Step Shear Strain Material Functions

**Kinematics:**

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

\[ \dot{\gamma} = \text{constant} = \gamma_0 \]

**Material Functions:**

\( G(t, \gamma_0) = \frac{-\varepsilon_{21} - \varepsilon_{32}}{\gamma_0} \)

First normal-stress relaxation modulus

\( G_N = \frac{-\varepsilon_{21}}{\gamma_0} \)

Second normal-stress relaxation modulus

\( G_{N2} = \frac{-\varepsilon_{32}}{\gamma_0} \)

What is the strain in this flow?

\[ \gamma_{21}(t, \epsilon) = \int_{\epsilon}^{t} \gamma_{21}(t') dt' \]

At small strains the relaxation modulus is independent of strain.

Linear viscoelastic limit

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

Damping function, \( h \)

\[ h(\gamma_0) = \frac{G(t, \gamma_0)}{G(t)} \]

The damping function summarizes the non-linear effects as a function of strain amplitude.

Small-Amplitude Oscillatory Shear Material Functions

**Kinematics:**

\[ \dot{\gamma}(t) = \gamma_0 \cos \omega t \]

\[ \gamma_0 = \frac{\gamma_0}{\omega} \]

**Material Functions:**

\( G'(0, \gamma_0) = G' \sin \omega t + G'' \cos \omega t \)

\( G'(0, \gamma_0) = \frac{\gamma_0}{\omega} \cos \omega t \)

Storage modulus

\( G''(0, \gamma_0) = \frac{\gamma_0}{\omega} \sin \omega t \)

Loss modulus

What is the strain in this flow?

\[ \gamma_{21}(0, t) = \int_{0}^{t} \gamma_{21}(t') dt' \]

\[ = \int_{0}^{t} \gamma_0 \cos \omega t' dt' \]

\[ = \frac{\gamma_0}{\omega} \sin \omega t' \]

The strain imposed is sinusoidal.
Generating Small Amplitude Oscillatory Shear (SAOS)

In SAOS the strain amplitude is small, and a sinusoidal imposed strain induces a sinusoidal measured stress.

\[-\tau_2(t) = \tau_0 \sin(\alpha t + \delta)\]

\[-\tau_3(t) = \tau_0 \sin(\alpha t + \delta)\]

\[\tau_v \cos \delta + \tau_0 \cos \alpha t \sin \delta\]

\[\tau_v \cos \delta \sin \alpha t + \tau_0 \sin \delta \cos \alpha t\]

\(\delta\) is the phase difference between the stress wave and the strain wave

\(\gamma_2(0, t) = \gamma_3(t)\)

SAOS Material Functions

\(-\tau_2(t) = \frac{\tau_0 \cos \delta}{\gamma_0} \sin \alpha t + \frac{\tau_0 \sin \delta}{\gamma_0} \cos \alpha t\)

For Newtonian fluids, stress is proportional to strain rate:

\(\tau_v = -\mu \dot{\gamma}\)

\(\mu\) is thus known as the viscoelastic loss modulus. It characterizes the viscoelastic contribution to the stress response.

\(\tau_v\) is thus known as the viscoelastic loss modulus. It characterizes the viscoelastic contribution to the stress response.

What types of materials generate stress in proportion to the strain imposed?

Answer: elastic solids

Hooke’s Law for elastic solids

\(\varepsilon_2 = -G \dot{\gamma}_2\)

\(\varepsilon_2 = -G \dot{\gamma}_2\)

Similar to the linear spring law

\(G^'\) is thus known as the viscoelastic storage modulus. It characterizes the elastic contribution to the stress response.
Steady Elongational Flow Material Functions

**Kinematics:**
\[
\dot{\varepsilon}(t) = \dot{\varepsilon}_0 = \text{constant}
\]

**Material Functions:**
\[
\begin{align*}
\varepsilon_0 & \quad \text{Uniaxial or Biaxial or First Planar Elongational Viscosity} \\
\varepsilon_0 & \quad \text{Second Planar Elongational Viscosity}
\end{align*}
\]

What is the strain in this flow?

**Hencky strain**
\[
\varepsilon(t_{\text{ref}}, t) = \int_{t_{\text{ref}}}^{t} \dot{\varepsilon}(t) \, dt \quad \text{(choose } t_{\text{ref}}=0) \]
\[
\dot{\varepsilon}_f = \text{The strain imposed is proportional to time.} \\
\ln \frac{l}{l_0} = \text{The ratio of current length to initial length is exponential in time.}
\]

What does the Newtonian Fluid model predict in uniaxial steady elongational flow?

\[
\dot{\varepsilon} = -\mu' \gamma = -\mu \left[ \nabla \gamma + (\nabla \gamma)^T \right]
\]

Again, since we know \( \gamma \), we can just plug it in and calculate the stresses.

What does the model we guessed at predict for steady uniaxial elongational flow?

\[
\dot{\varepsilon} = -M(\gamma) \left[ \nabla \gamma + (\nabla \gamma)^T \right]
\]

\[
M(\gamma) = \begin{cases} M_1 & \text{if } \gamma < \gamma_c \\ M_2 & \text{if } \gamma > \gamma_c \\ \gamma_0 & \text{if } \gamma = \gamma_c \end{cases}
\]

What if we make the following replacement?

\[
\frac{\partial \gamma}{\partial t} = \frac{\partial \mu}{\partial \gamma}
\]

This at least can be written for any flow and it is equal to the shear rate in shear flow.
Observations

- The model contains parameters that are specific to shear flow – makes it impossible to adapt for elongational or mixed flows.
- Also, the model should only contain quantities that are independent of coordinate system (i.e., invariant).

We will try to salvage the model by replacing the flow-specific kinetic parameter with something that is frame-invariant and not flow-specific.

The other elongational experiments are analogous to shear experiments (see text)

- Elongational stress growth
- Elongational stress cessation (nearly impossible)
- Elongational creep
- Step elongational strain
- Small-amplitude Oscillatory Elongation (SAOE)

Experimental Data (Chapter 6)

Steady shear flow
- Linear Polymers
- Limits on measurability
- Material effects - MW, MWD, branching, mixtures, copolymers
- Temperature and pressure

Unsteady shear flow (SAOS, step strain)
Steady elongation
Unsteady elongation

We will take out the shear rate and replace with the magnitude of the rate-of-deformation tensor (which is related to the second invariant of that tensor).

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

\[ M(\dot{\gamma}) = \begin{cases} M_r & |\dot{\gamma}| < \dot{\gamma}_c \\ 0 & |\dot{\gamma}| > \dot{\gamma}_c \end{cases} \]

Start-up of Steady Elongation

Steady shear viscosity and first normal stress coefficient

Unsteady shear flow makes it impossible to adapt.
Steady shear viscosity and first normal stress coefficient

```
Figure 6.2, p. 171 Menzes and Graessley conc. PB solution; c=0.0676 g/cm^3 813 kg/mol 517 kg/mol 350 kg/mol 200 kg/mol © Faith A. Morrison, Michigan Tech U.
```

**First normal stress effects: rod climbing**

\[ \tau_{11} - \tau_{22} < 0 \]

Extra tension in the 1-direction pulls azimuthally and upward (see DPL p63).

```
Newtonian - glycerin
Viscoelastic - solution of polyacrylamide in glycerin
```

Bird, et al., *Dynamics of Polymeric Fluids*, vol. 1, Wiley, 1987, Figure 2.3-1 page 63. (DPL)

**Second normal stress effects: inclined open-channel flow**

\[ \tau_{22} - \tau_{33} > 0 \]

Extra tension in the 2-direction pulls down the free surface where \( dv/dx_2 \) is greatest (see DPL p63).

```
Newtonian - glycerin
Viscoelastic - solution of polyethylene oxide in water
```

R. I. Tanner, *Engineering Rheology*, Oxford 1985, Figure 3.6 page 104

© Faith A. Morrison, Michigan Tech U.

Steady shear viscosity and first and second normal stress coefficient

```
Figure 6.5, p. 173 Binnington and Boger; PIB soln © Faith A. Morrison, Michigan Tech U.
```

**Second normal stress effects: inclined open-channel flow**

```
polyox WSR-301 in water
Separan AP-30 in water
Oppanol B200 in cetane
NBS/Nonlinear Fluid No. 1
```

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**Limits on Measurements: Flow instabilities in rheology**

- Cone and plate flow
- Capillary flow

Figures 6.7 and 6.8, p. 175 Hutton; PDMS

Figure 6.9, p. 176 Pomar et al. LLDPE

**Spurt instability**

![Spurt instability diagram](image)

- Spurt instability
- Various capillary rheometers

Figures 6.10, p. 177 Blyler and Hart; PE

**Steady shear viscosity and first normal stress coefficient - Molecular weight effects**

![Viscosity and first normal stress coefficient graph](image)

- Various MWs: 813 kg/mol, 517 kg/mol, 350 kg/mol, 200 kg/mol

Figures 6.2, p. 177 Menzes and Graessley; conc. PB solution; various MWs

**Variation of viscosity with molecular weight**

![Viscosity vs. molecular weight graph](image)

- Log $\eta_1$ + constant
- Slope = 3.4 - 3.5

Figures 6.12, p. 178 Berry and Fox, 1968; various polymers

**Entanglements strongly affect polymer relaxation**

- $M < M_c$: Unentangled relaxation is rapid
- $M > M_c$: Entangled relaxation is retarded

![Entanglement diagram](image)

Figures 6.14, p. 179 Berry and Fox; PVA solns in DEP

**Effect of Distribution of Molecular Weight**

![Effect of distribution graph](image)

- $A: M_w/M_m = 1.09$
- $B: M_w/M_m = 2.0$
- $C$: branched

Figures 6.16, p. 179 Berry and Fox; PVA solns in DLP
Types of polymer architecture

- short-chain branching
- long-chain branching
- star
- hyperbranching
- dendrimer

Motion of Branched Polymers

- Entangled linear polymer: chains move primarily along their contour
- Entangled branched polymer: branch points retard motion
- Once disentangled (high shear rate), branched polymers flow more freely

Effect of Branching on $\eta$

Figures 6.17, 6.18, pp. 181-183; Kraus & Gruver; PB

Steady shear rheology of PAMAM dendrimers

Figure 6.20, p. 183; from Uppuluri

Mixtures of Polymers with other materials - Filler Effect

For more on filled systems, see Larson, The Structure and Rheology of Complex Fluids, Oxford, 1999.

Steady shear viscosity - shear thickening

Figure 6.27, p. 188; Metzner and Whitlock; TiO$_2$/water suspensions
Steady shear viscosity - temperature dependence

Steady shear viscosity - pressure dependence

Steady shear flow - Summary

- **Linear Polymers - complex rheology**
- **Limits on measurability - instabilities**
- **Material effects - MW, MWD, branching, mixtures, copolymers - strongly affect rheology**
- **Temperature and pressure - T strongly affects rheology; P less of an effect, but can be important**

Next:
Unsteady shear flow (SAOS, step strain)
Steady elongation
Unsteady elongation