Rheology of Complex Materials
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Elasticity in fluids: normal stress differences and stress growth
Lecture - 52
Normal Stresses and Stress Growth

In this segment of lectures we are looking at normal stress differences and stress growth in materials. Earlier we have seen the oscillatory shear, stress relaxation creep of viscoelastic materials. And we saw that many of these characteristics were useful in the linear range or as a marker of linear viscoelastic response. And elasticity in fluids is an important indicator for understanding the overall behavior of materials. And therefore, normal stress differences in stress growth, which are generally observed under large deformations are very important.

So, what we saw last time was an example from macromolecules and a shear and we motivated the presence of the normal stresses in macromolecules under shear.

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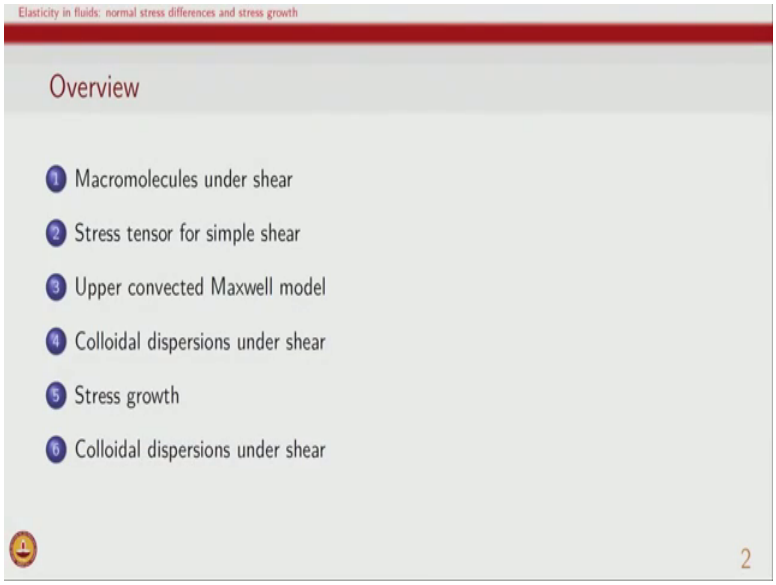

And then we looked at simple model, which could predict normal stress difference which is non-zero, because all the linear viscoelastic models as well as all the viscous models whether linear or non-linear viscous models, would all predict the normal stress differences to be 0. And then we motivated the stress growth response through a colloidal

dispersion under shear. And in this segment of the course we will see how do we define material function based on stress growth experiment, and look at the colloidal dispersion under shear.

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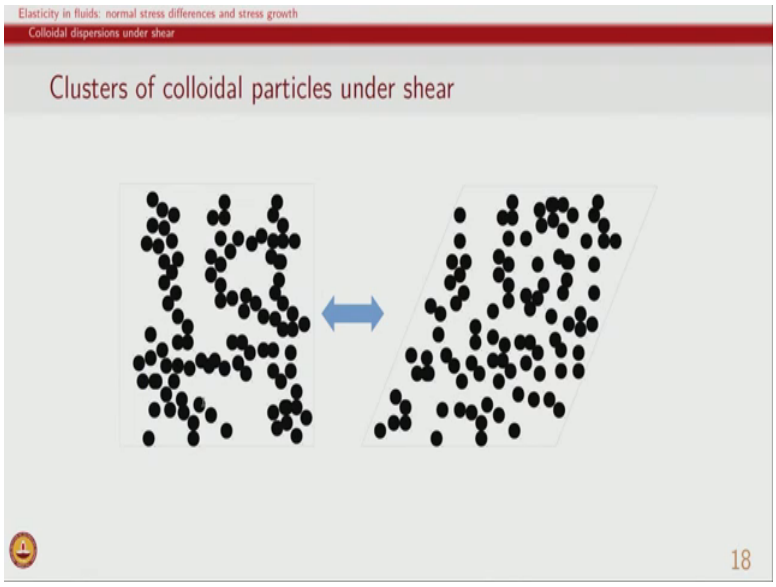

So, we looked at the idea that clusters actually break when we have shearing.

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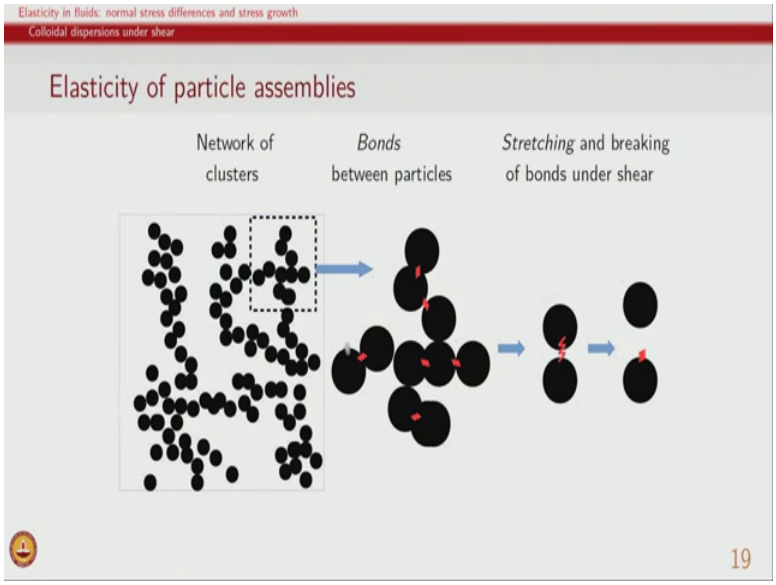

And the particles can be thought of as bonded to each other, because of the attraction between particles. And when shear is applied the bonds between these particles can stretch and the break under some conditions. So, therefore, this is the underlying

phenomena which is influential in determining the overall rheological response of such network of clusters. And so, if we think of these bonds with the certain life time, the fact that there are continuous thermal motions which are going on in the system and particles in general are vibrating, rotating, translating around their mean per around their positions.

So, in that case based on the thermal motion and depending on its magnitude with respect to the attractive interactions between the particles the bond may be present or bond may break over as a function of time. And so, in that case the transition between this will purely depend on what is the relationship between the attractive potential between the particles and the thermal energy which is present for the particles to move away from each other.

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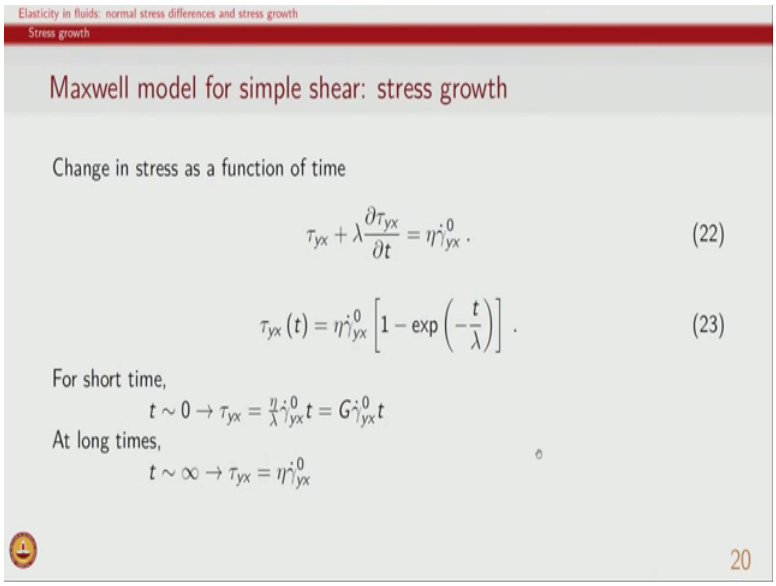

So, in such a scenario we could model the material as a Maxwell model with a relaxation time indicating what is the lifetime of such bonds. And so, in such case if we look at the materials under constant strain rate; and so, all of these experiments are when the strain rate is constant and so, we take a cluster of particles and apply a constant strain rate. So, that a linear velocity profile basically makes some of the particles to move faster than other set of particles and so, given a constant strain rate the Maxwell model reduces to an ordinary differential equation and solution of this is an exponential solution. And the solution can be examined under two limits that when time t is equal to 0 when we have.

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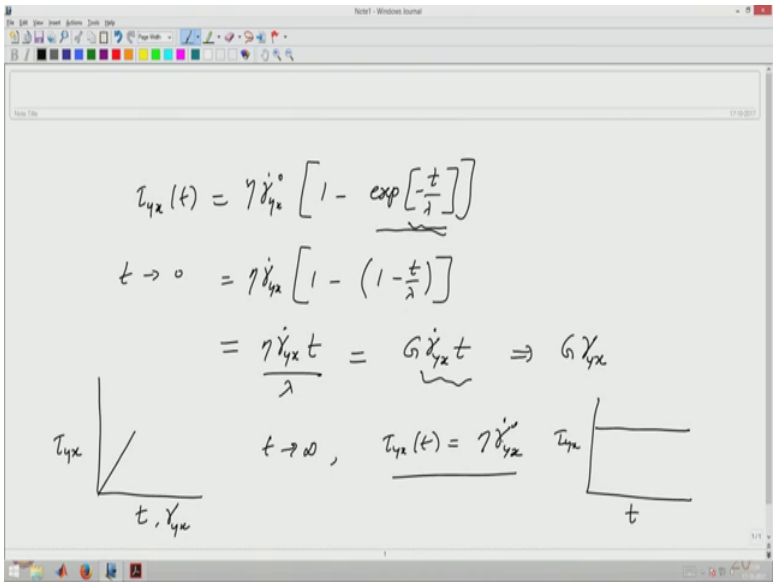

So, the stress is basically related to the coefficient eta times gamma dot yx naught to be applied strain rate and 1 minus exponential minus t by lambda. And given that this is the overall response of the material you could look at this under two extreme conditions when time t is equal to 0, the exponential function is very small and therefore, we one can write this as eta gamma dot yx 1 minus 1 minus t by lambda and therefore, this will be nothing, but eta gamma dot yx t by lambda or in other word given that eta by lambda is G, it is G times time.

So, that is what is for short time the behavior is where the stress increases linearly and in fact, gamma dot yx if the deformation is small can is directly related to the strain itself and. So, therefore, what we have is an elastic response and so, at very short time scale, the stress increases linearly or increases linearly with strain. So, this is the elastic response under these type of conditions with very small time imposed, what we have is basically the time scale short enough that each of these bond actually is formed and the time scales involved are such that the thermal motion of the particles, which leads to the bonds being broken is much much slower. And therefore it would appear at very short time scale that each of the bond exists. And therefore, the material pretty much responds like an elastic solid.

Now if you look at the other extreme or where the time is extremely large, in this case what happens is the life time of bond is defined by lambda then since we are now

looking at time which is very large in such cases basically the exponential function will reduce to 0 and therefore, tau yx as a function of time will reduce to eta times gamma dot yx and. So, this is the newtonian fluid response and in this case tau yx as a function of time will be just a constant value because gamma dot yx is fixed.

So, in this case the picturaization of the colloidal system is in this state. So, that basically the time scale given is such so large, that on an average the particles rather than remaining bonded to each other are free from each other. So, therefore, the system behaves as if it is a colloidal particles which are free to move without the bonds and therefore, we predominantly observe a viscous response. So, therefore, Maxwell model can capture this viscoelastic response, which is can generally be observed for variety of large class of viscoelastic materials, and that will be basically an increase in stress at shorter times and then a constant stress after sometime.

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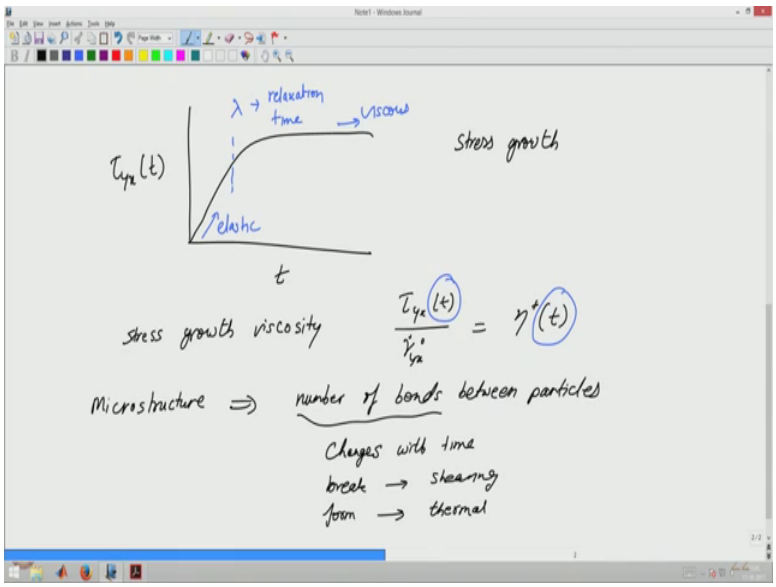

So, generally for large classes of viscoelastic materials, you would see a response where there is a stress growth. And so, this can be used to define a material function which we will call stress growth viscosity. The idea here is to say that given that we are applying a fixed strain rate, ratio of the strains which is being measured to the fixed strain rate which is being applied is defined as the stress growth viscosity and since the stress itself is a function of time, the viscosity also is a function of time.

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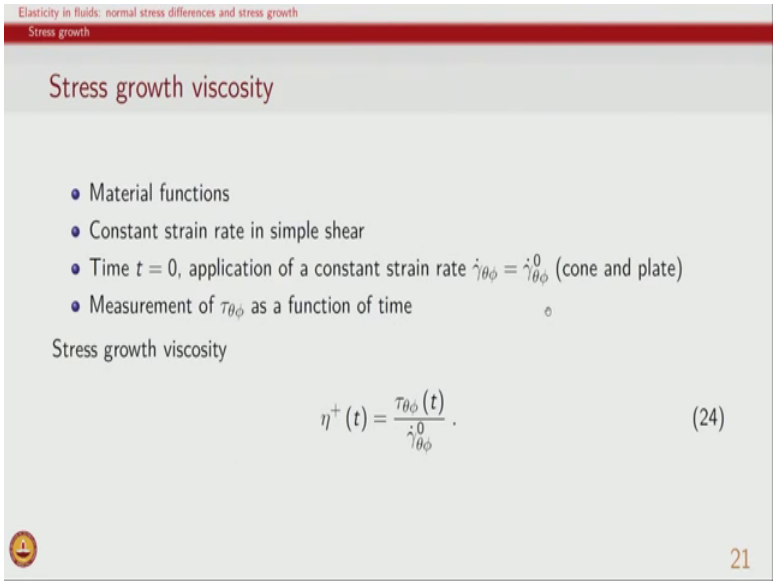

So, based on this we can define a material function which is stress growth viscosity, its a material function which is being measured at constant strain rate in a simple shear flow. At time t is equal to 0 a constant strain rate is applied and in this case we are writing the strain rate for a cone and plate device in which case theta phi or phi theta are the only non zero components, and then we measure tau theta phi as function of time and the stress growth viscosity is defined as ratio of the stress which is being measured divided by the strain rate, which was applied and this material function is a function of time.

So, similar to the other material function we define for example, viscosity itself for the function of strain rate, many of the oscillatory functions were the functions of frequency and therefore, we have now other stress material function which is stress growth viscosity which is the function of time. If you recall the relaxation modulus was also a function of time and similarly the creep compliance was also function of time.

So, stress growth viscosity given that it contains response of the material in the elastic limit as well as in the viscous limit; is a good indicator of viscoelastic response and this increase and at what time would the elastic or viscous response we observed, will depend on the relaxation time. So, similar to many other material function that we saw, under two extreme condition they either show viscoelastic response given that we are looking at Maxwell model in stress growth also we can see the two extreme responses otherwise the overall stress growth viscosity for Maxwell model is an exponential function. So,

now in case of material were the clusters can break down, but they have a finite time of taking and there is strength of these attractions is reasonably high.

So, that certain amount of shear is required and only then this braking can happen. The Maxwell model response we interpreted in terms of thermal fluctuation overcoming the attraction and therefore, these bonds could be broken only due to the thermal motions. But if these attractions are strong enough then what happens is the thermal motions are not efficient to break these bonds and degree of shearing is also required for the stretching and breaking.

So, therefore, stretching and breaking of bonds is possible in addition to thermal motion being there shear is must and only then this can happen. Of course, in all cases the reverse reaction can also happen. Earlier we saw with Maxwell model interpretation that given that the particles will fluctuate move around it can again bond back. And therefore, the bond is again formed similarly in case of shear breaking these bonds, if shear is removed then particles can again move and form bond. And again the network of clusters can be formed so many of the colloidal systems will undergo this change in micro structure from a network of clusters to broken clusters and this is mediated by shear. So, in such case a simple model which can be used to describe the behavior of response is called a structural model.

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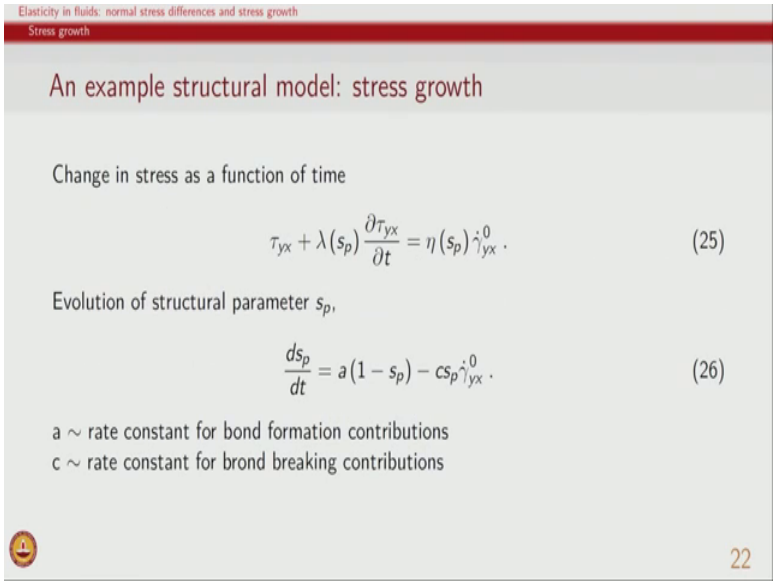

So, there is a structural model through the structural parameter which is indicated as Sp here is used. Now what we are trying to do here is to say that whatever is the micro structure of the material, that can be indicated and captured using a parameter. So, microstructure of a material which in our case is based on the number of bonds between particles and this changes as a function of time and we know that it forms and breaks. So, break happens because of shearing with the given rate and then formation happens that because the thermal motion again lead the particles to approach each other and so, due to thermal motion the formation can happen. So, therefore, in this case the idea of is to capture the variation of the micro structure through a structural parameter.

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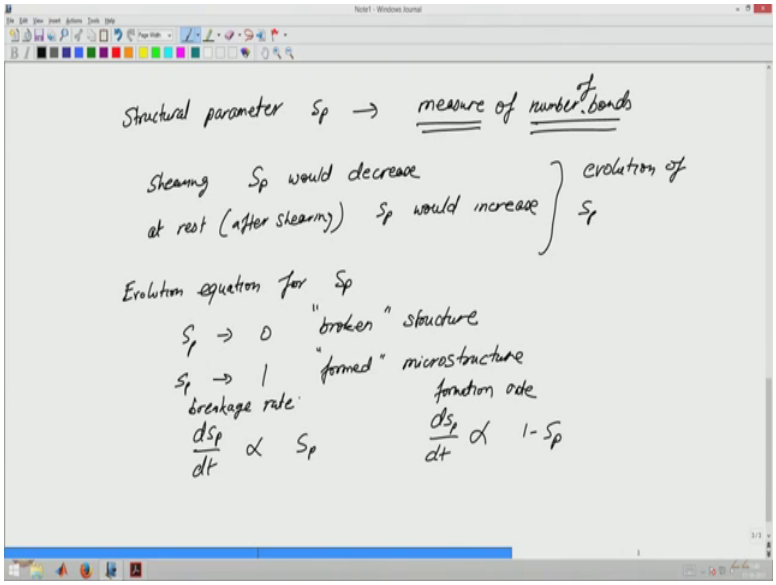

So, we make a hypothesis in such cases of a structural parameter, and clearly the structural parameter will in some way is measure of number of bonds between particles. So, with shearing Sp would decrease and at rest that is after shearing Sp would increase. So, clearly there is an evolution of Sp.

So, we need to understand the material behavior, we need to be able to write an evolution equation for Sp. And this needs to be combined with hypothesis of how the number of bonds actually influence the material behavior. So, in the example that I am showing here, the Maxwell model is itself chosen to represent the overall material response. However, the Maxwell model parameters are assumed to be dependent on the number of bonds which are present.

Given that the time scales of bond formation and breakage are very significantly influenced by shear we have to make an hypothesis that under shearing whenever structural parameter changes the overall relaxation time of material changes, and the parameter which signifies the viscous response may also change with structural parameter. So, now, this is Maxwell model where the model parameters are functions of structural parameter. And then the evolution of structural parameters itself is written as differential equation with terms which signifies formation as well as breakage. So, when Sp is 0 we imply completely broken structure and we should remember that this is only measure and some representation of what is the microstructure. Therefore, broken and formed should be viewed in as representing and not being completely measurable directly formed microstructure.

So, there is a rate of change of the parameter and of course, if all the bonds are formed which means Sp is high then what will happen is this rate will be higher. So, this rate will be directly proportional to Sp, but this will be rate of breakage. So, more Sp is the more breakage is possible. Because if bonds are completely broken in Sp 0 then the rate of change of Sp will be also 0 if Sp is 1, then the rate of change of Sp will be very high. Similarly dsp by dt will also be related to 1 minus sp, but in terms of formation if Sp is 0 then the formation can happen maximum rate when Sp is one all the bonds are already formed. So, therefore, formation rate will be 0.

So, this signifies the formation contribute rate and this signifies the breakage rate. So, therefore, the overall equation for evolution of Sp can be written as a differential equation in including two terms. The breakage rate as we been saying is also strongly dependent on the shearing. In the absence of shearing there is no breakage and in that case the material go to Sp equal to 1 when finally, even the formation rate will go to 0. In the absence of formation you will only have breakage and in that case there is no reverting back to the cluster that was there. So, therefore, we have both the formation and breakage term the rate constant a and c signify how fast or slow the formation and breakage rate are.

So, these two equations together govern the response of material and this is an example of a structural model because a structural parameter is being incorporated into a constantive model which we have already been seen many times. We have seen that the

response of this model alone if lambda and eta are constant for stress growth was just an exponential function.

Now given that the parameters themselves also depend on the structural parameter what happens this, these lambda and eta also evolve as a function of time when constant strain rate is applied. So, when you apply a constant strain rate that leads to constant rate of breakage in terms of c and gamma dot being constant, but Sp itself evolves and the evolution of Sp will eventually lead to again a steady state.

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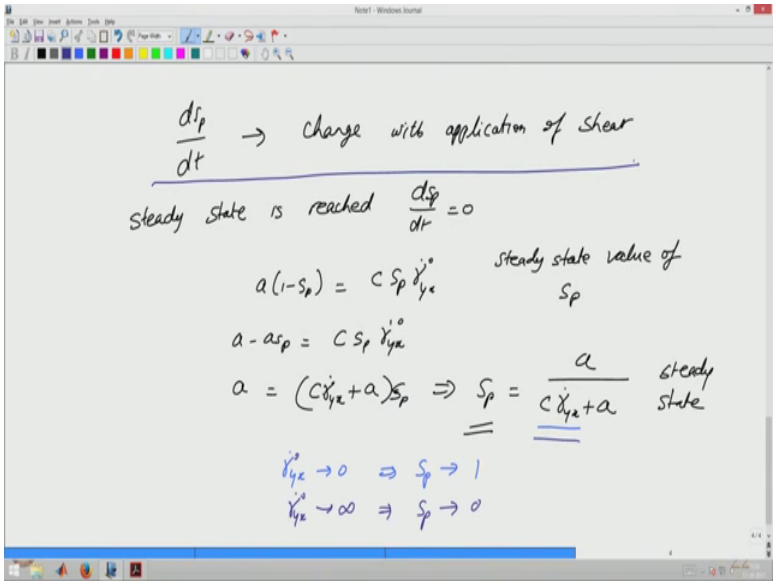

So, in general what you would have shear is applied on the material is the fact that dsp by dt will change with application of shear and steady state will be reached steady state is reached when of course, dsp dt is 0 what we have is the formation of breakage rate are same. So, therefore, the a 1 minus Sp is same as csp gamma dot yx and clearly so, this different steady state will be reached when you have different gamma dot. So, this equation can be solved to find out what is the steady state value of Sp. So, based on this one can get to know what is this steady state value of Sp.

So, we have basically a minus a times Sp same as C Sp gamma dot yx naught and clubbing them together we have a is equal to C gamma dot yx plus a times Sp therefore, Sp is a divided by c gamma dot yx plus a. So, the steady state value of the structural parameter would depend on how much is the strain rate that is being applied and what are the kinetic constants if no strain is applied strain differ gamma dot yx is 0, then in

that case if gamma dot yx is 0 then we have basically Sp tending to 1 a by a which is one and if gamma dot yx is very large if the value of gamma dot yx is very large then of course, we have the completely broken structure in steady state value of Sp is 0. So, therefore, the Sp actually evolves as a function of time and so, the response in also is that even lambda and eta vary as a function of time.

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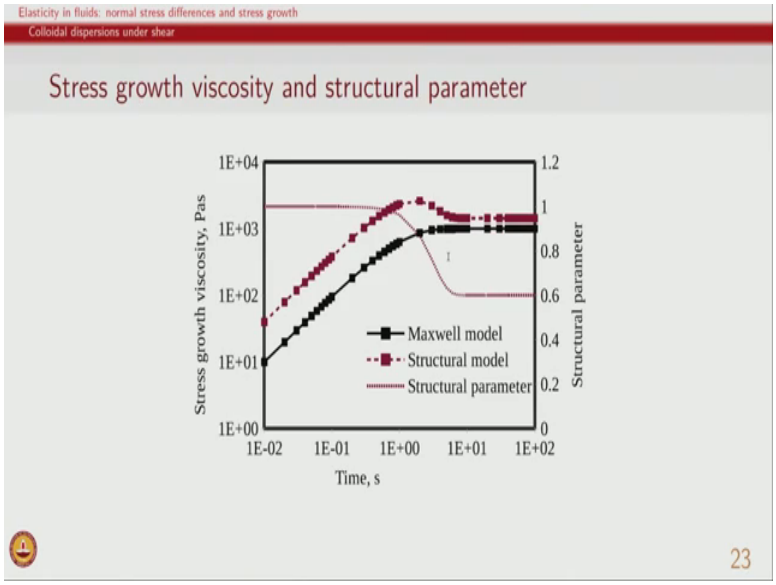

So, the overall response of this model to stress growth is given here we have already seen that the there is a Maxwell model and the exponential increase and the steady state is reached.

We had seen that this response was elastic response while the overall constancy of the stress growth viscosity is the viscous response at long time because of the structural parameter initially being one when all the bonds are formed and because of shearing there is an evolution and change in structural parameter and steady state value which is reached at long times basically structural parameter decreases and just to remind us that the structural parameter decreasing is because of the bonds the average number of bonds which are broken is higher and higher as the time goes on. However, at steady state the average number of bonds remains same because the rate of formation and rate of breakage are same.

And so, in this scenario therefore, initial response at short times is again related to the number of bonds being basically same as the sample at rest and so, completely elastic

response, and then at very large times since the number of bonds is less, but again remains constant we again see that an overall long time response which is viscous. However, in between the material shows a stress over shoot.

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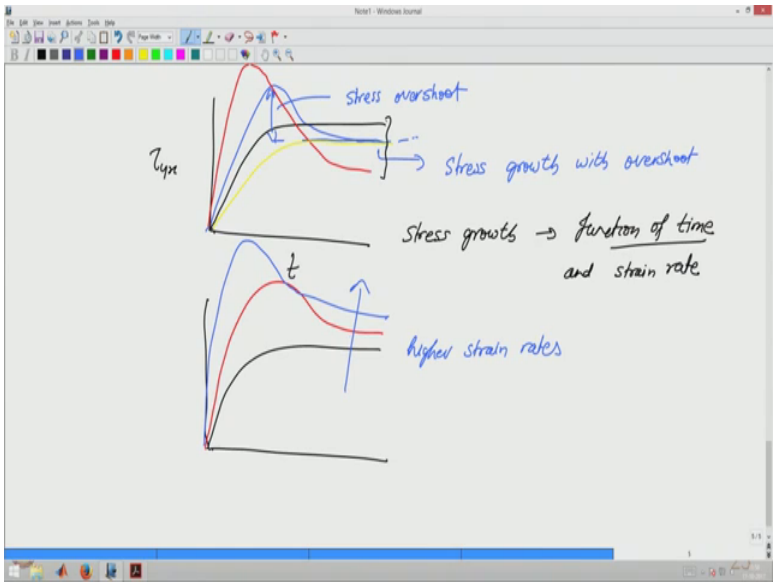

So, compared to earlier where we had seen the tau xy as a varying monotonically and an increase and then becoming constant, now what we are seeing is an overshoot and then it becoming constant. And so, this is stress growth with over shoot and this value given that this is the constant.

So, this is the stress over shoot and clearly what happens in this case is because the thus value of Sp would change, depending on what is the strain rate there as we seen that the not only steady value of structural parameter, but even the evolution of structural parameter would depend on strain rate, clearly the response of the model would depend on what is the strain rate; because the evolution of Sp is a function of strain rate. So, at different strain rates, we would observe that there may be different responses. So, for example, you may see response like this depending on the different strain rate that is being imposed.

So, therefore, now stress growth in these cases is a function of time and also the strain rate. It is a function of time which was the earlier case also and also strain rate so many of the non-linear response of materials is according to what we have discussed so, far that at very low strain rates where deformations are small we would observe stress

growth to be monotonic, but as the strain rate increasing in higher strain rate is applied a strain rate over shoot is observed, and you should see the stress over shoot is higher and higher when strain rate it is higher. Of course, the steady value of stress may depend on what is the overall the overall magnitude of strain rate being applied and in fact, in the drawing here what we should. In fact, look at is the fact that each of the stress value that you will get will be higher than the previous one as the stress will be higher, but the viscosity may be lower. So, at higher and higher strain rate we will have stress to be higher.

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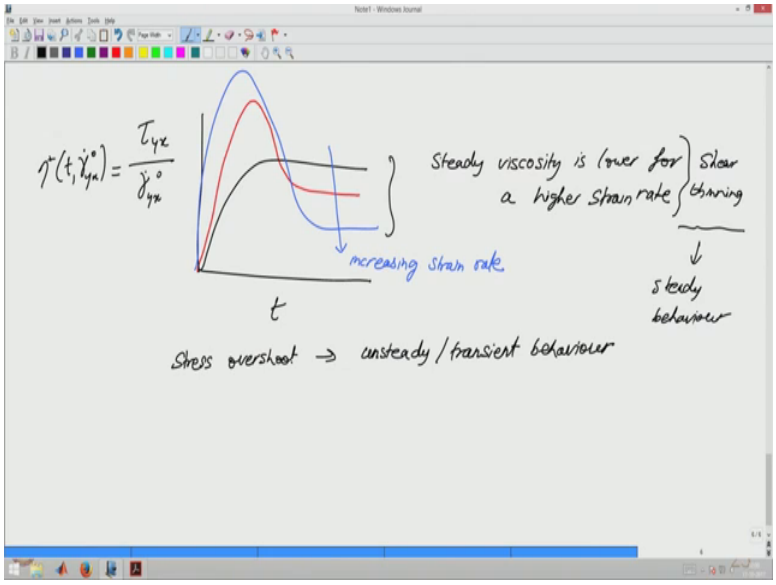

However, if I plot the data for the ratio of the stress and gamma dot yx which is being applied, then at a different function of different as a function of strain rates we will get response that I have drawn erroneously earlier as stress response and in fact, so, this is again in increasing strain rate and the fact that these steady value of viscosity is. So, steady viscosity is lower for a higher strain rate in the example that I have drawn here.

So, therefore, what has is being drawn here is for shear thinning material, but the shear thinning is described based on only the steady behavior. However, the stress overshoot descries the unsteady or transient behavior. So, we can define the stress growth material function which is again the stress growth viscosity, but it is a function of both time and the gamma dot. So, we have now the two versions of the same material function one which is defined for linear response where it is only a function of time.

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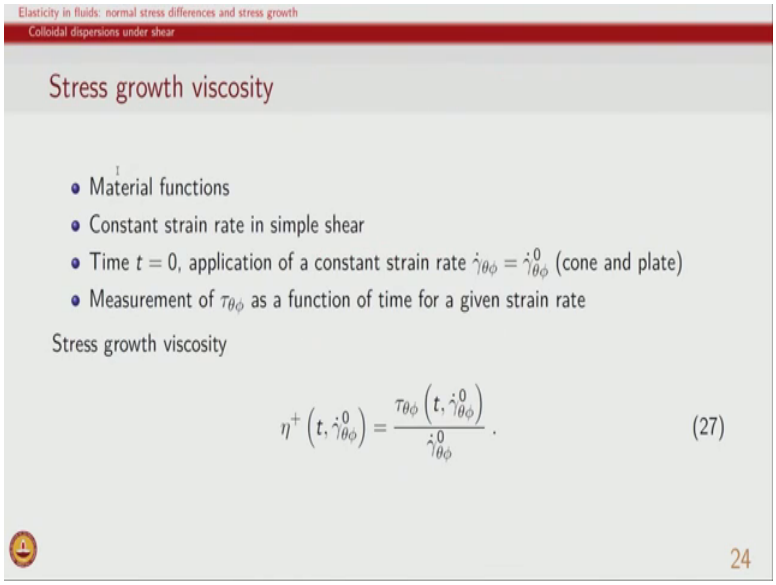

And then we have another function, which is called stress growth viscosity again only thing is this is being used for a non-linear response of the materials and therefore, the viscosity is a function of time as well as strain rate. So, in summary we have seen two important material functions common stress differences and stress growth viscosity, both of which are very useful in understanding the non-linear response of viscoelastic materials.