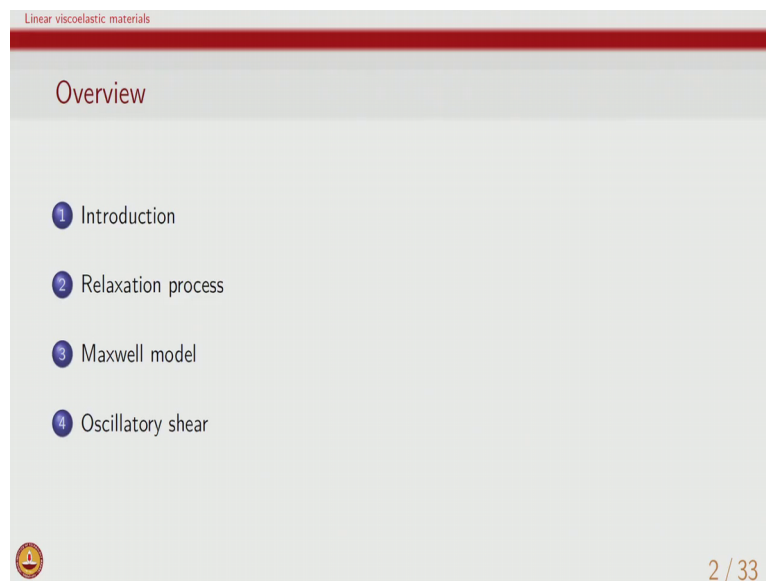


Rheology of Complex Materials
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Lecture – 19
Linear viscoelastic materials

We are discussing Linear Viscoelastic response of Complex Materials and this is the overall scheme which we are following after looking at some of the introductory concepts. We saw in detail the idea of a relaxation process because that is fundamental to the viscoelasticity and we of course, always said that material real material will have a collection of relaxation processes and of course, later on in the course when we look at real data for several material systems we will try to identify based on the rheological response, what is the relaxation process.

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And just to understand the viscoelasticity and overall development of several material functions we said we will look at Maxwell model closely. And in today's class we will finish up with looking at oscillatory shear, which forms the backbone of rheological analysis for viscoelastic materials. And just to remind us this is a framework we have been using we said that we will need to define the class of response. So, right now what we are discussing is linear viscoelastic response. We will look at material functions.

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Linear viscoelastic materials
Introduction

Response, material functions, constitutive models

- Material response**
 - Class of response, qualitative description
 - Viscous, viscoelastic, thixotropic, yield stress material
- Material functions**
 - Quantification of material response
 - Measurement under controlled conditions
 - Viscosity, relaxation modulus, storage modulus, creep compliance, extensional viscosity, stress growth viscosity, ...
- Constitutive models**
 - Phenomenological models
 - Carreau Yasuda model, Maxwell model, Structural model, Hershel Bulkley model, ...

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So, far we have defined material functions like viscosity and we have defined relaxation modulus. Today we will define material functions which are related to oscillatory shear and of course, we are continuing with Maxwell model as far as a simple model for doing this as concerned. So, in the last class we had discussed the Maxwell model.

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Linear viscoelastic materials
Maxwell model

Maxwell model

$$\tau_{yx} + \lambda \frac{\partial \tau_{yx}}{\partial t} = \eta \dot{\gamma}_{yx} \quad (2)$$

λ relaxation time
 η constant determining viscous contribution
 $G = \eta/\lambda$ constant determining elastic contribution

$\lambda \rightarrow 0$ $\tau_{yx} \approx \eta \dot{\gamma}_{yx}$ $\lambda \rightarrow \infty$ $\frac{\partial \tau_{yx}}{\partial t} \approx \frac{\eta}{\lambda} \frac{\partial \gamma_{yx}}{\partial t} = G \frac{\partial \gamma_{yx}}{\partial t}$

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And this is basically it incorporates both viscous as well as elastic contributions and lambda is relaxation time which incorporates, whether the material will have a predominantly viscous response or in elastic response.

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Linear viscoelastic materials
Maxwell model

Stress relaxation

Time $t = 0$, a constant strain $\gamma_{yx} = \gamma_{yx}^0$

$$\tau_{yx} + \lambda \frac{\partial \tau_{yx}}{\partial t} = 0 \quad ; \quad \tau_{yx}(0) = G \gamma_{yx}^0 \quad (3)$$
$$\tau_{yx}(t) = G \gamma_{yx}^0 \exp\left(-\frac{t}{\lambda}\right) \quad (4)$$
$$G(t) = \frac{\tau_{yx}(t)}{\gamma_{yx}^0} = G \exp\left(-\frac{t}{\lambda}\right) \quad (5)$$

For a perfectly viscous fluid,
 $\lambda \sim 0$ and the decay is instantaneous
For a perfectly elastic solid,
 $\lambda \sim \infty$ and no decay is observed.



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So, with this we had also seen that the stress relaxation modulus for a Maxwell model was an exponential function. And how fast the exponential decay is depends on the relaxation time. So, for fluid like materials relaxation time is very small and therefore, decay is instantaneous and these materials end up being dissipative while solid like materials have very large relaxation time and therefore, no decay and no dissipation.

So, with this we had defined the material function relaxation modulus and what we can also do is to use this relaxation model to recast the Maxwell model in an integral form.


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Linear viscoelastic materials
Maxwell model

Integral Maxwell model

$$\tau_{yx}(t) = \int_{-\infty}^t \left[G \exp\left(-\frac{t-t'}{\lambda}\right) \right] \dot{\gamma}_{yx} dt' \quad (7)$$

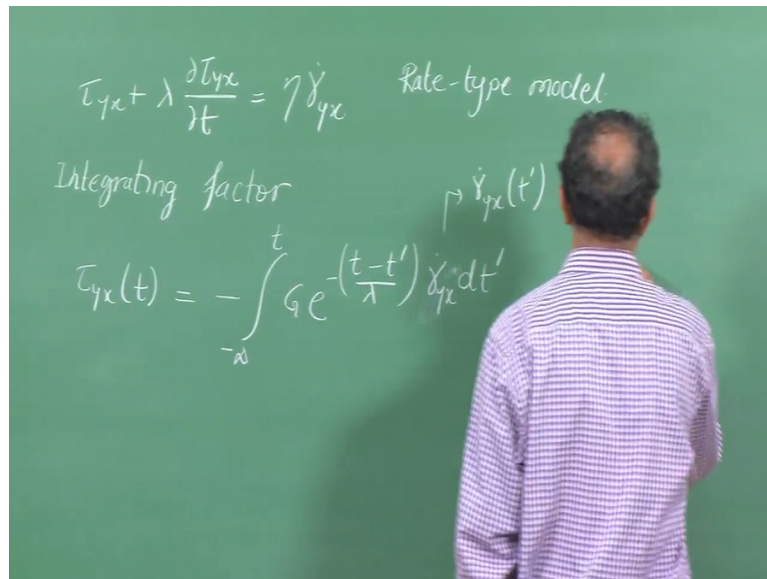
stress at time $t = \sum_{\text{past}} [G(t-t')] \times [\dot{\gamma}_{yx} \Delta t']$



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So, given that any differential equation in this case Maxwell model.

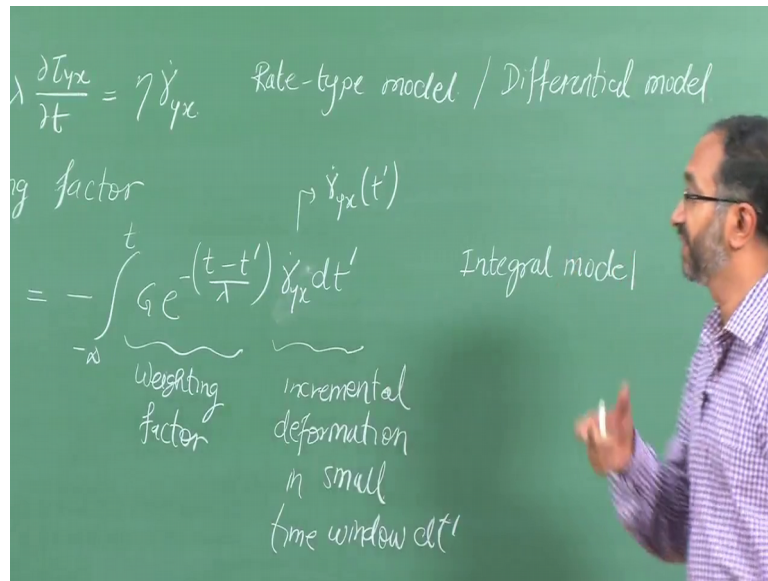
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Can be recast into the integral form for example, using integrating factor or any such method we can try to simplify this and by that what we can do is write an integral form of Maxwell model. In fact, in general in rheological analysis we generally talk of 2 types of models one is a rate type model. So, this is an example of a rate type model because we incorporate rates of different quantities and. So, it is called a rate type model and then same model can be expressed as the stress at present time which is an integral of all past deformations and we saw that in case of Maxwell model this can be written as the following.

So, this is the integral and. So, $\gamma \dot{y} x$ and the this $\gamma \dot{y} x$ is of course, at time t prime also. So, any t prime is the dummy integrating variable. So, that goes from any time in the past to present time. So, this is the integral Model.

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So, several models have rate type expression or they will have an integral expression and depending on the convenience we can use either of these and we will see later on for example, that we will for to look at let say normal stress differences in complex materials. We can have what is called a convected Maxwell model in which case rather than using the normal rate we will use convected rate and that will become an objective and frame invariant model which can be used for arbitrarily large deformation and in that case the convected model will be the rate type model and then similarly there is an equivalent which is called lodge rubber like liquid model.

So, both of these models are again same, but one of them is written as a differential model or a rate type model and the other one is written as an integral. So, this is also called as a differential model and we can quickly see this as this as the incremental deformation in a small time window dt' in small time window dt' and this of course, is the weighting factor and we had seen that this weighting factor is large for times which are not. So, distant and when time is much more distant in the past in this weighting factor falls off to 0 and it is an exponential function. So, with this ah review of Maxwell model and it is various versions.

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Linear viscoelastic materials
Oscillatory shear

Oscillatory shear

For small deformations or in linear regime

Periodic mechanical stimulus \rightarrow sinusoidal variation

$$\gamma_{\theta\phi} = \gamma_{\theta\phi}^0 \sin \omega t . \quad (8)$$

Stress response

$$\tau_{\theta\phi} = \tau_{\theta\phi}^0 \sin(\omega t + \delta) . \quad (9)$$

$$\tau_{\theta\phi} = G'(\omega) \sin \omega t + G''(\omega) \cos \omega t , \quad (10)$$

G' Storage modulus, G'' loss or viscous modulus and δ phase lag

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Now, we can look at the next probe of rheological response which is oscillatory shear. So, in case of oscillatory shear we impose either a strain or a strain rate or a stress which is sinusoidal function. So, in general you could have any of the different types of strains and this case I have used the notation, which is valid for a cone and plate cone and plate geometry which is used quite often for rheometry.

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Differential model / Differential model

Integral model

variables of interest $\gamma_{\phi}(r, \theta)$

$\theta = \frac{\pi}{2}; \gamma_{\phi} = 0$

$\theta = \frac{\pi}{2} - \theta_0, \gamma_{\phi} = Wr$

$\dot{\gamma}_{\phi} = \dot{\gamma}_{\phi}^0 \sin \omega t$

$\tau_{\phi} = \tau_{\phi}^0 \sin(\omega t + \delta)$ Newtonian fluid

Hookean solid $\tau_{\phi} = \tau_{\phi}^0 \cos \omega t$

$\dot{\gamma}_{\phi} = \omega \gamma_{\phi}^0 \cos \omega t$

And in this case what we have is a cone and a plate and fluid is in between and the cone is let say rotated. So, therefore, this direction is phi the rotation and the shear direction is theta. So,

we use spherical coordinates to describe this point with this as the origin and this going out is the radial direction and then the angle with respect to this axis is theta.

So, theta is equal to $\pi/2$ is which surface theta is equal to $\pi/2$ is the bottom plate right theta is 0 is the shaft and theta is equal to $\pi/2$ and of course, phi goes from 0 to 2π . So, this is there. So, therefore, in this case we have only v_ϕ and it is a function of r and theta because as you go radially outward the velocity will be higher and higher.

And it is a function of theta also because theta is equal to $\pi/2$ which is the bottom plate fluid will not be moving and theta is equal to $\pi/2$ minus theta naught let us say this angle is theta naught then we have these 2 boundary condition theta is equal to $\pi/2$ v_ϕ is 0 and theta is equal to $\pi/2$ minus theta not v_ϕ will be equal to $w r$ where w is the rotation rate of the top cone right.

Student: (Refer Time: 09:00).

Yes phi will be 0 to 2π theta will be 0 to π right the usual spherical coordinates.

So, therefore, theta goes from $z=0$ to π right what is your doubt.

Student: (Refer Time: 09:17).

No no phi will vary 0 to 2π yeah theta will vary from 0 to π . So, therefore, you can see that theta phi are the 2 components that is the shear component this is again an example of shear flow and theta phi will be the component which is non-zero while all the other components which are r r_θ r_ϕ or ϕ r all those components we will find them to be 0. So, therefore, in such a situation we will have either $\gamma_{\theta\phi}$ $\dot{\gamma}_{\theta\phi}$ or $\tau_{\theta\phi}$ as the quantities of interest.

So, any of these could be controlled and varied sinusoidally. So, if we have the top cone oscillating basically we are doing this or we could say that we will control the torque which is there on the top cone and we can say that it goes to maximum then it reverses goes to the negative maximum and then again goes like this. So, that is oscillatory shear. So, what we will look at initially is let us say strain imposing a strain which is an oscillatory strain.

So, now the experimental time scale is being manipulated with frequency if we apply the strain very quickly then we are giving material very less time to respond to the mechanical

stimulus. If you do the experiment extremely slowly then we are giving the material enough time to respond. So, therefore, frequency which is inverse of time is what is being manipulated in this case. So, we would expect that what is the long term behaviour will be observed when you have very low frequency being imposed on the material or very short time response of the material is equivalent to saying that I am doing the experiments at very large frequencies.

Student: (Refer Time: 11:28).

No strain this is that amplitude is there.

Student: (Refer Time: 11:39).

No no this is γ not to indicate it is constant not $\dot{\gamma}$. So, if at all we maintain strain rate then it will be $\dot{\gamma} \theta \phi$ equal to $\dot{\gamma}_0 \theta \phi$ I mean. So, naught we are just saying is a constant value it is an amplitude of the strain which is being imposed on the material and so given that we are imposing sinusoidal strain on the material the general stress response would also be a sinusoidal function, and in general that is will be a sin function most generally any function and it may or may not be in phase with the input.

For example, if we have a Hookean elastic solid then we know that if strain itself is a $\sin \omega t$ then stress also will be $\sin \omega t$ because wherever strain is maximum stress will be maximum.

So, for a Hookean solid we know that $\tau \theta \phi$ will be actually some amplitude and then $\sin \omega t$ itself because it has to be in phase with what about Newtonian fluid for Newtonian fluid. Newtonian fluid how will it be same yeah it proportional to strain rate right in case of Hookean solid stresses in phase with strain, but for a Newtonian fluid it is proportional to strain rate and strain rate from this is $\dot{\gamma} \theta \phi$ into $\omega \gamma \theta \phi$ naught $\cos \omega t$ right that is the strain rate. So, which is just a derivative and we again should remind ourselves that the transformation from going from strain to strain rate we are doing by simple time derivative because we are looking at linear response because we are looking at small deformation.

In general strain derivative partial derivative of strain is not strain rate only because we are working with small deformation we can do this transformation easily from strain to strain

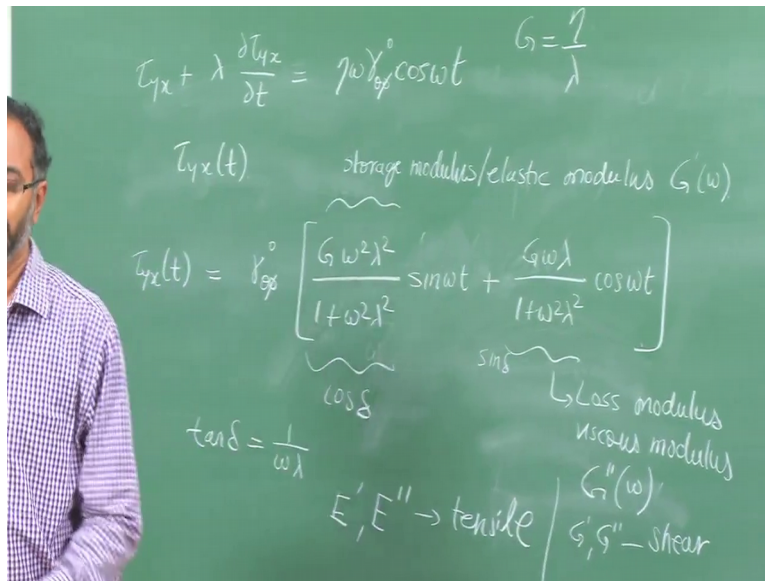
rate. So, this is the strain rate and then therefore, we would expect for a Newtonian fluid we would expect the stress to be some amplitude into $\cos \omega t$ right because stress is proportional to strain rate. So, therefore, we can see that for a Newtonian fluid strain and stress are completely out of phase. So, therefore, this that δ is $\pi/2$ while for Hookean solid the stress and strain rate strain and stress are in phase therefore, this δ is 0.

So, therefore, we have written general statement that for any linear response of the system in which way this is linear when I write these 2 together where is the assumption of linear being made when I yes small deformation. So, when I write this expression can you make out that it is linear response is it possible for you to see as soon as I say this is the strain response and if I write this is an expression for stress the only thing that we have said is most generally it could be any phase lag, but we are also saying that the response will be at the same frequency as that of input.

So, that is inherently only possible for small deformations only for linear systems the stimulating whatever frequency is being used to provide a stimulus the output is also at the same frequency, otherwise generally we will observe higher harmonics for a non-linear system response.

So, therefore, as soon as I have written this it is also assuming linear response within linear response this is a completely general expression. So, now, of course, this only says that the stress is expected to be also a sinusoidal function and if we were to solve this for Maxwell model then we need to substitute this in the Maxwell equation and then solve it.

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So, what we would need to do is just $\tau_{yx} + \lambda \frac{\partial \tau_{yx}}{\partial t} = \eta \dot{\gamma}_0 \cos \omega t$ right, because that is what is $\gamma_0 \dot{\theta} \cos \omega t$. So, this simple ordinary differential equation needs to be solved and we can then get τ_{yx} as a function of time which is this solution we are seeking ok.

So, generally what we do is the following we will solve for τ_{yx} and then based on those we will define material functions. So, let me first show what is the solution for Maxwell model and then we will come back and look at the solution. So, τ_{yx} if you were to solve this equation you can get it in terms of the pre factor which are $\gamma_0 \left[\frac{G \omega^2 \lambda^2}{1 + \omega^2 \lambda^2} \sin \omega t + G \omega \lambda \frac{1}{1 + \omega^2 \lambda^2} \cos \omega t \right]$. So, this is the overall solution according to Maxwell model.

Any generic visco elastic material will give this response, but according to this now there is a specific response and what is the phase lag is it why is it $\pi/2$ no it is not $\pi/2$ right the overall phase of τ_{yx} will depend on how significant these quantities are what this is saying is the overall stress response of the Maxwell model has some part which is in phase with the strain and some part, which is out of phase if let us say this term was 0, then we can say that it is completely in phase if this term was 0 then we can say it is completely out of phase.

So, by definition given that Maxwell model is a model of viscoelasticity we have a phase lag which is between 0 to $\pi/2$ and only at the 2 extremes of completely viscous response or completely elastic response it will go to 0 or $\pi/2$.

So, therefore, in fact, you can if you see there you can expand this right sin function as $\sin \omega t \cos \delta + \cos \omega t \sin \delta$. In fact, can you see that these are in fact, $\sin \delta$ and $\cos \delta$ right. So, this is $\cos \delta$ and this is $\sin \delta$. So, what is $\tan \delta = 1$ by $\omega \lambda$ right? So, that is $\tan \delta$ according to. So, that is the phase lag according to Maxwell model. So, the phase lag changes when you change the frequency of the material.

Now does it make sense that when frequency is very small what is δ when frequency is very small this is infinity? So, therefore, $\pi/2$ right when frequency is very small we are allowing material enough time to respond therefore, all relaxation processes can happen material will show dissipative response and viscous response. If we apply very high frequency we are not giving material enough time to respond because we are providing the mechanical stimulus very fast. So, then many relaxation processes will appear to be frozen and therefore, they will contribute elastically and therefore, material will be elastic or in other words phase lag will be 0.

So, that that is how the Maxwell model can actually show the responses which is both viscous and elastic depending on what is the frequency or depending on what is the relaxation time right. This is also another thing we have always been saying that you cannot isolation look at only the experimental time scale it is always with the comparison between experimental time scale and material time scale.

So, if the relaxation time of the material is already large to begin with then what happens is even at low frequency is itself I will have to go to very very low frequencies to see some viscous response. Otherwise I will automatically start seeing elastic response because λ is large $\tan \delta$ will already tend to 0, other way if λ is very small then I will have to go to very very high frequency to see any elastic contribution. Otherwise since λ is very small $\tan \delta$ will always be close to infinity or $\pi/2$ as the phase lag.

So, therefore, Maxwell model and these 2 terms actually contain what is the viscous and elastic response of the material. And so what we do is we choose to use these terms to define the 2 material functions. So, we say that the part of and you can see this is strain and this whole thing is stress. So, these factors are units of stress because the left hand side is stress.

So, therefore, this is analogous to a modulus stress is overall proportional to strain right of course, with the time dependent function because the strain itself is also time dependent function and therefore, we say that this is a storage modulus or elastic modulus and the quantity which is the second modulus what will it be if you have to guess what will be it is name viscous modulus or loss modulus it is called.

So, we some again storage versus loss elastic versus viscous, because if this modulus were to be 0 then we know we have a Hookean solid because stress and strain are completely in phase if this term is 0 elastic modulus is 0 then we have a viscous fluid. So, these are therefore, called the these are 2 new material functions that we have specified and we will indicate this as G' and this as G'' . So, most common reporting of rheological property this is in terms of G' G'' . Why are we using G are you saying what is this G or what is this G that G is η by λ right our Maxwell model parameter we can express in terms of η and λ or we can express it in terms of. So, that is the Maxwell model parameter.

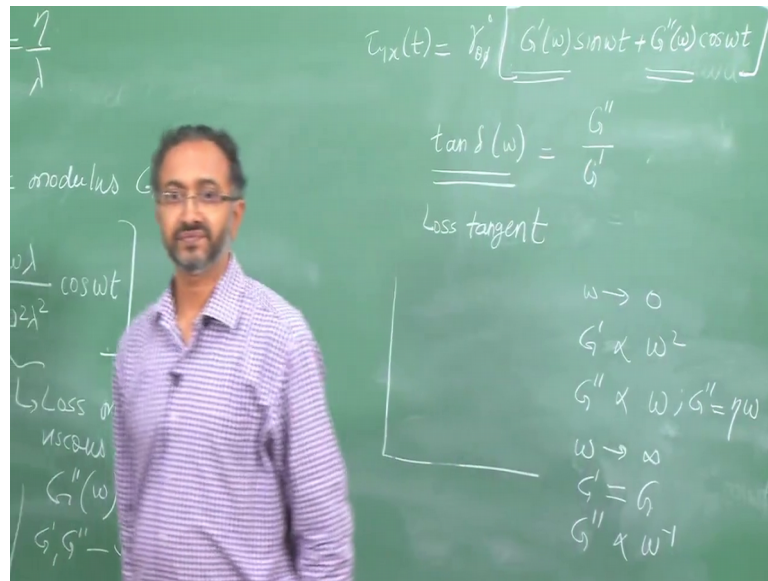
So, which one you please check what is dimensions on η viscosity is a Pascal second then dimension on λ is second. So, therefore, it is dimensions of Pascal it is modulus right. So, therefore, since it is dimension will be yeah we are using the symbol G to indicate that we are working with shear.

So, in fact, some experiments and especially for solid viscoelastic materials you can also do tension easily. So, then in that case many time they will refer to e' and e'' . So, this is a normally followed convention that E as a symbol is used for tensile mode of a deformation. So, we can take a rod and then you can do a tensile oscillator experiment.

So, then you will have an elastic modulus and again loss modulus or viscous modulus and we use G' and G'' for generally indicating shear. So, most of the times whenever materials are fluid like we would can do shear response and these are again material functions because it is functions are frequency. So, given that we have storage and loss modulus for a material we can find out what is it is overall viscoelastic response, because in the end what we have done is we have for the governing equation of viscoelasticity we have substituted what is the mechanical stimulus and then solved and got this response.

So, this G' and G'' contain information about what is the module like.

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So, in general we can write τ_{yx} as $\gamma_{By} [G'(\omega) \sin \omega t + G''(\omega) \cos \omega t]$ which is the function of $\omega \sin \omega t$ plus $G''(\omega) \cos \omega t$. And we also define one more material function which is given as $G''(\omega) / G'(\omega)$, which is either called loss tangent or $\tan \delta$. So, sometimes it is referred to as loss tangent or just $\tan \delta$ itself. So, these are the 3 material functions.

So, naturally when I am looking at a new material system and when I do shear experiment in cone and plate by applying sinusoidal deformation I can obtain these 3 material functions and then I will need to figure out how is the response compared to what I expected. So, for a Maxwell if I find a material meets is very similar to Maxwell model then I will get a response which is exactly given by these and if you look at the overall response it is always helpful as I have been saying an rheological.

So, it is look at terminal response. So, let us first look at terminal what if frequency is very small. So, what is the response? So, if frequency is very small then what is G' it is a I mean when frequency is very small yes the, but will rather than just saying 0 what you can see is a frequency is small then compared to one and this one can be taken and the you can ignore this.

So, therefore, G' is proportional to ω^2 right that is a terminal response. So, as viscosity tends to 0 you would see that G' and ω relationship will be a power

law and what about G'' it will be proportional to ω right because again you can ignore.

Now, if you go to the higher frequency on the other hand then what happens to G' if ω is very large then you can ignore one and therefore, G' becomes constant and G'' is inversely proportional to ω right. So, this is the terminal response does it make sense from what we discussed in terms of fluid like and solid like response do any of these make sense to you saying that we are said that if I do very high frequency then I am perturbing the material very fast and therefore, I will see elastic contributions and largely material will behave elastically.

So, for therefore, I would expect that elastic modulus to be a constant and under those conditions whatever little loss is there it is going to be inversely proportional to ω , what happens is true many elastic materials like steel we ignore this part because it is not very relevant and it is very also very small. So, for all practical applications we say that we will ignore this.

Similarly, what about this does it make sense any of these at low frequencies we are giving material enough time. So, that all the viscous contribution is there all the relaxation processes can take place purely dissipative response. So, does it make sense that G'' is proportional to ω , what is G'' if you just look at this it is $\eta \omega$ right. In fact, if you write the expression it is $\eta \omega$ yes of course, because they are functions of frequency only the idea of varying ω is because we would like to explore the viscoelasticity of the material when you keep ω constant then you are saying that only that frequency of interest.

So, generally we vary ω to do the experiment for example, when we are doing steady shear experiment we vary the strain rate right and therefore, viscosity is function of strain rate. So, in this case what we vary is frequency and in general let us say we are developing a gel for cold cream applications. So, then we would like to know how would it response at low frequencies because that is when it will be in the bottle or when I take out on the hand it will remain almost stationary. So, with we it will little shear how does it respond, but then when I start spreading it or rubbing it then it is very short time scales. So, which means high frequency? So, in general it is a good idea for me to put the material in rheometer and then look at the whole frequency range as possible.

So, we can do the strain rate also, but it is only a steady test and we saw that whenever we do a steady test we cannot get overall idea about viscoelasticity in the material it gives us only partial information, because we are only looking at the steady state the structure of the material and therefore, it is only steady state response by doing oscillatory shear we are. In fact, saying that we will impose a time dependent deformation and therefore, look at time dependent response of the material.

So, does this make sense that G'' is $\eta \omega$. So, what we will be able to visualise is.