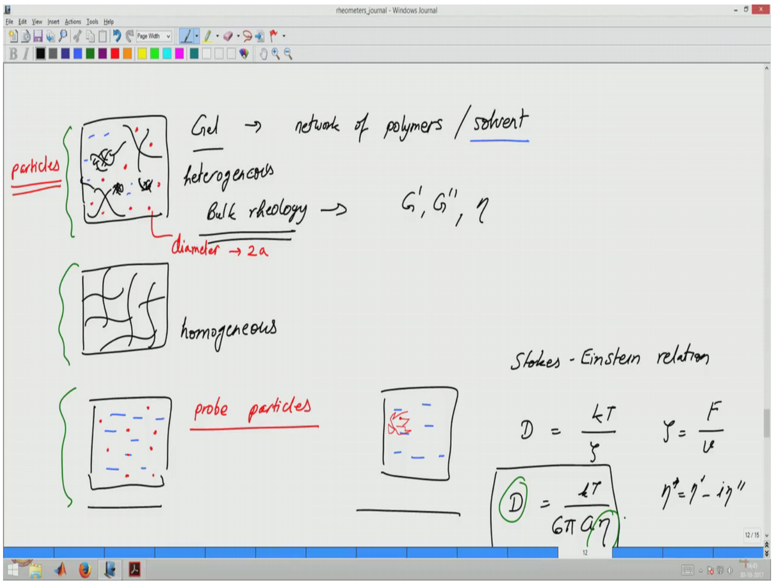

So, in dielectric spectroscopy we apply current or voltage, and based on the input and output we can then again analyze and then get an in phase and out of phase component.

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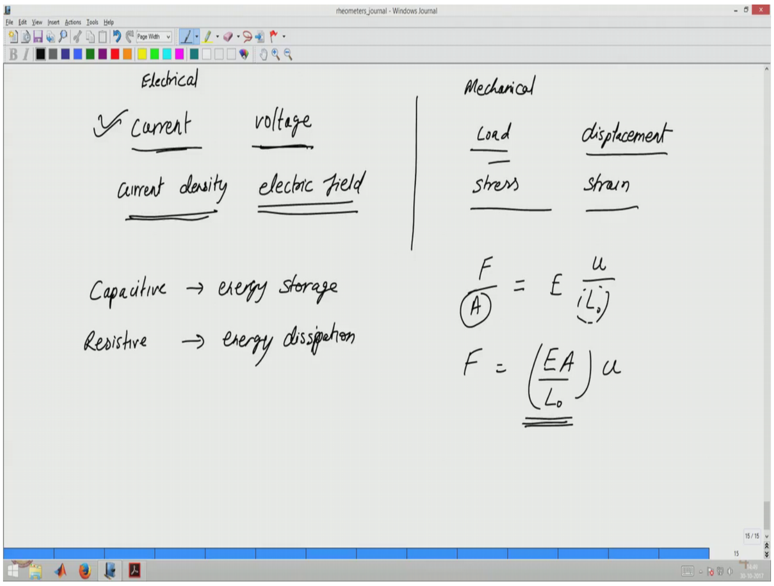

So, when current and voltage of course, we also can talk in terms of current density and electric field can you think of the analogous variable in the mechanical domain? So, generally when we do experiments we will measure current and voltage, but generally when we talk of material behavior we will say current density and electric field. So, similarly in mechanical domain, this is what is in electrical domain. So, in mechanical domain what are; so stress and strain are again not directly measurable. So, they are in fact, analogous to current density and electric field. In fact, the material behavior is defined in terms of stress and strain, but when the measurement is done with respect.

Student: (Refer Time: 02:04).

Load and right. So, we generally we will measure load and then displacement.

Student: (Refer Time: 02:15).

Load versus displacement curve we will say sometimes right or deformation. Deformation will still imply that we are processing the data and dividing by the original length, but displacement is basically what is being measured, and the load versus displacement will depend whether let us say I do a one inch diameter rod or if I do two inch diameter rod, because load displacement or not material properties, but they are actually dependent on the type of geometry which is being used. But stress versus strain property will not depend on whether I use a one inch diameter or two inch diameter because they are material properties. So, same ways here when you do current and voltage discussion, it depends on the resistor dimensions or the capacitor dimensions and the area between plates in case of capacitor and so on, the diameter of the resistor and the size of the resistor and so on, but current density and electric field are material properties.

So, generally just the way you can talk in terms of load displacement and say or in terms of current and voltage, but more correctly when we describe material behavior we should talk in terms of current density in electric field. So, depending on whether current density and electric field are in phase or out of phase, we will have the energy storage and energy dissipated phenomena. So, do you recall from your earlier studies on electromagnetism as to for a capacitor, how is current density and electric field related to each other and for a resistor how is current density in electric field related to each other.

Student: For register the rate is inversely proportional registers.

No resistance is the co see. So, just in this case Hooke’s law of the modulus.

Student: (Refer Time: 04:03).

Or the viscosity are proportionality constants. So, similarly for electrical domain of course, the capacitance or resistance are such proportionality constant. Remember again capacitance and capacitance and resistance are being measured in this domain, because it depends on the element itself. So, if I use load displacement and divide with load by displacement I will get modulus right, but that is not a material modulus, it depends on what size do I use. So, therefore, resistance is not really a material property, but resistivity is just the way modulus is material property, but load by displacement will depend on what is the size cross sectional area that I use here. Because load is let us say F by A will be equal to the Young's modulus right which let us say we denote by E into the displacement divided by original length right.

So, displacement divided by original length this is how stress versus strain is right. So, depending on the geometry being used the displacement load relation will change. So, if I were to define a coefficient it will be E, A by L naught into u. So, therefore, the geometry will determine and in fact, if you remember current and voltage relationship you similarly have the electrode area and the distance between electrodes coming into the picture along with dielectric constant. So, the dielectric constant is the material property, which relates current density and electric field while the capacitance is actually element property. Just the way here also this is the element property it is no longer material property.

So, in just the way we talked about stress strain and strain rate, here also we can talk of change of rate of change of electric field, rate of change of current density, and current density electric field and we can have materials which are both capacitive and resistive as we had visco inelastic. Capacitive will imply energy storage right and the resistive will imply energy dissipation. So, if we have a material, which has the mechanisms by which it conducts or the mechanisms by which it stores energy electrical energy, then we can do a dielectric spectroscopy on it by which what we mean is we will apply current at different frequencies, and then look at whether it is mostly capacitive or mostly resistive. So, for example, just the way we saw that there is a basic primitive model for viscoelasticity was Maxwell model right, which said that predominantly viscous response at low frequencies and then elastic response then we saw also standard linear solid model, which was elastic response which was rubbery and then elastic response which is glassy.

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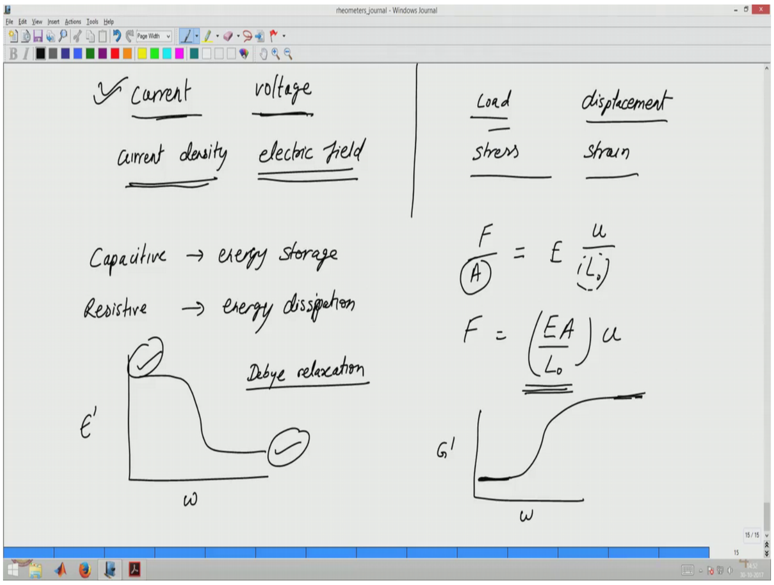

So, what we saw was G prime as a function of frequency was something like this. So, at very low frequency also you get elastic rubber elasticity, at very high frequency you get glassy elasticity and G prime varied like this.

So, if you look at the dielectric constant and the real part which again denotes the capacitive or energy storage contribution, generally this kind of a behavior is seen for many materials and this is called a Debye relaxation in the material. Dielectric constant remember is the ability of an a material to store energy. So, if I am applying let us say some constant. So, this is again frequency. So, if I apply small let us say frequency then what I am doing I am giving material enough time for the dipoles to orient. Many of these Debye relaxation processes are related to dipoles within the material. So, they orient therefore, they store the energy when the electric field is removed, they will come back and therefore, the stored energy can come back.

But when you go to very high frequencies then this is not possible the now the frequency is changing the electric field is changing too fast, and the dipoles really cannot respond therefore, they do not store as much energy and therefore, the relaxation the dielectric constant comes down. But there is some residual dielectric because there are some dipole some other mechanism which can actually respond at very high frequency. So, therefore, there is small amount of dielectric material dielectric constant is there.

So, you can see that both dielectric and mechanical responses mimic each other in terms of the frequency response. Here also at very low frequency the segments can move and therefore, we get rubber elasticity and very high amount of deformation is possible. At very high frequency only with small deformation the material will break, but the modulus is very high because you will require a lot more energy for small deformation. So, therefore, from rubber to elastic similarly here also if I go here I have more flexible behavior, here I have more rigid behavior. In the sense in this case dipoles can orient therefore, flexibility is there in this case dipoles cannot orient therefore, there is no flexibility.

So, you can do both dielectric spectroscopy and mechanical spectroscopy simultaneously and sometimes you can highlight changes which will affect dielectric properties more compared to the mechanical properties for example, let us say if you have a polymer molecule which has let us say dipoles and So, if let us say there is a polymer molecule and it has dipoles, and these dipoles are all let us say arranged in the direction of the polymer right. So, like this there are dipoles everywhere.

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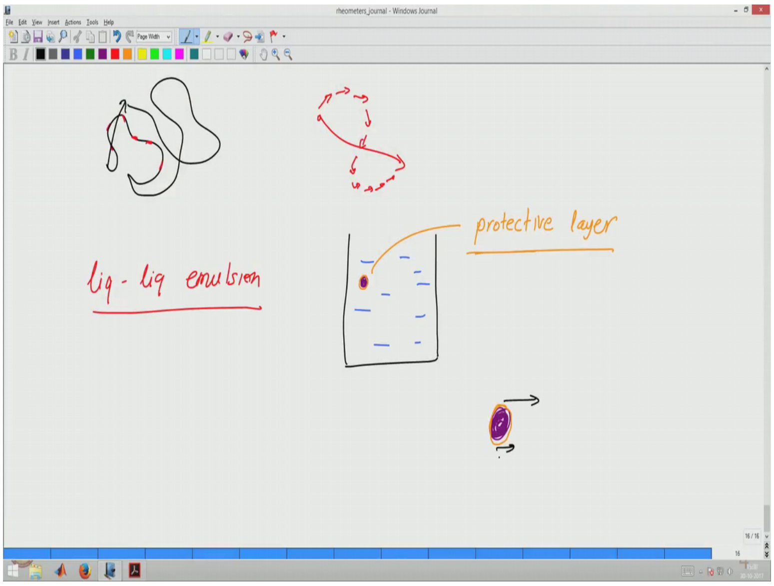

So, when now this material is you are doing the electric, when you are doing shearing of course, we know that there are segmental motions there is entanglement and all of these things, which affect.

Similarly when you are applying electric field how these dipoles are able to move will determine, whether the energy will be stored or not for example, if I take this polymer to melt to melt then I know that dipole orientation will be possible, but if I take this polymer to below glass transition where it becomes frozen, then the dipole orientation will not be possible. So, therefore, I can magnify the properties or simultaneously study two different aspects of the material behavior. In fact, one other thing you can do is, if you look at each and every dipole you if you add all the vectors together in the end what you can do is you can get into end distance right. So, it is like saying that I have lots and lots of small vectors, if I add all of these vectors then I will get my eventual end to end distance, and this end to end distance is based on addition of all these dipoles.

So, by knowing how the dipoles are orienting in general, I can also have an idea about how the overall molecule itself is oriented so. In fact, you can distinguish between reptation motion which is the whole molecule itself moving using dielectric spectroscopy. You will not be able to do that in what we did in all of our rheology was to speculate, that you know since we observed viscous response the relaxation time must be such that the overall polymer is reptating; which means entanglements are relaxing away and the whole polymer can move. But by looking at dielectric spectroscopy you can. In fact, try to distinguish between two different frequencies one frequency at which the overall polymer can move, and the other frequency at which the polymer does not seem to be moving and that is possible because dipoles are dipoles are actually tracking the individual polymer motion while when we are doing mechanical spectroscopy we are just looking at bulk behavior and not really tracking an individual molecule.

So, therefore, it is advantageous at times to do this simultaneously, whenever you can try to highlight what is the for example, if you are two components in the system and your suspicion is one of them is leading to viscosity increase, then what you can do and you can hope that one of them is only responding has dipoles. So, you can do dielectric spectroscopy on it also. If you see that the dipoles are also getting slowed down then you know that whichever has dipoles is the one which is slowing down. But if you see that there is mechanically things are slowing down, but dielectric it does not slow down then you know that the other component is probably responsible for the overall mobility decrease in the material.

So, therefore, you can compliment and do dielectric spectroscopy and rheology together. Magnetorheology of course, is an for those fluids which respond to magnetic field. So, many of the commercial rheometers these days will come up with these attachments, where you can apply magnetic field at the same time do shearing and for break fluids or several such application by application of magnetic field you can change the properties.

For example with iron oxide particles, you can if you apply magnetic field suddenly they will align and they will form a network and viscosity will be very high and otherwise the viscosity is very low. So, you can manipulate the properties and so, for such fluids you may want to study the properties as a function of magnetic field. Rheomicroscopy is again a phrase in which you observe the material while you are doing rheology. So, as opposed to microrheology where we add the particles, if we just observe the microscopy of the particle, for example, we talked about a particulate gel.

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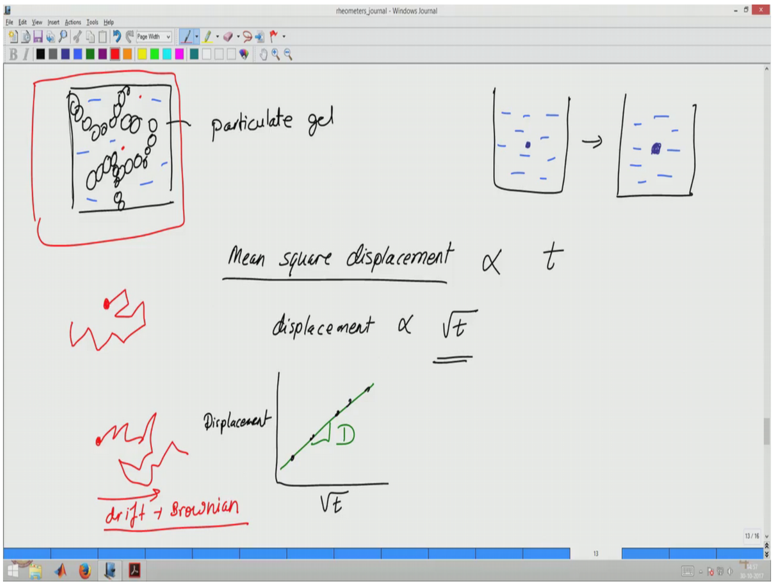

So, this kind of a particulate gel. So, if we view it under microscope we may come to know that whether clusters are breaking or what is happening to the particles as we are shearing the material. So, therefore, rheomicroscopy refers to basically looking at microscopically the material while it is being sheared also.

For example one application could also be that let us say I have a capsule which is a liquid and liquid emulsion. So, let us say we have a liquid in liquid emulsion and this is done by having let us say one fluid. So, again maybe let us say oil or some fluid and then we have another fluid, but then separating these two we have a. So, that is why it is called a capsule. So, there is a protective layer, which separates. And now this emulsion is used as a product somewhere where it flows it is forced to go through narrow openings and all that and one question we may want to know is under what shearing does this protective layer break down alright. So, what we can do then is, to put this overall sample in the rheometer start systematically shearing it, and at the same time try to observe microscopically.

If we can see the overall capsules remaining then we know that shear is not enough to break it, but we suspect that at some particular high shear rate because what is happening is this fluid and it is protective coating which is outside, when we subject it to shear basically what we have is some part of the because of the shearing we will see that the forces on the capsule surface will cause it to break. In fact, this is a principle which is used in recovering materials from a cell biological cell right. If you break the cell wall then whatever are the contents inside can easily be used so. In fact, you can shear it; if you shear it at high shear rates then the cell wall will break down then the internal components can be recovered.

So, therefore, in such cases it becomes useful to do rheology at the same time also examine under what condition the breakage happens and. So, microscopically is done or if we have any colloidal system which our rod like particle and we want to know whether they are orienting. So, we can again do microscopy along with rheology to see whether orientation is happening. So, there are several applications, in which microscopy is done along with rheometry itself.

And then other important aspect of rheometry in the last five ten years has been that we do not assume the flow, we actually examine the flow that is happening.

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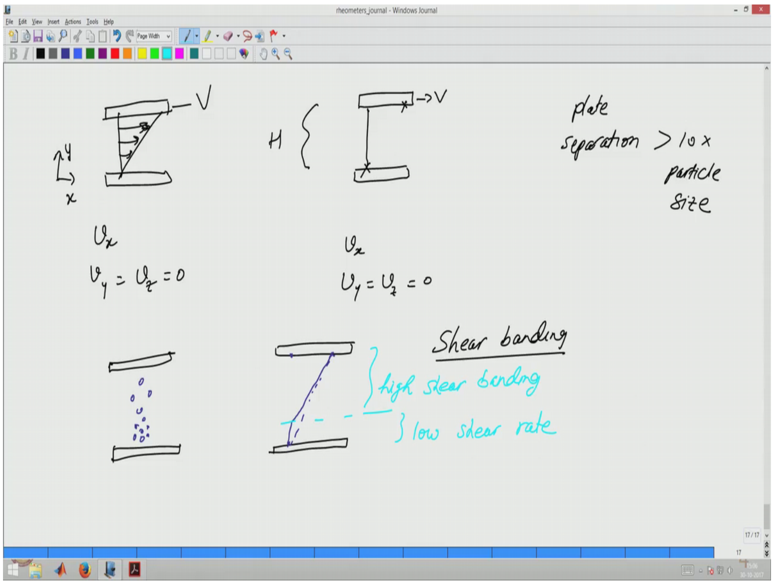

For instance we have been always saying that between two parallel plates of you take the fluid right and we assume that because the top plate is moving at certain velocity we will have a linear velocity profile. The only thing we are ensuring when we conduct experiments of this kind is that at the top plate velocity should be v and the bottom plate the velocity should be 0. So, if we look at there are only two points we are fixing this point is being fixed this point is being fixed.

Now, one of the solutions to this flow problem is the linear velocity profile that we have solved, but can you think of situations where maybe linear velocity profile may not be valid, or can you think of what are the assumptions that went into. So, that we get the linear velocity profile

Student: Suspensions.

Suspensions what would suspensions do.

Student: (Refer Time: 18:55).

Because of suspensions why would we not get linear velocity profile alright?

Student: Must have (Refer Time: 19:01).

So, what do we mean by instabilities.

Student: Secondary flows.

No. So, secondary flows is one aspect. So, in that case what happens is we will still have one dimensional flow. So, let us. So, if we have secondary flows then what happens is there is flow in the other two direction.

For example we are generally mentioning that there is only v x and we say that v y and v z is 0 in fact, right that is the assumption that we are making. So, secondary flows whenever we say; that means, that v y and v z are also there. So, let us still assume that we are able to do flow where v y and v z is still predominantly 0.

Student: Completes the process velocity gradually increases.

Yeah.

Student: If there is (Refer Time: 19:47) at the increase will not be in regular (Refer Time: 19:48).

Yeah why; so, that is one aspect that we always have to worry about, given that whenever we talk of suspension there is always heterogeneity in the material by definition material is heterogeneous. So, generally in such cases what we say rheometry is that the separation right the plate separation should be at least 10 times the particle size. Generally if we are ensuring this then the fact that there are local variations and because a particle is there or not there all that with average out, and linear velocity profile is still very good in terms of giving us the bulk behavior of materials.

So, generally we will still get bulk behavior even though the sample itself is heterogeneous at microscopic scale.

Student: Plate separation.

Plate separation is this right.

Student: (Refer Time: 20:55).

Yeah distance between two plates.

Student: Can we have (Refer Time: 20:59).

So, that is one possibility. So, in general of course, the sample undergoing some change right. So, in this case let us say there is a settling of particles, then at the bottom plate they may settle and, but what will that do. If let us say particles start settling we have a flow and then more particles now below. So, effectively we have a situation where we have let us say more number of. So, we will have some particles here, but here there will be more number of particles right. So, what do we expect now the velocity profile to be.

Student: The bottom.

Let us assume that if we were to have no part no settling like this, then the velocity profile would have been these two points are fixed right. So, this would have been the velocity profile. So, what would you expect the velocity profile to be the.

Student: Sir.

Velocity profile would be lower than what is expected. So, let us say the velocity profile will be like this it is very low and then it.

Student: (Refer Time: 22:06).

Increases linearly right.

Student: Sir concentration of the suspension will.

Will also vary will also vary yeah.

Student: (Refer Time: 22:14).

Yeah.

Student: (Refer Time: 22:16).

Yeah. So, this; so, what we have saying therefore, is we are not no longer sure as to what the variation of velocity within will be, because the material itself shows certain behavior which leads to we when we derive this we assumed material properties to be constant throughout and so. In fact, we have this phenomena of what is called shear banding where the flow it breaks down into two domains. So, what we discussed was a case of where we have two domains, one where the effective shear rate is low while one where effective shear rate is high. So, two regions where one low shear rate region and high shear rate region. So, the flow has broken into two parts. So, that is why it is called band there are two bands which have appeared.

One question that always could be asked is should we be measuring rheology of such materials, when there is settling because we in the end we would like to measure the properties of material themselves and if there is settling involved, then clearly we are not characterizing the material, but the settling phenomena. So, therefore, one may argue that there for this kind of materials, you should not really measure properties because settling is a very significant feature right. But in other case if let us say for settling slurries itself we need to have some estimate of properties, then we must do such experiments we have to be careful that while analyzing our data, we must know that the overall flow is not really what is assumed which is linear velocity profile.

Then best way to look at this is through flow visualization and again in this case also what we can do is we take the overall material of interest and this overall material of interest we again put let us say one small set of particles.

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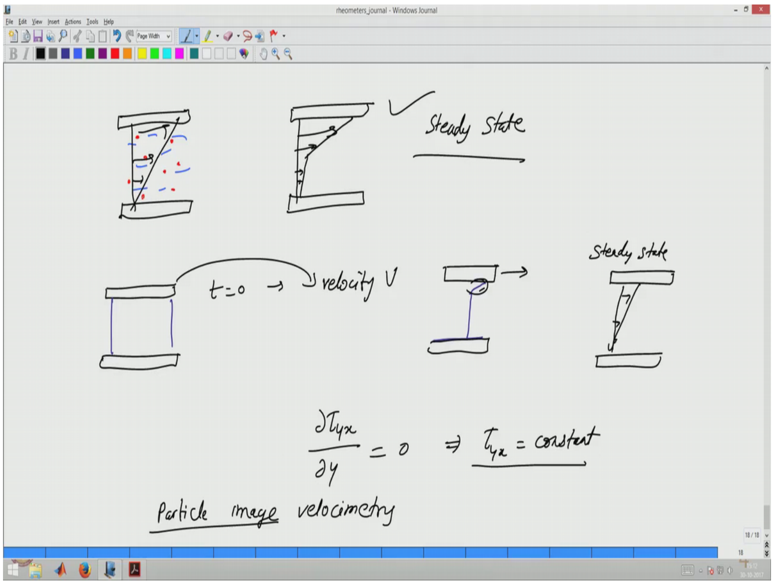

And as again using laser and scattering we can follow how these particles are moving. If they are and we can measure the velocity that way and if we see that the velocity is what we expect in terms of linear velocity profile, then we say there is no artifacts in terms of flows being different than the linear velocity profile therefore, we can do analysis. But if there is a we using the particle motion we find out that some particles are moving slowly while some other particles are moving fast, then we have basically a banding in the material.

So, in general it helps to do flow visualization and examine what is the type of flow which is being observed between the geometry in the rheometer geometry as opposed to what is the assumption. This is a steady state profile right what we are talking right now is a steady state profile. So, generally yield stress material what you might see is. So, let us say we have an yield stress material, and then we start at time t is equal to 0 we start the flow right the top plate becomes moves with velocity V. So, what will happen generally in such case is since the top plate is moving now, and the material which is at the top would have undergone the yield and then the rest of the velocity will be 0 right where and then slowly as time goes on more and more material will undergo yield and more and more material will start moving. So, that is the difference.

Student: (Refer Time: 26:09).

But at again the steady state steady state what you would see is generally provided the shear stress that is being applied is higher than the thing then you will again see a linear velocity profile.

Student: Sir how do you know that the (Refer Time: 26:27).

The; so, that depends on what is the velocity with which you are applying and therefore, what is the stress being applied on the material. See let us say given that you are expecting some part of the material to flow; that means, the stress is higher than yield stress because if you remember if you look at the linear momentum balance or equation of motion of motion for a parallel plate geometry, the governing equation says let us say in this case it is tau y x by del y is equal to 0 which means tau y x is constant this is by the no assumption involved in terms of which type of fluid it can be viscoelastic, it can be just viscous. So, this is a governing equation for all materials.

So, therefore, if some part of the material is yielded with this stress, other part will also yield it is just that it takes finite amount of time for the healing process to go. So, at steady state you would again expect a linear velocity profile, and what we are talking here also are steady state profiles only. The fact that most fluids will take a finite time to come to a steady state is an also important property, but generally we in rheology when we do we assume that that time is much shorter than the time for which we are examining the material properties.

For example we will assume that maybe it takes milliseconds or hundreds of a second, to actually reach the steady state and everything that we are examining is the material behavior itself. So, there are class of materials, which show some density gradients like what we saw in case of particle gradients. So, whenever such gradients are possible it shows shear banding phenomena, because the material overall breaks into a low viscosity and high viscosity material regime and therefore, it breaks into a high shear rate and low shear rate regime.

So, for examination of shear binding or any such features in rheometric flows flow visualization is done and there are multiple ways. So, what I explained was right now using optical method, that you put particles and this technique is called particle image velocimetry. Basically measurement of velocity using images of particles. So, this is a very popular technique which from aerodynamics, which is a fairly large scale phenomena to rheometer flows which is a small scale flow you can examine the overall flow profiles in detail at a plane using.

Student: (Refer Time: 29:20).

Particle image velocimetry yeah a region of interest can be looked at basically what you do is you take pictures again of specific region and look at how particles are moving and again by doing image analysis you can find out what is the velocity, again the assumption is the particle addition is not doing anything to the fluid that is under study because the amount of particles that are being added is very small. Of course, additionally the particles that are being added have the same density as the surrounding fluid. So, that they themselves do not have any inertia they themselves do not settle down and so on they actually follow the fluid faithfully. So, therefore, by looking at their motion we get to know; what is the fluid motion.

Similar measurements could be done based on NMR or any other spectroscopic measurement which is basically related to how molecules are moving at the molecular scale and based on that you can then try to measure what may be the velocity. So, there are several such techniques which are available to capture the velocity of the material and. So, all of this is called flow visualization. And then in terms of rheometry with scattering we always would like to know information about structure of the material. So, depending on the length scale of the structure, we can use either light or x ray or neutron to probe different length structure for example, if particles are large and they can be seen using microscopy, then we do not even need to do any of these, but if particles are smaller then we can look at light scattering and then get to know about what is their position what is their orientation and so on and therefore, what is the microstructure of the material.

If they are still smaller then we can do x ray or neutron scattering and. So, using these scattering techniques, we will get to know about what is the length scale dominant length scale in the material, and hopefully that we can relate to either a cluster of the particles or in case of macromolecules a region where micro molecules are either crystalline or amorphous and so on. So, depending on the variety of how the scattering of light x ray or neutron happens based on the microstructure we can find out and most often we know that when we do rheology, we are shearing the material and shearing effects microstructure.

So, quite often we come up with this hypothesis that under shear things may be getting oriented under shear cluster may be breaking down, under shear orientation of molecules may happen. So, therefore, it is important to do this scattering along with when shearing is going on. So, many of the neutron scattering or x ray scattering equipment or light scattering equipment can allow a small shearing cell to be attached on them. Alternately these days rheometers also come up with attachment where you can attach x ray scattering or light scattering or neutron scattering is of course, very difficult because you need the neutron beam which is only possible with a nuclear facility.

So, therefore, nucle the neutron scattering attachment is not available, but x rays can be generated in lab. So, therefore, x ray scattering and light scattering attachments are available with commercial rheometer also, and neutron scattering is usually done with a rheometer or a shearing cell attached wherever there is neutron beam availability in a nuclear facility.

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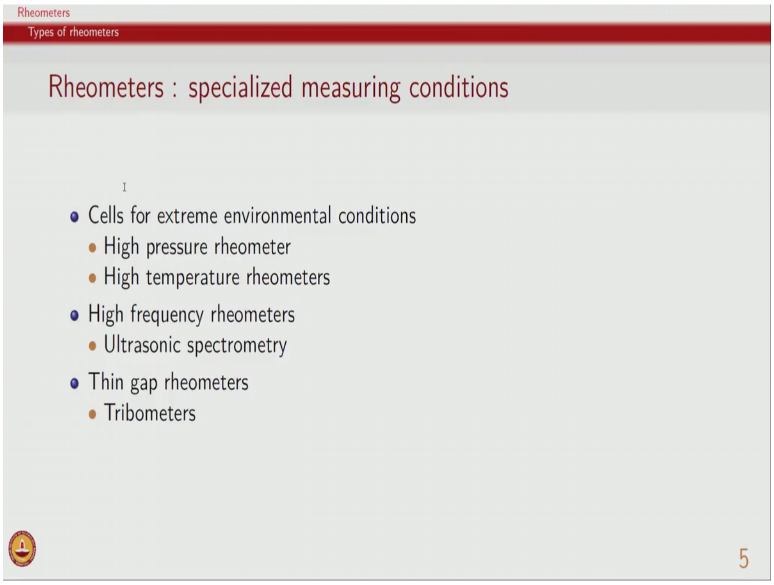

Rheometers : specialized measuring conditions

- Cells for extreme environmental conditions
  - High pressure rheometer
  - High temperature rheometers
- High frequency rheometers
  - Ultrasonic spectrometry
- Thin gap rheometers
  - Tribometers

And then to finish there are some specific cells along with rheometers, which come for extreme measurement conditions. For example, if we are dealing with oil and gas exploration we have to deal with very high pressure phenomena. So, therefore, high pressure rheometer where you can apply extremely high pressure and then measure the properties for example, water viscosity at the sea subsurface is very different compared to what we know of it as one centipoise, because the pressures we are talking about is like three kilometers of water column above it. So, pressure is extremely different and under those conditions. In fact, viscosity will also be a function of pressure and so, such properties whether high temperature when we have ceramic materials and their processing, temperatures are fifteen hundred degree Celsius and so on. So, there are high temperature attachments also for measuring the viscosities of materials under those conditions.

There is also of course, you can use some other rather than looking at purely mechanical, sound interacts with material and you can get to know about mechanical properties of the material through this interaction. So, for example, sound is nothing, but pressure waves. So, how pressure waves travel through the material is dependent on the elastic modulus of the material. So, therefore, by using ultrasonic probes and if you use a vibrating probe then you can then again do calculations and try to find out what are the material properties. So, this is usually done at high frequencies, because mechanical instruments have upper limit of generally hundreds of hertz or hundreds of radians per second beyond which they cannot go.

One last aspect sometimes is very thin film rheology for example, when we eat something the final feel that we get of the material being very good or bad will depend on a very microscopic layer, and how it is shared within our mouths and what kind of feel. Do we get do we feel it is rich do we feel it is sticky. So, that will be very different something which is very sticky we will say oh it does not feel good, but something which nicely shear thins and flows at the same time gives us when we first take the bite it gives us a rich feeling, but then it spreads very nicely and disappears in the mouth we will say it melts in the mouth.

So, then it is actually it. So, that thin film rheology sometimes also extremely important the first bite second bite is just gives us a preliminary idea, but it eventually what happens. So, therefore, in such cases you may want to understand the flow behavior of material when they are micron thick while most of our rheology measurements are hundreds of microns at least 50 microns and higher. So, therefore, but the problem with thin gap rheometer is the material structure is again the same order of magnitude as the gap itself.