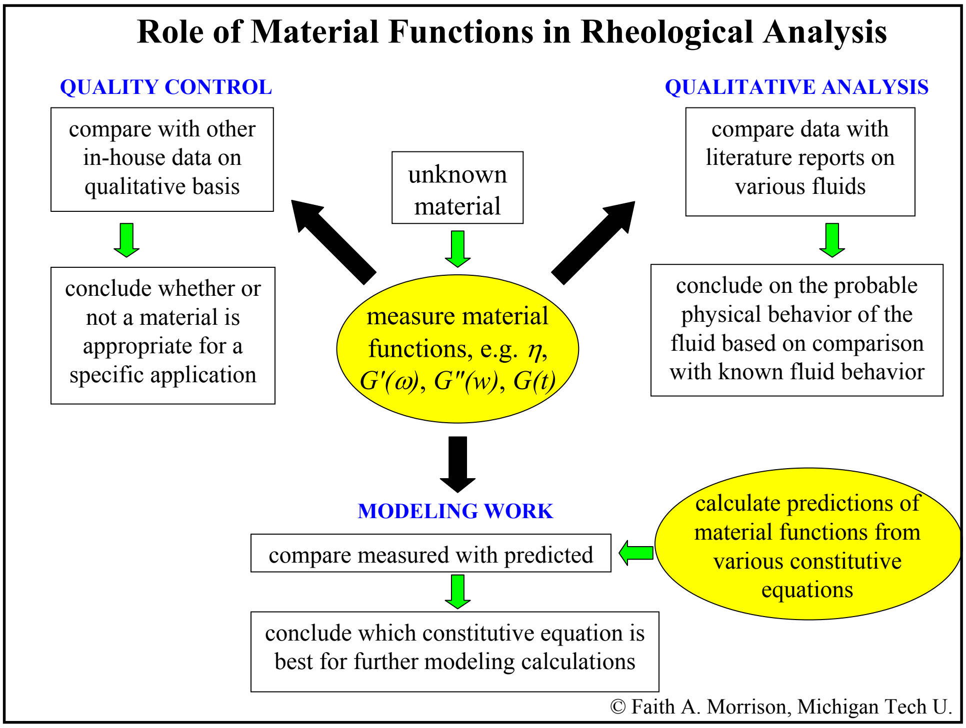
Role of Material Functions in Rheological Analysis
QUALITY CONTROL
compare with other in-house data on qualitative basis
conclude whether or not a material is appropriate for a specific application
unknown material
measure material functions, e.g. η, G'(ω), G"(w), G(t)
QUALITATIVE ANALYSIS
compare data 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
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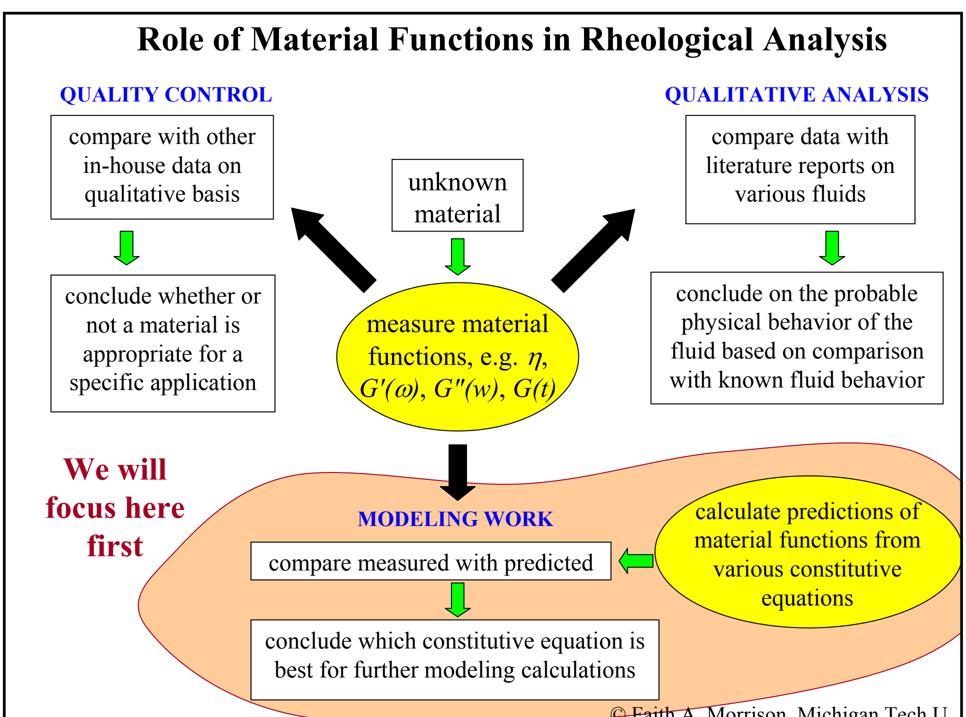
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QUALITATIVE ANALYSIS
compare data with literature reports on various fluids
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We will focus here first
MODELING WORK
compare measured with predicted
calculate predictions of material functions from various constitutive equations
conclude which constitutive equation is best for further modeling calculations
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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 τ_{21}, N_1, N_2 in shear or $\tau_{33} - \tau_{11}, \tau_{22} - \tau_{11}$ in elongational flows.

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:

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

Viscosity

First normal-stress coefficient

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

Second normal-stress coefficient

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

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?

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

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

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Steady shear viscosity and first normal stress coefficient

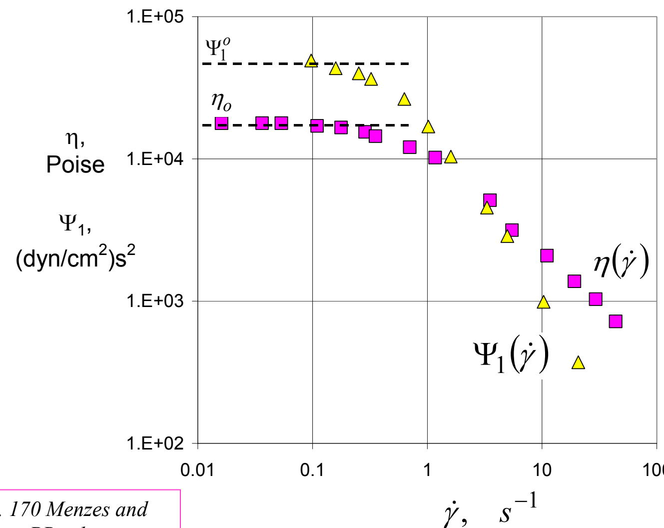


Figure 6.1, p. 170 Menzes and Graessley conc. PB solution

Steady shear viscosity and first normal stress coefficient

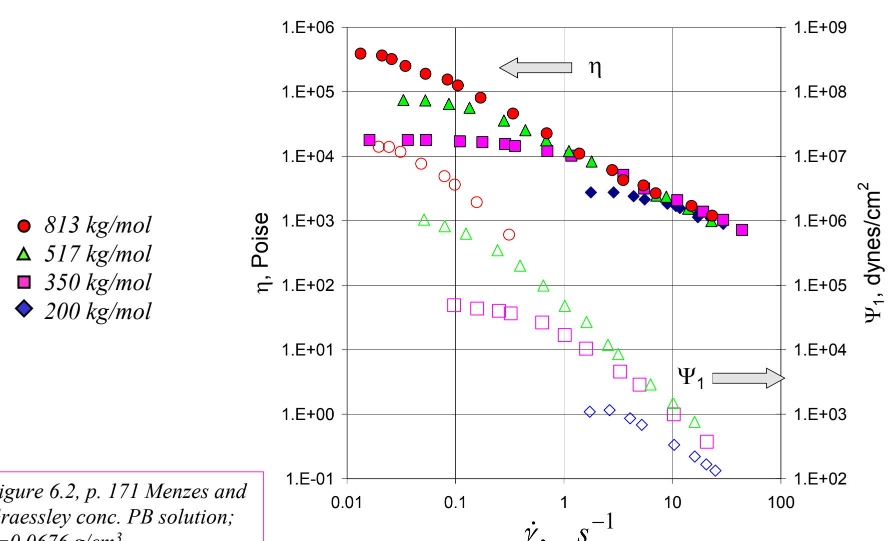


Figure 6.2, p. 171 Menzes and Graessley conc. PB solution; c=0.0676 g/cm^3

Steady shear viscosity for linear and branched PDMS

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

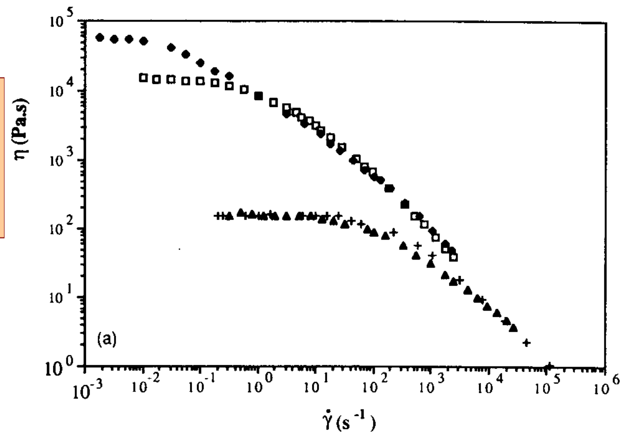


Figure 6.3, p. 172 Piau et al., linear and branched PDMS

What have material functions taught us so far?

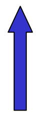
•Newtonian constitutive equation is inadequate

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)

Can we fix the Newtonian Constitutive Equation?

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



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

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

What does this model predict for steady shear viscosity?

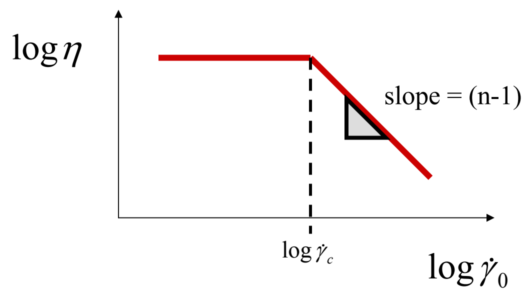
$$\underline{\underline{\tau}} = -M(\dot{\gamma}_0)\left[\nabla \underline{v} + (\nabla \underline{v})^T\right]$$

Answer:

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

If we choose:

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



Problem solved!

But what about the normal stresses?

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

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

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

Try something else . . .

$$\underline{\underline{\tau}} = -\mu \dot{\underline{\underline{\gamma}}} + \underline{\underline{I}}\, f(\underline{v})$$
$$\underline{\underline{\tau}} = f(\underline{v})\, \nabla v \cdot (\nabla v)^T$$
$$\underline{\underline{\tau}} = A\left[\nabla v \cdot (\nabla v)^T\right] + B\nabla v + C(\nabla v)^T$$
$$\ldots$$

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:

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

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

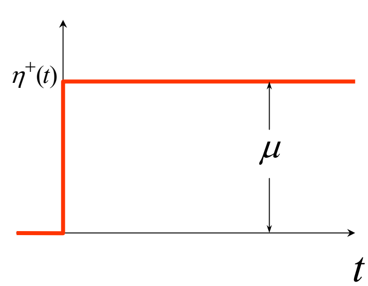
What does the **Newtonian** Fluid model predict in start-up of steady shearing?

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

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

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

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



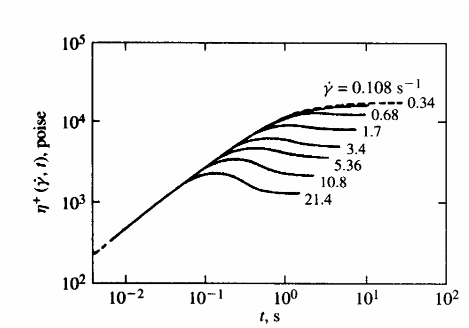
$$\Psi_1^+ \equiv \frac{-(\tau_{11} - \tau_{22})}{\dot{\gamma}_0^2} = 0$$

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

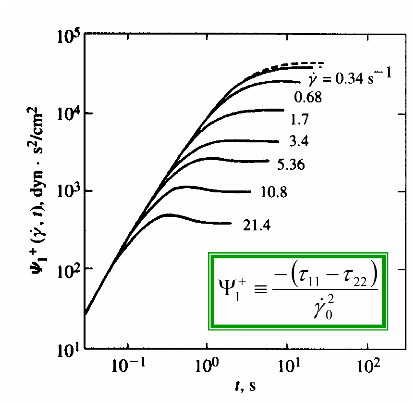
Do these predictions match observations?

Startup of Steady Shearing

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



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



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

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

What about other non-steady flows?

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:

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

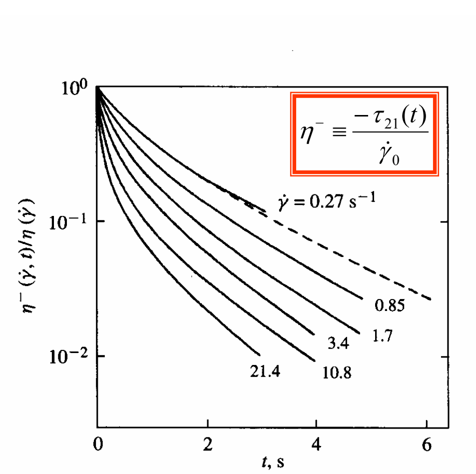
Shear stress decay function

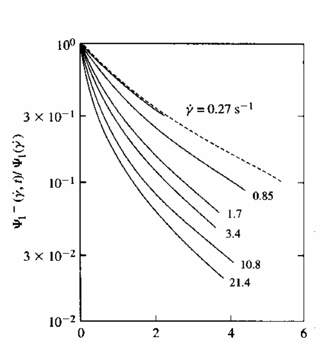
First normal-stress decay function $\Psi_1^- \equiv \dfrac{-(\tau_{11} - \tau_{22})}{\dot{\gamma}_0^2}$

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

Cessation of Steady Shearing

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





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

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

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

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

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

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

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

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

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

Observations

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

- 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

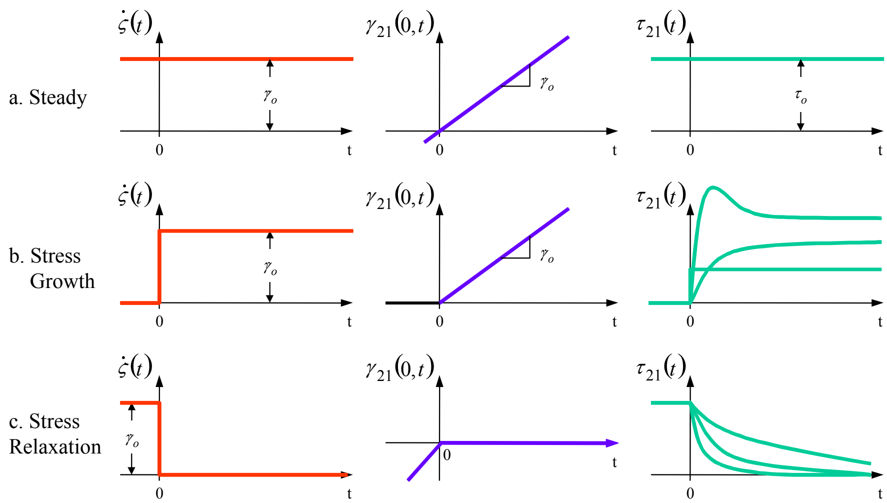
$$\eta^+ = \eta^+(t, \dot{\gamma}_0)$$ ← **Progress here**

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

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.

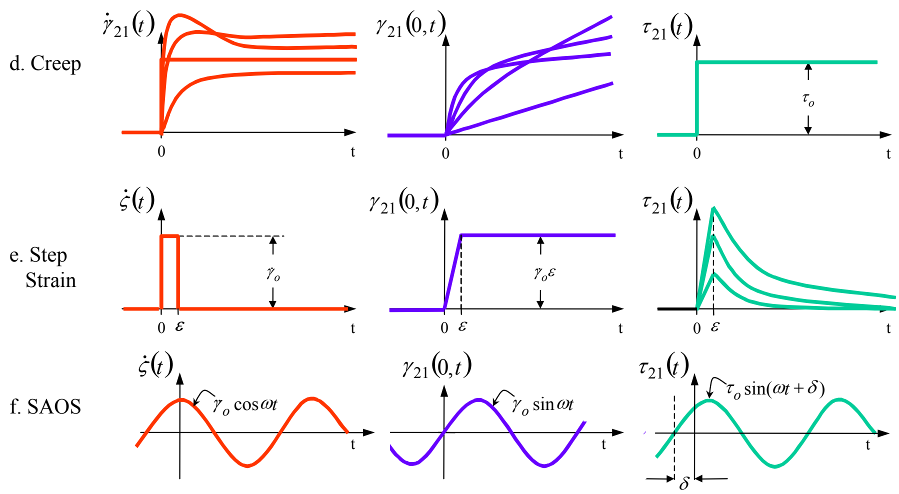
- More non-steady material functions (material functions that tell us about memory)
- Material functions that tell us about nonlinearity (strain)

Summary of shear rate kinematics *(part 1)*



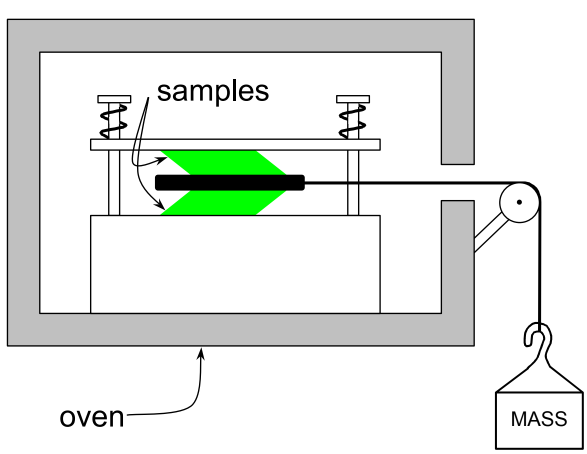
The next three families of material functions incorporate the concept of strain.

Summary of shear rate kinematics *(part 2)*



Shear Creep Flow

Constant shear stress imposed



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

Creep Shear Flow Material Functions

Kinematics:

It is unusual to prescribe stress rather than $\dot{\varsigma}(t)$

$$\underline{v} \equiv \begin{pmatrix} \dot{\gamma}_{21}(t) x_2 \\ 0 \\ 0 \end{pmatrix}_{123} \qquad \tau_{21}(t) = \begin{cases} 0 & t < 0 \\ \tau_0 & t \geq 0 \end{cases}$$

Material Functions:

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.

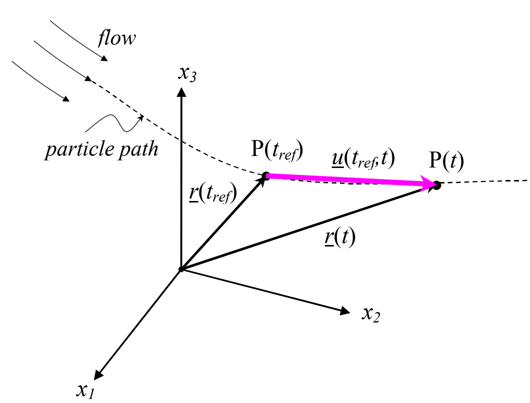
Deformation (strain)

$$\gamma_{21}(t_{ref}, t) \equiv \frac{\partial u_1}{\partial x_2}$$ **Shear strain**

$$\underline{u}(t_{ref}, t) \equiv \underline{r}(t) - \underline{r}(t_{ref})$$ **Displacement function**

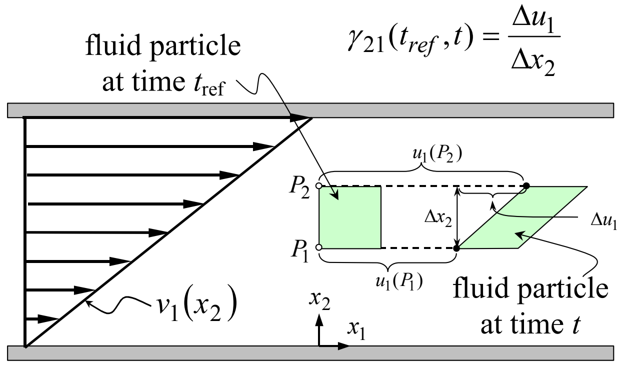
$$\underline{r}(t_{ref}) = \begin{pmatrix} x_1(t_{ref}) \\ x_2(t_{ref}) \\ x_3(t_{ref}) \end{pmatrix}_{123}$$

$$\underline{r}(t) = \begin{pmatrix} x_1(t) \\ x_2(t) \\ x_3(t) \end{pmatrix}_{123}$$



Physical interpretation of strain in shear

$$\gamma_{21}(t_{ref},t) = \frac{\Delta u_1}{\Delta x_2}$$



The strain is the inverse of the slope of the side of the deformed particle.

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

Deformation in shear flow (strain)

$$\underline{r}(t_{ref}) = \begin{pmatrix} x_1(t_{ref}) \\ x_2(t_{ref}) \\ x_3(t_{ref}) \end{pmatrix}_{123}$$

$$\gamma_{21}(t_{ref},t) \equiv \frac{\partial u_1}{\partial x_2}$$ **Shear strain**

$$\underline{r}(t) = \begin{pmatrix} x_1(t) \\ x_2(t) \\ x_3(t) \end{pmatrix}_{123} = \begin{pmatrix} x_1(t_{ref}) + (t - t_{ref})\dot{\gamma}_0 x_2 \\ x_2(t_{ref}) \\ x_3(t_{ref}) \end{pmatrix}_{123}$$

$$\underline{u}(t_{ref},t) \equiv \underline{r}(t) - \underline{r}(t_{ref}) = \begin{pmatrix} (t - t_{ref})\dot{\gamma}_0 x_2 \\ 0 \\ 0 \end{pmatrix}_{123}$$ **Displacement function**