Rheology of Complex Materials
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Lecture - 18
Linear viscoelastic materials

So, this relative ratio of the time scale of interest and the material relaxation time is called Deborah number and. So, we quantify the material response time using this relaxation time and of course, we always have a time scale of interest, which could depend on an engineering application, it could depend on what is the a material we are studying and so on. For example, for a structural application we are looking at 30 or 50 years of lifetime and so that is the time scale of interest. Sometimes when we are processing something let us say injection moulding of polymer objects like a plastic let us say an optical disk or a CD or a DVD, then in those cases we are looking at extremely fast production rates and some time scales we are interested in are milliseconds and so on.

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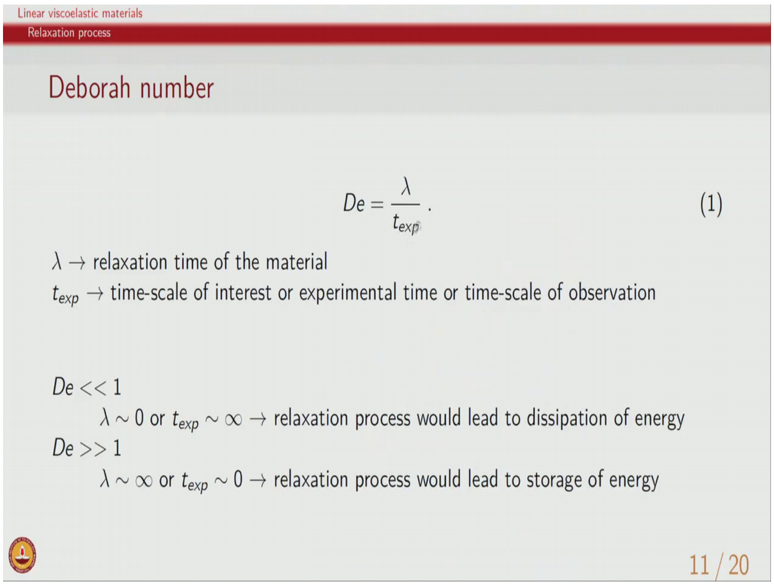

So, therefore, timescales of engineering application vary and so, that is why that is something that varies and so, there will the ratio of these two can tell us what may be the material response, And for example, if Deborah number is less than 1 which implies that relaxation time is close to 0 or the experimental time scale or time scale of interest is very large geological time scale, then in that case definitely relaxation process would lead to dissipation of energy.

So, either of the two, either the relaxation times are very small or our length time scales of interest is very large. And opposite is true if Deborah number is very large, that would be the case when either the relaxation process is very very slow, the relaxation times are very large or our time scale of interest is very small. So, in that case we would see that the relaxation process would actually lead to storage of energy ok.

So, in this case the what we saw earlier the deformation of atoms can lead to dissipation only if defect also move, otherwise it will not lead. But if we wait millions of years then certainly at the those rate defects will move and therefore, we will have dissipation.

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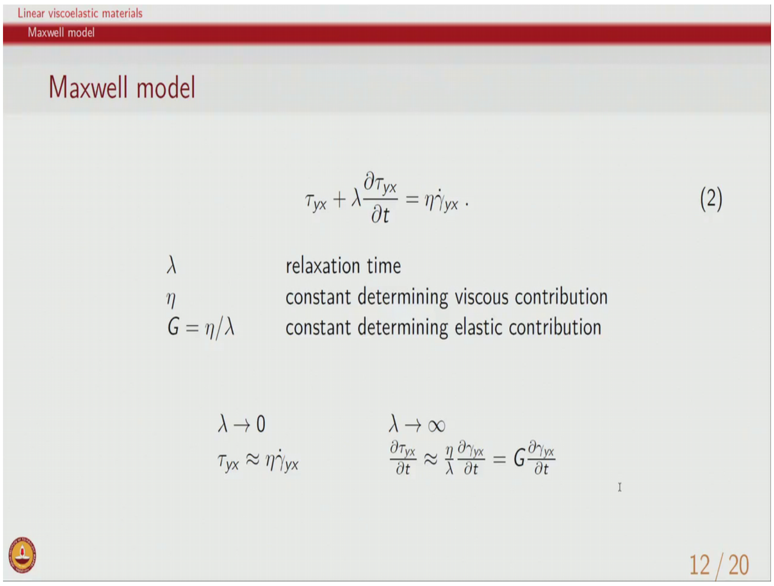

So, just two now look at the overall aspect quantitatively we will look at Maxwell model and Maxwell model is basically given by the stress being related to stress rate and strain rate.

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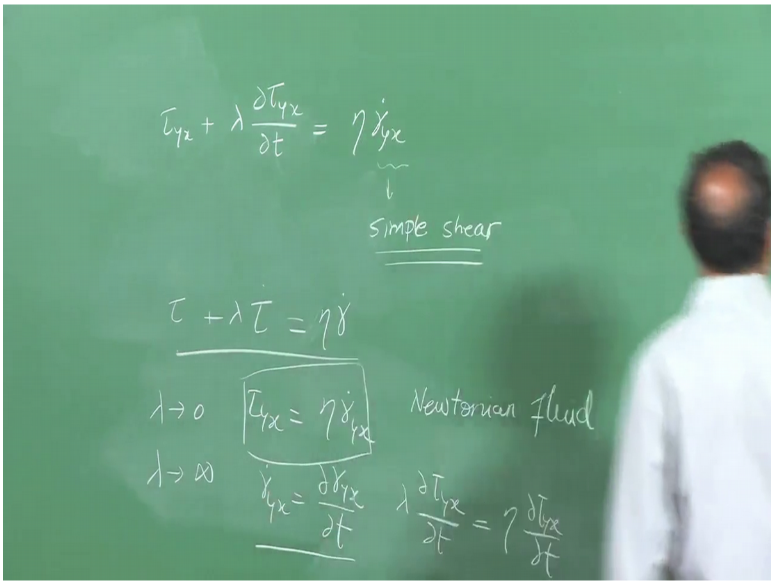

So, that is what I meant when we said viscoelasticity, we will have different variables which may be interrelated to each other. We are using this subscript just to imply that we are using simple shear as our mode of deformation and we are looking at only one component of stress, and one component of strain rate. We know overall that in a material there are 9 components and given that stress is symmetric there are 6 components and similarly 6 components of strain rate also. So, to completely specify the state of the system, we will need to solve for all of these, but given that we are subjecting the material to only simple shear, we only have these other relevant ones.

So, therefore, we will continue to use these subscripts even though many times people will try to describe these things just as a model like this right you could use this also to describe a Maxwell model. But we are just making sure that we will always remind ourselves that we are looking at a specific situation, and this is the statement of Maxwell model which is valid for simple shear. In general the overall Maxwell model which is valid for three dimensions, we will write down later on and you can see that if lambda is 0 then tau y x is nothing, but e t a gamma dot y x.

So, that is nothing, but Newtonian fluid. And similarly when lambda is very large what we have is this term and this term this term dominates over this term and so, only these two terms are present and this can be visualized as gamma dot y x is nothing, but del gamma y x by del t. And again we have already said this multiple times before that this is valid only when deformations are small right. In general rate of strain is not same as strain rate tensor right we will need to find the convicted rates of strain to get strain rate, but given that deformations is small and we are going to only look at linear viscoelasticity for now this relationship is fine.

So, therefore, we have lambda del tau y x by del t is same as eta del tau y x by del t. And since the two derivatives are related to each other for any arbitrary amount of time, we have basically the tau y x itself equal to e t a by lambda gamma y x.

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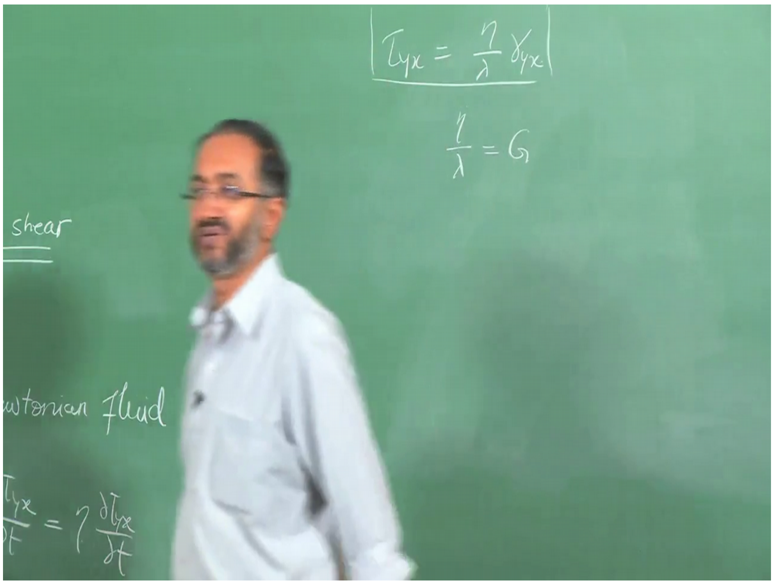

So, which is nothing, but an elastic that stress is proportional to strain and. So, this is the other parameter which we use to characterize the Maxwell model. So, Maxwell model is a two parameter model, lambda and eta or lambda and g and lambda is the relaxation time. So, we have already seen that when relaxation is 0, relaxation time is 0, material behaves like Maxwell model reduces to viscous fluid. When relaxation time is large it behaves like an elastic solid. So, it combines both viscous and elastic responses phenomenologicaly. It says that this is the relationship for fluid, it says this is the relationship for elastic solid, let me combine the two and therefore, I will get viscoelastic response.

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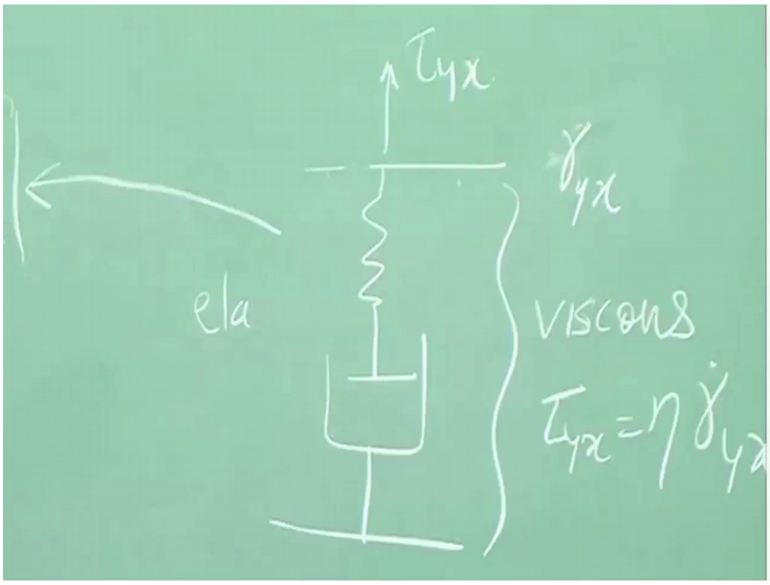

Many times mechanical analogues are used to describe the viscoelastic models, these serves as representations of how viscous an elastic response is combined in a given model. For example, Maxwell model is a series combination of spring which represents elastic response and a dashpot, which represents viscous response. These analogues are also useful to understand how to arrive at different terms of a given model. Just the way a complex circuit the electric circuit can be simplified by realizing current or voltage going through different resistances and capacitances, we can simplify mechanical analogues by analyzing how stress and strain are subjected to in these different springs and dashpots.

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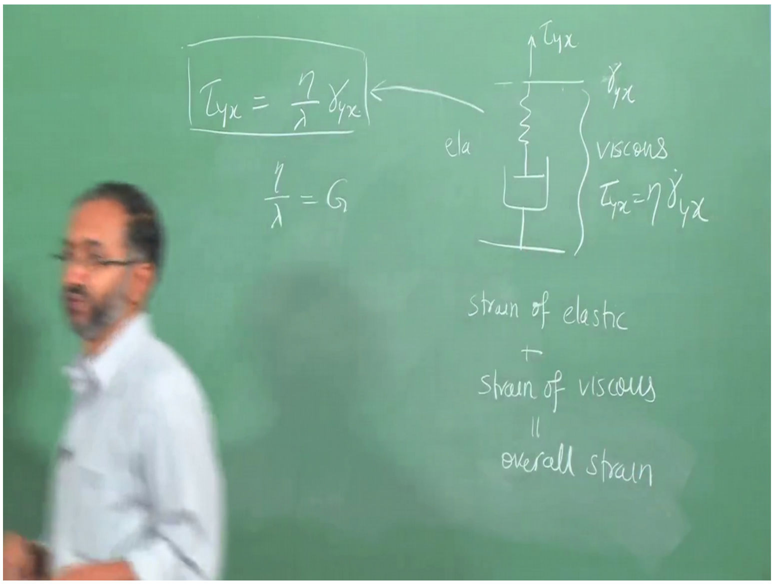

What you will see is strain of elastic element plus strain of viscous element is the overall strain and this if you put together then you have the Maxwell model of visco elasticity.

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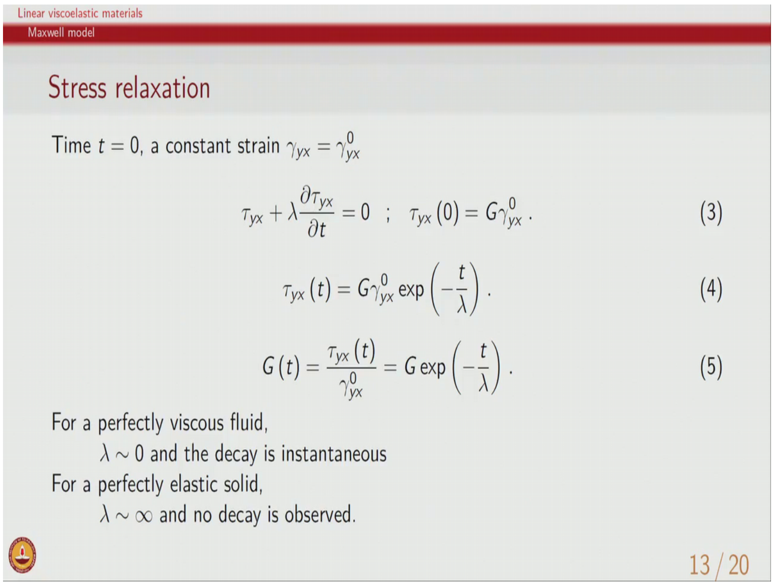

So, now let us define another mode of mechanical deformation which we will call stress relaxation. So, stress relaxation is an experiment in which we apply a constant strain on the material.

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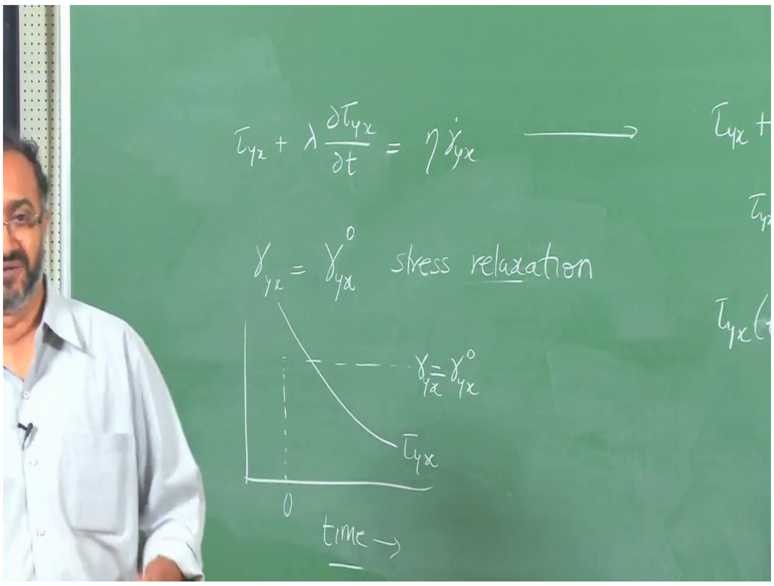

So, we apply gamma y x a constant strain and by this superscript 0 we indicate that its a constant value, it does not change as a function of time and. So, this is called the stress relaxation experiment.

So, what we have is we take a material and at time t is equal to 0, we basically apply a strain which is constant. And this is what we have discussed already in the previous class that when we apply a constant strain what happens to an elastic or a viscous material. Now we can try to understand what happens to a viscoelastic material by just looking at the response of Maxwell model itself and since gamma y x is constant the governing equation for Maxwell model will be lambda delta y x by del t is 0 right.

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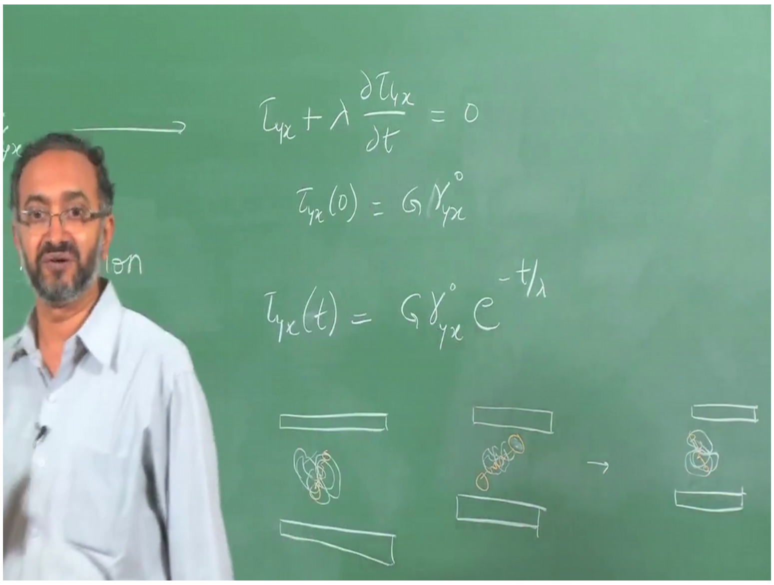

So, it is an ordinary differential equation and the solution of this is an exponential. And the initial condition we can write that at time t is equal to 0 stress response is completely elastic. So, whatever deformation that is put and the g which is a parameter which describes the elastic response of a Maxwell model, that is the amount of stress which is required in the initial at time t is equal to 0. And with time because of the solution of this what we find is with time the stress decays.

There is a stress decay in the material and therefore, what you would see is stress goes down, and this is called a stress relaxation phenomenon. So, the amount of stress that is required to hold the material in the new deformed state decreases as a function of time and the rate at which this happens is characterized by lambda. If lambda is 0 then this will be 0 right stress will be immediately 0 if lambda is very large then basically you have this quantity becoming 1and therefore, then its an elastic response.

So, Maxwell responds clearly of course, has both the terminal responses, the reverse can also be done by changing the time scale at which I do the stress relaxation experiment. I can the stress relaxation experiment for a millisecond, then for many materials I will observe that all the energy is stored and nothing is relaxed or I can do the stress relaxation experiment for years, then I will see that many solid like object which appear to be solid like seem to actually relax stress, and there is some plastic or other contributions which lead to energy dissipation the material.

Student: There is some something called yielding.

Yielding yeah. So, the in case of crystalline solids, yielding is the threshold of deformation beyond which the plastic deformation the mechanisms, which leads to plastic de deformation take place, but what we are talking about here is the deformation is still small, but since we are waiting long enough.

Student: Yes.

That can happen. So, the processes which may happen during yield at normal rates may happen over years at small deformation. So, let us say if 4 percent is the strain beyond which plastic deformation happens, if I deform the material to 2 percent, I would expect no nothing to happen right its elastic. But if I wait years and years then with the grain boundary and grain boundary deformations and all that those things which happen during plastic deformation will happen over much longer periods.

So, that is why then material will relax at very long timescales and so, that is what is summarized here that when lambda is 0 for a perfectly viscous fluid the decay is instantaneous, which means stress is relaxed away immediately instantaneous dissipation for a perfectly elastic solid no decay is observed and. So, this is what is the stress response, for a constant step input of strain increase we have stress basically decreasing exponentially and we can sort of think of this in terms of macromolecule right because it is always helpful for us to think in terms of microstructure molecular mechanism, such that is one of the important things for rheology.

So, let us say if we have a solution of polymer molecule and then now we are applying a strain on it right. So, what do we mean by stress relaxation. So, if its only water molecules then what happens is instantaneous decay, but now because we have a macro molecule which has other relaxation process is possible which means these segments can move the overall molecule can also move. So, what we have is.

So, if I apply this a small deformation, this molecule will get extended at instantaneously right. So, the spring and dashpot that we had visualized earlier, it will be longer as opposed to. So, it suddenly got stretched, but over time what happens is since the segments since there are fluctuations present in the material, and molecular flexibility segmental flexibility is there this particular molecule in the new state which is the deform state will again occupy the same spherical conformation. So, which means it will come back to same length of course, its orientation may also continuously keeps on fluctuating.

So, that is why this what we can say is the macro molecule is able to relax, through segmental relaxation and other modes which are present. So, the macro molecule is undergoing mechanical relaxation, because of its segments can move there is bond rotation around the macro molecular chain and because of these things this molecule which got stretched at 0 time, is able to come back to equilibrium state. So, now, a new equilibrium stress Free State is again obtained yeah.

Student: We call it equilibrium state or steady state.

In this case it is an equilibrium state right.

Student: (Refer Time: 15:50) some fragment may fluctuate.

No if fluctuation does not imply non equilibrium right water a jar of water with its random molecules fluctuating is not a non equilibrium state, the fluctuations at molecular scale. In fact, are no indication of its non equilibrium nature right with those fluctuations material is at equilibrium only at molecular scale fluctuations are there. On the average when you look at average velocity is not present, there is no temperature your non uniformity, there is no pressure non uniformity and so on.

So, any macroscopic variable there are no gradients or they are not changing as a function of time. But if you look at individual molecule or individual bond they are always fluctuating, only a temperature 0 all these fluctuations will die away right.

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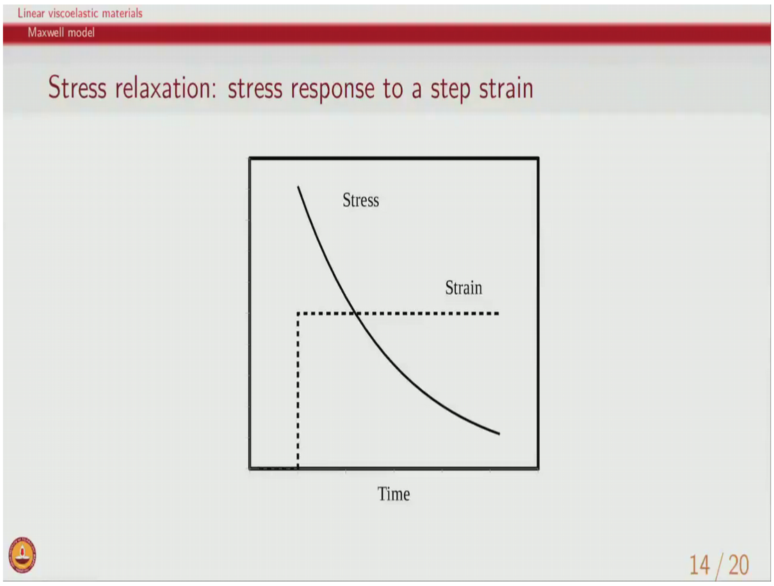

So, therefore, fluctuations do not imply non equilibrium state, because fluctuations whenever we say we are talking molecular scale phenomenon. So, to define equilibrium what we should do is, find average of those fluctuations.

Student: (Refer Time: 16:57).

Right because if we are applying a constant stress the fluid will continue to keep on the molecules will continue to see the molecules in a fluid in a gas or a liquid, are not really in energy minimum state right they are fluctuating thermal energy sufficient for molecules to move about. So, therefore, when you apply a force and a stress molecule can continue to move.

Student: If we remove the (Refer Time: 17:26) then it will come.

Then it will come to a halt yeah equilibrium again, which is a new equilibrium state and the only fine point which we have not specified, but it is important to mention is that in the process there was some mechanical energy which was input into the system, and that has dissipated. So, the temperature between this and this will be slightly different, and that is what if we keep on stirring for a long time then the fluid temperature will of course, go up right.

So, the mechanical energy has been converted to the internal energy thermal energy. So, the average temperature may go up, but many of the cases when we are doing these flows we are either controlling the temperature or the amount of viscous dissipation may be minimal. So, therefore, we are just saying that this is an equilibrium state and this is also an equilibrium state, it may not be exactly the identical equilibrium state there may be a small difference in both the equilibrium states.

But they are both equilibrium states because in this condition also average velocity is 0, there are no temperature gradients, there are no pressure gradients, everything while when you apply a constant stress there is a velocity gradient in the system and therefore, that is a non equilibrium situation. So, any time either temperature gradient is their, velocity gradient is their, concentration gradient is there these are all non equilibrium transport phenomena yeah.

Student: Sir the flexibility story of compressible fluid will be different or will be remain same.

Come what is that.

Student: Compressible fluid various case of (Refer Time: 19:03).

And un non compressible fluids as far as viscous flow and dissipation is concerned are similar, in that case only thing is the pressure is also another variable. In our case we are never discussing pressure as. So, I am only saying temperature will be different in two cases right, but incompressible flow pressure is also another variable, but from a molecular standpoint from the point of view of relaxation processes, incompressible and compressible fluids will have similar features, they will have viscoelast viscous response only dissipative responds only. So, the at time t is equal to 0 is this stress that we talked about right.

So, therefore, any viscoelastic material initially will show an elastic response. So, if let us say I do the same experiment and observe it for a microsecond, then I will see only response like this, and then I will say oh macromolecular solution is almost elastic. But if

I do the same experiment over seconds or minutes, then I will say that all the disappe energy is all dissipated the molecule actually got t form, but it came back to equilibrium state and therefore, it dissipated the energy away. So, therefore, by doing stress relaxation experiment I can probe what is the relaxation process present in the material, I can do my stress relaxation experiment at different for different times and characterize this lambda and quite often what will happen is I will have.

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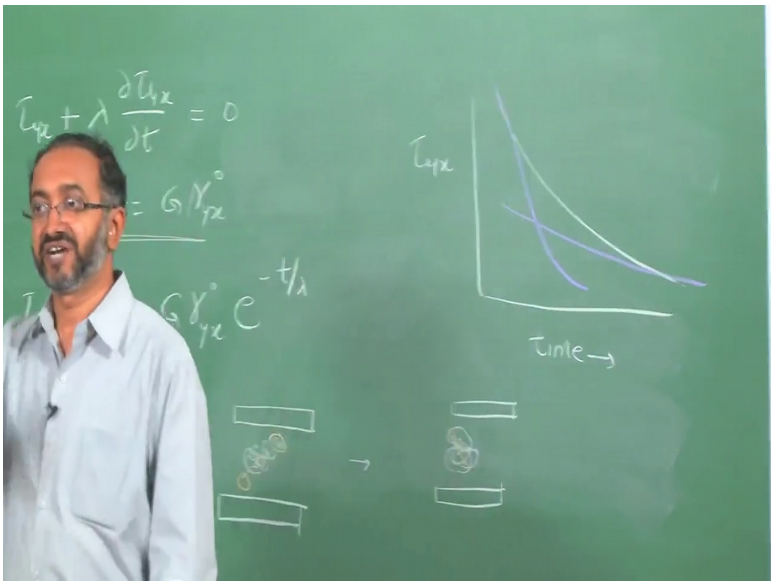

the overall stress relaxation like this, and this may not be it may not be possible to fit to a one relaxation time, one exponential process. If I try to fit let say exponential curve to this it may happen that I will get a fit like this or I will get a fit like this right if I try to fit exponential curve.

So, what does this imply, what would this imply if i. So, in the graph here I am showing is a nice exponential, this is actually an exponential decay, but let us say if the experimental data was like this, the way I am showing or experimental data then you would not be able to fit one particular exponential to it. So, what does that imply? Based on Maxwell model each and every relaxation process which is characterized by one relaxation time should give us exponential decay, but combinations of exponential can be actually.

So, therefore, I can try to fit multiple exponentials, and then I will say that oh looks like the material that I am studying has. In fact, multiple relaxation processes and if I assume then I have to look at of course, the material makeup I will have to make a hypothesis of what might be the relaxation processes, and I will know that over there are some bond level or segment level phenomena. So, that will be less time scale then let us say if it is an entangled polymer melt the way we discussed polymer molecules are entangled. So, therefore, they will be very very slow relaxation processes. So, then I can clearly see by studying stress relaxation I can try to see what are the relaxation times or relaxation modes which are present in the material and we should remember that all of this we are doing at constant strain and also strain value which is small.

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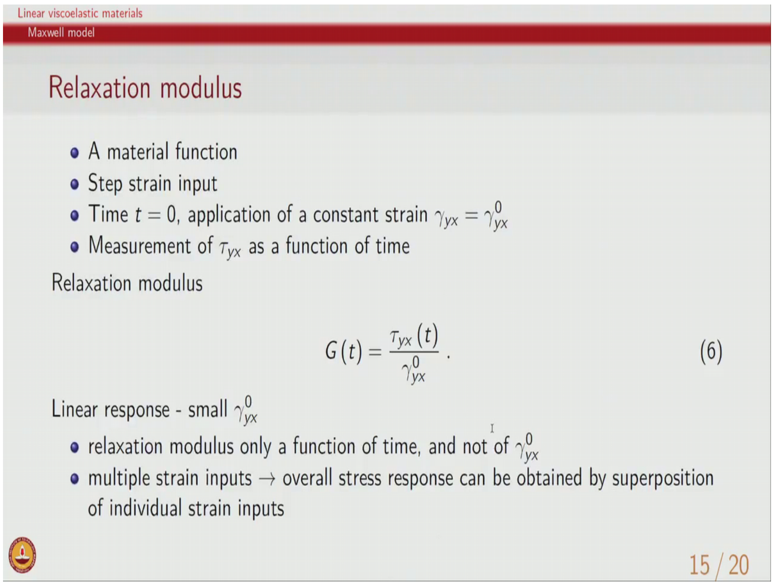

So to do this quantification effectively what we do is we define material function called relaxation modulus.

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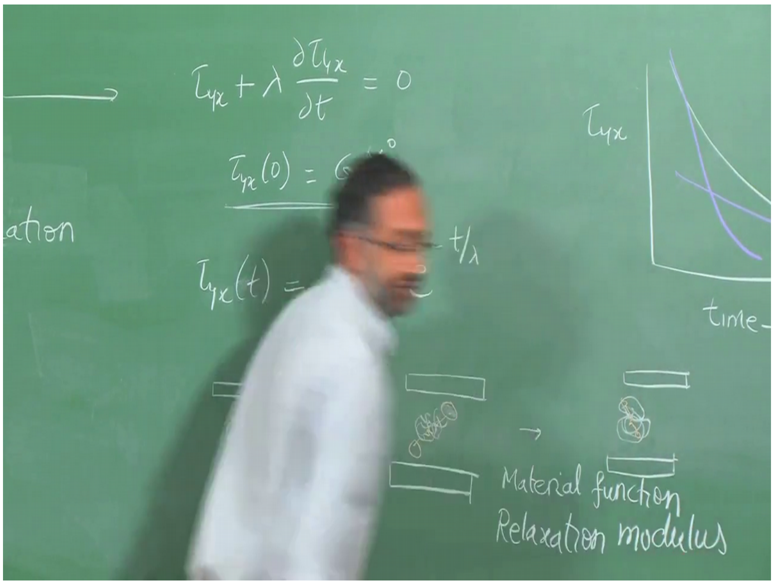

So, which is defined here. So, the this is a material function which is done when a step strain input is given or step strain perturbation is given to a material, at time t equal to 0 a constant strain is applied and stress is measured. We will we should remind ourselves that of course, how this measurement is done will depend on with geometry right and so on. And then the relaxation modulus is defined as G of t stress divided by gamma.

So, in this case therefore, we are not evaluating one constant right the whole curve itself is an indication of the material response. If I get an exponential curve right away I know this is good, this material has one relaxation process and I can also say what is its relaxation time. But in general most common materials we will find will not be able to fit one exponential, and then it is our job to try to find out what is the meaning of multiple relaxation processes that are there in the material and.

So, all of this is of course, also very important in terms of the amount of deformation, the stress relaxation modulus right which we wrote we can write here is G of t is equal to G e to the power minus t by lambda.

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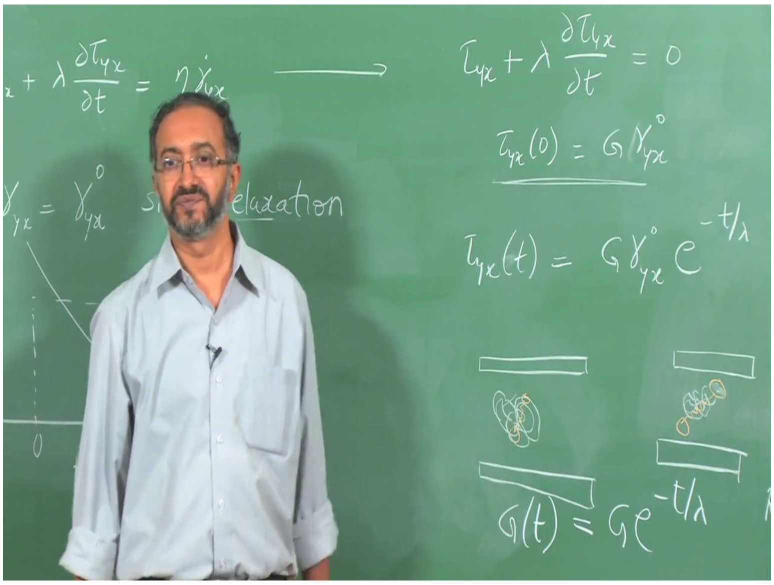

So, it is independent of the strain amplitude right. So, whether I apply one person in 1 percent strain or 0.5 percent strain, does not affect the relaxation modulus. So, I am characterizing the material response using a linear regime, and that is where I said earlier that the overall equilibrium structure of the material is sufficient to describe the phenomenon. So, if I apply 0.5 percent or one percent strain, both the cases the responses can be captured using this relaxation modulus. We will see that for non-linear viscoelasticity G will be a function of time, and the strain amplitude that was applied on the material.

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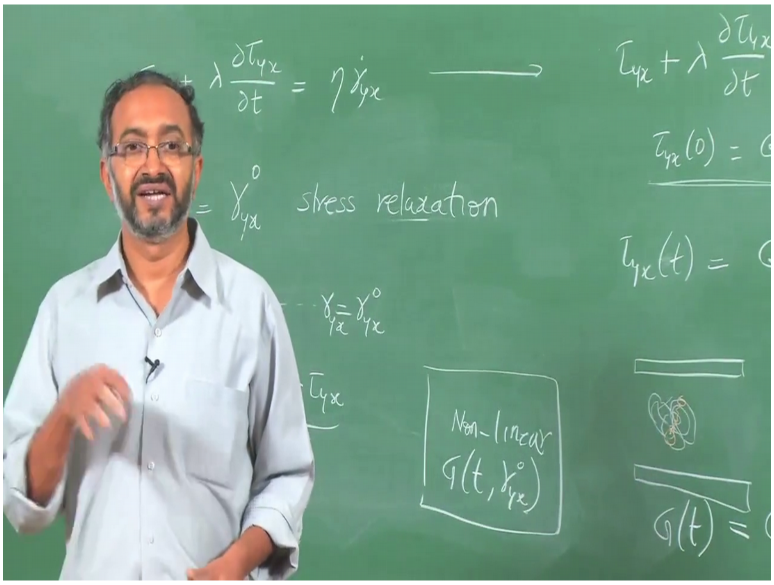

Because we are taking the material far away from equilibrium its new structure is also relevant in determining, how far away from equilibrium you have taken and. So, the relaxation modulus itself will be a function of strain amplitude itself.

So we are only looking at linear amplitude and therefore, G of t is not a function of gamma y x. Secondly, just the way I can think of overall stress response as combinations of several, I can also do experiments where I put one strain, and after some time I put another strain. And I should be able to actually get the overall response by just summing.

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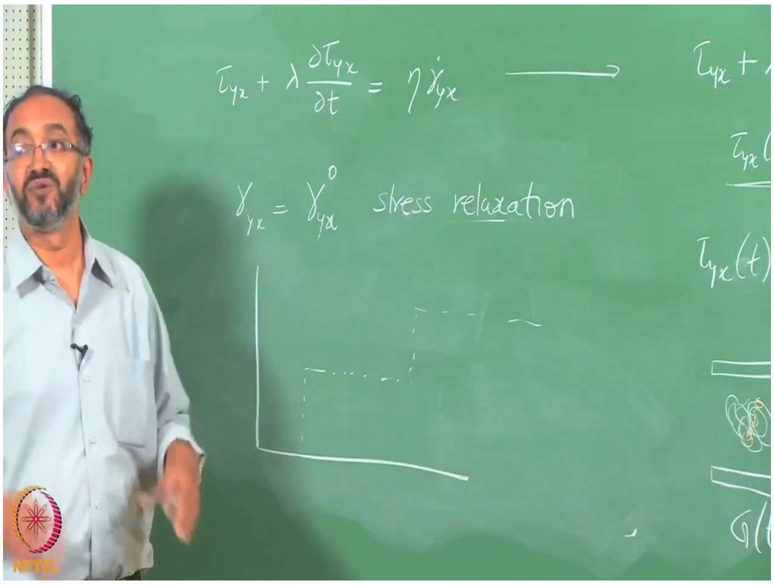

So, instead of doing this experiment now let me see if I can do this experiment, one strain and then I put another strain. So, I can individually do a solution for this, then I can do a solution for this and I can add both of them together, to give me what is the overall stress response. So, this is called superposition right which is again possible only because the material function is independent of the strain amplitude. The stress of course, depends on strain amplitude, but it is a scaled output, if I double the strain amplitude the overall stress also everything gets doubled and.

So, therefore, the relaxation modulus is independent of that strain amplitude, but in non-linear regime we will see that that will not be the case, the stress will not be directly related to the strain in a linear way right. So, there will be a non-linear response.

Student: (Refer Time: 27:44) remain same or.

Where.

Student: The superposition.

Yeah. So, the overall what we can do is, we can I can do two experiments, I can do one experiment where I just apply this and beyond a certain time I can do another experiment where I just applied this, and I can say that the overall response will be summation of this plus summation of this.

Student: I am asking about stress, stress will remain same we are applying same stress or.

No if you apply strain then you measure stress right you do not you cannot control both of them at the same time. See when I apply on an elastic solid, I apply a constant strain I cannot again apply some stress right stress will be determined based on the material. I cannot independently control both of them because both of them are related to each other through a proportionality constant do you follow.

Student: Yes yes.

So, therefore, both of them are not independently controlled, in this case strain is the one which is controlled and stress is what is being measured. So, what we are saying is the overall stress response can be a linear combination of responses to individual strains, and that is only possible because of small deformations and. So, maybe we will stop here, beyond this we will do in the next class.