# Rheology of Complex Materials
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## Lecture – 26
## Rheometers

This segment of the course, we are looking at few examples of types of rheometers and what are their advantages disadvantages and what are the main types of flows that are used in these rheometers.

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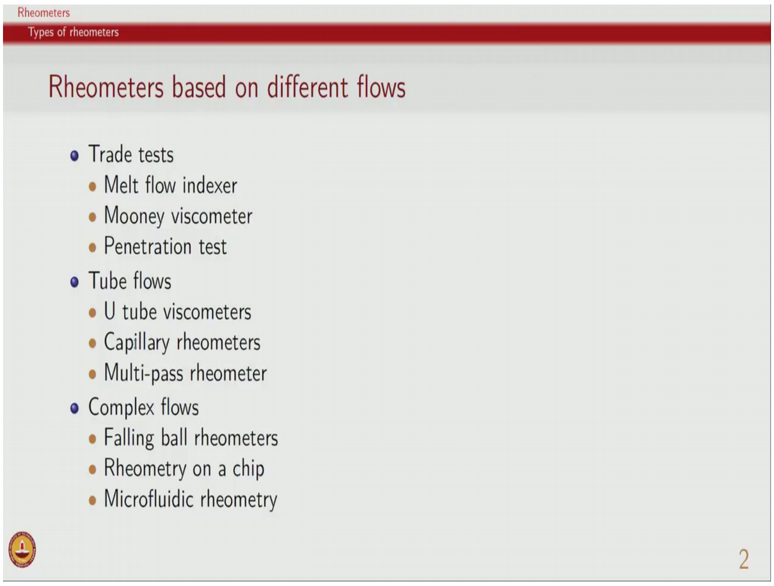

Rheometers

Types of rheometers

Rheometers based on different flows

- Trade tests
  - Melt flow indexer
  - Mooney viscometer
  - Penetration test
- Tube flows
  - U tube viscometers
  - Capillary rheometers
  - Multi-pass rheometer
- Complex flows
  - Falling ball rheometers
  - Rheometry on a chip
  - Microfluidic rheometry

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So, we initially looked at trade tests and also some rheometers, which are based on more complicated flows such as flow remolds through or spherical object falls through a fluid, which can also be used to determine the viscosity. Then we looked at the rotational rheometers, which are really the bulk of instruments which are used as far as rheology is concerned.

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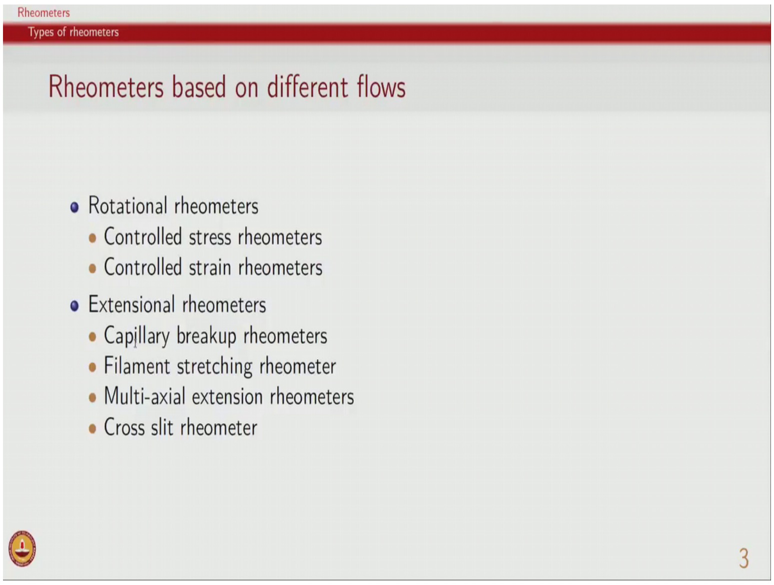

Rheometers

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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And we also saw that in last 10, 15 years more and more extensional rheometers are being used though, they are still far more tricky in terms of operations because the achievement of control and having a flow which is needed is not always possible with extensional flows. And then we started looking at some of the rheometers, which are more specialized and each of them serves a specific purpose of what needs to be estimated or what needs to be measured.

So, for example, as far as solid samples, samples which are more solid like we can use a torsional mode of deformation. In fact, the parallel plate that we use in rheometry is also a torsional mode when the material is fluid, but let us say if you have a more solid rod, like material then you can you will have to have clamps and again the same way torsion can be applied and you can do the oscillatory rheology as we have done.

Dynamic mechanical analyzer is also similar to a rheometer, but it is for solid like materials. So, here also generally oscillatory shear or oscillatory tensile examination is done also creep stress relaxation, so many of the things that we discussed for fluid like materials are applied to solid like materials.

So, generally viscoelastic solids are more often than not characterized using dynamic mechanic analyzer, because you need clamps to actually hold the sample, while in case of fluid like materials we keep them under parallel plate or between two cylindrical surfaces and so on, well in the other case we will design clamps and then have them let us say this is a tensile oscillatory shear, oscillator tensile oscillatory deformation. We can also put the same solid object between two plates and do shear deformation as we have done for fluids. So, dynamic mechanical analyzers are basically rheometers for solid materials.

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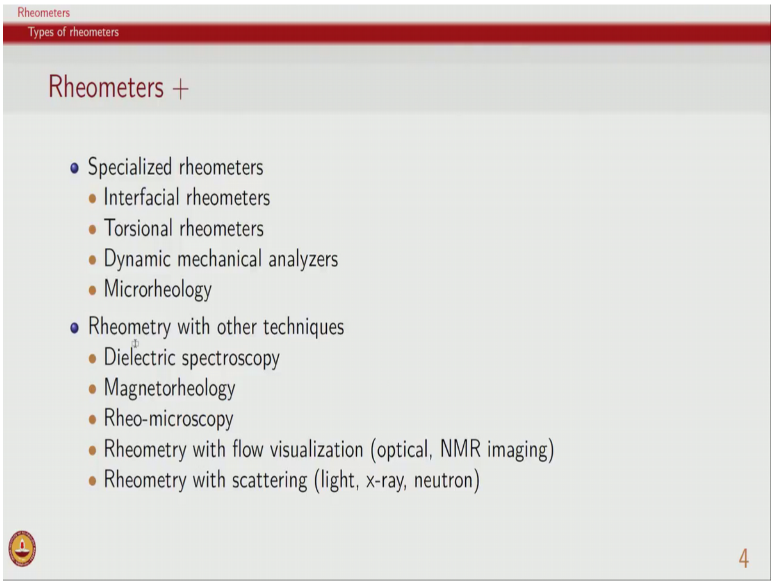

Rheometers
Types of rheometers

## 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)

And then we also have what is called micro rheology as a technique, which is evolved in the last 10 or years or so. The idea of micro rheology is to look at the rheology of the material at the microscopic scale and the advantages for example, could be very small amount of sample because you are going to examine very small using a microscope. So, you need very small amount of sample, and other advantage could be let us say if you have a heterogeneous sample, and you would like to get to know about the heterogeneity of the sample.

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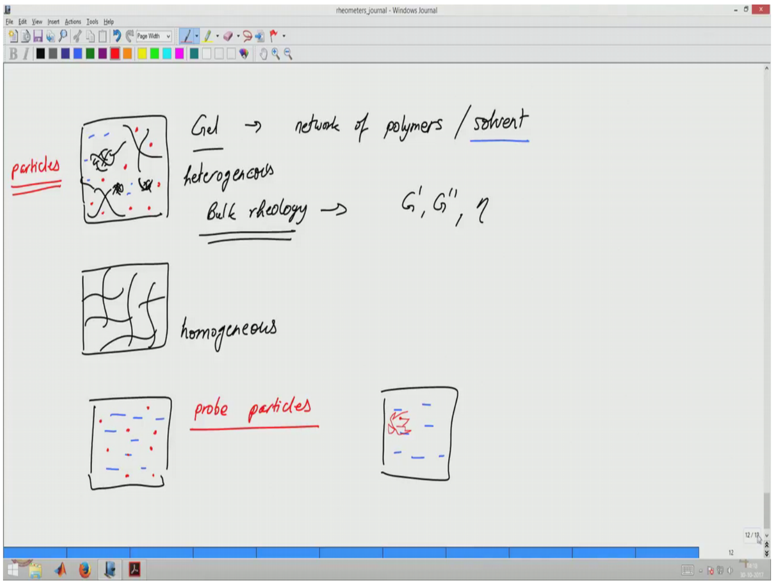

So, for example, if you have a sample, which has some denser regions, and then there are some lighter regions, and then there are some denser regions right. So, if you examine this material in the rheometer you are going to get an average response of the material. And but let us say, you want to know how much of it is this denser region and how much of it is this not so dense region, what you can do is you can embed a particle or a set of particle in this, and then view them using microscopy.

And what will happen to these particles when we put them let us say in this material, let us say that this material which is dense in parts and not so dense in other parts is a gel material, which means it has some network and let us assume that it is some maybe let us say network of polymers to be just take one example, right and then there the solvent also right, that is why we call it a gel, soft gel material.

So, there is a solvent which is there everywhere and then the polymer molecule which are also there. So, now this is a gel material which has let us say biomaterial or such applications. And we want to examine that when we prepare such a gel is it how homogeneous it is or how heterogeneous is it. So, when we do bulk rheology. So, now we are trying to distinguish between bulk rheology and micro rheology.

So, throughout the course whatever we have discussed is bulk rheology because we get macroscopic properties. So, we can measure let us say G prime and G double prime and or viscosity and so on. All the properties can be measured, but this property is sum total of contributions from the denser and not so dense regions, of course, if we make two three such gels and we get higher and higher eta then maybe we can make a hypothesis that the fraction of denser region is increasing therefore, eta is increasing or g prime is increasing and so on.

But let us say, if we have one particular sample and we measure its properties by looking at G prime G double prime, it may not be easy to speculate as to how much of it is heterogeneous, how heterogeneous the sample is in the sense presumably, it is possible that the same G prime will be also exhibited by another material which is far more homogeneous.

So, the two material, one which is homogeneous and the one which is heterogeneous may show us exactly the same behavior, because in the end when you are trying to do a bulk sample the overall cross link density and the overall properties are important, but in biological samples as I said biomaterials we may specifically need to know as to how heterogeneous the sample is. And so in that case, it becomes important to look at micro rheology. So, the idea of micro rheology is to embed a small set of particles. So, which is what is indicated here?

So, we put some particles in the gel. So, what would happen to these particles when we are trying to view them under the microscope? So, if I just take let us say water alone right, if I just take water alone and or because in this case let us say, solvent is water and in this I put the same set of particles, what do I expect will happen to the particles, particles are very small right micro particles.

Student: (Refer Time: 07:23)

No it is a very small amount of particles that we see. So, these are probe particles right we are using them as probe. So, our idea is that in this case the particle should not influence the material which is being tested. So, therefore, we add an exceedingly small amount of particles.

So, for example, our hypothesis is that the gel response is the same whether we add particles or not just the way in water if I add particles, we assume that water viscosity is not going to change, because we are adding very small amount of particles, but by looking at what particles are doing can I get to know about, what is the surrounding material. So, if I take water and if I look at these particles, what will happen to such particles? Let us say we choose a set of particles, which have almost the same density as that of water.

Student: (Refer Time: 08:17)

No that is what, now we are choosing a set of particles which are exactly same density as water. So, they will neither float as she was suggesting nor will they sink as because they have the same density. So, what happens to a small particle of course, if I use a word then immediately all of you will say that, yes that is what will happen?

Student: (Refer Time: 08:42)

The motion of the particles given that their microscopic Brownian motion right, you would expect that the particles would be randomly going about because they are exceedingly small particles, we are not imposing any flow on the material. So, therefore, overall water phase is stationary, but because of the interactions between solvent molecules and the surface of the particle there is a random force which the particle experiences and due to this random force the generally, if I pick let us say one particular particle.

Student: (Refer Time: 09:17)

One minute I will get back. So, if let us say we pick one particle and we look at what happens to it we would most often expect that it will start moving about and maybe it will have a path, which is given by something like this right, it may just go around and that is why we call it Brownian motion. But the question that you are asking is also possible let us say instead of a polymeric gel.

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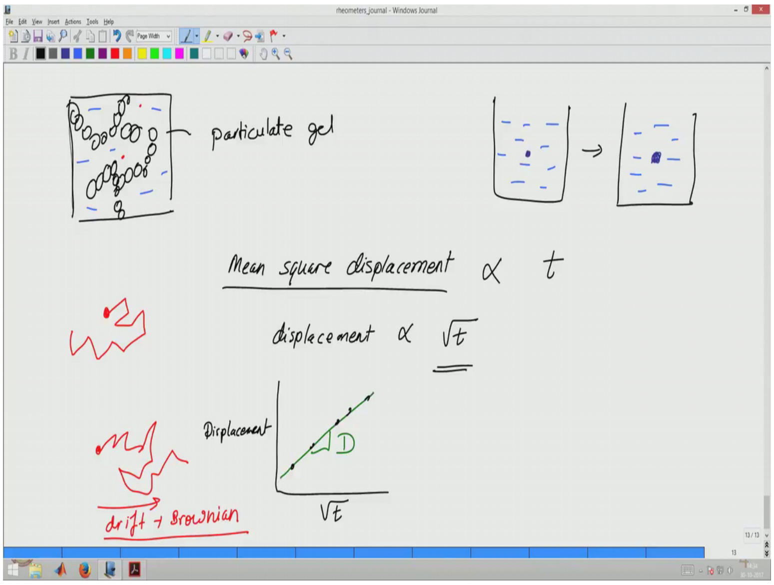

If I have let us say a particulate gel right, in which case, if I have let us say a particulate gel then what I will have is let us say a set of particles, which are forming a network together and then again I am interested in knowing how is this gel behavior right. So, this is a set of particles, this is a particulate gel since, it is a gel we will again have solvent in it, and again we put a small Brownian particle right.

So, in each case what we are trying to do is there is motion locally possible, because we are putting an extremely small particle when this particle moves by observing the Brownian motion of this particle can we get to make statements about what surrounds this Brownian particle. For example, if we look at this earlier case, we put it in water what do we expect.

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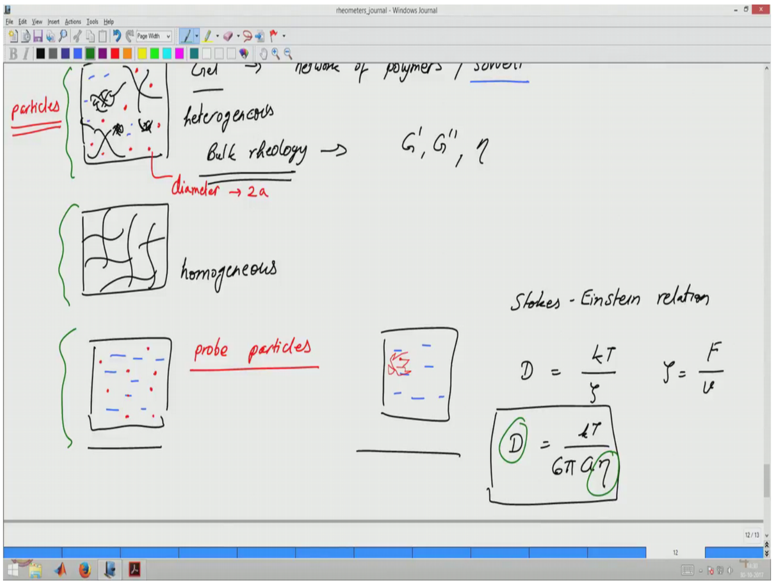

The Brownian particle to do what, how do we define Brownian motion? What are the features of Brownian motion? One specific feature is that the particle will move randomly right, its move in random directions do you have any other knowledge about what are the other features of Brownian particles.

Student: scatter (Refer Time: 11:21)

So, if we were by doing light scattering we can actually get to know at what rate the particle is moving and therefore, its diffusivity and based on the diffusivity we can also get to know its size so. In fact, size measurement is done using the same principle the fact that, if I put a set of particles given their Brownian motion, they will scatter light. I can analyze the scattered light and therefore, get to know how they are diffusing and based on that I can also find out their size.

So, let us just ask as to what is the relationship between diffusion of this particle, and its size. How are they related to each other? Let me also ask another question as to, how do you feel the diffusion of this particle is related to the viscosity of the surrounding medium.

Student: it will be inversely.

It will be inversely proportional right. So, that is a far more, easier sort of judgment to make that if the surrounding fluid viscosity is higher, we would expect this particle to diffuse slower similarly, what about the size.

Student: inversely.

Again inversely proportional, so this is based on the relationship between the diffusion of Brownian particle and is based on stokes Einstein relation, where the diffusion of such a particle is depends on the thermal energy that is available in relation to a friction coefficient.

That is experienced by the particle when its moving about if frictional coefficient is higher than the diffusion coefficient would be lower and clearly the friction coefficient will be higher, for higher viscosity fluids friction coefficient will be higher for higher sized particle, we have already said that can you now try to guess as to what that friction coefficient would be.

Student: viscosity (Refer Time: 13:25)

Given that we have already identified two parameters right. So, I will write the size let us say is the diameter of the particle is let us say a, 2 a is equal to 2 a where a is the radius. So, we were we already said that it will be inversely proportional to a, it will inversely proportional to the viscosity. So, what else do you know of a formalism in fluid mechanics, which will give you a friction coefficient between a particle and its surrounding fluid.

Student: 6 pi eta

6 pi eta a right, stokes law; we can use stokes law to estimate this friction coefficient because the friction coefficient is nothing, but the force on the particle divided by its velocity right. So, and that is nothing, but 6 pi eta a. So, therefore, if we know the if we can measure the diffusion coefficient, basically we can then find out the viscosity of the fluid, if I start with an unknown viscosity fluid, I can do micro rheology. I can look at the probe particle it I can find how fast it is diffusing based on that I can then estimate the viscosity.

So, this is the principle of micro rheology, now in diffusion motion how does position of a particle change as a function of time any judgment on that, as to how much does a particle move with respect to its own original position, when diffusion happens you would of course, have seen this in terms of a classical experiment that is talked about many times is that if we take fluid right, let us say water and in that if I put a blob of ink right with time it will diffuse out.

So, in the next instant of time it will become bigger and the concentration would reduce in the center, but it will start spreading right. So, what is the rate at which this diameter of this blob will grow? So, what is the, because that is what is happening right with the ink contains many particles which are all Brownian motion and therefore, they are spreading out, but how does it vary as a for the displacement of these Brownian particles how does the position vary as a function of time.

So, we can measure see because the Brownian particle as we saw let us say is traveling in all random directions right. So, generally to find out its displacement. How do we and there are multiple such particles right. So, the diffusion coefficient is based on the mean square displacement of particles, or if I take a particle and then average it over a certain amount of time window then what is the displacement. So, therefore, measure of diffusion is basically mean square displacement.

Student: this method will give exact position (Refer Time: 16:55)

Position of the particle is being captured based on microscopy. So, as good a microscope is that will determine how accurately the position is being determined, and given that lets say these particles are 2 microns or 5 microns its relatively easy to spot them through any microscope and image analysis will have to be done to find out the position of particle at each in every instant.

Basically what you do is you take a video of the material of examination and depending on the frame rate of the camera that you are using you will get videos per unit time. So, 30 frames per second or 100 frames per second or even 10,000 frames per second, if it is a very fast camera and so on and. So, then image analysis will have to be done to try to figure out where the particles are and how is it moving.

So, what is captured is the mean square displacement of particles and mean square displacement is proportional to time. So, if you go back to the analysis of diffusion problems you will be able to see that the mean square displacement is or displacement. So, root mean square displacement is proportional to square root of time.

So, this is what happens during diffusion in motion that is why, this size of this increases because with time particles are diffusing out and the amount of distance that they cover is proportional to square root of time So, whenever let us say you have a set of particles and if you look at their displacement and you plot it as a function of square root of time, if you get a straight line right.

So, if you look at displacement of particle, and if you plot it and you get a data where the its all nicely fitting straight line then you know that this is a diffusive process. The particles are undergoing diffusion motion the extreme case is also lets say if it is not diffusion then what is the relationship how will the distance covered be related to time. If let us say a particle rather than moving randomly like this it is moving with a velocity v.

Student: (Refer Time: 19:11)

It is directly proportional to t right. So, that is called the ballistic motion in which case basically an object is moving with a certain velocity and in that case distance traveled will be directly proportional to time, given that this is a diffusive motion the distance traveled is actually square root of time.

So, now what you can see is in such therefore, using micro rheology if I do displacement versus square root of time, then the slope of this line will be directly proportional to the diffusion coefficient and diffusion coefficient as we saw is directly related to the viscosity. So, if I can do video microscopy, measure the displacement of particles using image analysis and then using those the image analysis data of displacement, I plot it as a square root of time from the slope I can find diffusion coefficient and I know the size of the particles that I have taken the temperature at which the measurement is being done. So, therefore, viscosity can be measured.

So, now what can be done is we can focus on set of particles in different regions and we were in a case which is heterogeneous what we will get is certain regions the particles have higher viscosity they are facing fluids of higher viscosity some other regions the particle is. In fact, has a region of lower viscosity

So, therefore, you can look at how many particles are showing higher viscosity region how many particles are showing lower viscosity region and get some idea of the heterogeneity of the sample, because in case of water for example, we will see that all particles will have pretty much similar mean square displacement, because all of them are seeing water around it.

If you have a homogeneous sample then also again you will see similar phenomena, where all particles will have similar mean square displacement, but if it is a heterogeneous sample you hope to actually pick up the heterogeneity of sample, because you will have 2 or 3 or 4 sets of populations of particles some of them are displacing quite a bit, some of them are displacing little less.

We are in micro rheology shear is not being applied right, this is not under shear, what we are doing is its a stationary fluid, but because the solvents and solvent molecules and particles interact through forces and the random collision of solvent molecule leads to a effective force at each and instant of time and this force direction keeps on changing and therefore, which is called the Brownian force and therefore, particle keeps on moving in different directions.

Now, if you were to do same experiment with a shear, what you will see is there is a drift velocity and there is a diffusive component. So, let us say if this particle which was undergoing Brownian motion, what you will see is the overall diffusion motion maybe like this. So, if you look at there is a drift. So, there is a drift plus there is Brownian motion, if you put it under shear. In fact, this is one way to when we are doing these microscopy experiment, if you do MSD and if you see that there is a preferential motion always in one direction you know because of the fan or because of the air conditioning or because of whatever other drafts. In fact, there are some currents in the fluid and these currents are forcing all the particles to move in one direction which is like shearing that he was talking about

So, therefore, in addition to random motion or due to Brownian motion there will also be a velocity, drift velocity and also what we do is of course, it will be difficult for us to just put one particle and then follow it through microscope. So, generally we tend to put a few particles still very much in dilute rain. So, that they are not interacting with each other they in no way are modifying the properties of the fluid, but at the same time they are they can be their motion can be captured and in turn using that we can know the what is the surrounding material.

So, the other possibility is also there because we are we know that many of these gels or these fluids will be viscoelastic and. So, how do we then say what will happen to the particle, because if it is a Newtonian fluid this relation that we have written holds, right because eta is the viscosity of the fluid. Now, if you have a viscoelastic material will the diffusive motion of Brownian particles give us an idea about viscoelasticity of the material.

Student: if they are not affecting the fluid property.

Student: So, what is the significance of means the trying the displacement profile like that.

No using the displacement profile only you can calculate the diffusion coefficient, because displacement when you know and you plotted as a function of square root of time the slope of that is diffusion coefficient and this diffusion coefficient is related to the viscosity. What is the fluid that is surrounding these particles is viscoelastic, what would you expect, the other thought experiment that is useful to do is to say that lets say if I start with a material which can undergo gelation.

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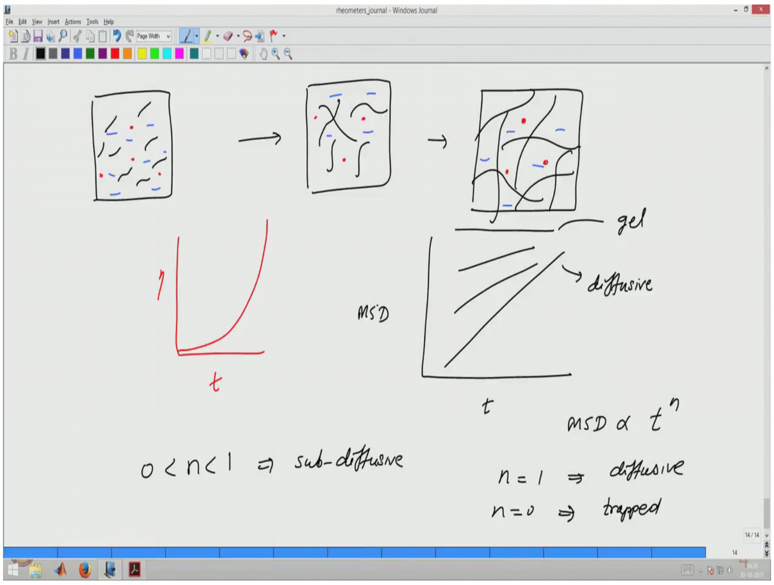

So, that initially let us say I start with small fragments of these molecules and of course, there is water also some solvent and then I have these particles right, which are the probe particles. Now with time these small fragments of molecules they start interacting reacting with each other, and what you get is little longer set of molecules again still the solvent would be there and the same set of particles that we have will also be there and then eventually, when the reaction is complete this is what we saw also when there is a three dimensional network form and there is a gelation.

So, what might happen at the end is basically a cross linked network and again we still have the solvent and we still have the particles. So, what would we expect in the three different cases, in this case the surrounding fluid would pretty much be, low viscosity material and as the gelation happens we know that viscosity goes up. In fact, it becomes infinite as the gelation is completed. So, if you were to plot viscosity as a function of time it will basically be some function like this.

So, therefore, diffusion also you will see initially will be high and eventually. In fact, it wills the particles will become trapped in the overall mesh that has been built by the molecules and the particle will become trapped.So, generally if you look at let us say the MSD, the mean square displacement as a function of time this is now mean square displacement. So, what will be the slope in the diffusive regime what will be the slope between MSD and time, because the displacement versus square root of time, it will be proportional to, but I am saying is it will it be proportional to time or will it be time squared or what.

Student: (Refer Time: 27:10)

Proportional to time right, so slope is one basically as far as time with respect to time goes and slope is also related to diffusion coefficient. So, this is when the motion is diffusive. At the other extreme when the particle, get trapped the overall there will not be any diffusion. So, this is when the gel has been formed, and so at different instants of time you will see that MSD versus time will be some exponent and this exponent, if it is one we know its diffusive and n is equal to 0 would imply its trapped and.

So, in between whenever, n is equal to n is less than 1 n, but greater than 0, we have what is called a sub diffusive motion. So, by characterizing this n we can actually find out as to how the properties of the fluid are changing or how viscoelasticity is developing in the material and there are also theories to look at the overall stoke Einstein relation in terms of complex quantity.

We know that the overall eta star is eta prime, minus i eta double prime right, where the eta prime is the real part of the viscosity or the dissipative contribution while eta double prime is the elastic part of viscosity. So, therefore, the overall MSD can also be analyzed to give us an elastic modulus and storage modulus. So, therefore, the same data stokes Einstein relation, can be used also in the complex domain to find out G prime and G double prime or basically eta prime and eta double prime.

If we assume the surrounding fluid to be Newtonian, then we directly use stokes Einstein relation, if we know that the surrounding fluid is a viscoelastic fluid, we know rather than it being eta it will be eta star and therefore, we can then find out what is the elastic and viscous contributions. So, therefore, micro rheology as a technique has been used over the last 10 years for samples which either are very small or the samples which are biological in origin which may be heterogeneous and then people have explored how does their rheology vary as a function of time or how does the rheology vary in as a function of position within the gel.

So, then we will move on to other aspect of rheometry where we use rheometry with other set of techniques. So, in the next segment of the course we will look at simultaneous techniques where rheology is used with other techniques in order to learn more about how the microstructure is evolving.