Rheology of Complex Materials

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

Lecture - 17
Linear viscoelastic materials

So, in the last class we discussed about the viscous response of materials. One of the first things we pointed out was the fact that whether the behaviour is viscous or viscoelastic may in fact depend on our interest. So, the same material may be treated as viscous or viscoelastic depending on the problem at hand.

So, with that in our background, in our thoughts we will now today look at the viscoelastic materials and more specifically we will only look at viscoelasticity at small deformations. As we will see later on, whenever there are small deformations the material is taken only slightly away from equilibrium and therefore, the structure at equilibrium is a good indication in terms of how the material may respond. But if you deform the material to a large extent then it gets taken away much more from equilibrium and then the structure at equilibrium is no longer relevant to describe the properties of the material.

So, therefore, we have to look at material behaviour in these two different regimes, one is the linear regime where deformation is small and then the non-linear regime. In the context of solids mechanics of solids we use Hooke's law and we know that it is valid for small deformations beyond small deformations there is plasticity and other phenomena which take place. And clearly the way crystals deform in case of elastic deformation and plastic deformation are different. So, same we can expect in terms of colloidal systems or a macro molecular system. That small deformation the overall structure the way it responds to shearing or extension will be different when we subject the same material to very large deformations.

So, the overall outline that we will follow for this discussion is we will first look at the overall format that we have been using to discuss different materials and their response, and then we will look at the idea of relaxation process.

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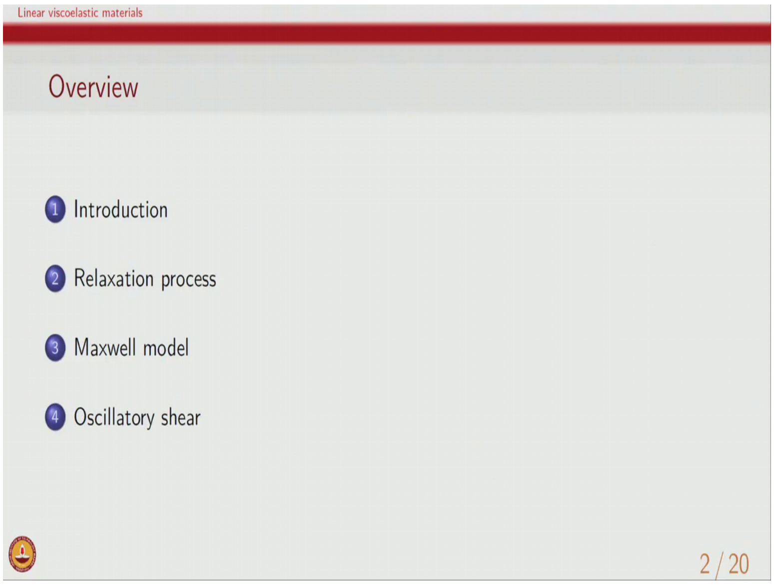

This is fairly fundamental to whatever we will discuss in terms of linear and non-linear viscoelasticity. Then we will look at a simple model which is used as a primitive model to describe some elemental viscoelastic behaviour and then we will finish up by looking at oscillatory response. Earlier when we were discussing viscous materials we looked at steady response. So, we looked at steady shear and steady extension and so clearly we were looking for a material apply a constant strain rate and wait for constant stress to reach. We will see that that is not the only way to examine materials we will define two such different probes or ways to examine the materials.

So, let us just summarize how we are looking at. We are basically looking at 3 things simultaneously the response of material, the quantification of it using material functions and of course, side by side a model which will be helpful in terms of understanding. So, we look at the material response in terms of different classes. We have already finished looking at viscous we are now going to today look at viscoelastic and in the future we will look at some other classes also. Within viscoelastic we have already specified that we will be looking at two distinct classes, the linear viscoelastic as well as non-linear viscoelastic.

The next is to look at it quantitatively because the class of material only qualitatively describes, what is the expected behaviour? But when we are looking at rheology of a particular material we ought to be able to quantitatively say how this material behaves.

For example, in case of Newtonian fluid viscosity quantifies everything because qualitatively the behaviour is same regardless of what Newtonian fluid we are following, but the Reynolds number among the various other thing is defined by viscosity. So, therefore, viscosity is a key property of the material which needs to be specified to get anything quantitative.

Similarly we need to specify material functions which are quantitative and these material function are measured under controlled conditions. So, as we saw steady shear viscosity was measured when constant strain rate was applied and steady value of stress was measured.

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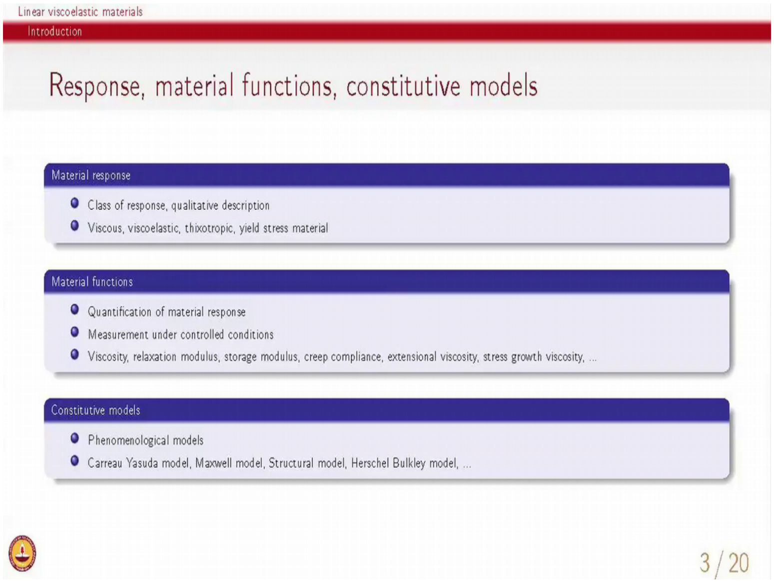

So, therefore, measurements are done under controlled conditions and we define things like viscosity, in today's class and the next class we will define relaxation modulus storage modulus and further down in the course we will define creep compliance, stress growth viscosity. So, several such quantification functions are there which then we can use to contrast materials and understand their behaviour more closely. And the other thing we need to make sense of all of this is few simple models. Because models again give us a quantitative response and model also through mathematical expressions capture what is the phenomenology. So, therefore, by using models along with this discussion hopefully we will be able to have a comprehensive understanding of viscoelastic response of materials.

And this is what we did for viscous materials also. We looked at the overall response in terms of shear thinning or shear thickening. We then looked at steady shear and steady extensional as the two probes and steady shear viscosity and steady extensional viscosity as to material functions and then we looked at Carreau-Yasuda as one of the models which can capture some of the features which are described by many of the material systems.

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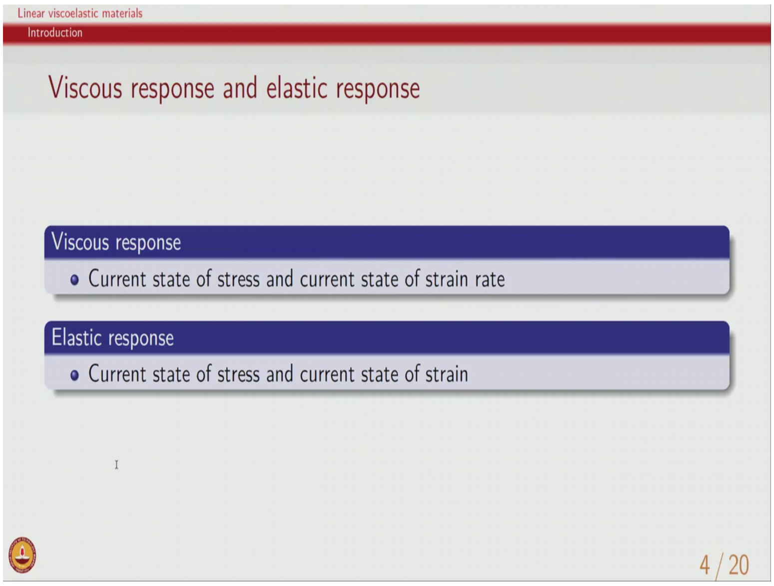

So, now let us look at and paraphrase again what is viscous and elastic response. In viscous response we said that the current state of stress and current state of strain rate are only relevant. The past strain rate past strain none of that is relevant. Similarly for elastic response the current state of stress and current state of strain are relevant. If I specify the current state of strain I can specify the current state of stress and this includes linear elastic as well as non-linear elastic. Similarly this includes linear viscous Newtonian fluid and non-linear viscous Carreau-Yasuda model.

So, all the features are included in this by only saying that the current state of stress is related to current state of strain rate or current state of stress is related to current rate of strain. So, this is one way of understanding viscous and elastic response.

The other way of course, is the fact that viscous response is dissipative in terms of energy dissipating, whatever mechanical energy is being input in terms of a mechanical stimulus the energy gets dissipated while in case of elasticity it gets stored. And that is true even for a material like rubber which is a non-linear elastic material, it still stores all the energy and when we leave it, it comes back. So, therefore, it is a non-linear elastic material and Carreau-Yasuda is a non-linear viscous model which means that the rate of dissipation depends on also the strain rate because otherwise rate of dissipation is stress into strain rate, but given that stress itself depends on strain rate right because it is a non-linear relationship we find that the viscous dissipation will depend will be different for a Carreau-Yasuda fluid as opposed to a Newtonian fluid. But the fact still remains is that it is only all the energy is getting dissipated in case of a viscous fluid.

Now, when we have a viscoelastic response we will have combinations of both which means we will have both dissipative and storage response. We will also have not only current state relevant, but maybe past state relevant in other words we also might have not just stress and strain and strain rate we might have all the other derivatives of these quantities. So, many variables may be of interest in terms of specifying the state of the material system.

So, therefore, in terms of formulation we may see that the current states of stress strain strain rate, rate of strain rate, rate of stress and all such rate quantities may be involved in terms of specifying and by this what we mean is if I just specify the strain of the material I may not be able to specify it stress unless I specify also rate of stress. So, that is one model then that is one type of material response. So, similarly there will be various such combinations possible.

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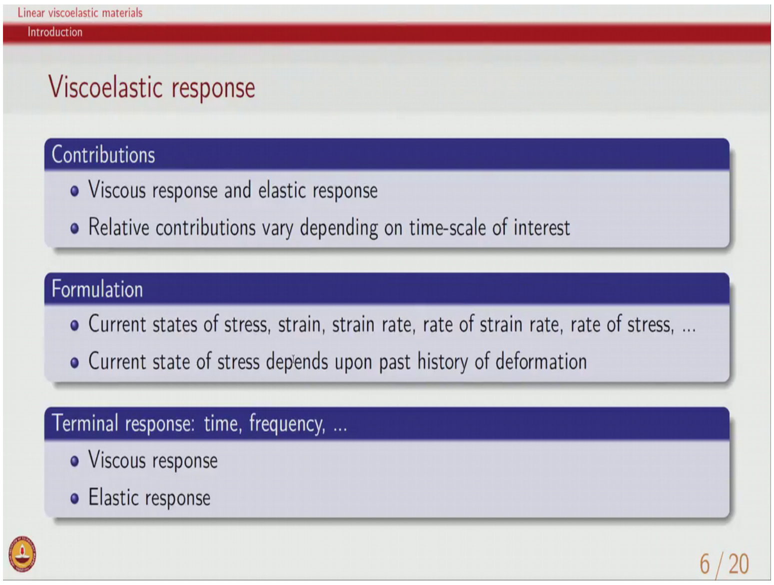

Similarly the current state of stress may depend on what the material underwent in the past. So, there is because of causality in something that is going to happen in the future cannot determine the current state of stress, but certainly whatever has happened in the past will certainly be influential in determining the current state of stress.

So, this is also another feature of viscoelastic materials that we will see. Of course, what we will expect I do not know whether you can think of this that, the more distant past may not be as relevant as the near past. So, if the material has undergone deformation in the recent past that deformation history we will find is far more important compared to some deformation which was much more time in distant in the past. So, you think about why this may be the case and we will come to this point little further in the lecture.

And naturally because it is a combination of both viscous and elastic response it will be helpful for always for us to try to see the terminal response, by terminal we mean can we look at very short timescale, very large timescale, very small frequency, very high frequency. So, terminal response in the sense that does this material which is viscoelastic under some condition show maybe viscous response or maybe elastic response. So, this is one useful check to always look at and understand what are the mechanisms for viscoelasticity because under some condition we should be able to get completely viscous response or elastic response depending on the material.

And if let us say the terminal response is absent for example, in a cross linked rubber we will find that the viscous response is absent a solid rubber will never flow like a fluid right. So, clearly then we know something is there at the molecular level which prevents this polymeric material from behaving like a fluid. On the other hand some other polymer material which appears solid like, but over long term it will actually show flow like behaviour. So, clearly there is a distinguishing feature and in this case it is called cross linked. So, rubbers are cross link material that prevents any viscous terminal response in them while other plastic materials may show terminal flow like behaviour. So, therefore, it is always helpful to check whether under some conditions can we observe either viscous or elastic response.

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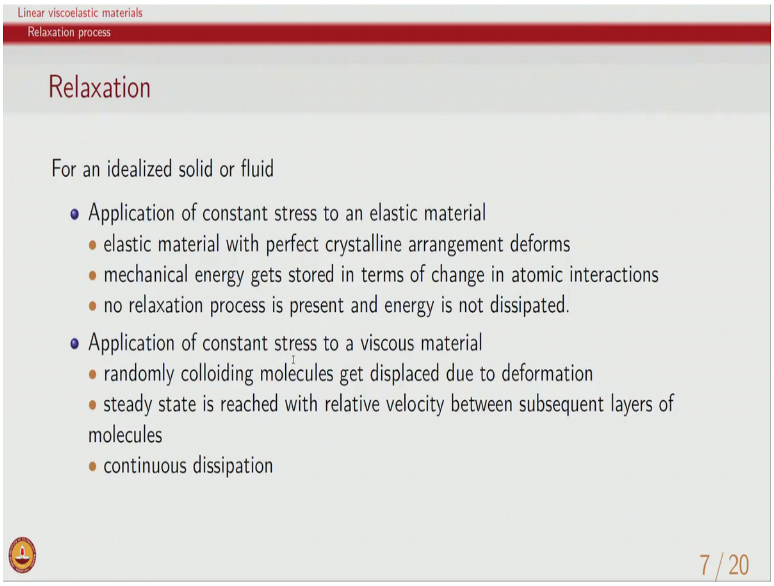

So, the central idea behind trying to look at viscoelasticity is phenomenon called relaxation. So, when I say relaxation what comes to your mind, I mean what would you say is relaxation. So, of course, things which happen at atomic and molecular scale are responsible for the relaxation right, because the equilibrium state is defined based on with respect to the energy states of that different microscopic entities in the material occupy.

If you look at from a mechanical point of view, let us first look at what do we mean by relaxation. So, if we apply a constant stress to an elastic material what do we have if we apply a constant stress it will deform and for example, we know that the solid and let us look at a ideal crystal, we may be able to represent it like this and then when we deform it let us say shear deformation you are basically changing the atomic arrangement.

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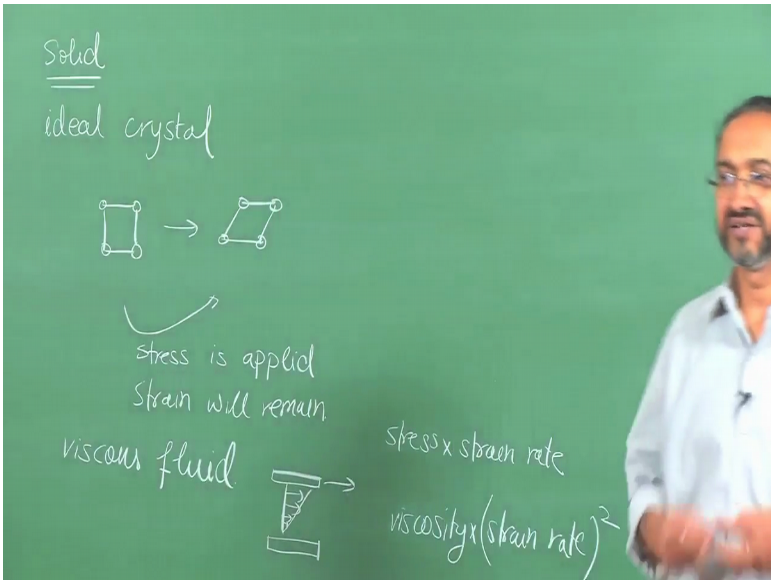

And the average separation between the atoms which were the equilibrium has now changed. So, we have modified the interaction between these atoms and our idea is that the mechanical energy which was input is offset by the change in the interaction energy. And since these two are balancing each other whenever we release the stress the material will come back and therefore, we call it elastic material. So, and as long as we continue to apply the stress, as long as stress is applied strain will remain right. So, we say there is a lack of any relaxation in the material.

The material is not able to dissipate and very important aspect of relaxation process what we mean in mechanical relaxation is the ability to dissipate. So, in this case because the interatomic potential defines some interaction between atoms and given we are changing the separation between the atoms the interaction energy changes and that is balanced by the strain energy and both of these basically give a new state which remains forever and there is no relaxation in the material. So, therefore, no relaxation is present in the material and energy is not at all dissipated.

Now, same thing if we apply for on a fluid right the molecules are anyway randomly displayed getting going about here and there, and then when we apply a constant stress what happens is we achieve a steady state. So, for a viscous fluid what we end up doing is achieving a steady state right in which multiple layers have each has a different velocity.

So, in general of course, all the molecules are getting displaced, but they continue to get displaced because the velocity field is set up and there is a continuous rate of dissipation and of course, that rate of dissipation depends on the stress that was applied and the strain rate which is there in the material. So, there is a continuous the molecule because of their random motions are able to dissipate energy and this dissipation goes on and of course, the amount of dissipation depends on stress and strain rate stress itself depends on viscosity into strain rate. So, therefore, viscosity into strain rate squared is actually the rate of viscous dissipation. So, that is why viscosity is a measure of how much energy can be dissipated by a fluid. And it of course, is dependent on the intermolecular interactions and how different layers of molecules their interaction changes when they are moving with some relative velocity and so a steady state is reached with relative velocity between subsequent layers and there is continuous dissipation. So, this is as far as the relaxed, so in this case we say that relaxation is happening continuously right.

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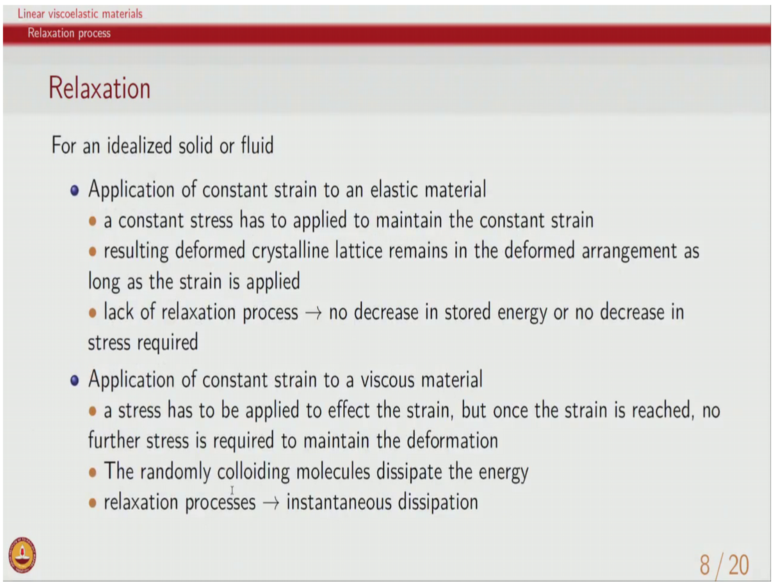

Now, let us look at the same phenomena now under constant strain. So, now, we are doing another mechanical stimulus in this case instead of applying a constant stress we apply a constant strain.

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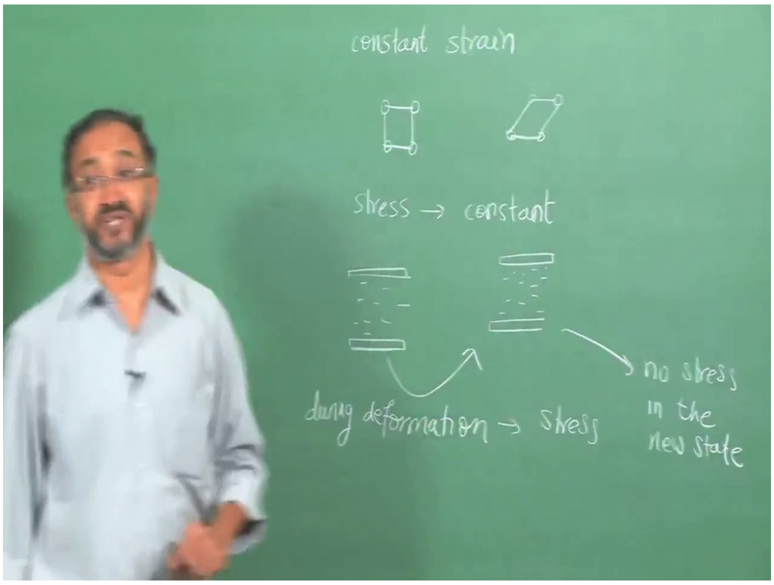

So, again what we find is that an ideal crystalline solid deforms and again we will say that it is a shear strain. So, again deforms and I will have to apply a constant stress to maintain the constant strain. And again the value of the stress will not change with respect to time because as long as the strain is maintained the amount of mechanical energy that is there has to be maintained which is stress into strain. So, the mechanical energy that is input which actually offsets the change in interaction between atoms is given by stress into strain. So, that remains constant because there is no other atomic motion possible. So, inter atomic energy does not really change as a function of time and therefore, the stress value also remains fixed. So, stress also remains constant and again there is no relaxation, there is no relaxation happening.

Student: The same case will be in the fluid also.

No, because fluid will continuously dissipate right, it will continue to dissipate as long as you keep the constant stress on the material it will continue to dissipate.

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It is continuously going on, that is why it is a steady state of dissipation in fact, see it is a steady state we do not really taut. So, therefore, this particular state is not an equilibrium state. Fluid will never achieve an equilibrium if you apply constant stress on it, it will continue to it will only achieve a steady state steady state at which velocity becomes constant and it is not a function of time, strain rate therefore also becomes constant it is not a function of time and the rate of dissipation is also constant it is not a function of time

So, fluid achieves a steady state in which molecule still continue to randomly collide and go around accept the fact that average velocity in subsequent layers of molecules are different and that is a shear flow that we talked about. So, coming back to this case again there is lack of relaxation process and therefore, there is no decrease in stored energy or no decrease in the stress required. So, the value of stress that I require to keep the new deformation remains constant throughout and it does not change. On the other hand if I apply now the same thing to a fluid right. So, I take fluid between two plates and now I apply a constant deformation we are applying a constant stream here.

So, what happens in this case is to just to displace the top plate by a small amount I will need certainly some force, but in the new state I will not require any more force for the fluid to be kept. You can visualize this as between I take two plates and between them there is some fluid when I move the top plate and leave it, it is going to remain there right and I will not require any more force to keep the plate in the new position. So, therefore, in this case what has happened is when I was applying the force when I was deforming the material. So, during deformation some stress is required, but once the new state is reached no stress required in the new state and now this is again an equilibrium state. It is a stress free state again right. Once I move the material it is like saying when I take it from one beaker and I pour it in the plate, while pouring of course, some amount of stress is required, but once the fluid again is in the plate and it is become stationary again it is a completely stress free state.

So, what has happened is whatever mechanical energy that was required has instantaneously been dissipated because certainly there was some mechanical energy input when we were deforming, but in the new state no stress is required. So, the mechanical energy which was applied has been instantaneously dissipated into the material. So, therefore, we can say that basically the randomly colliding molecules dissipated the energy and the relaxation process actually was led to instantaneous dissipation.

So, the contrast between the two material is that there is no relaxation process and there is presence of relaxation processes in fluids and so therefore, dissipation either at steady state or instantaneous dissipation happens. And one other way to again state that by trying to argue that look in solids relaxation process will happen if you wait in finite time because that is basically by saying that relaxation processes are very very slow and of course, we know that there are sometimes defects in crystals and so it is possible that atoms can migrate there are defects at grain boundaries. So, therefore, those are the things, but they will happen at much slower rate. So, for many purposes we can assume than say that the relaxation times of the processes which happen in solid are in finite. So, we can say that the timescale of relaxation process is infinite for solid and it is very close to 0 instantaneous in case of fluids.

And so this is an important idea called relaxation time, time scale of relaxation and that is what we will start using to quantify viscoelasticity of the materials because as we said is the viscoelastic material will have elements of viscous and elastic response and this relaxation time will be key quantity to actually depict what is the time scale of relaxation process.

So, therefore, relaxation process is associated with a relaxation time. If you look at let us say a macro molecule right, what are the relaxation processes possible there? If you start from electronic cloud itself that itself is fluctuating, that itself will respond when molecule changes when molecular separation happens atoms come closer or far away, electronic cloud itself responds, then similarly bonds themselves also have fluctuations bond length keeps on changing, bond there is rotation around bonds. So, these are all examples of relaxation processes.

Then we saw that in case of macro molecule a segment of macro molecule can move. Then we also saw that the whole macro molecule itself can move. Then we also saw that the molecule and its surrounding fluid interact with each other. So, each and every mechanism it is possible that that will have its own characteristic time and each of them is associated with a relaxation process.

So, we will also use this term called relaxation mode. So, the fact that inter particle interaction is may be one characteristic time the interaction between a particle and surrounding fluid is another characteristic time. So, each of them we will call relaxation mode. So, we visualize the material to contain various relaxation modes and the overall viscoelastic response of material is how these different modes respond to the particular mechanical perturbation. So, real materials will have several mechanisms and therefore, several relaxation processes and therefore, they will contain several relaxation modes.

And depending on the time scale of interest a particular relaxation mode may participate and I am using the emphasize emphasis here just to imply that this is somewhat sort of colloquial way of talking about what relaxation mode is doing. So, if relaxation mode participates then we expect that it will contribute to both dissipation as well as storage. So, which means it will give us viscoelastic response. If the relaxation mode is very fast for example, bond vibration right in water the mechanical deformation is always at seconds and even higher level. So, clearly the bond vibration and other things will instantaneously lead to dissipation. There is no mechanism in water which can actually relax at seconds and hours level and therefore, water has perfectly viscous response at room temperature conditions.

If you take water to confinement where now the separation between two surfaces which you are mechanically perturbing is similar order of magnitude as the bond, so nano meters and so on, then now the water structure may respond differently at different time scales. So, therefore, viscoelasticity of water may become relevant only there. For many of the engineering and other problems water for all practical purposes we can say that all its relaxation modes dissipate whatever are the relaxation modes, whether its bond fluctuations whether its hydrogen bonding fluctuations all of those fluctuations they all lead to dissipation. On the other hand we can say that the relaxation mode is frozen.

For example, in this case let us say if there is a defect then the defect can migrate right, but we can say that the defect migration is frozen in the sense that we are asking question only over an hour or a few hours or a few days and over that time period the relaxation mode is practically frozen. So, it is not available for energy to be dissipated therefore, such type of materials will only lead to elastic or storage response. So, and that is the complication involved with viscoelastic materials. The fact that we have a collection of relaxation modes and each of them will respond depending on what is our timescale of perturbation. So, this idea is captured through Deborah number and that is what we will see in the next lecture.