Plasticity and Deformation Process

Viscoelasticity and Viscoplasticity
Remember that even elastomers become Hookean (perfectly elastic) below their glass transition temperatures and exhibit enthalpic elastic deformation.

Enthalpic energy stored in the intermolecular bonds is reflected in the mechanical behavior at this condition.

Their Brownian motion becomes possible above this energy limit and increases with further increasing temperature.

Above the glass transition temperature materials gain freedom (entropy) that enable them to respond differently to applied mechanical energy.

- entropic elastic deformation
- viscous heat dissipation
- viscous plastic deformation

All materials at practical engineering conditions are viscoelastic to some extent. They give both viscous (liquid-like) and elastic (solid-like) responses to stresses.

Hence all materials flow.
Viscoelasticity

‘παντα ροι’ (panta roi) or ‘everything flows’ as Heraclitus said

‘the mountains flow before the Lord’ as prophetess Deborah said

Mountains flow if the time scale of observation is extended to geological scale.

Using an every-day time scale we can define a solid as a material which either does not flow or flows plastically.

Plastic flow requires a stress larger than a definite stress, the yield stress, and a plastic solid does not flow under the action of a stress below that yield stress.

If we observe the objects for a very long time we see that the limiting stress below which the materials do not flow is quite low
Time-temperature equivalence

The difference between the mechanical behavior of a solid and a liquid material at the same temperature results only from their glass transition temperatures.

The response of matter under stress at high temperature for a short time is identical to the response of matter under stress at low temperature for a long period of time.

Solids need more time to respond to a stress applied within a time period at a constant temperature than liquids.

They flow very slowly due to their sluggish molecular motion by diffusion mechanism.

Creep is the resulting engineering concept (more on this later).
Consider homogeneous suspensions that consist of both liquid and solid as a model to analyze the viscoelastic flow behavior of matter.

Suspensions exhibit different degrees of elasticity and viscosity depending on their structure.

Consider water as the binder phase of the suspension. Water behaves purely viscously because its molecules move very rapidly; it does not contain structure. Its resistance to flow under stress is defined as its viscosity, $\eta$.

$$\tau = \eta \gamma$$

where $\tau$ is the shear stress (Pa) and $\gamma$ is the shear rate (1/s).

Consider alumina powder as the filler of the suspension. Alumina is a hard, brittle ceramic and behaves mostly like an elastic solid under shear stress:

$$\tau = G\gamma$$

where $\tau$ is the shear stress, $G$ is the shear modulus, $\gamma$ is the shear strain.

$$\tau = F/Area$$

$$\gamma = dx/dy$$
Simple shear flow of water between two plates of infinite lengths deforms the liquid according to Newtonian flow:

Shear stress \( \tau_{xz} = \frac{F}{\text{Area}} \)

Shear strain rate \( \dot{\gamma} = \frac{\partial V_x}{\partial y} = \frac{V_0}{H} \)

Velocity gradient is linear \( V_x = \frac{V_0 \cdot y}{H} \)

\[ \eta = \frac{\tau_{yz}}{\dot{\gamma}} = \frac{F \cdot H}{A \cdot V_0} \]
The ideal suspension is a homogeneous mixture of water and alumina, powders are well dispersed in water without agglomerations.

By virtue of the interactions between the binder and filler particles (surface adhesion, wetting, hydration), the flow behavior of the mixture changes from Newtonian to non-Newtonian viscosity:

\[ \tau = m\dot{\gamma}^n \]

where \( m = \mu \) is the non-Newtonian viscosity, \( n \) is the shear rate dependency index. For Newtonian materials \( n=1 \) and shear thinning occurs when \( n<1 \).

Non-Newtonian fluids respond with a more or less than doubled shear rate when the force is doubled, depending on whether they show shear thinning or shear thickening.

Most aqueous ceramic suspensions show shear thinning, so that doubling the force will more than double the shear rate, thus making deformation of the material relatively easier at higher shear rates.

\[ \mu = \frac{\tau}{\dot{\gamma}^n} = \frac{F \cdot H^n}{A \cdot V_0^n} \]
The stress-strain relation of non-Newtonian suspensions has been analyzed by combination of a purely elastic and a purely viscous component using Maxwell’s model:

![Maxwell's model diagram]

The shear stress of purely viscous damper (dashpot) is proportional to the shear rate \( \dot{\gamma} \)

\[ \tau_{yx} = \eta \dot{\gamma} \]

The shear stress of purely elastic spring is proportional to the shear strain \( \gamma \)

\[ \tau_{yx} = G \gamma \]

The relation according to the model is a combination of these (additive strains, equal stresses):

\[ \tau_{yx} + \left( \frac{\eta}{G} \right) \frac{d\tau_{yx}}{dt} = \eta \dot{\gamma} \]

Under steady flow, stress response of the suspension should be constant (independent of time) and the flow will be of viscous character.

Under sudden flow, stress response of the suspension should be time dependent and \( \frac{d\tau_{yx}}{dt} \gg \tau_{yx} \)

So the suspension behaves like a pure elastic solid under sudden deformation.
\[ \tau_{yx} + \left( \frac{\eta}{G} \right) \frac{d\tau_{yx}}{dt} = \eta \dot{\gamma} \]

Maxwell model is applicable to all materials since all materials are viscoelastic to some extent.

The ratio of the viscosity of a material to its shear modulus \( \left( \frac{\eta}{G} \right) \) is termed the relaxation time \( \lambda \).

The relaxation time is basically the time it takes for the molecules in the unit cell of the material to respond to the surrounding stresses and return to equilibrium structure by Brownian motion.

\( \lambda \) determines the extent of elastic response of a material to stresses and is a function of temperature.

Low relaxation time means the material quickly returns to equilibrium structure after the stress is removed.
Prophetess Deborah: ‘even the mountains flow before the Lord’, M. Reiner’s translation of Bible, Judges 5:5

Deborah number is the ratio of the relaxation time to deformation time which is the inverse of shear rate:

$$De = \frac{\lambda}{t_d}, \quad t_d \approx \frac{1}{\dot{\gamma}}$$

The higher the Deborah number (deformation time smaller than the relaxation time), the more elastic is the response of the material.

Molecular structure of a material is close to equilibrium conditions when the deformation or the deformation rate (inversely proportional to deformation time) is small.

The response of the material to deformation in that large time frame reflects the molecular arrangements as in creep.
Nothing seems more solid-like than the rocks of the earth, but even they flow by creep.

Geologists found the viscosities of many rock samples by subjecting the samples to a constant load:

- a. for a long time
- b. at an elevated temperature
- c. under hydrostatic pressure

These very long time scales appropriate for geological studies mean that even very high viscosities and the resultant very low shear rates are significant and measurable.

Long-term creep experiments on natural quartzites led to viscosities in the region of $3–4 \times 10^{15}$ Pa $s$.

Cooled lava viscosity is $10^{12}$ Pa $s$ and the viscosities for lower crust and upper mantle of Earth are found as $3 \times 10^{19}$ and $3 \times 10^{18}$ Pa $s$ respectively.

<table>
<thead>
<tr>
<th>Typical examples for each viscosity decade from $10^{21}$ down to $10^6$ Pa $s$, arranged in log$_{10}$ increments:</th>
</tr>
</thead>
<tbody>
<tr>
<td>21-the earth’s mantle</td>
</tr>
<tr>
<td>20-glass</td>
</tr>
<tr>
<td>19-steel</td>
</tr>
<tr>
<td>18-mortar</td>
</tr>
</tbody>
</table>
The relaxation time for low molecular weight liquids at $T \gg T_g$ are very ($10^{-12}$ s) low so that local arrangement of molecules relaxes quickly through Brownian motion.

A particle with 200 nm diameter can move 10000 nm in 30 s due to Brownian motion. However, liquids with such fast relaxation can behave as elastic solids depending on the deformation time.

Examples

Liquid water
Relaxation time = $10^{-12}$ s
Deformed at a shear rate = 1000/s
Deformation time = 1/1000 s
$De = 10^{-12}/0.001 = 10^{-9}$

Polymer
Relaxation time = $10^3$ s
Deformed during molding at a shear rate = 1/s
Deformation time = 1 s
$De = 1000/1$

Mountains
Relaxation time = $10^{21}/10^{10} = 10^{11}$ s
Deformed in 100 years at a shear rate = 1/100000
Deformation time in 100 years = 100000
$De = 10^{11}/10^5 = 1000000$
How do solids behave when loaded below their yield stress, especially when examined over very long time periods of stress?

Frost and Ashby found an answer to this question by analyzing the creep behavior of many types of materials under carefully controlled conditions.

The answer: If brought within the range of measurability by increasing the test temperature, almost all materials will show creep, however low the applied stress.

Creep is the steady-state, continuous deformation of a material when a stress below yield stress is applied, and this is usually after an initial linear elastic deformation and may take some time to arrive at steady state.

Pressurized specimen was taken to a high-enough temperature \((T>0.5T_m)\) to avoid the initiation and propagation of cracks and seal up any opening cracks to observe pure creep behavior.

![Strain time curve for a creep test](image-url)
At temperatures $>0.5T_m$ atomic diffusion occurs and grains grow but the material is still solid. Creep rates for all materials are brought within the measurable range, i.e. $>10^{-9} \text{ s}^{-1}$

Creep behavior of solids display three identical characteristics:

1. After a long-enough time, a steady creep rate is achieved.
2. This creep rate, at low-enough applied stress, usually becomes a linear function of applied stress (Newtonian flow)—and is governed by atomic diffusion.
3. At higher stresses, the creep rate increases faster than the stress, and usually shows a power-law-like non-Newtonian behavior.
Creep is a performance-based behavior since it is not an intrinsic materials response.

It is defined as time-dependent deformation at absolute temperatures greater than one half the absolute melting.

Remember that time-dependent deformation (or flow) of fluids is characterized by the coefficient of **viscosity** $\eta$, which is the resistance to flow: $\tau = \eta \gamma$.

Diffusion-controlled mechanisms have significant effect on high temperature mechanical properties and performances.

- Dislocation climb
- Concentration of vacancies
- New slip systems
- Grain boundary sliding
- Corrosion or oxidation

Approximate values of the Ellis model parameters that describe the creep of some ‘solid’ materials

<table>
<thead>
<tr>
<th>Material</th>
<th>Grain size</th>
<th>Temp.</th>
<th>$\eta_0$</th>
<th>$\sigma_0$</th>
<th>$m$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spinel, a mineral</td>
<td>10</td>
<td>1000</td>
<td>$4.64 \times 10^{16}$</td>
<td>$7.4 \times 10^7$</td>
<td>1.2</td>
</tr>
<tr>
<td>$\alpha$-Alumina</td>
<td>10</td>
<td>1200</td>
<td>$1.25 \times 10^{16}$</td>
<td>$4.8 \times 10^7$</td>
<td>1.1</td>
</tr>
<tr>
<td>Zinc carbide</td>
<td>10</td>
<td>1600</td>
<td>$2.00 \times 10^{16}$</td>
<td>$1.5 \times 10^8$</td>
<td>2.9</td>
</tr>
<tr>
<td>Lithium fluoride</td>
<td>50</td>
<td>500</td>
<td>$2.45 \times 10^{14}$</td>
<td>$2.7 \times 10^6$</td>
<td>4.6</td>
</tr>
<tr>
<td>Sodium chloride</td>
<td>50</td>
<td>400</td>
<td>$3.02 \times 10^{14}$</td>
<td>$1.7 \times 10^6$</td>
<td>4.3</td>
</tr>
<tr>
<td>304 Stainless steel</td>
<td>100</td>
<td>600</td>
<td>$6.20 \times 10^{15}$</td>
<td>$2.5 \times 10^7$</td>
<td>3.6</td>
</tr>
<tr>
<td>Titanium</td>
<td>100</td>
<td>900</td>
<td>$1.00 \times 10^{15}$</td>
<td>$1.0 \times 10^6$</td>
<td>2.9</td>
</tr>
<tr>
<td>Ice</td>
<td>100</td>
<td>8</td>
<td>$1.02 \times 10^{13}$</td>
<td>$3.2 \times 10^5$</td>
<td>2.1</td>
</tr>
</tbody>
</table>

$\eta_0$, the zero shear rate viscosity (Pa s); $\sigma_0$, the critical stress (Pa); and $m$, the non-linearity index [\-].

The grain size ($\mu$m) and test temperature data ($^\circ$C) are also included. The data has been read off graphs in E. Ashby’s book [109] and has been fitted to the Ellis model. The grain size is included because it controls the behavior of $\eta_0$ and $\sigma_0$ (but not the value of $m$). Fig. 18.

18. Viscosity versus stress data at 1000°C, derived from [109], for various grain sizes of: (a) magnesium (b) olivine (a rock).
General creep equation 
\[ \frac{d\varepsilon}{dt} = \frac{C \sigma^m}{d^b} e^{-\frac{Q}{kT}} \]

where \( \varepsilon \) is the creep strain, \( C \) is a constant dependent on the material and the particular creep mechanism, \( m \) and \( b \) are exponents dependent on the creep mechanism, \( Q \) is the activation energy of the creep mechanism, \( \sigma \) is the applied stress, \( d \) is the grain size of the material, \( k \) is Boltzmann's constant, and \( T \) is the absolute temperature.

The total strain-time relation is
\[ \varepsilon = \varepsilon_i + \varepsilon_t (1 - \exp(rt)) + t\varepsilon_{ss} \]

where \( r \) is a constant, \( \varepsilon_t \) is the strain at the transition from primary to secondary creep and \( \varepsilon_{ss} \) is the steady-state strain rate.
Experimental measurements of viscoelastic behavior

Two types of rheological tests enable us understand the viscoelastic behavior of materials

- Static tests
  - Strain build-up under constant stress (creep test)
  - Stress relaxation under constant strain

- Dynamic tests
  Sinusoidally fluctuating strains or stresses are applied to the material and responses are measured as a function of
  - Time
  - Frequency
  - Strain amplitude or stress amplitude

Stresses applied or generated during dynamic tests are commonly below the yield strength of the material
Strains applied or generated cyclicly range from 0.001 to 1000 (0.1% to 100000%)
Dynamic tests involve fatigue tests for solids and rheological tests for suspensions, melts
Creep test
A sample is subjected to constant stress and deformation is measured as a function of time

A perfectly elastic solid deforms instantaneously according to the Hooke’s law and there is no further deformation with time

A viscoelastic solid strains with time because of the motion of molecules relative to each other at a rate controlled by the viscosity of the material, the stress, the temperature and the time for which the material has been stressed

Polymers creep at room temperature so their creep behavior is more critical than metals

e.g. cellulose acetate has been subjected to constant loads for up to 7000 hours

Strain (increasing with time) divided by constant stress gives the creep compliance J (inverse of modulus)
Stress relaxation test
A sample is deformed (stretched or compressed) to a given value of strain and the stress necessary to maintain that strain within the microstructure is measured as a function of time

It is mostly applied to polymers which have molecular structure such as long chains As the sample relaxes, the chains change their conformations, disentangle or slide over each other As a result of this microstructural change, stress within the material decreases

The results are reported as the relaxation modulus $E_r$
Similar to the elastic modulus, relaxation modulus is found by dividing stress (changing with time here) by the constant strain

Usually involves testing at multiple temperatures because of the equivalence of time and temperature for viscoelastic solids (A test at a high temperature will give the same curve at shorter times than a test at a low temperature)
The Maxwell model is applicable to this experiment where the length is held constant, \( \frac{de}{dt} = \dot{\gamma} = 0 \)

\[
\tau_{yx} + \left( \frac{\eta}{G} \right) \frac{d\tau_{yx}}{dt} = \eta \dot{\gamma} = 0
\]

By rearrangement of the equation we obtain:

\[
\frac{d\tau_{yx}}{\tau_{yx}} = -\left( \frac{G}{\eta} \right) dt
\]

Since \( \tau_{yx} = \tau_0 \) at \( t=0 \), at the start of the experiment, integration the above equation gives:

\[
\tau_{yx} = \tau_0 \exp \left( -\frac{t \cdot G}{\eta} \right)
\]

This means that the stress (may be shear or normal stress) decays exponentially with time for a simple viscoelastic material with a relaxation time of \( \frac{\eta}{G} \)

Since the strain is constant, and time is linearly increasing, \( t \) in the equation is equal to the instantaneous deformation time which is equal to the inverse of strain rate

So the creep behavior becomes a function of the Deborah number (which decreases with time):

\[
\tau_{yx} = \tau_0 \exp \left( -\frac{1}{De} \right) = \tau_0 \exp(De)
\]
A similar time dependence of strain results for creep when the Voigt model is used in place of the Maxwell model

$$
\varepsilon = \varepsilon_0 \exp \left( \frac{-t \ast G}{\eta} \right)
$$

$$
\varepsilon = \varepsilon_0 \exp(De)
$$

Maxwell model can not be applied to creep experiments because it only gives the viscous contribution at constant load ($$\frac{d\tau_{yx}}{dt} = 0$$)

$$
\tau_{yx} + 0 = \eta \dot{\gamma}
$$

Similarly the Voigt model is not realistic when stress-relaxation is considered, as it omits viscous character of the material and just gives the elastic solid contribution

These shortcomings of the two model are overcome by their serial or parallel combination as in standard linear solid model

Here the number of Voigt or Maxwell elements can be increased in order to fit the creep or stress relaxation behavior of real viscoelastic materials
We can model the behavior of any material at practical engineering conditions by combination of these models.

Consider the behavior represented by these models in terms of plots of strain versus time when a stress is applied at time $t_1$ and it is removed at time $t_2$. 

![Strain versus time plots for Spring, Dashpot, Maxwell model, Voigt model and Elastoplastic behavior](image_url)
Viscoelastic behavior of plastics

Polymers that can be strained significantly at stresses above their yield point are termed plastics. Their time-dependent deformation at stresses well below the yield strength is viscoelasticity.

All polymers have complex microstructure consisting of molecules with a wide distribution of molecular weights, i.e., many different sizes of molecules.

If we know the exact number of molecules with each size which can be represented by a Maxwell or Voigt element, we can precisely model their viscoelastic behavior by adding that number of elements to the combined model.

Short molecules have less degree of freedom and can relax in a shorter time (return to their most probable orientation).

Long molecules can move, rotate, and entangle more which makes their relaxation time longer.

The chemistry of the molecules, temperature, time frame of deformation also determine the viscoelastic response observed.
Viscoelastic behavior of plastics

Graph 1: Log G(t) vs. Log time (sec)
- Glassy region
- Transition
- Rubbery plateau
- Low molecular weight
- High molecular weight

Graph 2: Log E (Pa) vs. Temperature
- Glassy region
- Rubbery plateau
- Low molecular weight
- Cross-linked elastomers
- Melt
Creep of plastic materials

Some materials do not seem to deform below their yield strengths and deform extensively above it. Plastics refer to these materials with low yield strengths. Plastics at practical engineering conditions are viscoelastic: they also deform viscously.

A common example is plasticine or play-doh. It is a mixture of clay and mineral oil.

This material deforms easily and to a large extent. It is often used to model metal working operations such as forging, rolling, milling, extrusion, and cutting due to the similarity of its plastic behavior to hot metals.

Its response to deformation is represented as $\sigma = \sigma_Y + \mu \dot{\gamma}^n$ Herschel-Bulkley Equation

where $\sigma_Y$ is the yield strength. Viscoplastic materials have yield strengths.
The creep behavior of plasticine was investigated by Barnes et al. under very long-time testing (days).

Its flow behavior at loads under yield stress was seen as typical non-Newtonian, steady-state liquid behavior:

This means that materials do not really have yield strengths when tested under precise rheometrical conditions, where very small shear rates are capable of being measured at very small stresses at very long times.

Yield strength is assigned to ductile solids for engineering purposes based on measurements obtained under limited conditions.
Dynamic tests for measurement of viscoelasticity

An oscillatory stress or strain is applied to the sample (it varies sinusoidally)

If the material is perfectly elastic, the resultant strain or stress should be completely in-phase with the applied stress or strain and vary as:

$$\gamma = \gamma_0 \sin(\omega t)$$

Where $\omega$ is the angular frequency in radian/s, equal to $2\pi f$ where $f$ is the frequency in cycles/s

Hooke’s law applied for small amplitudes of oscillation so that

$$\tau(t) = G\gamma_0 \sin(\omega t)$$

For a Newtonian viscous fluid, the resulting stress should be exactly 90° out-of phase with the strain because

$$\tau(t) = \eta \ast \dot{\gamma}(t) = \eta \ast \frac{d}{dt} [\gamma_0 \sin(\omega t)]$$

$$\tau(t) = \eta \ast \gamma_0 \ast \omega \ast \cos(\omega t)$$

![Purely elastic response](image1)

![Viscoelastic response](image2)
The response of a viscoelastic material to an oscillatory strain or stress is characterized by a phase angle between $0^\circ$ and $90^\circ$.

Its response is partly viscous and partly elastic.

A purely viscous response to strain is such that the resulting stress is highest at the highest strain rate which occurs at zero strain. Stress is lowest at the lowest strain rate which occurs at the highest strain. The stress-strain figure is a circle for viscous materials.
It is possible to measure the modulus of the material at the highest strain ($\gamma_0$) which corresponds to the storage modulus $G'$ or the real component of the complex shear modulus $G^*$.

Similarly, the modulus measured at the highest strain rate corresponds to the loss modulus $G''$ or the imaginary component of the complex shear modulus $G^*$.

$G^*$, $G'$, $G''$ and $\delta$ are related by a simple relationship:

\[
\tau_0 = G^* \gamma_0 \sin(\omega t + \delta)
\]
\[
\tau_0 = (G^* \cos \delta) \gamma_0 \sin(\omega t) + (G^* \sin \delta) \gamma_0 \cos(\omega t)
\]
\[
\tau_0 = G' \gamma_0 \sin(\omega t) + G'' \gamma_0 \cos(\omega t)
\]

\[
\tan \delta = \frac{G''}{G'}
\]

The magnitude of complex viscosity is obtained according to the relationship

\[
\eta^* = \frac{G^*}{\omega}
\]

$G^* = G' + iG''$
The measured values of the shear moduli $G'$ and $G''$ determine the elastic and viscous character of
the material. They depend on frequency (shear rate) and temperature but the effects are inverse

Elastic response (high $G'$) is observed at high frequencies and low temperatures
Viscous response (high $G''$) is observed vice versa
Damping (dissipation of energy relative to its storage) is seen when loss modulus is high relative to storage modulus (high $\delta$)