What exactly do we observe when we subject non-Newtonian fluids to deformation?

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Rheology uses a sort of an ASTM or ISO-like technical standards approach to organize observations:

1. Choose a standard flow (shear or elongation)
2. Choose a set of flow kinematics (the speed and time-profile of the specific test)
3. Measure specified quantities (related to stress or deformation)
4. Report a standardized reported function (material function)
What exactly do we observe when we subject non-Newtonian fluids to deformation?

<table>
<thead>
<tr>
<th>Standard flow</th>
<th>( \dot{\gamma}(t) = )</th>
<th>Standard kinematics</th>
<th>What do we observe?</th>
</tr>
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<tbody>
<tr>
<td>Shear</td>
<td>( \begin{pmatrix} \dot{\gamma}(t) x_2 \ 0 \ 0 \end{pmatrix} )</td>
<td></td>
<td>( \begin{array}{c} \text{Shear} \ \text{Material Functions} \end{array} )</td>
</tr>
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<td></td>
<td></td>
<td>( \sigma_{ij} )</td>
<td>( \begin{array}{c} \text{a) Steady} \ \text{b) Start-up} \ \text{c) Cessation} \ \text{d) Step-strain} \ \text{e) SAOS}^* \end{array} )</td>
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\( (*SAOS = \text{small-amplitude oscillatory shear}) \)

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\( \sigma_{ij} = \frac{\partial \ddot{\gamma}_{ij}}{\partial \dot{\gamma}_{ij}} \)
What exactly do we observe when we subject non-Newtonian fluids to deformation?

**Material Functions**

Summarized on “recipe cards”

- Vocabulary (framework) of material comparison
- Used to characterize a material as Newtonian vs. non-Newtonian

### Newtonian

- \( \eta = \mu = \text{constant} \)
- \( \Psi_1 = \Psi_2 = 0 \)
- \( G' = 0 \)
- etc.

### Non-Newtonian

- \( \eta = \eta' \)
- \( \Psi_1 \neq 0; \Psi_2 \neq 0 \)
- \( G', G'' \neq 0 \)
- etc.

• Within non-Newtonian fluids, used to further categorize materials
  - Cross-linked rubber: \( G' = G_0 = \text{constant} \)
  - Entangled melt: characteristic \( G'(\omega), G''(\omega) \) shapes
  - Shear thinning, shear thickening melt: characteristic \( \eta' \)
  - Branched polymer: characteristic \( G'(\omega), G''(\omega) \) shapes
Part II-A. Continuum versus molecular modeling

**Shear Material Functions**

\[ \gamma \equiv \begin{pmatrix} \dot{\gamma}(t)x_1 \\ \frac{1}{2}\dot{\gamma}(t)x_2 \\ \frac{1}{3}\dot{\gamma}(t)x_3 \end{pmatrix} \]

a) Steady

b) Start-up

c) Cessation

**Elongation Material Functions**

\[ \gamma \equiv \begin{pmatrix} \dot{\gamma}(t)x_1 \\ \frac{1}{2}\dot{\gamma}(t)x_2 \\ \frac{2}{3}\dot{\gamma}(t)x_3 \end{pmatrix} \]

da) Steady

e) SAOS

f) Creep

(c currently unobservable)

(exists, but easily converted to SAOS so is redundant)

(exists)
### Steady Shear Flow Material Functions

**Imposed Kinematics:**

\[
y(t) = \begin{pmatrix} 
\dot{\gamma}(t) \chi_{2} \\
0 \\
0 
\end{pmatrix}_{123}
\]

\[\dot{\gamma}(t) = \dot{\gamma}_0 = \text{constant}\]

**Material Stress Response:**

\[\bar{\tau}_{21}(t)\]

\[N_1(t)\]

**Material Functions:**

Viscosity \[
\eta(\dot{\gamma}_0) = \frac{\bar{\tau}_{21}}{\dot{\gamma}_0}
\]

First normal-stress coefficient \[
\psi_1(\dot{\gamma}_0) = \frac{\bar{\tau}_{11} - \bar{\tau}_{22}}{\dot{\gamma}_0}
\]

Second normal-stress coefficient \[
\psi_2(\dot{\gamma}_0) = \frac{\bar{\tau}_{22} - \bar{\tau}_{33}}{\dot{\gamma}_0}
\]

### Start-up of Steady Shear Flow Material Functions

**Imposed Kinematics:**

\[
y(t) = \begin{pmatrix} 
\dot{\gamma}(t) \chi_{2} \\
0 \\
0 
\end{pmatrix}_{123}
\]

\[\dot{\gamma}(t) = \begin{cases} 
0 & t < 0 \\
\dot{\gamma}_0 & t \geq 0
\end{cases}\]

**Material Stress Response:**

\[\bar{\tau}_{21}(t)\]

\[N_1(t)\]

**Material Functions:**

Shear stress growth function \[
\eta^+(t, \dot{\gamma}_0) = \frac{\bar{\tau}_{21}(t)}{\dot{\gamma}_0}
\]

First normal-stress growth coefficient \[
\psi_1^+(t, \dot{\gamma}_0) = \frac{\bar{\tau}_{11} - \bar{\tau}_{22}}{\dot{\gamma}_0}
\]

Second normal-stress growth coefficient \[
\psi_2^+(t, \dot{\gamma}_0) = \frac{\bar{\tau}_{22} - \bar{\tau}_{33}}{\dot{\gamma}_0}
\]
Cessation of Steady Shear Flow Material Functions

**Imposed Kinematics:**
\[
y(t) = \begin{pmatrix} \dot{\gamma}(t)x_2 \\ 0 \\ 0 \end{pmatrix}
\]
\[
\dot{\gamma}(t) = \begin{cases} \dot{\gamma}_0 & t < 0 \\ 0 & t \geq 0 \end{cases}
\]
\[
\gamma(t, 0) = \begin{cases} \gamma_0 & t < 0 \\ 0 & t \geq 0 \end{cases}
\]

**Material Stress Response:**
\[
\mathbf{F}_1(t) = \begin{pmatrix} \tilde{F}_{11}(t) \\ \tilde{F}_{12} \\ \tilde{F}_{13} \end{pmatrix}
\]
\[
N_1(t) = \begin{pmatrix} N_{11} \\ N_{12} \\ N_{13} \end{pmatrix}
\]

**Material Functions:**
- Shear stress decay function:
  \[
  \eta(t, \dot{\gamma}_0) = \frac{\tilde{F}_{21}(t)}{\gamma_0}
  \]
- First normal-stress decay coefficient:
  \[
  \Psi_1(t, \dot{\gamma}_0) = \frac{\tilde{F}_{11} - \tilde{F}_{22}}{\gamma_0}
  \]
- Second normal-stress decay coefficient:
  \[
  \Psi_2(t, \dot{\gamma}_0) = \frac{\tilde{F}_{22} - \tilde{F}_{33}}{\gamma_0}
  \]

Step Strain Shear Flow Material Functions

**Imposed Kinematics:**
\[
y(t) = \begin{pmatrix} \dot{\gamma}(t)x_2 \\ 0 \\ 0 \end{pmatrix}
\]
\[
\dot{\gamma}(t) = \begin{cases} \dot{\gamma}_0 & t < \varepsilon \\ 0 & t \geq \varepsilon \end{cases}
\]
\[
\gamma(t, 0) = \begin{cases} \gamma_0 & t < \varepsilon \\ 0 & t \geq \varepsilon \end{cases}
\]

**Material Stress Response:**
\[
\mathbf{F}_1(t) = \begin{pmatrix} \tilde{F}_{11}(t) \\ \tilde{F}_{12} \\ \tilde{F}_{13} \end{pmatrix}
\]
\[
N_1(t) = \begin{pmatrix} N_{11} \\ N_{12} \\ N_{13} \end{pmatrix}
\]

**Material Functions:**
- Relaxation modulus:
  \[
  G(t, \gamma_0) = \frac{\tilde{F}_{21}(t, \gamma_0)}{\gamma_0}
  \]
- First normal-stress relaxation modulus:
  \[
  G_{\Psi_1}(t, \gamma_0) = \frac{\tilde{F}_{11} - \tilde{F}_{22}}{\gamma_0}
  \]
- Second normal-stress relaxation modulus:
  \[
  G_{\Psi_2}(t, \gamma_0) = \frac{\tilde{F}_{22} - \tilde{F}_{33}}{\gamma_0}
  \]
Small-Amplitude Oscillatory Shear Material Functions

**Imposed Kinematics:**

\[
y(t) = \begin{pmatrix} \xi(t) \nu_2 \\ 0 \\ 0 \end{pmatrix}_{123}
\]

\[
\dot{\xi}(t) = \dot{\gamma}_0 \cos(\omega t)
\]

\[
\dot{\gamma}_0 = \frac{\dot{\gamma}_0}{\omega}
\]

**Material Stress Response:**

\[
\delta = \text{phase difference between stress and strain waves}
\]

\[
\gamma_{21}(t) = \gamma_{21}(0, t) = \gamma_{21}(0, t) = \gamma_{21}(0, t)
\]

\[
N_1(t) = N_2(t) = 0 \quad \text{(linear viscoelastic regime)}
\]

**Material Functions:**

**SAOS stress**

\[
\frac{\gamma_{21}(t)}{\gamma_0} = \frac{\dot{\gamma}_0}{\gamma_0} \sin(\omega t + \delta) = G' \sin(\omega t) + G'' \cos(\omega t)
\]

**Storage modulus**

\[
G'(\omega) = \frac{\gamma_0}{\gamma_0} \sin(\delta)
\]

**Loss modulus**

\[
G''(\omega) = \frac{\gamma_0}{\gamma_0} \sin(\delta)
\]

Creep Shear Flow Material Functions

**Imposed Stress**

\[
y(t) = \begin{pmatrix} \nu_{21}(t) \nu_2 \\ 0 \\ 0 \end{pmatrix}_{123}
\]

\[
\nu_{21}(t) = \begin{cases} 0 & t < 0 \\ \bar{\nu}_0 & 0 \leq t < t_2 \\ 0 & t \geq t_2 \end{cases}
\]

**Material Kinematic Response:**

For creep, the material response is the form of deformation (stress is specified).

**Material Function:**

Shear creep compliance

\[
J(t, \bar{\nu}_0) = \frac{\gamma_{21}(0, t; \bar{\nu}_0)}{\bar{\nu}_0}
\]
**Steady Elongational Flow Material Functions**

**Imposed Kinematics:**
\[
\dot{\mathbf{y}} = \begin{pmatrix}
\dot{\varepsilon}(t)x_1 \\
-\frac{1}{2}\dot{\varepsilon}(t)x_2 \\
-\frac{1}{2}\dot{\varepsilon}(t)x_3
\end{pmatrix}_{123}
\]
\[
\dot{\varepsilon}(t) = \dot{\varepsilon}_0 = \text{constant}
\]

**Material Stress Response:**
\[
\tau_{11}(t) - \tau_{22}(t)
\]

**Material Functions:**
- **Elongational Viscosity**
  \[
  \eta_e(\dot{\varepsilon}_0) \equiv \frac{\tau_{11} - \tau_{22}}{\dot{\varepsilon}_0}
  \]
  Alternatively, \( \eta^*(\dot{\varepsilon}_0) \)

---

**Start-up of Steady Elongation Material Functions**

**Imposed Kinematics:**
\[
\dot{\mathbf{y}} = \begin{pmatrix}
\dot{\varepsilon}(t)x_1 \\
-\frac{1}{2}\dot{\varepsilon}(t)x_2 \\
-\frac{1}{2}\dot{\varepsilon}(t)x_3
\end{pmatrix}_{123}
\]
\[
\dot{\varepsilon}(t) = \begin{cases}
0 & t < 0 \\
\dot{\varepsilon}_0 & t \geq 0
\end{cases}
\]

**Material Stress Response:**
\[
\tau_{11}(t) - \tau_{22}(t)
\]

**Material Functions:**
- **Elongational Start-up Function**
  \[
  \eta^*_e(t, \dot{\varepsilon}_0) \equiv \frac{\tau_{11} - \tau_{22}}{\dot{\varepsilon}_0}
  \]
  Alternatively, \( \eta^*_e(t, \dot{\varepsilon}_0) \)
Summary

Rheological Material Functions

- Are the answer to the question “What exactly do we observe when we subject non-Newtonian fluids to deformation?”
- Are based on continuum view
- Provide a framework/vocabulary of comparison
- Help to categorize and organize observed material responses

Material Functions do not:

- Identify a material conclusively
- Tell us the form of \( f(B) \)

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Material Functions do **not**:

- Identify a material conclusively
- Tell us the form of \( f(\mathbf{e}) \)

Except for Newtonian fluids, the structure of the model for stress is not known \( f(\mathbf{e}) = ?, \) and remains a mystery.

Cannot conclusively identify, but can classify and can be used to assess proposed models.