Rheology of Complex Materials

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Structural materials: yield stress and thixotropy

Lecture - 50

Structured Materials-Yield Stress

So, in the course on rheology we have seen several classification and several types of materials. We have also observed many material functions which are defined to describe the characteristics of several complex materials. In this set of lectures we will look at two very important classifications. These are very important because many engineering systems many materials systems which are used in practice belong to one of these categories for example, cement paste is a very common example of a thixotropic fluid, while several food materials are example of yield stress materials. And so quite often it is very important to quantify the nature of these materials, and in today's in this set of lectures we will take a look at what is meant by these class of materials.

We refer to them as structural materials because in all discussion related to yield stress as well as thixotropy we will always refer back to these structural aspects of the material.

We will see that the breakup and rebuilding are essential processes that happen when we speak of yield stress as well as thixotropy. And therefore, the structure of material keeps on undergoing changes during when we are looking at its rheological response. And so, structure is a very important component of defining properties of these set of materials and therefore, we will refer to them as a structural materials. Now looking at the overall outline, we will start with colloidal dispersions under shear and some discussions related to what happens at particle level and then define yield stress, and look at how this yield stress is present in the material and we will look at one specific example of Herschel Buckley model and then move on to looking at thixotropy in structural materials.

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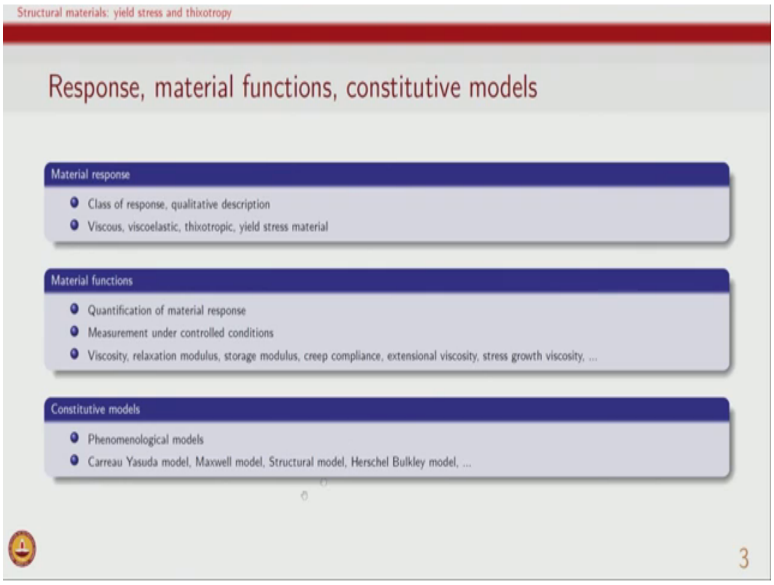

Structural materials: yield stress and thixotropy

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, Herschel Bulkley model, ...

We had been following this outline throughout our course, we want to observe material response and we try to classify this. So, that it is easier to analyze and we have seen viscous and viscoelastic response, and in next two set of lectures we will look at yield stress material and thixotropic response. The idea here is qualitatively first try to describe as what do we mean by this class of response and therefore, that is what we will do.

Parallely of course, we try to define material function because this we can use to quantify the material response, and we define viscosity relaxation modulus and creep compliance and today we will see that yield stress is one example of a material function, that can be defined for these materials also parallely we have looked at some simple models, which give us an idea of how the response can be an functional form of how stress or strain or strain rate are related to each other and so, in this set of discussion where we are looking at yield stress and thixotropy, we will look at examples of Herschel Buckley model as well as a structural model.

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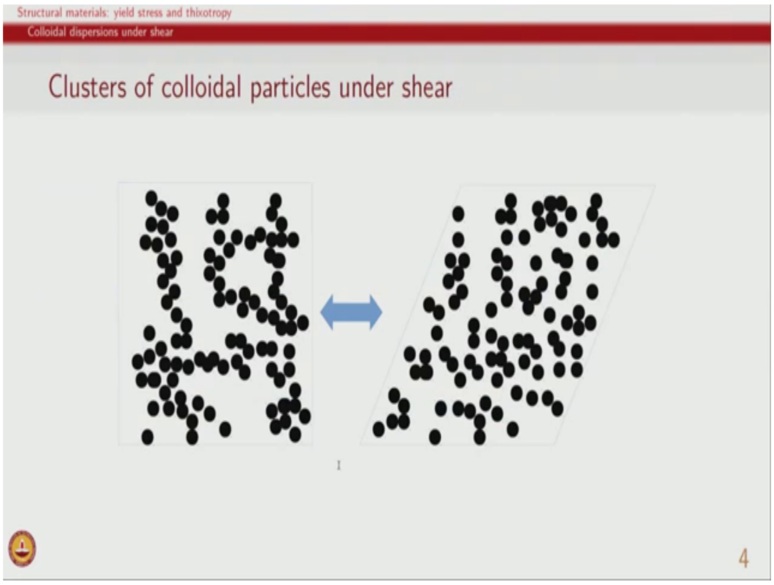

Structural materials: yield stress and thixotropy

Colloidal dispersions under shear

Clusters of colloidal particles under shear

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So, now looking at the colloidal system, we know that the particles of colloids are held together because of attractions or interactions between these particles and as this slide shows that eh we have what is called percolating network if I start from one end I can easily see that almost all the particles are connected. So, I can start from one end and I can reach the other end where particles are almost connected to each other. So, therefore, there is a cluster of these particles and they are connected to each other through network.

And when we disturb this network by applying a shear when we apply deformation on the material, then the clusters get broken and the particles appear to be more isolated then they are together as was the case when the material is under rest. So, therefore, we have this going back and forth between these two states. So, we have basically going from flow to rest we have rebuilding, and similarly from rest to flow we have breaking. So, in many of these situations, we will talk of breaking and rebuilding processes that happen in a material.

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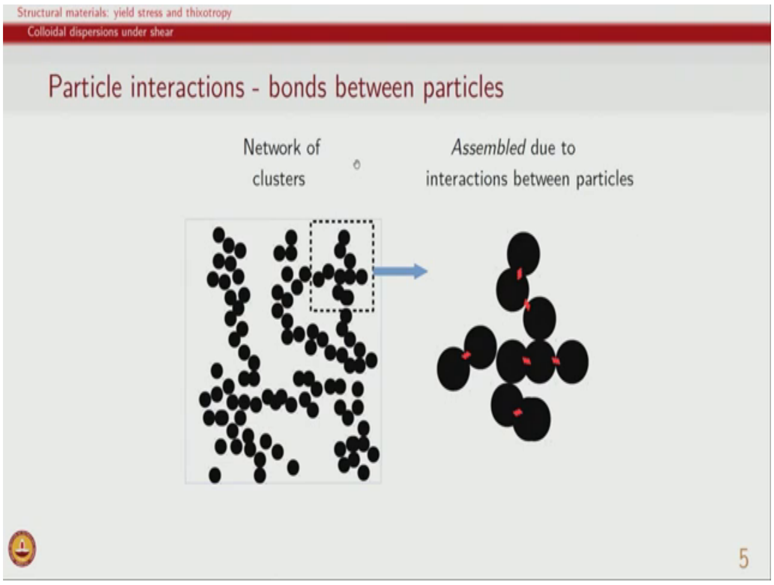

Structural materials: yield stress and thixotropy

Colloidal dispersions under shear

Particle interactions - bonds between particles

Network of clusters

Assembled due to interactions between particles

So, if we look at let us say the particle interactions and consider basically that the two particles are next to each other and they are bonded to each other because there is an attraction. So, therefore, these particle are assembled due to interaction between particles and so, the there is an energy required to pull these particles apart because they are as if they are connected to each other with the spring. So, the assembly of particles in such a case is due to interaction between particle. So, now, the question is that is to what happens assembly or what happens to this network of clusters when we apply shear on it.

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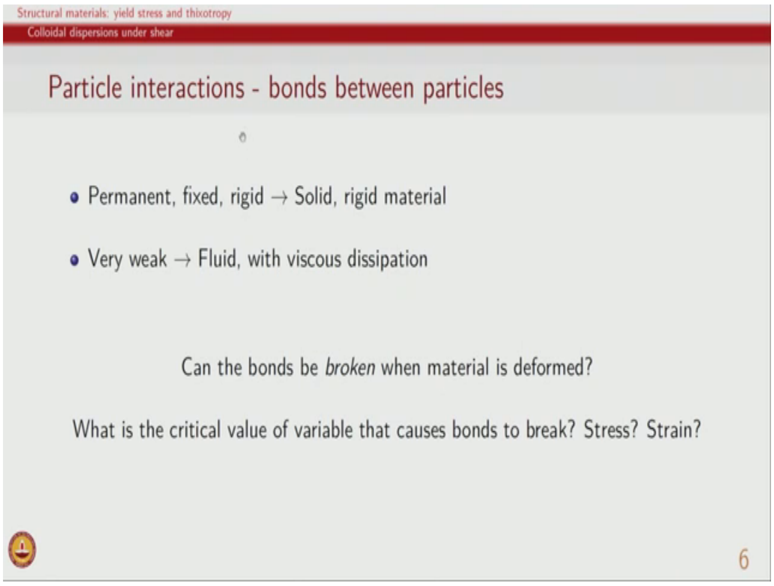

Structural materials: yield stress and thixotropy

Colloidal dispersions under shear

Particle interactions - bonds between particles

- Permanent, fixed, rigid → Solid, rigid material
- Very weak → Fluid, with viscous dissipation

Can the bonds be *broken* when material is deformed?

What is the critical value of variable that causes bonds to break? Stress? Strain?

So, if we look at generally the bonds between particles if these bonds are very fixed or they very strong, they are very permanent, then basically we will have a solid rigid material. An example of this would be if let us say all these bonded particles are perfectly cinterred with each other in which case they are fused together.

So, if particles are fused together then we know that they cannot separate at all in that case the bonds will be permanent and such a porous structure will have the very solid like response it will be very rigid material its basically solid material. Of course, what we have is the fluid and then solid particles and these particles are bonded to each other through interactions and therefore, it is possible that these particles can be separated. We can have other extreme where the particles do not really have an attractive interactions at all. So, therefore, the bonds between particles are extremely weak or not present at all, in which case the overall response of the material is going to be fluid with because these two particles though are they are neighbors this can easily separate from each other and move about.

So, in that case we will obtain an overall viscous response dissipative response and therefore, the overall response will be fluid. So, the many materials will not have either of these extremes. So, the bonds between particles will not be permanent which means particles can be separated, provided sufficient amount of deformation is applied. Similarly the particles may or may not have very weak bond in which case there is certain amount of energy required for us to separate the particles and make them move.

So, the question at can be asked is, can the bonds be broken when material is deformed. And if the answer to this question is yes then what we will see is material which was otherwise solid if a sufficient amount of deformation is applied or the material is extend deformed to a certain extent, then the material can undergo a transition to a fluid like system. Because if the bonds are broken then initially material will be rigid, but once the bonds starts breaking it will go more and more it will become more and more fluid like. So, the natural question that arises is also is there a critical value of variable and which variable will that be. So, is there a critical value of stress at which bonds start to break, is there a critical value of strain or deformation at which bonds start to break.

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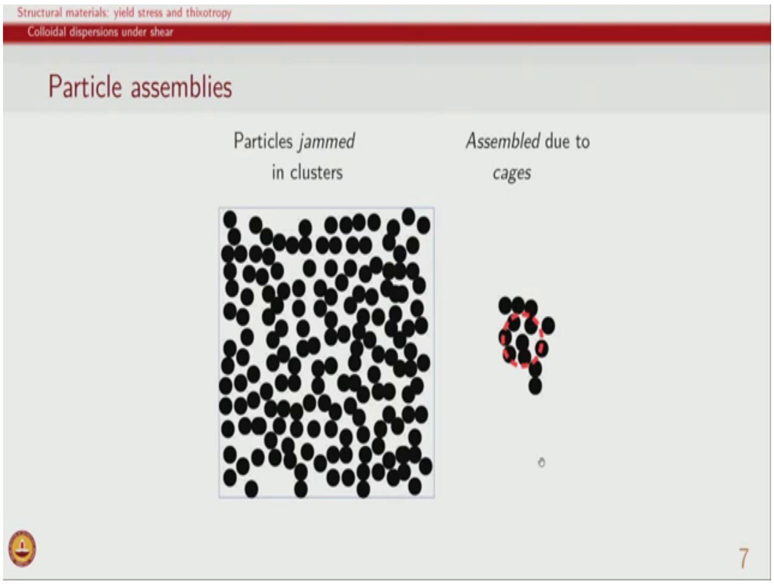

Structural materials: yield stress and thixotropy

Colloidal dispersions under shear

Particle assemblies

Particles *jammed* in clusters

Assembled due to *cages*

We can also look at the overall colloidal system in another con context, if we have the particle assemblies where particles are together in a jammed state and by that we mean is basically there are this happens at very high concentration, and particles seem to form chains and they are forming chains just because they are in neighborhood of each other.

So, this chain basically then not allow individual particle to move and even if we try to shear this material it will resist that. And therefore, this state is called the jammed state. So, because of jamming of these particles like analogous to what happens in case of a traffic jam, where vehicles cannot move because in the neighborhood there are all other vehicles and since each vehicle can only moves so much, each vehicle is confined because of all its neighbors. Similarly here also we have a particle basically confined because of a cage.

So, each particle can be thought of as being in a cage and this cage is formed because there are all the other particles surrounding it. So, given that this particle cannot really move out of this cage, we have a situation where the overall material response will be quite solid like. And if the cage is broken then the particle can be move about and in that case it is possible that the overall response can be fluid.

So, in general for particle assemblies the particles are jammed in clusters and therefore, very little mobility is there due to the cages being present and so, the cage particles which no scope of mobility implies that, we have solid or rigid material.

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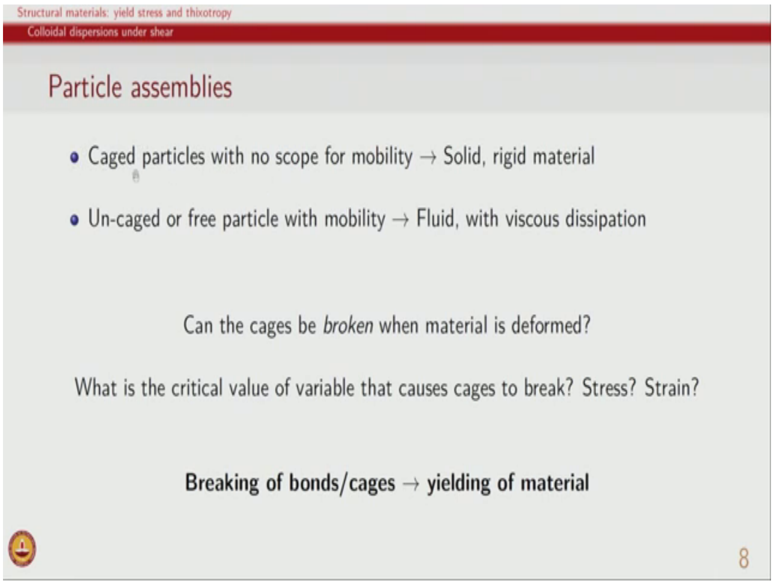

Particle assemblies

- Caged particles with no scope for mobility → Solid, rigid material
- Un-caged or free particle with mobility → Fluid, with viscous dissipation

Can the cages be *broken* when material is deformed?

What is the critical value of variable that causes cages to break? Stress? Strain?

Breaking of bonds/cages → yielding of material

If let us say the particles are uncaged or there are particles which are free to move or they have sufficient mobility, then we will observe a fluid like response which is of course, viscous and also dissipative response. And so, for such materials the jammed states are observed because the interparticle attraction is not a significant factor. So, the particles do not come together because there is an attraction between them the particles come together because there is a excessive population. The concentration of particles is so, high that they are forming these cages and because of the formation of the cages they are do not allow motion for each other and that case they are jammed.

So, therefore, the question that is very relevant it for such materials system as if cages can be broken. If the cages can be broken then we know that when material when cage state will have a solid like response, but if cages have broken then we can end up having a fluid like response and so, the question is whether it is possible for the cages to be broken when deformation happens. What that implies is if it is possible that when deformation is applied that there is some rearrangement of the particles would take place.

So, there it is relatively easier for the particles to move about. Again the question that arises is there a critical value of either stress or strain, which causes the cage break and if yes then we can say that at this critical stress, the material goes some of the solid rigid like material to a fluid like material or if there is a critical strain at which such phenomena happen, then we can say that material goes from solid like to a fluid like state. And all of this discussion as we have said we are only talking about breaking of bonds and cages.

So, we can have the cages being broken so, that particle can move out or we can have the bonds being broken so, that particles are free to move. So, in both the cases we are talking about breaking of bonds and cages, and this breaking of bonds cages is set to lead to yielding of material. So, material yields by which bonds and cages are broken and it becomes more fluid like. So, yield is a concept to try to describe the phenomena, where a material which appears to be solid like due to deformation becomes fluid like and underlying the concept is related to the breaking of bonds and cages. This of course, yield is a concept which we look at very often in metals when we look at stress strain behavior of metals.

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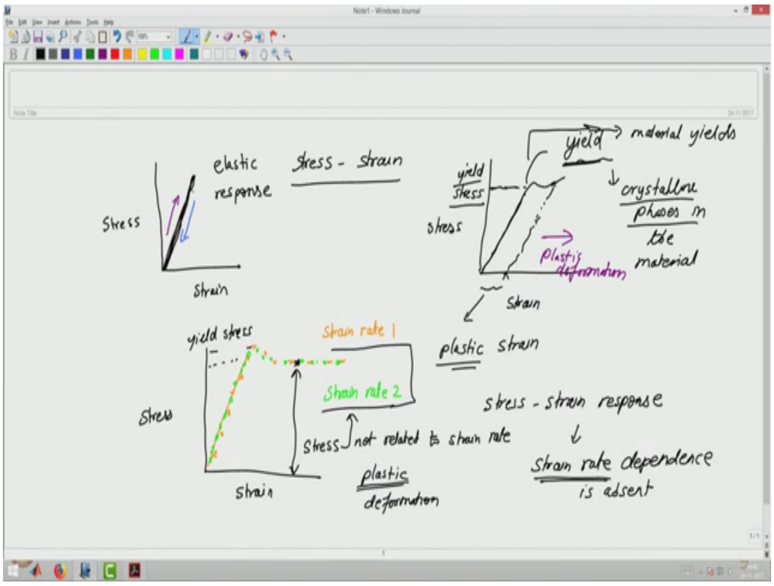

So, if we look sat stress verses strain, we know that at low small strains we will have elastic deformation in the material, and where stretches proportional to strain and also quite importantly, if I increase the stress I will go and then when if I decrease the stress I will come and I will trace the same path.

So, if no matter what the stress strain is, the stress is determined completely by strain and strain is determined completely by stress and so, this is the elasticity. But in when we take the material to higher strains in case of metals, what we see is a yield point beyond which we see nonlinearity beginning and the other important aspect is if I release the material, if I reduce the load on it and therefore, comes back with a plastic strain. And in this context the yield processes are related to crystalline crystals crystalline phases in the material and they yield. So, there is flow of crystalline material due to various defects, it could be a across due to defects which are present at the crystal grains, it could be due to the point and line defect which are present within the crystal itself.

So, what we say is beyond this strain the material yields and or the material also is set to flow, while below this strain the material is elastic and stress and strain are proportional to each other. So, this concept of an yield stress is used here also. So, stress at which yield has happen is also called the yield stress. And so, when we look at many metallic materials and we want to design them for structural application, it is the very useful for us to keep the design stresses to be much lower than yield stress to ensure that material does not yield during an application. For example, if will beam is being used we do not want it to deform drastically during application, we would want it to remain this range. So, yield stress is very important characteristic of solid like material and in this case what we have seen is for example, for metallic materials and so, we see in this case that there is an yielding phenomena which associated with the structure of the material.

So, we are of course, discussing fluid like materials and in this case the colloidal particles and their assemblies, the colloidal particle are along with fluid they are dispersed in a fluid and this is an example of a multiphase system as we have been discussing in this course. So, what we can say is yield this material yields if it shows of fluid like response, the material are below yield if the overall response is solid like.

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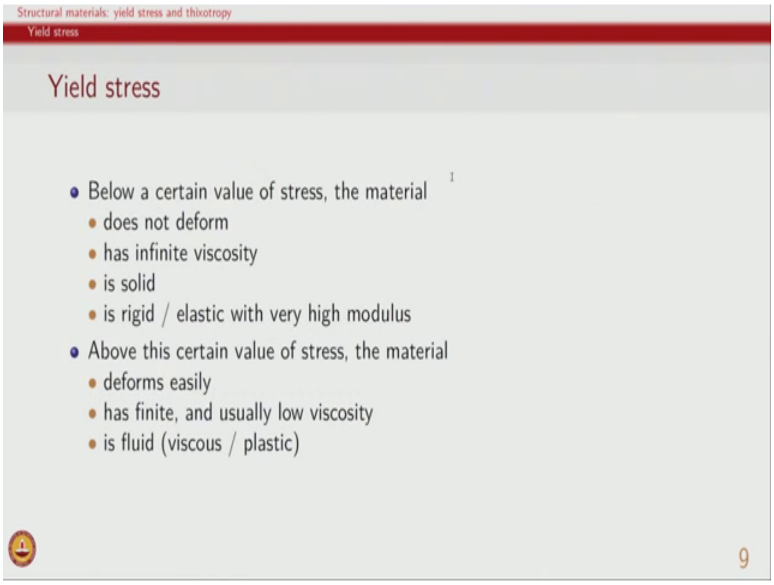

Structural materials: yield stress and thixotropy

Yield stress

Yield stress

- Below a certain value of stress, the material
  - does not deform
  - has infinite viscosity
  - is solid
  - is rigid / elastic with very high modulus
- Above this certain value of stress, the material
  - deforms easily
  - has finite, and usually low viscosity
  - is fluid (viscous / plastic)

So, therefore, in the materials that we will discuss in this course we can also define something called a yield stress. So, below a certain value of stress if the material does not form which means it remains very solid like its strain is very small, the other way of saying this is also that it has an infinite viscosity or this is very important for many of the food for example, jam it has very high viscosity when the material is just scoped out because its a solid material and when we start spreading it spreads it very easily. So, therefore, its viscosity decreases beyond an yield point.

So, we can talk of many of these materials which we use in the kitchen as yield stress material, that below a certain value of stress they would pretty much be like solid, but are also for example, it will remain like a solid block, but then if we use knife to spread it, it can be spread and therefore, it has a finite viscosity. So, below a certain value of stress the material does not deform as infinite viscosity, it is said to be solid and basically either is very rigid which means deformation is very small or elastic with very high modulus.

Just to remember that when we say a material is elastic, stress is proportional to strain when we say material is rigid basically it does not deform at all. So, therefore, the limit of elasticity being extremely where modulus is a finite is what is meant by rigid. So, generally in the below yield stress we say basically that the material is solid and therefore, it does not deform or it has infinite viscosity above the same value of stress above.

So, above this certain value of stress the material deforms a relatively easily which means it has a acquired a fluid like characteristic now it is either a viscous or a plastic material, it has finite and therefore, low viscosity. One key is that we should try to understand is this notion of viscous behavior and plastic behavior. So, as we saw in case of metal plastic material that in this regime, we had plastic deformation.

So, generally when we observe plasticity in metals, as an ideal case the stress verses strain response is not really dependent on strain rate strain rate dependence is absent. So, what; that means, is if I do same test at different strain rates. So, let us say if I do stress verses strain rate at two different strain rates. So, I will see that initially the data points will be all elastic. So, they are all in a straight line and then later on and then we have the yield point and so, because of the yield point and then there will be at constant stress the strain will continue to increase we are talking of only strain being plotted here; now if I do it at.

So, this is at one particular strain rate. So, this is strain rate 1 now let us say if I do the same test for strain rate 2 the strain rate does not really matters in case of elastic deformation. So, what we will see is again we will get essentially the same response and similarly in this case also we will see the same response.

So, basically the stress verses strain behavior in case of metal plasticity as an ideal case does not depend on strain rate. So, then this phenomena is called plasticity. So, this is plastic deformation. If you look at the state here the stress is not related to strain rate not related to strain rate. Of course, we call it plastic deformation because stress is also not related to strain. At same value of stress which is the yield stress we have basically a if a strain in keeps on increasing and therefore, this is called the plastic deformation.

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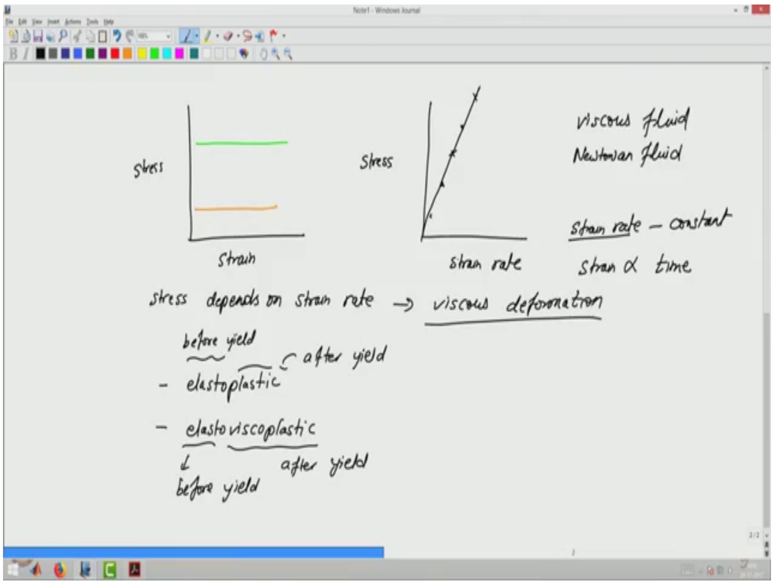

Viscous fluid
Newtonian fluid

Strain rate – constant
Strain $\propto$ time

stress depends on strain rate → viscous deformation

before yield
after yield
- elastoplastic
- elastoviscoplastic
before yield
after yield

On the other hand when we say discuss deformation we have seen that for viscous dissipation and for the stress and strain how are they related this to answer this question, first you can also think of how is stress and strain rate related.

So, we know that for a viscous fluid and let us take an example of a Newtonian fluid the linear viscous fluid. In this case what I would see is that stress and strain rate are proportional to each other. So, therefore, I will only get a basically straight line of response and so, in this case what I will see is as stress increases. The strain rate as the strain rate increases the stress also will continue to increase given that its a linear flu viscous fluid we would expect the stress and strain rate to be related to each other through a linear relation.

So, if we do now experiment at different strain rate if the stress is constant and strain rate is constant. So, if strain rate is constant this would imply that strain will be proportional to time because strain rate is derivative of strain with respect to time. So, therefore, strain will continue to increase, but at any other stress we will have different. So, each of this are different strain rates. So, drawing analogously to what we had done in the previous discussion, if we do the experiment at one strain rate we will get one value of stress if we do it at a different strain rate we will get another value.

So, therefore, in this case is stress depends on strain rate and this is viscous deformation in the material. So, quite often given that there are researchers and practitioners different backgrounds working on different set of materials, we tend to use several phases to describe the phenomena and we need to be careful and understand the meaning of each of the phrases and what context this is being used for.

So, the yield stress as a concept is used by people describing metal plasticity to describe plastic deformation, and we also use this yield stress in the context of fluid like materials to describe the viscous deformation. In both cases the term flow is used or fluid like response is used; however, there is a distinction in terms of what the basic mechanism is and how it is related to strain rate and therefore, in general when we look at let us say the class of materials, which are yield stress materials we could have their response being described as elasto plastic, viscoelastic or elasto viscoplastic.

So, therefore, these are the phrases that you will hear people talk about, when we describe the overall response. So, elasto plastic implying this is before yield and this is after yield. Similarly elasto visco plastic again implying that this is after yield and this is before yield. So, again the materials which have yields stress as the basic characteristics will always have this solid like response and fluid like response the fluid like response could be combination of viscous and plastic type of responses we whenever there is a strain rate dependency.

We will say that its viscous dissipation which is the underlying feature and is we will call it viscous when the deformation is independent of strain rate and then we will say that it is plastic mechanisms.

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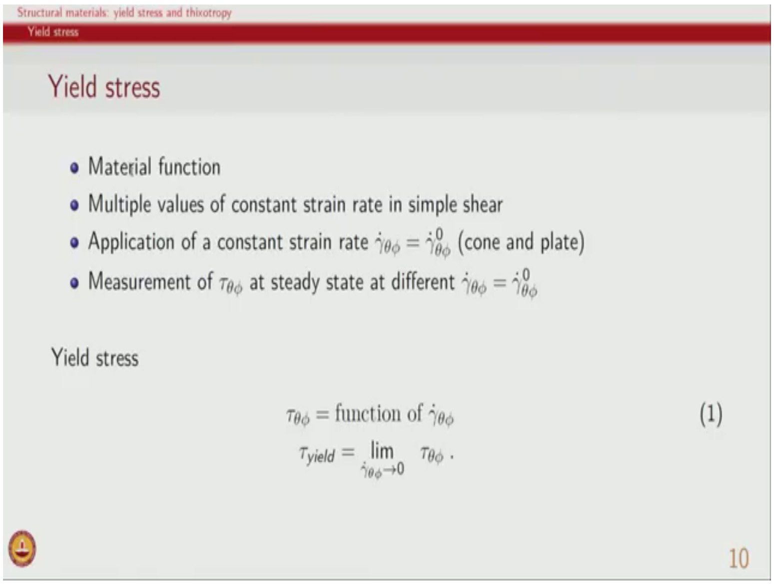

Structural materials: yield stress and thixotropy

Yield stress

Yield stress

- Material function
- Multiple values of constant strain rate in simple shear
- Application of a constant strain rate $\dot{\gamma}_{\theta\phi} = \dot{\gamma}^0_{\theta\phi}$ (cone and plate)
- Measurement of $\tau_{\theta\phi}$ at steady state at different $\dot{\gamma}_{\theta\phi} = \dot{\gamma}^0_{\theta\phi}$

Yield stress

$$\tau_{\theta\phi} = \text{function of } \dot{\gamma}_{\theta\phi} \tag{1}$$

$$\tau_{yield} = \lim_{\dot{\gamma}_{\theta\phi}\to 0} \tau_{\theta\phi} .$$

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And so, we can define a material function in these kind of for to characterize the response of these material, basically the there are several ways to determine yield stress and we will also soon see that the quantity called yield stress subject to the way it is being measured and quite like in case of polymers the glass transition as a glass transition temperature is not very well understood, because we are going from thermodynamic equilibrium rubber state to a non-equilibrium glassy state.

Similarly the yield dress also is a as a material function as a there is the considerable amount of uncertainty and there is considerable amount of lack of understanding about what is exactly it means and so, in this case also we are going from a fluid like material to locked in cages or clusters which are formed, and in that case again whether the materials is non equilibrium and to what extent it is equilibrium are questions which bare not very well understood.

So, from a theoretical point of view and from research point of view yield stress as a quantity is still being debated and various people are trying to understand what is what materials can have yield stress and in under what circumstances, we can use the word yield stress for several materials. However, as I pointed out earlier given that many materials in our day to day application as well as an engineering application show these phenomena of yielding. Yield stress as an experimental feature or as a material characteristic is used quite often and it is found to be very useful in terms of designing materials and to make decisions regarding what type of material to use or what type of mechanism to use in what type of application. So, therefore, yield stress measurements are done most commonly by applying constant strain rate in simple shear.

So, therefore, we do steady shear on the material and when we apply a constant strain rate and let us say for a cone and plate geometry we apply gamma dot theta phi naught and we what we do is we measure the stress at steady state. So, we apply a constant strain rate we wait for the stress to reach a study value and that value is measured.

So, this basically experiment is done at different values of strain rate and then yield stress is defined basically the general stress itself tau theta phi will depend on the whichever is the strain rate being applied. So, at different value of strain rates we will get different value of tau theta phi. Now yield stress is defined as that value of stress when strain rates are very small, there is the value of stress which in the limit of gamma dot going to 0. Remember that for a Newtonian fluid if gamma dot goes to 0 tau theta phi will also go to 0.

So, as we expect and as we know Newtonian fluid is not an yield stress fluid of course, it does not have any yielding phenomena. So, therefore, in that case yield stress is 0, but most materials which belong to this yield stress category will have a certain amount of stress even if strain rates are very small and that stress is called the yield stress.

So, in the next lecture we will then see how to look measure these stresses using couple of different type of experiments and then we will also look at phenomena of thixotropy.