Role of Material Functions in Rheological Analysis

**QUALITY CONTROL**
- compare with other in-house data on qualitative basis
- conclude whether or not a material is appropriate for a specific application

**QUALITATIVE ANALYSIS**
- unknown material
- measure material functions, e.g. $G'(w), G''(w), G(t)$
- compare measured with predicted
- conclude which constitutive equation is best for further modeling calculations

**MODELING WORK**
- calculate predictions of material functions from various constitutive equations
- compare data with literature reports on various fluids
- conclude on the probable physical behavior of the fluid based on comparison with known fluid behavior
- compare with other in-house data on qualitative basis
- conclude whether or not a material is appropriate for a specific application

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**Material Function Definitions**

1. Choice of flow (shear or elongation)
   - $\frac{\partial \gamma}{\partial t} = 0$
   - $\frac{\partial \chi}{\partial t} = 0$
   - $\frac{\partial \delta}{\partial t} = 0$

2. Choice of details of $\dot{\gamma}(t)$ or $\dot{\chi}(t)$.

3. Material function definitions: will be based on $\tau_{21}, N_1, N_2$ in shear or $\tau_{33} = \tau_{11}, \tau_{22} = \tau_{11}$ in elongational flows.

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**Steady Shear Flow Material Functions**

**Kinematics**
- $\gamma = \begin{pmatrix} \tau_{00} \\ 0 \\ 0 \end{pmatrix}$
- $\dot{\gamma}(t) = \gamma_0 = \text{constant}$

**Material Functions**
- First normal-stress coefficient $\eta_1 = \frac{-\tau_{11} - \tau_{33}}{\gamma_0}$
- Second normal-stress coefficient $\eta_2 = \frac{-\tau_{22} - \tau_{33}}{\gamma_0}$
- Viscosity $\eta = \frac{-\tau_{23}}{\gamma_0}$

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**How do we predict material functions?**

**ANSWER:** From the constitutive equation.

$\tau = f(\gamma)$

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**What do we measure for these material functions?**

**Newtonian Fluid model predict in steady shearing?**

$\tau = -\mu \nabla \cdot (V \times V) + (V \cdot V)$
Steady shear viscosity and first normal stress coefficient

Let's replace $\mu$ with a function of shear rate because we want to predict a non-constant viscosity in shear.

What does this model predict for steady shear viscosity?

$\tau = -M(\dot{\gamma}) [\nabla \dot{\gamma} + (\nabla \dot{\gamma})^T]$

Answer:

$\eta = M(\dot{\gamma})$
If we choose:

\[ M(\gamma_0) = \begin{cases} M_S & \gamma_0 < \gamma, \\ m\gamma_0 & \gamma_0 \geq \gamma. \end{cases} \]

log \( \eta \)

slope = (n-1)

log \( \gamma_0 \)

Problem solved!

But what about the normal stresses?

\[ \varepsilon = -M(\gamma_0)(\nabla \mathbf{v} + (\nabla \mathbf{v})^T) \]

\[ \nabla_\mathbf{x} = \begin{pmatrix} 0 & 0 & 0 \\ \gamma_0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \]

\[ \varepsilon = \begin{pmatrix} 0 & \gamma_0 & 0 \\ \gamma_0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \]

It appears that \( \varepsilon \) should not be simply proportional to \( \varepsilon \).

Try something else . . .

\[ \varepsilon = -\mu \nabla_\mathbf{x}^\varepsilon \cdot \nabla \mathbf{v} \]

\[ \varepsilon = (\nabla_\mathbf{x}^\varepsilon) \nabla \mathbf{v} \cdot (\nabla_\mathbf{x}^\varepsilon)^T \]

\[ \varepsilon = \lambda (\nabla_\mathbf{x}^\varepsilon) \nabla \mathbf{v} + \mu (\nabla_\mathbf{x}^\varepsilon)^T \]

But which ones?

To sort out how to fix the Newtonian equation, we need more observations (to give us ideas).

Let’s try another material function that’s not a steady flow (but stick to shear).

Start-up of Steady Shear Flow Material Functions

**Kinematics:**

\[ \varsigma = \begin{pmatrix} \gamma(0) \\ 0 \\ 0 \end{pmatrix} \]

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

**Material Functions:**

\[ \eta^* = -\frac{\varepsilon^*}{\gamma_0} \]

First normal-stress growth function

\[ \Psi_1^* = \frac{-(\tau_{11} - \tau_{22})}{\gamma_0} \]

Shear stress growth function

\[ \Psi_2^* = \frac{-(\tau_{22} - \tau_{33})}{\gamma_0} \]

Second normal-stress growth function

Material functions predicted for start-up of steady shearing of a Newtonian fluid

\[ \eta^*(t) = \begin{cases} 0 & t < 0 \\ \mu & t \geq 0 \end{cases} \]

\[ \Psi_1^* = \frac{-(\tau_{11} - \tau_{22})}{\gamma_0} = 0 \]

\[ \Psi_2^* = \frac{-(\tau_{22} - \tau_{33})}{\gamma_0} = 0 \]

Do these predictions match observations?
**Kinematics**

\[ \dot{\gamma}(t) = \begin{cases} \frac{20\mu t}{\eta_0} & 0 < t < 0 \\ \frac{20\mu}{\eta_0} & t \geq 0 \end{cases} \]

\[ \gamma = \begin{cases} \frac{20\mu t}{\eta_0} & 0 < t < 0 \\ \frac{20\mu}{\eta_0} & t \geq 0 \end{cases} \]

**Material Functions**

- First normal-stress decay function: \( \eta_1 = -\frac{\tau_{11}(t)}{\eta_0} \)
- Second normal-stress decay function: \( \eta_2 = -\frac{\tau_{22}(t)}{\eta_0} \)
- First normal-stress tensor: \( \tau_{11} = \frac{\tau_{11}}{\eta_0} \)
- Second normal-stress tensor: \( \tau_{22} = \frac{\tau_{22}}{\eta_0} \)

**Observations**

- The model predicts an instantaneous stress response, and this is not what is observed for polymers.
- The predicted unsteady material functions depend on the shear rate, which is observed for polymers.
- No normal stresses are predicted.
Observations

• The model predicts an instantaneous stress response, and this is not what is observed for polymers. **Lacks memory**
• The predicted unsteady material functions depend on the shear rate, which is observed for polymers.
• \( \eta^* = \eta^* (t, \dot{\gamma}_s) \) **Progress here**
• No normal stresses are predicted. **Related to nonlinearities**

To proceed to better-designed constitutive equations, we need to know more about material behavior, i.e. we need more material functions to predict, and we need measurements of these material functions.
• More non-steady material functions (material functions that tell us about memory)
• Material functions that tell us about nonlinearity (strain)

Summary of shear rate kinematics (part 1)

The next three families of material functions incorporate the concept of strain.

Summary of shear rate kinematics (part 2)

Shear Creep Flow

Constant shear stress imposed
Shear Flow Material Functions

to prescribe stress rather than shear

Because shear rate is not prescribed, it becomes something we must measure.

The strain is related to the change of shape of the deformed particle.

For steady shear, with \( t_{ref}=0 \):

\[
\gamma_r(t) = \frac{du_i}{dx_2} = 1 \gamma_r
\]

For a long time interval, we add up the strains over short time intervals.

\[
\gamma_3(t_{ref}, t) = \sum_{j=0}^{n} \gamma_3(t_{ref}, t_{j-1})
\]

Same, because flow is steady.

Deformation (strain)

Since we set the stress in this experiment (rather than measuring it), the material functions are related to the deformation of the sample. We need to discuss measurements of deformation before proceeding.

Intro to strain (continued):

For steady shear, with \( t_{ref}=0 \):

\[
\gamma_r(0, t) = \frac{du_i}{dx_2} = 1 \gamma_r
\]

For a long time interval, we add up the strains over short time intervals.

\[
\gamma_3(t_{ref}, t) = \sum_{j=0}^{n} \gamma_3(t_{ref}, t_{j-1})
\]

Same, because flow is steady.

Deformation in shear flow (strain)

For unsteady shear:

\[
\gamma_r(t_{ref}, t) = \frac{du_i}{dx_2} = 1 \gamma_r(t_{ref}) \Delta t
\]

For a long time interval, we add up the strains over short time intervals.

\[
\gamma_3(t_{ref}, t) = \sum_{j=0}^{n} \gamma_3(t_{ref}, t_{j-1})
\]

Taking the limit as \( \Delta t \) goes to zero,

\[
\lim_{\Delta t \to 0} \sum_{j=0}^{n} \Delta \gamma_3(t_{ref}, t_{j}) = \int t_3(t) dt
\]

Strain at \( t_0 \) with respect to fluid configuration at \( t \) in unsteady shear flow.

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Shear Creep - Recoverable Compliance

\[ J(t) = R(t) + \frac{t}{\eta_s} \]

At long times the creep compliance \( J(t, \tau_0) \) becomes a straight line.

\[ \frac{dJ}{dt} \bigg|_{\text{steady state}} = \frac{d}{dt} \left( \frac{1}{\tau_0} \right) \]

\[ = \frac{\dot{\gamma}}{\tau_s} \]

\[ = \frac{1}{\eta(\dot{\gamma}_0)} \]

the slope at steady state is the inverse of the steady viscosity

\[ \frac{dJ}{dt} \bigg|_{\text{steady state}} = \frac{1}{\eta(\dot{\gamma}_0)} \Rightarrow J(t)_{\text{steady}} = \frac{1}{\eta(\dot{\gamma}_0)} t + C \]

Steady-state compliance \( J_s(\tau_0) \)

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**Creep Recovery** - after creep, stop pulling forward and allow the flow to reverse

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

- Recoverable strain
- Strain at the end of the forward motion
- Strain at the end of the recovery

\[ J(t, \tau) = \int_{\tau}^{t} \gamma(t') \, dt' \]

- Recoverable creep compliance

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**Linear Viscoelastic Creep**

\[ \gamma(t) = \gamma_f(t) + t \dot{\gamma}_f \]

- Recoverable strain
- Non-recoverable strain

\[ J(t) = R(t) + \frac{t}{\eta_0} \]

This is a way to get \( R(t) \) without measuring it.

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**Shear creep material functions**

- **Linear-viscoelastic limit**

\[ J(t) \]

- Constant slope = \( \frac{\gamma_f}{\eta} \)

- Steady-state compliance

\[ R(t) \]

- Ultimate recoil function

\[ R_c' = J_c' \]

- \( t, \text{ creep} \)

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