Introduction to Rheology of complex fluids
Brief Lecture Notes

Kinematics and material functions for shear flows
Contents

• Introductory Lecture
• Simple Flows
• Material functions & Rheological Characterization
• Experimental Observations
• Generalized Newtonian Fluids
• Generalized Linearly viscoelastic Fluids
• Nonlinear Constitutive Models
Kinematics of Couette flow
Couette flow in parallel plates

\[ v_x(H) = V_w(t) = \dot{\gamma}(t)H \]

\[ \dot{\gamma} = \dot{s}(t)y \varepsilon_x \]

\[ \dot{s}(t) \text{ Deformation rate} \]

\[ \dot{s}(t) = \frac{\partial v_x}{\partial y} \]

Path lines

Steady Shear

Transient flow

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Rate of deformation tensor for shear flow

Velocity Fields

\[ \mathbf{v} = \dot{\gamma}(t) y \mathbf{e}_x \]
\[ \dot{\gamma}(t) = \frac{\partial v_x}{\partial y} \]

Rate of deformation tensor

\[ \dot{\mathbf{\gamma}} = \begin{pmatrix} 0 & \dot{\gamma}(t) & 0 \\ \dot{\gamma}(t) & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \]

Rate of deformation magnitude

\[ \dot{\gamma}(t) = \left\| \dot{\mathbf{\gamma}} \right\| = \left\| \nabla \mathbf{v} + (\nabla \mathbf{v})^T \right\| = \frac{\sqrt{\dot{\gamma} : \dot{\mathbf{\gamma}}}}{2} = \left| \dot{\gamma}(t) \right| \]

Always positive

The rate of deformation may depend on time, but not in space.

It can be positive or negative

These flows are called homogeneous.
Why shear-flow is a standard flow;

- It is the simplest flow field
- It represents various, more complex laminar flows
- The stress tensor has a simple form: 2x2 nonzero entries
Shear Flows
All possible shear flows

1. Steady shear flow

Velocity field

\[ v_x = \dot{\gamma}_o y \]

2. Small amplitude oscillatory shear

Velocity field

\[ v_x = \dot{\gamma}_o \cos(\omega t) y \]
All possible shear flows

3. Stress Growth

\[ \dot{\gamma} = 0 \]

\[ v_x = 0 \]

\[ V_w = 0 \]

\[ t < 0 \]

4. Stress relaxation

\[ \dot{\gamma} = \dot{\gamma}_o \ y \]

\[ v_x = \dot{\gamma}_o \ y \]

\[ V_w = 0 \]

\[ t < 0 \]

\[ \dot{\gamma} = 0 \]

\[ v_x = 0 \]

\[ V_w = 0 \]

\[ t \geq 0 \]
All possible shear flows

5. Step strain

\[ \dot{v}_x = 0 \]

\[ t < 0 \]

6. Creep

\[ \tau_{yx} = 0 \]
\[ v_x = 0 \]

\[ t < 0 \]

\[ \dot{v}_x = \dot{\gamma}_o \delta(t) y \]

\[ t \geq 0 \]

\[ \dot{\gamma}(t) = \dot{\gamma}_o \delta(t) \]

Fixed shear stress

\[ \tau_{yx} = \tau_0 \]
\[ v_x = \dot{\gamma}(t) y \]

\[ t \geq 0 \]
All possible shear flows

7. Constrained Recoil after steady Shear Flow

\[ \tau_{yy} = \tau_0 \]
\[ v_x = \dot{\gamma}_0 y \]

\[ t < 0 \]

\[ \tau_{yy} = 0 \]
\[ v_x = \dot{\gamma}(t) y \]

\[ t \geq 0 \]
Steady Shear Flow
Steady shear flow

Velocity Field
\[ v_x(x, y, z) = \dot{\gamma}_o y \]
\[ v_y(x, y, z) = 0 \]
\[ v_z(x, y, z) = 0 \]

Material properties

Viscosity
\[ \eta = \frac{\tau_{xy}}{\dot{\gamma}} \]
\[ \eta = \eta(\dot{\gamma}) \]

Coefficient of 1\textsuperscript{st} normal stress difference
\[ \psi_1 = \frac{\tau_{xx} - \tau_{yy}}{\dot{\gamma}^2} \]
\[ \psi_1 = \psi_1(\dot{\gamma}) \]

Coefficient of 2\textsuperscript{nd} normal stress difference
\[ \psi_2 = \frac{\tau_{yy} - \tau_{zz}}{\dot{\gamma}^2} \]
\[ \psi_2 = \psi_2(\dot{\gamma}) \]

Kinematics
\[ \dot{\gamma}(t) = \dot{\gamma}_o \]

Notation
\[ v_w \]
\[ 1, 2, 3 \leftrightarrow x, y, z \]
At low shear rates the viscosity is independent of the shear rate. It is called zero shear rate viscosity $\eta_o$. 

$$\eta = \frac{\tau_{xy}}{\dot{\gamma}}$$

$$\eta_o = \lim_{\dot{\gamma} \to 0} \eta(\dot{\gamma})$$

A typical polymeric fluid
Material properties: $\Psi_1$

For Newtonian Fluids

$$\psi_1 = 0$$

A typical polymeric fluid

$$\psi_{1,o} = \lim_{\dot{\gamma} \to 0} \psi_1(\dot{\gamma})$$
Material properties: shear viscosity for melts

$$\eta = \frac{\tau_{xy}}{\dot{\gamma}}$$

Viscosity of LDPE melts at various temperatures
Material properties: shear viscosity for solutions

Intrinsic viscosity:

\[
[\eta] \equiv \lim_{c \to 0} \left( \frac{\eta - \eta_s}{c \eta_s} \right)
\]

c: polymer concentration

Higgins Law:

\[ \eta_r = \frac{\eta}{\eta_s} = 1 + [\eta]c + k'[\eta]^2 c^2 + \ldots \]

The intrinsic viscosity \([\eta]\) of polystyrene in various solvents, as a function of a normalized rate of deformation, \(\beta\).

\([\eta]_o\): zero shear value, \(\eta_s\) solvent viscosity.
Startup of Steady Shear Flow or Stress Growth
Steady Shear Flow Startup

Material properties

Startup

Viscosity

Coefficient of 1\textsuperscript{st} normal stress difference

\[ \eta^+ = \frac{\tau_{xy}}{\dot{\gamma}} \]

Coefficient of 2\textsuperscript{nd} normal stress difference

\[ \psi_1^+ = \frac{\tau_{xx} - \tau_{yy}}{\dot{\gamma}^2} \]

\[ \psi_2^+ = \frac{\tau_{yy} - \tau_{zz}}{\dot{\gamma}^2} \]

Kinematics

\[ \dot{\gamma}(t) = \begin{cases} 0 & t < 0 \\ \dot{\gamma}_0 & t \geq 0 \end{cases} \]
Material properties: Startup shear viscosity
Initially entangled chains, later disentangled

\[ \eta^+(t) = \frac{\tau_{xy}}{\dot{\gamma}} \]

\[ \eta_o = \lim_{\dot{\gamma}_o \to 0} \eta(\dot{\gamma}_o) \]

\[ \eta(\dot{\gamma}_o) = \lim_{t \to \infty} \eta^+(t; \dot{\gamma}_o) \]

Polystyrene solution
Material properties: \textbf{Startup }\Psi_{1}^{+}

\[ \Psi_{1}^{+}(t) = \frac{\tau_{xx} - \tau_{yy}}{\dot{\gamma}^2} \]

\textbf{Linear elastic behavior}

\textbf{Polystyrene solution}
Cessation of a Steady Shear Flow or Stress Relaxation
Cessation of shear flow

Material properties

<table>
<thead>
<tr>
<th>Cessation</th>
<th>Coefficient of 1\textsuperscript{st} normal stress difference</th>
<th>Coefficient of 2\textsuperscript{nd} normal stress difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Viscosity</td>
<td>$\eta^- = \frac{\tau_{xy}}{\dot{\gamma}}$</td>
<td>$\psi^- = \frac{\tau_{xx} - \tau_{yy}}{\dot{\gamma}^2}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\psi^+ = \frac{\tau_{yy} - \tau_{zz}}{\dot{\gamma}^2}$</td>
</tr>
</tbody>
</table>

Kinematics

$t < 0$

$V_w = 0$

$t \geq 0$

Stress relaxation

$\dot{\gamma} = \begin{cases} \dot{\gamma}_0 & t < 0 \\ 0 & t \geq 0 \end{cases}$
Material properties: Cessation shear viscosity

\[ \eta^{-}(t) = \frac{\tau_{xy}}{\dot{\gamma}} \]

Polyisobutylene solution

Linear elastic behavior
Material properties: Cessation $\Psi_1^-$

$$\psi_1^-(t) = \frac{\tau_{xx} - \tau_{yy}}{\dot{\gamma}^2}$$

Polyisobutylene solution

Linear elastic behavior
Small Amplitude Oscillatory Shear: SAOS
Small Amplitude Oscillatory Shear (SAOS)

Location of a wall-point under steady shear

\[ l(t) = V_w t = H\gamma_o t \]

Location of a wall-point under oscillatory shear

\[ l(t) = H\gamma_o \sin(\omega t) = \frac{H}{\omega} \gamma_o \sin(\omega t) \]

\[ \gamma_{yx}(t) = \gamma_o \sin(\omega t) \]

\[ \gamma_o = \omega \gamma_o \]

\[ \dot{\gamma}_{yx}(t) = \omega \gamma_o \cos(\omega t) \]

\[ v_x = \dot{\gamma}_o \cos(\omega t) y \]
Small Amplitude Oscillatory Shear (SAOS)

**displacement**

\[ \gamma_{yx} = \frac{\gamma_o}{\omega} \sin(\omega t) = \gamma_o \sin(\omega t) \]

**stress**

\[ \tau_{yx} = \tau_o \sin(\omega t + \delta) \]

\[ = (\tau_o \cos(\delta)) \sin(\omega t) + (\tau_o \sin(\delta)) \cos(\omega t) \]

- **Solid** \( \delta = 0 \)
  - “In phase” with the applied displacement

- **Fluid** \( \delta = 90 \)
  - “Out of phase” with the applied displacement

\( \delta \): phase difference
SAOS

Viscous fluid

\[ \tau_{yx} = \dot{\gamma}_o \eta'' \cos(\omega t) \]

Viscous behavior, completely “out of phase” with deformation

Elastic solid

\[ \tau_{yx} = \gamma_o G \sin(\omega t) \]

Elastic behavior, completely “in phase” with deformation
Complex shear modulus $G^*$

\[ \tau_{yx} = \gamma_o G' \sin(\omega t) + \gamma_o G'' \cos(\omega t) \]

Storage modulus \[ G' \equiv \frac{\tau_o}{\gamma_o} \cos(\delta) \] Elastic behavior, in phase with deformation

Loss modulus \[ G'' \equiv \frac{\tau_o}{\gamma_o} \sin(\delta) \] Viscous behavior, out of phase with deformation

Complex shear modulus \[ G^*(\omega) \equiv G'(\omega) + iG''(\omega) \]
Complex viscosity \( \eta^* \)

\[
\tau_{yx} = \dot{\gamma}_o \eta' \sin(\omega t) + \dot{\gamma}_o \eta'' \cos(\omega t)
\]

\[
\eta' \equiv \frac{\tau_o}{\dot{\gamma}_o} \sin(\delta) = \frac{G''}{\omega} \quad \eta'' \equiv \frac{\tau_o}{\dot{\gamma}_o} \cos(\delta) = \frac{G'}{\omega}
\]

Complex viscosity

\[
\eta^*(\omega) \equiv \eta'(\omega) - i \eta''(\omega)
\]
Material functions for SAOS

Magnitude of shear modulus
$$|G^*| = \sqrt{G''^2 + G'^2}$$

Loss angle
$$\tan(\delta) = \frac{G''}{G'}$$

Dynamic viscosity
$$\eta' = \frac{G''}{\omega}$$
$$\eta'' = \frac{G'}{\omega}$$

Out of phase component of $\eta^*$
$$|\eta^*| = \sqrt{\eta'^2 + \eta''^2}$$

Magnitude of complex viscosity
$$|J^*| = \frac{1}{|G^*|}$$

Magnitude of complex compliance
$$J' = \frac{1/G'}{1 + \tan^2(\delta)}$$
$$J'' = \frac{1/G''}{1 + \tan^{-2}(\delta)}$$

Storage compliance
Loss compliance
Storage and loss moduli

SUPER BALL

LOSS (G'')

STORAGE (G')

TENNIS BALL

LOSS (G'')

STORAGE (G')
How strongly viscoelastic is a material?

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

<table>
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<tr>
<th>Viscous behavior</th>
<th>Viscoelastic behavior</th>
<th>Elastic behavior</th>
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</thead>
<tbody>
<tr>
<td>G'' &gt;&gt; G'</td>
<td>G'' &gt; G'</td>
<td>G'' = G'</td>
</tr>
<tr>
<td>G' &gt; G''</td>
<td></td>
<td>G' &gt;&gt; G''</td>
</tr>
<tr>
<td>tan(\delta) &gt;&gt; 1</td>
<td>tan(\delta) &gt; 1</td>
<td>tan(\delta) = 1</td>
</tr>
<tr>
<td>(\rightarrow \infty)</td>
<td>tan(\delta) = 1</td>
<td>tan(\delta) &lt; 1</td>
</tr>
<tr>
<td></td>
<td>tan(\delta) &lt; 1</td>
<td>(\rightarrow 0)</td>
</tr>
</tbody>
</table>
The amplitude of deformation can be chosen arbitrarily, but it should be small enough.
Loss Angle

It is a function of temperature, frequency and polymer structure

$$\tan(\delta) = \frac{G''}{G'}$$
In the linear region, $G$ is constant. In the non-linear region, $G = f(\gamma)$. The end of LVR occurs at a critical strain $\gamma_c$. 

Non-linear region $G = f(\gamma)$
Concept of Linear Viscoelastic Region

“If the deformation is small, or applied sufficiently slowly, the molecular arrangements are never far from equilibrium. The mechanical response is then just a reflection of dynamic processes at the molecular level which continue constantly, even for a system at equilibrium. This is the domain of LINEAR VISCOELASTICITY. The magnitudes of stress and strain are related linearly, and the behavior for any liquid is completely described by a single function of time.” (Bill Graessley, Princeton University)

Reference:
Magnitude of complex viscosity

\[ |\eta^*(\omega)| = \frac{\sqrt{G'(\omega)^2 + G''(\omega)^2}}{\omega} \]
Calculation of $\lambda$, $\eta_0$, $J_s^o$ from SAOS

RC-3 polybutylene $M_w=940,000$ $M_w/M_n<1.1$, $T_g=-99^\circ C$

\[ \eta_0 = \lim_{\omega \to 0} \left( \frac{G''(\omega)}{\omega} \right) = \lim_{\omega \to 0} \left( \eta'(\omega) \right) \]

\[ J_s^o = \lim_{\omega \to 0} \left( \frac{G'(\omega)}{G''^2(\omega)} \right) \]

\[ A_G = J_s^o \eta_0^2 \]

For a cycle the period is given by $2\pi/\omega$

For $\omega = 10^{-4}$ rad/sec, $2\pi/\omega \cong 1$ day
Cox-Merz’s rule

At the limit of low frequencies \( \omega \to 0 \)

\[
\eta(\dot{\gamma}) = \left| \eta^*(\omega) \right|_{\omega=\dot{\gamma}} = \sqrt{\left( \frac{G'}{\omega} \right)^2 + \left( \frac{G''}{\omega} \right)^2} \bigg|_{\omega=\dot{\gamma}}
\]

At low frequencies the elastic behavior is weak

\[
\eta(\dot{\gamma}) = \left| \eta'(\omega) \right|_{\omega=\dot{\gamma}}
\]
Laun’s rule

At the limit of low frequencies \( \omega \rightarrow 0 \)

\[
\Psi_1(\dot{\gamma}) = 2\left( \frac{G'(\omega)}{\omega^2} \right) \left\{ 1 + \left( \frac{G'(\omega)}{G''''(\omega)} \right)^2 \right\}^{0.7}
\]

\( \omega = \dot{\gamma} \)
A summary of standard shear flows, deformations and stresses
Flow  Deformation  stress

a. Steady
\[ \dot{\gamma}(t) \]
\[ \gamma_{yx}(0, t) \]
\[ \tau_{yx}(t) \]

b. Stress Growth
\[ \dot{\gamma}(t) \]
\[ \gamma_{yx}(0, t) \]
\[ \tau_{yx}(t) \]

c. Stress Relaxation
\[ \dot{\gamma}(t) \]
\[ \gamma_{yx}(0, t) \]
\[ \tau_{yx}(t) \]
Flow  Deformation  Stress

d. Creep

\[ \dot{\gamma}(t) \]

\[ \gamma_{yx}(0, t) \]

\[ \tau_{yx}(t) \]

e. Step Strain

\[ \dot{\gamma}(t) \]

\[ \gamma_{yx}(0, t) \]

\[ \tau_{yx}(t) \]

f. SAOS

\[ \gamma_o \cos \omega t \]

\[ \gamma_o \sin \omega t \]

\[ \tau_o \sin(\omega t + \delta) \]
Summary of flows and Material Properties

<table>
<thead>
<tr>
<th>Flow</th>
<th>Material Function</th>
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<tbody>
<tr>
<td>Steady shear flow</td>
<td>$\dot{\gamma}_{yx} = \dot{\gamma} = \text{constant}$</td>
</tr>
<tr>
<td>Small-amplitude oscillatory shear</td>
<td>$\dot{\gamma} = \dot{\gamma}_0 \cos \omega t$</td>
</tr>
<tr>
<td>stress growth upon inception of steady shear flow</td>
<td>$\dot{\gamma} = 0 \ t &lt; 0, \ \dot{\gamma} = \dot{\gamma}_0 \ t \geq 0$</td>
</tr>
<tr>
<td>Stress relaxation after cessation of steady shear flow</td>
<td>$\dot{\gamma}_{yx} = \dot{\gamma}<em>0 \ t &lt; 0, \ \dot{\gamma}</em>{yx} = 0 \ t \geq 0$</td>
</tr>
<tr>
<td>Stress relaxation after a sudden shearing displacement</td>
<td>$\dot{\gamma}_{yx} = \dot{\gamma}_0 \delta(t)$</td>
</tr>
<tr>
<td>Creep</td>
<td>$\tau_{yx} = 0 \ t &lt; 0, \ \tau_{yx} = \tau_0 \ t \geq 0$</td>
</tr>
<tr>
<td>Constrained recoil after steady shear flow</td>
<td>$\tau_{yx} = \tau_0 \ t &lt; 0, \ \tau_{yx} = 0 \ t \geq 0$</td>
</tr>
</tbody>
</table>

- $\eta(\dot{\gamma}), \Psi_1(\dot{\gamma}), \Psi_2(\dot{\gamma})$
- $\eta'(\omega), \eta''(\omega)$
- $G'(\omega) = \eta'' \omega, \ G''(\omega) = \eta' \omega$
- $\eta^+(t, \dot{\gamma}_0), \Psi^+_1(t, \dot{\gamma}_0), \Psi^+_2(t, \dot{\gamma}_0)$
- $\eta^-(t, \dot{\gamma}_0), \Psi^-_1(t, \dot{\gamma}_0), \Psi^-_2(t, \dot{\gamma}_0)$
- $G(t, \gamma_0), G_{\Psi_i}(t, \gamma_0)$
End of lecture
Creep and recoil
Complex compliance \( J^* \)

\[
J^*(\omega) \equiv \frac{1}{G^*(\omega)} = J'(\omega) - iJ''(\omega)
\]

where

\[
G' = \frac{J'}{(J')^2 + (J'')^2} \quad G'' = \frac{J''}{(J')^2 + (J'')^2}
\]
6. Creep

Application of constant shear stress

\[ \tau_{yx} = \tau_0 \]

\[ v_x = \dot{\gamma}(t) y \]

7. Constrained Recoil after steady Shear Flow

Zeroing of applied shear stress

\[ \tau_{yx} = 0 \]

\[ v_x = \dot{\gamma}(t) y \]
Viscoelastic recoil
Shear Creep

The shear stress is imposed and we measure the deformation

\[ \tau_{yx}(t) = \begin{cases} 0, & t < 0 \\ \tau_o, & t \geq 0 \end{cases} \]

- At steady state, both shear stress and shear rate are constant.
- Thus at steady state (e.g. viscosity curve), the results are the same whether one imposes the shear rate or the shear stress.
- However, the transient behaviors are described by different material functions.
Shear creep and recoil

• Shear creep: A stress starts to be applied at $t_1$. The deformation $\gamma(t)$ is plotted as function of time.

• Recoil: Stress is zeroed at $t_2$, and deformation $\gamma(t)$ is measured as function of time.

\[ \tau_{yx}(t) = \begin{cases} 0, & t < t_1 \\ \tau_o, & t_2 \geq t \geq t_1 \end{cases} \]
Creep kinematic and Material Functions

Kinematic

\[ \nu \equiv \dot{\gamma}_{yx}(t) y e_x \]

Material functions

\[ J(t, \tau_o) \equiv \frac{\gamma_{yx}(0, t)}{\tau_o} \]

Shear compliance

\[ J_r(t', \tau_o) \equiv \frac{\gamma_r(t')}{\tau_o} \]

 Recoverable compliance

\[ \tau_{yx}(t) = \begin{cases} 0, & t < 0 \\ \tau_o, & t \geq 0 \end{cases} \]
Shear creep and recoil:
Elastic and Viscous Materials

- For $t>t_1$ the deformation is constant
- For $t>t_2$ the deformation is zero

Elastic Material

- For $t>t_1$ the rate of deformation is constant
- For $t>t_1$ the deformation increases in time
- For $t >t_2$ the rate of deformation is 0

Viscous Material
Shear creep and recoil: Viscoelastic Material

Rate of deformation reduces up to a constant value.

Viscoelastic fluid recoils, and reaches at a steady state, having a permanent deformation.

\[ \tau_o > 0 \quad \tau_o = 0 \]

\[ t_1 = 0 \quad t_2 \quad \text{time} \]

Recoverable deformation
Creep compliance

Compliance

\[ J(t, \tau_o) = \frac{\gamma_{yx}(0,t)}{\tau_o} \]

the flow ability of a material as a response of an applied stress (~ 1/ (shear rate) )

At steady state

\[ J(t, \tau_o) = J_s(\tau_o) + \frac{t}{\eta(\dot{\gamma}_{t=\infty})} \]

Steady state compliance
Creep compliance at steady state

At large times, the compliance exhibits a linear variation

$$\left. \frac{dJ(t, \tau_o)}{dt} \right|_{\text{steady state}} \equiv \frac{d\gamma_{yx}(0,t)}{dt} \frac{1}{\tau_o} = \frac{\dot{\gamma}_\infty}{\tau_o} = \frac{1}{\eta(\dot{\gamma}_\infty)}$$

The slope

If we integrate it in time, we get:

$$\left. \frac{dJ(t, \tau_o)}{dt} \right|_{\text{steady state}} = \frac{1}{\eta(\dot{\gamma}_\infty)} \Rightarrow J(t, \tau_o)\Bigg|_{\text{steady state}} = \frac{1}{\eta(\dot{\gamma}_\infty)} t + C$$

Compliance at steady state
Compliance of a Newtonian Fluid

\[ J(t) \]

\[ \frac{1}{\eta} \]
Creep recovery

- After the imposition of creep, the applied stress is zeroed.
- Elastic and viscoelastic materials will recoil in the opposite direction of the creep.

$$J(t, \tau_o)$$

1

$$\eta(\dot{\gamma}_{t=\infty})$$

$$R(t', \tau_o)$$

$$R_\infty(\tau_o)$$

Ultimate recoil function
Kinematic and Material Functions

Deformation recovery in recoil

As function of $t$

As function of $t'$

Recoverable compliance or recoil function:

\[
\gamma_r \equiv \gamma_{21}(0, t_2) - \gamma_{21}(0, t)
\]

\[
\gamma_r(t) \equiv -\int_{t_2}^{t} \gamma(t'')dt''
\]

\[
\gamma_r(t') \equiv -\int_{0}^{t'} \gamma(t'')dt''
\]

\[
J_r(t', \tau_o) = R(t', \tau_o) \equiv \frac{\gamma_r(t)}{\tau_o}
\]
Recovery functions

\[ J(t) \Big|_{\text{steady state}} \equiv J_s^0 + \frac{t}{\eta_o} \]

\[ J(t) \equiv R(t) + \frac{t}{\eta_o} \]

\[ \frac{1}{\eta_o} \]

\[ J_s^0 \]

\[ J(t) \]

\[ 0 \]

\[ -t_2 \]

\[ t_2 \]

\[ t, \text{ creep} \]

\[ t', \text{ recovery} \]
Shear recoil

PS melt

\[ \gamma(t) = \gamma_r(t) + t \dot{\gamma}_\infty \]

recoverable strain

total strain

non-recoverable strain

\( \log \left[ I_p(t) - I_{\text{th}} \right], \text{cm}^2/\text{dyn} \)

\( \log t, \text{s} \)

\( \log \left[ I_p(t) - I_{\text{th}} \right], \text{cm}^2/\text{dyn} \)

\( \log t/\alpha_r, \text{s} \)
Step stain in shear
Step strain in shear

5. Step strain in shear

\( v_x = 0 \)  

\( t < 0 \)

\( v_x = \dot{\gamma}_o \delta(t) y \)

\( t \geq 0 \)

\( \ddot{\zeta}(t) = \dot{\gamma}_o \delta(t) \)

Stress relaxation
Step strain for elastic materials

- Deformation is not a flow, unless the material is viscoelastic.
- If we impose an elastic solid in such a deformation, we can calculate the shear modulus as $G$.

\[ G = \frac{\tau_{xy}}{\gamma_o} \]

\[ \gamma_o = \frac{\delta x}{H} \]
Relaxation experiment for an elastic material
Stress relaxation experiment

Elastic solid
Hookean Solid

Stress for $t>0$ is constant

Viscous fluid
Newtonian Fluid

Stress for $t>0$ is 0
Relaxation experiment for a viscoelastic material

• Shear stress is decreasing function of time.

• In small deformations (in LVE), the ratio stress to deformation is only function of time.

• It is called shear modulus \( G(t) \):

\[
G(t) = \frac{\tau_{yx}(t)}{\gamma_0}
\]
Step strain in shear

Kinematic for step strain in shear

\[ \dot{\gamma}(t) = \lim_{\varepsilon \to 0} \begin{cases} 0 & t < 0 \\ \dot{\gamma}_o & 0 \leq t < \varepsilon \\ 0 & t \geq \varepsilon \end{cases} \]

Relation between deformation and rate of deformation in shear flow:

\[ \frac{d\gamma_{yx}(t_{ref}, t)}{dt} = \dot{\gamma}_{yx} \quad \gamma_{yx}(-\infty, t) = \dot{\gamma}_0 \varepsilon \equiv \gamma_0 \]
Material functions for step strain

Relaxation modulus

\[ G(t, \gamma_o) \equiv \frac{\tau_{yx}(t, \gamma_o)}{\gamma_o} \]

Relaxation modulus for the 1st normal stress difference

\[ G_{\psi_1}(t, \gamma_o) \equiv \frac{\tau_{xx} - \tau_{yy}}{\gamma_o} \]

Relaxation modulus for the 2nd normal stress difference

\[ G_{\psi_2}(t, \gamma_o) \equiv \frac{\tau_{yy} - \tau_{zz}}{\gamma_o} \]
Linear Viscoelasticity

Viscoelastic relaxation modulus of flexible linear polymers.

*Polym J.* 2009, 41(11), 929.
Experimental observations

Relaxation Modulus:

$$G(t, \gamma_0) \equiv \frac{\tau_{yx}(t, \gamma_0)}{\gamma_0}$$

For small deformations

$$\lim_{\gamma_0 \to 0} G(t, \gamma_0) = G(t)$$

Lodge-Meissner's rule:

$$\frac{G(t, \gamma_0)}{G_{\Psi_1}(t, \gamma_0)} = 1$$
Experimental observations

\[ G(t, \gamma) \text{ (kPa)} \]

\[ \gamma = 0.52, 0.76 \text{ and } 1 \]

Linear viscoelastic limit, \( G(t) \)

\[ \gamma = 1, 2, 4, 8, 16 \]
Gleissle’s rule

Bird, Armstrong, Hassager (1987); Dealy & Wissbrun (1990)

\[ \eta^+(t) \approx \eta(\dot{\gamma}) \]

They are valid in the linear elastic region

\[ \Psi^+(t) \approx \Psi_1(\dot{\gamma}) \]

\[ \Psi_1(\dot{\gamma}) \approx -2 \int_{\dot{\gamma}/k}^{\infty} x^{-1} \left[ \frac{\partial \eta(x)}{\partial x} \right] dx \]

k varies between 2<k<3, and can be calculated with a fitting procedure

\[ \eta \leftrightarrow \eta^+ \]

\[ \Psi_1 \leftrightarrow \Psi^+ \]

\[ \Psi_1 \leftrightarrow \eta \]