# Chapter 5: Material Functions

CM4650
Polymer Rheology
Michigan Tech


*Steady* Shear Flow Material Functions

Kinematics:

$$\underline{v} \equiv \begin{pmatrix} \dot{\varsigma}(t) x_2 \\ 0 \\ 0 \end{pmatrix}_{123} \qquad \dot{\varsigma}(t) = \dot{\gamma}_0 = \text{constant}$$

Material Functions:

Viscosity
$$\eta \equiv \frac{-\tau_{21}}{\dot{\gamma}_0}$$

First normal-stress coefficient
$$\Psi_1 \equiv \frac{-(\tau_{11} - \tau_{22})}{\dot{\gamma}_0^2}$$

Second normal-stress coefficient
$$\Psi_2 \equiv \frac{-(\tau_{22} - \tau_{33})}{\dot{\gamma}_0^2}$$







## Role of Material Functions in Rheological Analysis

unknown material → measure material functions, e.g. $\eta$, $G'(\omega)$, $G''(w)$, $G(t)$

**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**

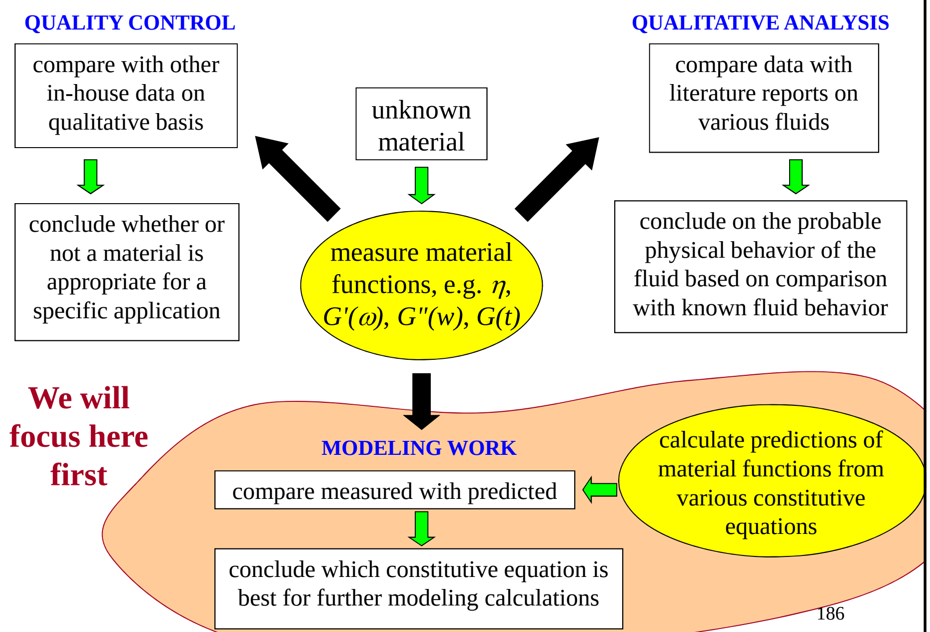
compare data with literature reports on various fluids → conclude on the probable physical behavior of the fluid based on comparison with known fluid behavior

**MODELING WORK**

compare measured with predicted ← calculate predictions of material functions from various constitutive equations

→ conclude which constitutive equation is best for further modeling calculations

## Role of Material Functions in Rheological Analysis

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## Material function definitions

kinematics

1. Choice of flow (shear or elongation)

$$\underline{v} \equiv \begin{pmatrix} \dot{\varsigma}(t) x_2 \\ 0 \\ 0 \end{pmatrix}_{123} \qquad \underline{v} = \begin{pmatrix} -\frac{1}{2}\dot{\varepsilon}(t)(1+b)x_1 \\ -\frac{1}{2}\dot{\varepsilon}(t)(1-b)x_2 \\ \dot{\varepsilon}(t)x_3 \end{pmatrix}_{123}$$

Elongational flow: b=0, $\dot{\varepsilon}(t) > 0$

Biaxial stretching: b=0, $\dot{\varepsilon}(t) < 0$

Planar elongation: b=1, $\dot{\varepsilon}(t) > 0$

2. Choice of details of $\dot{\varsigma}(t)$ or $\dot{\varepsilon}(t)$.

3. Material functions 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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(I call these my "recipe cards")

## *Steady* Shear Flow Material Functions

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Material Functions:

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Viscosity

First normal-stress coefficient

$$\Psi_1 \equiv \frac{-(\tau_{11} - \tau_{22})}{\dot{\gamma}_0^2}$$

Second normal-stress coefficient

$$\Psi_2 \equiv \frac{-(\tau_{22} - \tau_{33})}{\dot{\gamma}_0^2}$$

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## *How do we predict material functions?*

**ANSWER:** From the constitutive equation.

$$\underline{\underline{\tau}} = f(\underline{v})$$

What does the **Newtonian** Fluid model predict in steady shearing?

$$\underline{\underline{\tau}} = -\mu \underline{\underline{\dot{\gamma}}} = -\mu\left[\nabla \underline{v} + (\nabla \underline{v})^T\right]$$

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What does the **Newtonian** Fluid model predict in steady shearing?

$$\underline{\underline{\tau}} = -\mu \dot{\underline{\underline{\gamma}}} = -\mu\left[\nabla \underline{v} + (\nabla \underline{v})^T\right]$$

You try.

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

*(for polymer solutions, for example)*

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## Steady shear viscosity and first normal stress coefficient

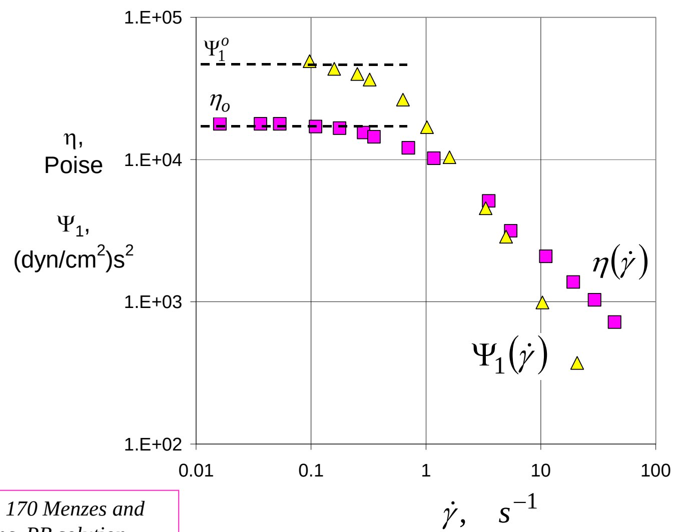


*Figure 6.1, p. 170 Menzes and Graessley conc. PB solution*

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## Steady shear viscosity and first normal stress coefficient

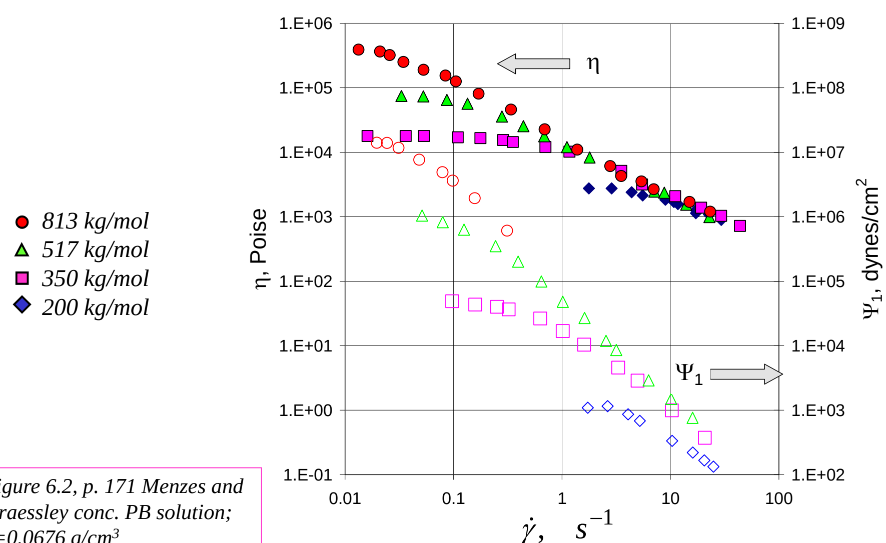


*Figure 6.2, p. 171 Menzes and Graessley conc. PB solution; c=0.0676 g/cm³*

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## Steady shear viscosity for linear and branched PDMS

+ linear 131 kg/mole
▲ branched 156 kg/mole
□ linear 418 kg/mol
◆ branched 428 kg/mol

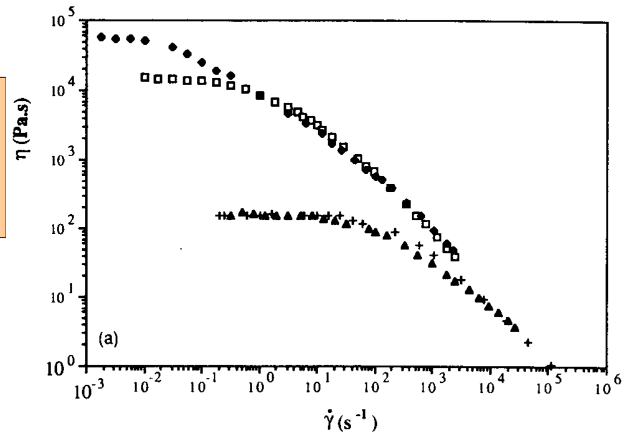


*Figure 6.3, p. 172 Piau et al., linear and branched PDMS*

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## What have material functions taught us so far?

•Newtonian constitutive equation is inadequate

1. Predicts constant shear viscosity (not always true)
2. Predicts no shear normal stresses (these stresses are generated for many fluids)

•Behavior depends on the material (chemical structure, molecular weight, concentration)

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## Can we fix the Newtonian Constitutive Equation?

$$\underline{\underline{\tau}} = -\mu\left[\nabla \underline{v} + \left(\nabla \underline{v}\right)^T\right]$$

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

$$\underline{\underline{\tau}} = -M\left(\dot{\gamma}_0\right)\left[\nabla \underline{v} + \left(\nabla \underline{v}\right)^T\right]$$

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## What does this model predict for steady shear viscosity?

$$\underline{\underline{\tau}} = -M\left(\dot{\gamma}_0\right)\left[\nabla \underline{v} + \left(\nabla \underline{v}\right)^T\right]$$

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What does this model predict for steady shear viscosity?

$$\underline{\underline{\tau}} = -M(\dot{\gamma}_0)\left[\nabla \underline{v} + (\nabla \underline{v})^T\right]$$

You try.

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What does this model predict for steady shear viscosity?

$$\underline{\underline{\tau}} = -M(\dot{\gamma}_0)\left[\nabla \underline{v} + (\nabla \underline{v})^T\right]$$

Answer: $\eta = M(\dot{\gamma}_0)$

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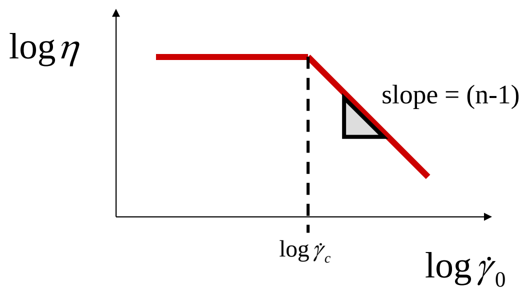
If we choose:

$$M(\dot{\gamma}_0)=\begin{cases} M_0 & \dot{\gamma}_0<\dot{\gamma}_c \\ m\dot{\gamma}_0^{n-1} & \dot{\gamma}_0\geq\dot{\gamma}_c \end{cases}$$




Problem solved!

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But what about the normal stresses?

$$\underline{\underline{\tau}}=-M(\dot{\gamma}_0)\left[\nabla\underline{v}+(\nabla\underline{v})^T\right]$$

$$\nabla\underline{v}=\begin{pmatrix} 0 & 0 & 0 \\ \dot{\gamma}_0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}_{123} \qquad \underline{\underline{\dot{\gamma}}}=\begin{pmatrix} 0 & \dot{\gamma}_0 & 0 \\ \dot{\gamma}_0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}_{123}$$

It appears that $\underline{\underline{\tau}}$ should not be simply proportional to $\underline{\underline{\dot{\gamma}}}$

Try something else . . .

$$\underline{\underline{\tau}}=-\mu\underline{\underline{\dot{\gamma}}}+\underline{\underline{I}}\ f(\underline{v})$$

$$\underline{\underline{\tau}}=f(\underline{v})\ \nabla v\cdot(\nabla v)^T$$

$$\underline{\underline{\tau}}=A\left[\nabla v\cdot(\nabla v)^T\right]+B\nabla v+C(\nabla v)^T$$

. . .

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**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).

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

Kinematics:

$$\underline{v} \equiv \begin{pmatrix} \dot{\varsigma}(t)x_2 \\ 0 \\ 0 \end{pmatrix}_{123} \qquad \dot{\varsigma}(t) = \begin{cases} 0 & t < 0 \\ \dot{\gamma}_0 & t \geq 0 \end{cases}$$

Material Functions:

$$\eta^+ \equiv \frac{-\tau_{21}(t)}{\dot{\gamma}_0}$$

Shear stress growth function

First normal-stress growth function

$$\Psi_1^+ \equiv \frac{-(\tau_{11} - \tau_{22})}{\dot{\gamma}_0^2}$$

Second normal-stress growth function

$$\Psi_2^+ \equiv \frac{-(\tau_{22} - \tau_{33})}{\dot{\gamma}_0^2}$$

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What does the **Newtonian** Fluid model predict in start-up of steady shearing?

$$\underline{\underline{\tau}} = -\mu \dot{\underline{\underline{\gamma}}} = -\mu\left[\nabla \underline{v} + (\nabla \underline{v})^T\right]$$

Again, since we know $\underline{\boldsymbol{v}}$, we can just plug it in and calculate the stresses.

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What does the **Newtonian** Fluid model predict in start-up of steady shearing?

$$\underline{\underline{\tau}} = -\mu \dot{\underline{\underline{\gamma}}} = -\mu\left[\nabla \underline{v} + (\nabla \underline{v})^T\right]$$

You try.

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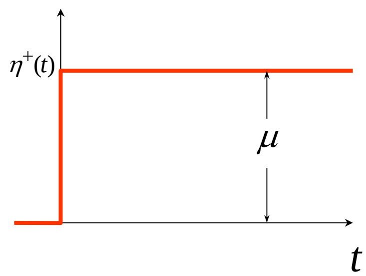
Material functions predicted for *start-up of steady shearing* of a Newtonian fluid

$$\eta^+(t) = \begin{cases} 0 & t < 0 \\ \mu & t \geq 0 \end{cases}$$




$$\Psi_1^+ \equiv \frac{-(\tau_{11} - \tau_{22})}{\dot{\gamma}_0^2} = 0$$

$$\Psi_2^+ \equiv \frac{-(\tau_{22} - \tau_{33})}{\dot{\gamma}_0^2} = 0$$

*Do these predictions match observations?*

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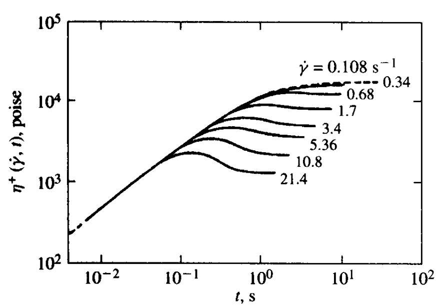
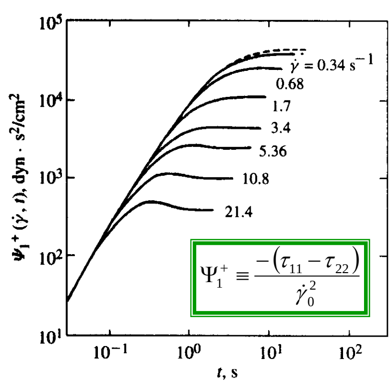
## Startup of Steady Shearing

$$\underline{v} \equiv \begin{pmatrix} \dot{\varsigma}(t) x_2 \\ 0 \\ 0 \end{pmatrix}_{123} \qquad \dot{\varsigma}(t) = \begin{cases} 0 & t < 0 \\ \dot{\gamma}_0 & t \geq 0 \end{cases}$$




$$\eta^+ \equiv \frac{-\tau_{21}(t)}{\dot{\gamma}_0}$$




*Figures 6.49, 6.50, p. 208*
*Menezes and Graessley, PB soln*

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What about other non-steady flows?

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## *Cessation of Steady* Shear Flow Material Functions

Kinematics:

$$\underline{v} \equiv \begin{pmatrix} \dot{\varsigma}(t) x_2 \\ 0 \\ 0 \end{pmatrix}_{123} \qquad \dot{\varsigma}(t) = \begin{cases} \dot{\gamma}_0 & t < 0 \\ 0 & t \geq 0 \end{cases}$$

Material Functions:

$$\eta^- \equiv \frac{-\tau_{21}(t)}{\dot{\gamma}_0}$$

Shear stress decay function

First normal-stress decay function

$$\Psi_1^- \equiv \frac{-(\tau_{11} - \tau_{22})}{\dot{\gamma}_0^2}$$

Second normal-stress decay function

$$\Psi_2^- \equiv \frac{-(\tau_{22} - \tau_{33})}{\dot{\gamma}_0^2}$$

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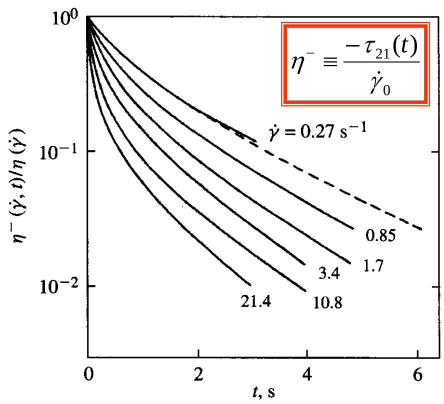
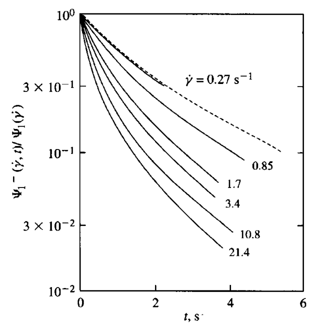
## Cessation of Steady Shearing

$$\underline{v} \equiv \begin{pmatrix} \dot{\varsigma}(t) x_2 \\ 0 \\ 0 \end{pmatrix}_{123} \qquad \dot{\varsigma}(t) = \begin{cases} \dot{\gamma}_0 & t < 0 \\ 0 & t \geq 0 \end{cases}$$




$$\eta^- \equiv \frac{-\tau_{21}(t)}{\dot{\gamma}_0}$$




$$\Psi_1^- \equiv \frac{-(\tau_{11} - \tau_{22})}{\dot{\gamma}_0^2}$$

*Figures 6.51, 6.52, p. 209 Menezes and Graessley, PB soln*

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What does the model we guessed at predict for start-up and cessation of shear?

$$\underline{\underline{\tau}} = -M(\dot{\gamma}_0)\left[\nabla \underline{v} + (\nabla \underline{v})^T\right]$$

$$M(\dot{\gamma}_0) = \begin{cases} M_0 & \dot{\gamma}_0 < \dot{\gamma}_c \\ m\dot{\gamma}_0^{n-1} & \dot{\gamma}_0 \geq \dot{\gamma}_c \end{cases}$$

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What does the model we guessed at predict for start-up and cessation of shear?

You try.

$$\underline{\underline{\tau}} = -M(\dot{\gamma}_0)\left[\nabla \underline{v} + (\nabla \underline{v})^T\right]$$

$$M(\dot{\gamma}_0) = \begin{cases} M_0 & \dot{\gamma}_0 < \dot{\gamma}_c \\ m\dot{\gamma}_0^{n-1} & \dot{\gamma}_0 \ge \dot{\gamma}_c \end{cases}$$

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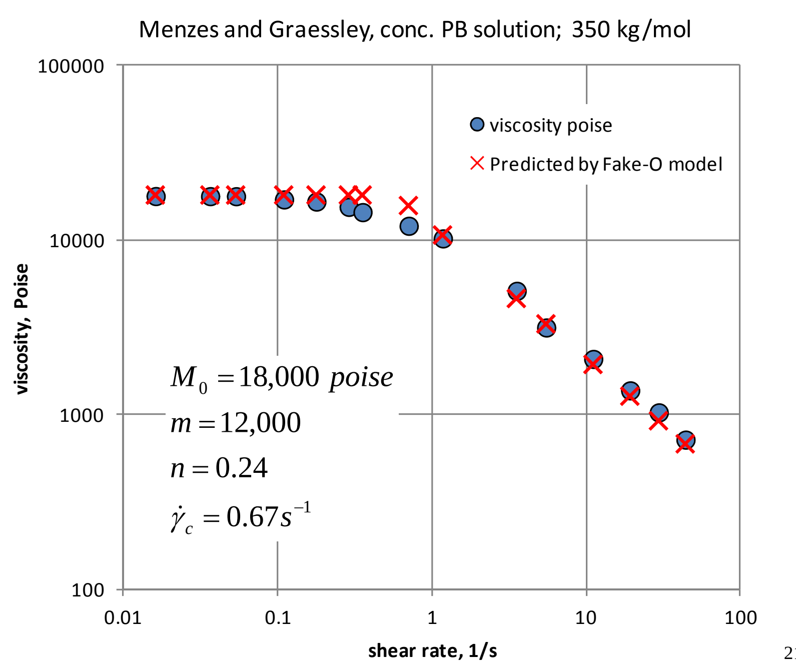


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$$\underline{\underline{\tau}} = -M(\dot{\gamma}_0)\left[\nabla \underline{v} + (\nabla \underline{v})^T\right]$$

$$M(\dot{\gamma}_0) = \begin{cases} M_0 & \dot{\gamma}_0 < \dot{\gamma}_c \\ m\dot{\gamma}_0^{n-1} & \dot{\gamma}_0 \geq \dot{\gamma}_c \end{cases}$$

## 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

$$\eta^+ = \eta^+(t, \dot{\gamma}_0)$$ ← **Progress here**

•No normal stresses are predicted

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$$\underline{\underline{\tau}} = -M(\dot{\gamma}_0)\left[\nabla \underline{v} + (\nabla \underline{v})^T\right]$$

$$M(\dot{\gamma}_0) = \begin{cases} M_0 & \dot{\gamma}_0 < \dot{\gamma}_c \\ m\dot{\gamma}_0^{n-1} & \dot{\gamma}_0 \geq \dot{\gamma}_c \end{cases}$$

## 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

$$\eta^+ = \eta^+(t, \dot{\gamma}_0)$$ ← **Progress here**

•No normal stresses are predicted ← **Related to nonlinearities**

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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)

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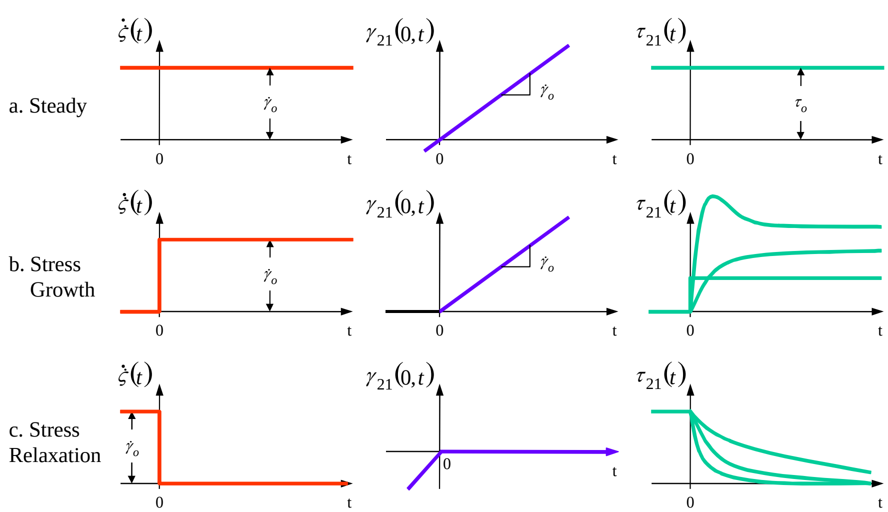
## Summary of shear rate kinematics *(part 1)*

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

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