

On to ... Polymer Rheology ...





We now know how to model Newtonian fluid motion, $\underline{v}(\underline{x},t)$, $p(\underline{x},t)$:

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \underline{v}) = 0$$

$$\rho \left(\frac{\partial \underline{v}}{\partial t} + \underline{v} \cdot \nabla \underline{v} \right) = -\nabla p - \nabla \cdot \underline{\tau} + \rho \underline{g}$$

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

Continuity equation

Cauchy momentum equation

Newtonian constitutive equation

119

Rheological Behavior of Fluids – Non-Newtonian

How do we model the motion of Non-Newtonian fluid fluids?

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \underline{v}) = 0$$

Continuity equation

$$\rho \left(\frac{\partial \underline{v}}{\partial t} + \underline{v} \cdot \nabla \underline{v} \right) = -\nabla p - \nabla \cdot \underline{\underline{\tau}} + \rho \underline{g}$$

Cauchy Momentum Equation

$$\underline{\tau} = f(\underline{x}, t)$$

Non-Newtonian constitutive equation

120

© Faith A. Morrison, Michigan Tech U.

Rheological Behavior of Fluids - Non-Newtonian

How do we model the motion of Non-Newtonian fluid fluids?

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \underline{v}) = 0$$

Continuity equation

$$\rho \left(\frac{\partial \underline{v}}{\partial t} + \underline{v} \cdot \nabla \underline{v} \right) = -\nabla p - \nabla \cdot \underline{\tau} + \rho \underline{g}$$

Cauchy Momentum Equation

 $\underline{\underline{\tau}} = f(\underline{x}, t)$

Non-Newtonian constitutive equation

This is the missing piece

121

Chapter 4: Standard Flows for Rheology

Chapter 4: Standard flows
Chapter 5: Material Functions
Chapter 6: Experimental Data

To get to constitutive equations, we must first **quantify** how non-Newtonian fluids behave

Chapter 7: GNF

Chapter 8: GLVE

Chapter 9: Advanced

Constitutive equations

122

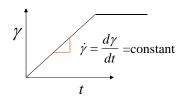
© Faith A. Morrison, Michigan Tech U.

What do we observe?

Rheological Behavior of Fluids - Newtonian

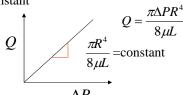
- 1. Strain response to imposed shear stress *2†
- •shear rate is constant





- 2. Pressure-driven flow in a tube (Poiseuille flow)

•viscosity is constant

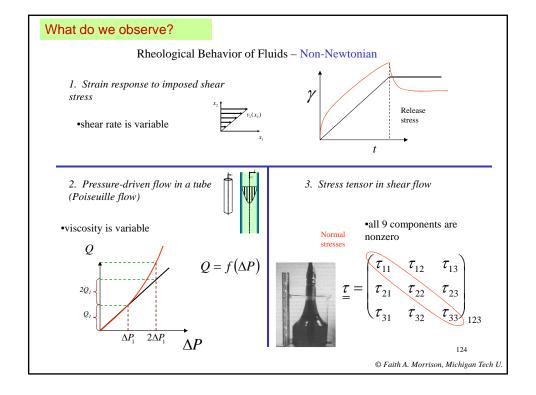


- 3. Stress tensor in shear flow
 - •only two components are nonzero



$$\underline{\underline{\tau}} = \begin{pmatrix} 0 & \tau_{12} & 0 \\ \tau_{21} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}_{123}$$

123

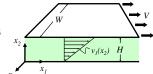




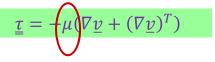
- We have observations that some materials are not like Newtonian fluids.
- How can we be systematic about developing new, unknown models for these materials?

Need measurements

For Newtonian fluids, measurements were easy:



- · shear flow
- one stress, τ_{21}
- one material constant, μ (viscosity)



125

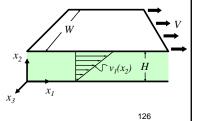
Non-Newtonian Constitutive Equations

Need measurements

For non-Newtonian fluids, measurements are **not easy**:

- shear flow (not the only choice)
- Four stresses in shear, τ_{21} , τ_{11} , τ_{22} , τ_{33}
- <u>Unknown</u> number of material constants in $\underline{\tau}(\underline{v})$
- <u>Unknown</u> number of material *functions* in $\tau(v)$

$$\underline{\tau} = ???$$



© Faith A. Morrison, Michigan Tech U.

Non-Newtonian Constitutive Equations



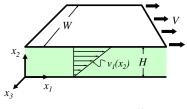
Need measurements

For non-Newtonian fluids, measurements are **not easy**:

We know we need to make measurements to know more,

- shear flow (not the only choice)
- Four stresses in shear, τ_{21} , τ_{11} , τ_{22} , τ_{33}
- Unknown number of material constants in $\underline{\tau}(\underline{v})$
- Unknown number of material functions in $\underline{\tau}(\underline{v})$

$$\tau = ???$$



127

Non-Newtonian Constitutive Equations

Need measurements

For non-Newtonian fluids, measurements are **not easy**:

We know we need to make measurements to know more,

- shear flow (not the only choice)
- Four stresses in shear, τ_{21} , τ_{11} , τ_{22} , τ_{33}
- <u>Unknown</u> number of material constants in $\underline{\underline{\tau}}(\underline{\nu})$
- Unknown number of material functions in $\tau(v)$

 $\underline{\tau} = ???$

But, because we do not know the functional form of $\underline{\underline{\tau}}(\underline{v})$, we don't know what we need to measure to know more!

128

© Faith A. Morrison, Michigan Tech U.

Non-Newtonian Constitutive Equations

What should we do?

129

Non-Newtonian Constitutive Equations

What should we do?

- 1. Pick a small number of simple flows Chapter 4: Standard flows
 - Standardize the flows
 - Make them easy to calculate with
 - Make them easy to produce in the lab

130

© Faith A. Morrison, Michigan Tech U.

Non-Newtonian Constitutive Equations

What should we do?

- 1. Pick a small number of simple flows Chapter 4: Standard flows
 - Standardize the flows
 - Make them easy to calculate with
 - Make them easy to produce in the lab
- 2. Make calculations
- 3. Make measurements

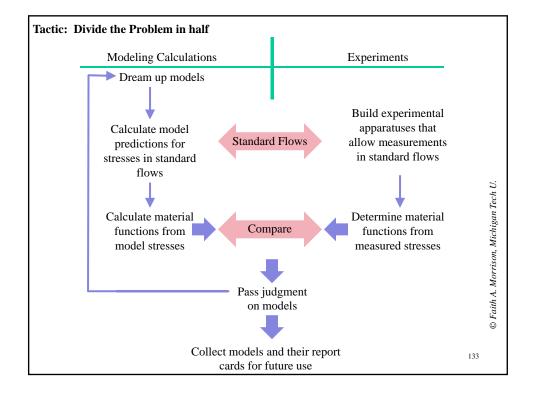
}

Chapter 5: Material Functions Chapter 6: Experimental Data

131

Non-Newtonian Constitutive Equations What should we do? Pick a small number of simple flows Chapter 4: Standard flows Standardize the flows Make them easy to calculate with Make them easy to produce in the lab Make calculations Make measurements Try to deduce <u>T</u>(<u>v</u>) Chapter 5: Material Functions Chapter 6: Experimental Data Try to deduce <u>T</u>(<u>v</u>) Chapter 7: GNF Chapter 8: GLVE Chapter 9: Advanced

132



<u>Standard flows</u> – choose a velocity field (not an apparatus or a procedure)

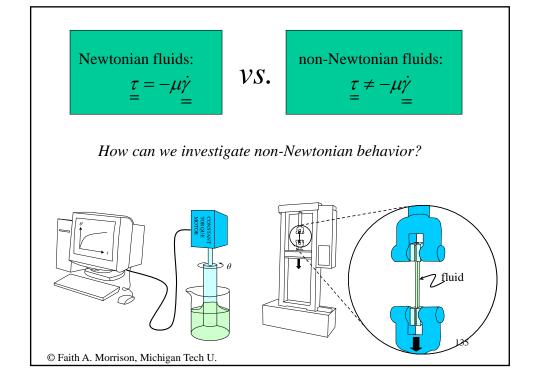
- •For model predictions, calculations are straightforward
- •For experiments, design can be optimized for accuracy and fluid variety

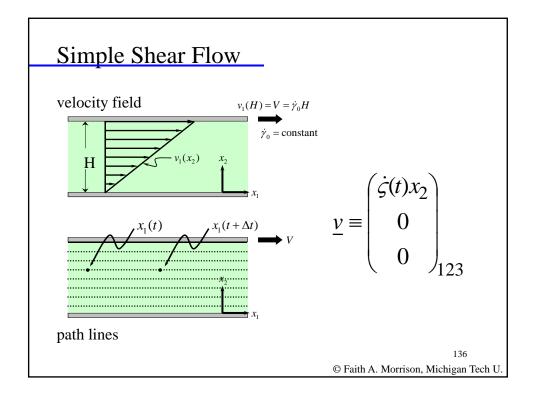
<u>Material functions</u> – choose a common vocabulary of stress and kinematics to report results

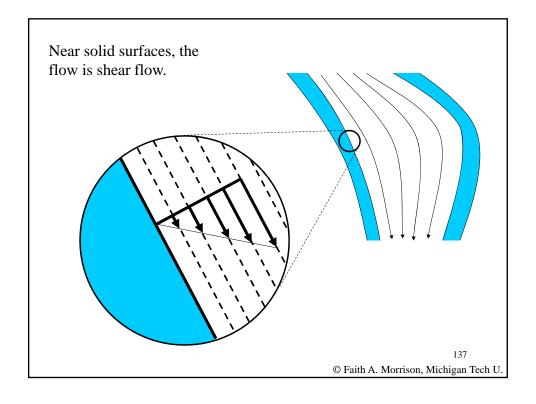
- •Make it easier to compare model/experiment
- •Record an "inventory" of fluid behavior (expertise)

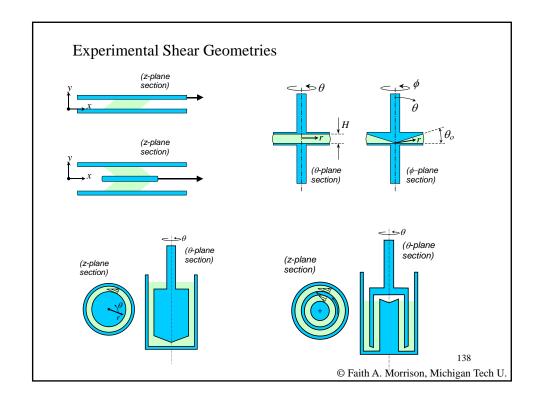
134

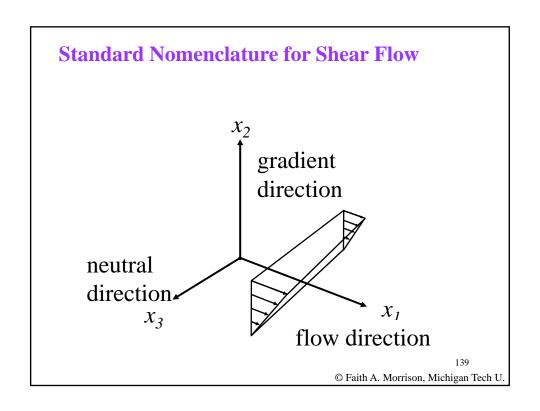
@ Faith A. Morrison, Michigan Tech U.

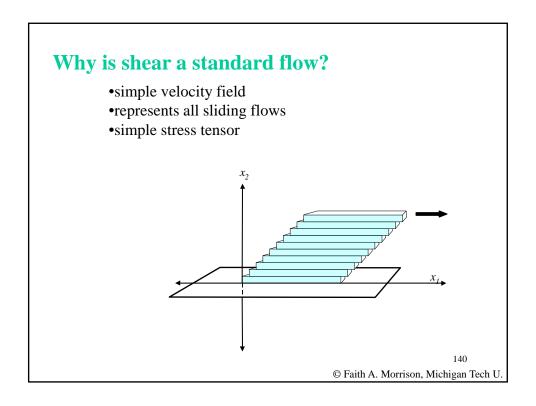


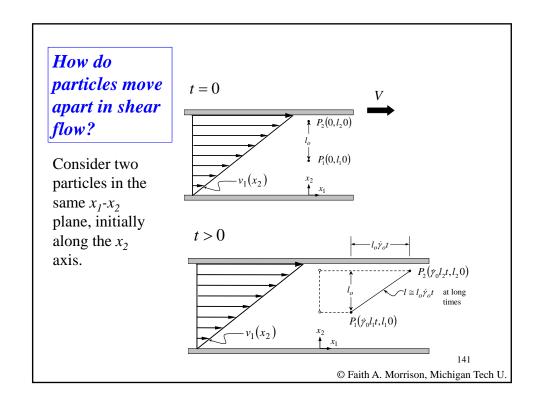












How do particles move apart in shear flow?

 $\underline{v} = \begin{pmatrix} \dot{\gamma}_0 x_2 \\ 0 \\ 0 \end{pmatrix}_{12}$

Each particle has a different velocity depending on its x_2 position:

 $v_1 = \dot{\gamma}_0 x_2$

Consider two particles in the same x_1 - x_2 plane, initially along the x_2 axis $(x_1=0)$.

 $P_1: v_1 = \dot{\gamma}_0 l_1$ $P_2: v_1 = \dot{\gamma}_0 l_2$

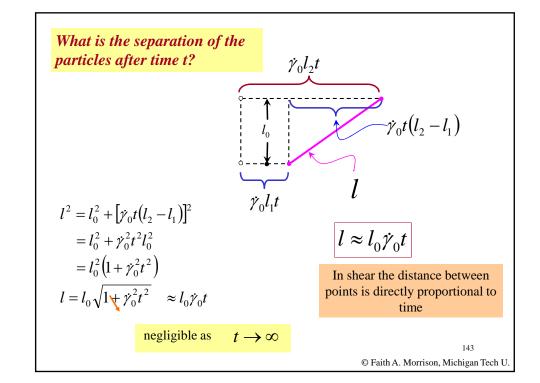
The initial x_I position of each particle is x_I =0. After t seconds, the two particles are at the following positions:

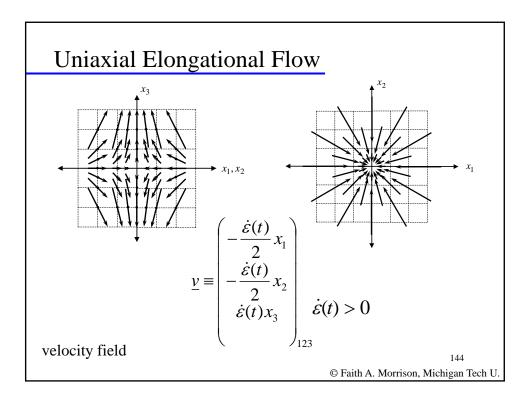
$$P_{1}(t): \quad x_{1} = \dot{\gamma}_{0}l_{1}t$$

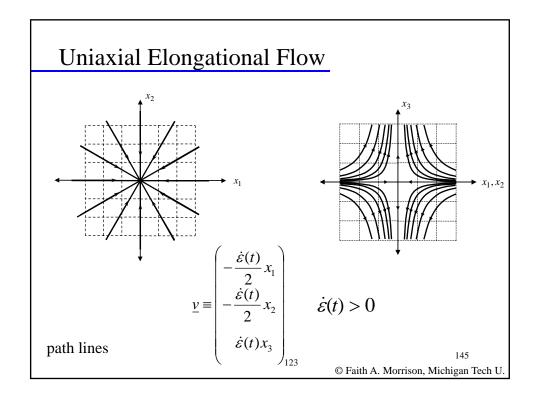
$$P_{2}(t): \quad x_{1} = \frac{\dot{\gamma}_{0}l_{2}t}{t}$$

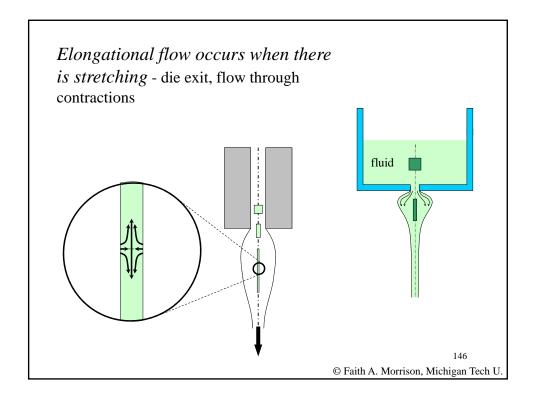
$$location = initial + \left(\frac{length}{time}\right)(time)$$

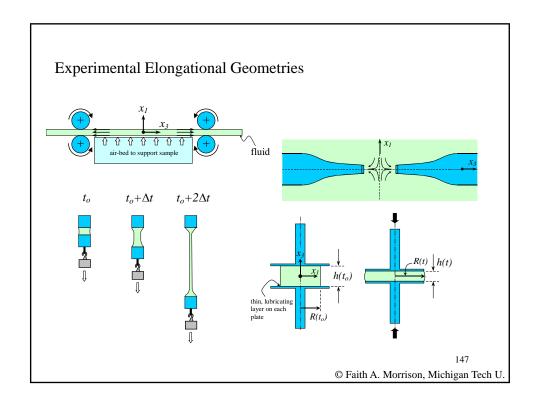
142





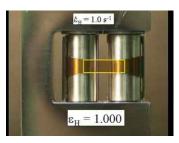






Sentmanat Extension Rheometer (2005)

- •Originally developed for rubbers, good for melts
- •Measures elongational viscosity, startup, other material functions
- •Two counter-rotating drums
- •Easy to load; reproducible



www.xpansioninstruments.com

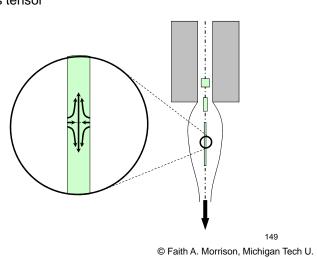
148

© Faith A. Morrison, Michigan Tech U.

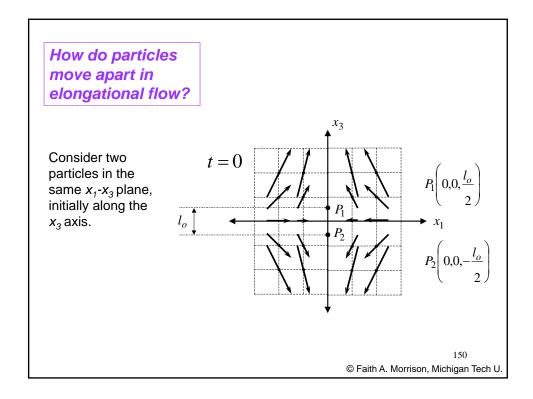


Why is elongation a standard flow?

- •simple velocity field
- •represents all stretching flows
- •simple stress tensor



16



How do particles move apart in elongational flow?

Consider two particles in the same x_1 - x_3 plane, initially along the x_3 axis.

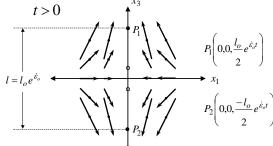
$$x_1 = 0$$

$$x_2 = 0$$

$$x_3 \text{ varies}$$

$$\underline{v} = \begin{pmatrix} -\frac{\varepsilon_0}{2} x_1 \\ -\frac{\dot{\varepsilon}_0}{2} x_2 \\ \dot{\varepsilon}_0 x_3 \end{pmatrix}_{123} = \begin{pmatrix} 0 \\ 0 \\ \dot{\varepsilon}_0 x_3 \end{pmatrix}_{123}$$

$$v_3 = \frac{dx_3}{dt} = \dot{\varepsilon}_0 x_3$$
$$\frac{dx_3}{x_3} = \dot{\varepsilon}_0 dt$$
$$\ln x_3 = \dot{\varepsilon}_0 t + C_1$$
$$x_3 = x_3(0)e^{\dot{\varepsilon}_0 t}$$

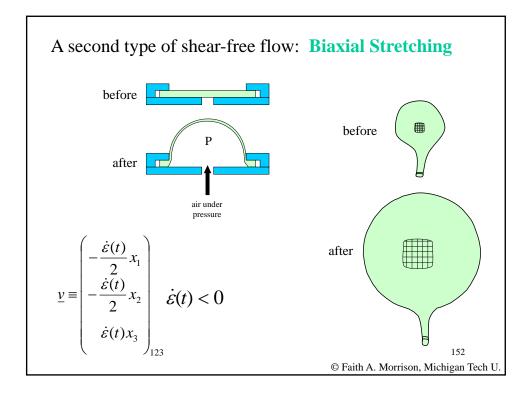


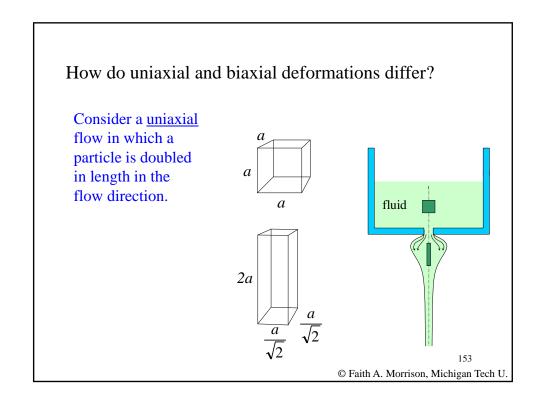
 $l = l_0 e^{\dot{\varepsilon}_0 t}$

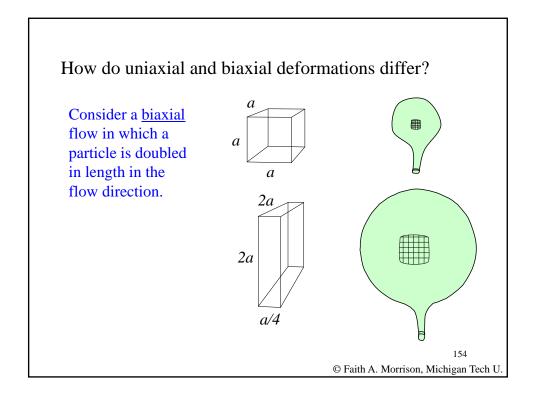
Particles move apart exponentially fast.

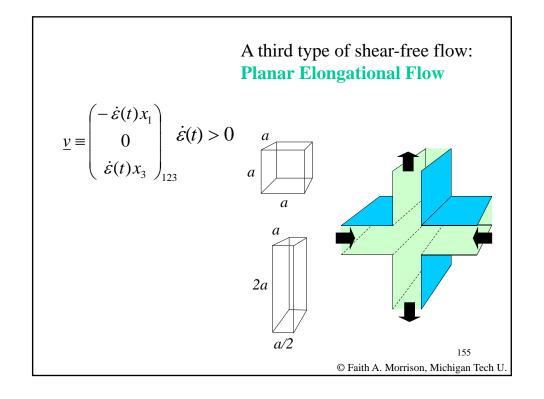
© Faith A. Morrison, Michigan Tech U.

151









All three shear-free flows can be written together as:

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

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

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

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

156

© Faith A. Morrison, Michigan Tech U.

Why have we chosen these flows?

ANSWER: Because these simple flows have symmetry.

And symmetry allows us to draw conclusions about the stress tensor that is associated with these flows *for any fluid* subjected to that flow.

157

In general:

$$\underline{\underline{\tau}} = \begin{pmatrix} \tau_{11} & \tau_{12} & \tau_{13} \\ \tau_{21} & \tau_{22} & \tau_{23} \\ \tau_{31} & \tau_{32} & \tau_{33} \end{pmatrix}_{123}$$

But the stress tensor is <u>symmetric</u> – leaving 6 independent stress components.

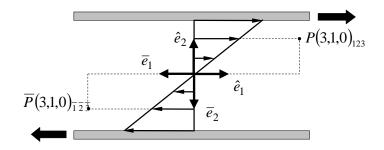
Can we choose a flow to use in which there are fewer than 6 independent stress components?

Yes we can - symmetric flows

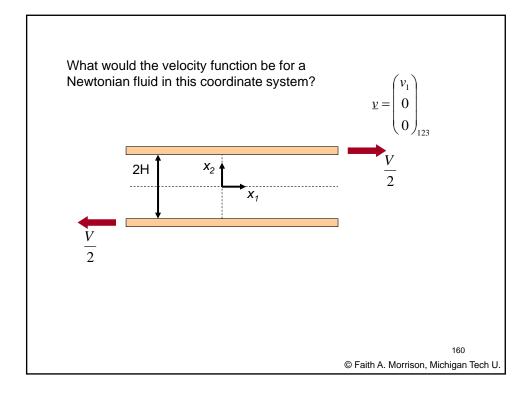
158

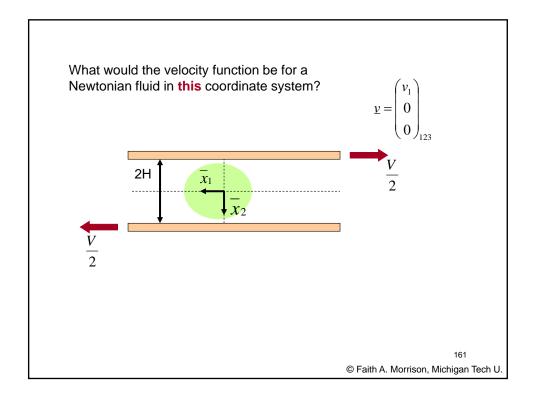
© Faith A. Morrison, Michigan Tech U.

How does the stress tensor simplify for shear (and later, elongational) flow?



159





Vectors are independent of coordinate system, but in general the coefficients will be different when the same vector is written in two different coordinate systems:

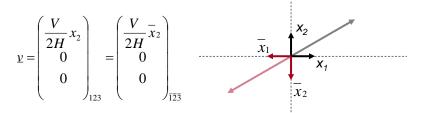
$$\underline{v} = \begin{pmatrix} v_1 \\ v_2 \\ v_3 \end{pmatrix}_{123} = \begin{pmatrix} \overline{v}_1 \\ \overline{v}_2 \\ \overline{v}_3 \end{pmatrix}_{\overline{123}}$$

For shear flow and the two particular coordinate systems we have just examined, however:

$$\underline{v} = \begin{pmatrix} \frac{V}{2H} x_2 \\ 0 \\ 0 \end{pmatrix}_{123} = \begin{pmatrix} \frac{V}{2H} \bar{x}_2 \\ 0 \\ 0 \end{pmatrix}_{\bar{1}\bar{2}\bar{3}}$$

162

© Faith A. Morrison, Michigan Tech U.



If we plug in the **same number** in for x_2 and \bar{x}_2 , we will NOT be asking about the same point in space, but we WILL get the same exact velocity vector.

Since stress is calculated from the velocity field, we will get the same exact stress components when we calculate them from either vector representation.

$$v_n = \bar{v}_n \\ \tau_{pk} = \bar{\tau}_{pk}$$

 $\begin{array}{c} v_n = \bar{v}_n \\ \tau_{pk} = \bar{\tau}_{pk} \end{array} \qquad \begin{array}{c} \text{This is an unusual} \\ \text{circumstance only true for} \\ \text{the particular coordinate} \\ \text{systems chosen.} \end{array}$

163

What do we learn if we formally transform \underline{V} from one coordinate system to the other?

164

© Faith A. Morrison, Michigan Tech U.

What do we learn if we formally transform $\underline{\underline{\tau}}$ from one coordinate system to the other?

$$\hat{e}_{1} = -\bar{e}_{1}$$
 $\hat{e}_{2} = -\bar{e}_{2}$
 $\hat{e}_{3} = \bar{e}_{3}$

165

What do we learn if we formally transform \underline{V} from one coordinate system to the other?

$$\underline{\tau} = \tau_{ms} \hat{e}_m \hat{e}_s = \overline{\tau}_{ms} \overline{e}_m \overline{e}_s$$

(now, substitute from previous slide and simplify)

You try.

166

© Faith A. Morrison, Michigan Tech U.

Conclusion:

Because of symmetry, there are only 5 nonzero components of the extra stress tensor in shear flow.

SHEAR:

$$\underline{\tau} = \begin{pmatrix} \tau_{11} & \tau_{12} & 0 \\ \tau_{21} & \tau_{22} & 0 \\ 0 & 0 & \tau_{33} \end{pmatrix}_{123}$$

This greatly simplifies the experimentalists tasks as only four stress components must be measured instead of 6 (recall $\tau_{21} = \tau_{12}$).

167

Summary:

We have found a coordinate system (the shear coordinate system) in which there are only 5 non-zero coefficients of the stress tensor. In addition, $\tau_{21}=\tau_{12}$.

This leaves <u>only four stress components</u> to be measured for this flow, expressed in this coordinate system.

168

© Faith A. Morrison, Michigan Tech U.

How does the stress tensor simplify for elongational flow? There is 180° of symmetry around all three coordinate axes. 169 © Faith A. Morrison, Michigan Tech U.

Because of symmetry, there are only 3 nonzero components of the extra stress tensor in elongational flows.

ELONGATION:

$$\underline{\tau} = \begin{pmatrix} \tau_{11} & 0 & 0 \\ 0 & \tau_{22} & 0 \\ 0 & 0 & \tau_{33} \end{pmatrix}_{123}$$

This greatly simplifies the experimentalists tasks as only three stress components must be measured instead of 6.

170

© Faith A. Morrison, Michigan Tech U.

Standard Flows Summary

Choose velocity field:

Symmetry alone implies: (no constitutive equation needed yet)

$$\underline{v} = \begin{pmatrix} \dot{\varsigma}(t)x_2 \\ 0 \\ 0 \end{pmatrix}_{123}$$

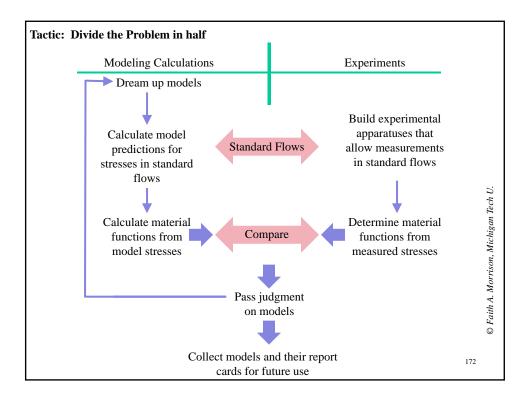
$$\underline{\tau} = \begin{pmatrix} \tau_{11} & \tau_{12} & 0 \\ \tau_{21} & \tau_{22} & 0 \\ 0 & 0 & \tau_{33} \end{pmatrix}_{123}$$

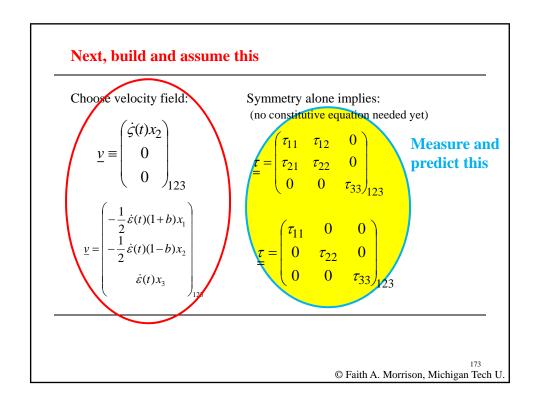
$$\underline{v} = \begin{pmatrix} -\frac{1}{2}\dot{\varepsilon}(t)(1+b)x_1\\ -\frac{1}{2}\dot{\varepsilon}(t)(1-b)x_2\\ \dot{\varepsilon}(t)x_3 \end{pmatrix}$$

$$\underline{\tau} = \begin{pmatrix} \tau_{11} & 0 & 0 \\ 0 & \tau_{22} & 0 \\ 0 & 0 & \tau_{33} \end{pmatrix}_{123}$$

By choosing these symmetric flows, we have reduced the number of stress components that we need to measure.

71





One final comment on measuring stresses. . .

What is measured is the total stress, $\underline{\Pi}$:

$$\underline{\underline{\Pi}} = \begin{pmatrix} p + \tau_{11} & \tau_{12} & \tau_{13} \\ \tau_{21} & p + \tau_{22} & \tau_{23} \\ \tau_{31} & \tau_{32} & p + \tau_{33} \end{pmatrix}_{123}$$

For the normal stresses we are faced with the difficulty of separating p from τ_{ii} .

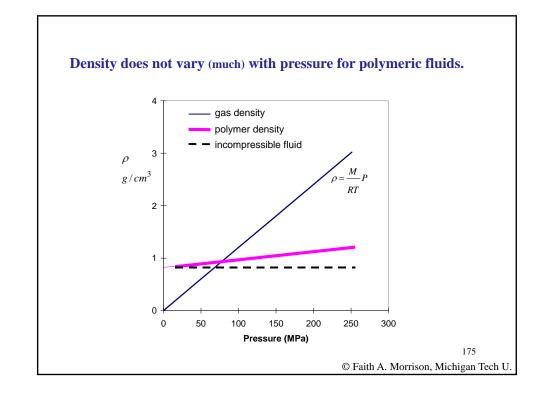
Compressible fluids:

 $p = \frac{nRT}{V}$

Get *p* from measurements of *T* and *V*.

Incompressible fluids:





For incompressible fluids it is not possible to separate p from τ_{ii} .

Luckily, this is not a problem since we

only need
$$\nabla \cdot \underline{\underline{\Pi}} = \nabla p + \nabla \cdot \underline{\underline{\tau}}$$

Equation of motion

$$\frac{\partial \underline{v}}{\partial t} + \underline{v} \cdot \nabla \underline{v} = -\nabla \underline{\underline{\Pi}} + \rho \underline{g}$$
$$= -\nabla P - \nabla \cdot \underline{\underline{\tau}} + \rho \underline{g}$$

Solution? Normal stress differences

176

© Faith A. Morrison, Michigan Tech U.

We do not

need τ_{ii} directly to

solve for velocities

Normal Stress Differences

First normal stress difference

$$N_1 \equiv \Pi_{11} - \Pi_{22} = \tau_{11} - \tau_{22}$$

Second normal stress difference

$$N_2 \equiv \Pi_{22} - \Pi_{33} = \tau_{22} - \tau_{33}$$

In shear flow, three stress quantities are measured

$$\tau_{21}, N_1, N_2$$

In elongational flow, two stress quantities are measured

$$\tau_{33} - \tau_{11}, \, \tau_{22} - \tau_{11}$$

177

Normal Stress Differences

First normal stress difference

$$N_1 \equiv \Pi_{11} - \Pi_{22} = \tau_{11} - \tau_{22}$$

Second normal stress difference

$$N_2 \equiv \Pi_{22} - \Pi_{33} = \tau_{22} - \tau_{33}$$

In shear flow, three stress quantities are measured

 $\tau_{21} (N_1, N_2)$ Are shear normal stress differences real?

In elongational flow, two stress quantities are measured

$$au_{33} - au_{11}, \, au_{22} - au_{11}$$

178

© 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 p65).



Newtonian - glycerin

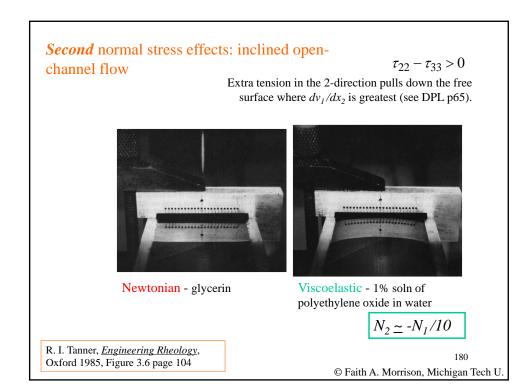


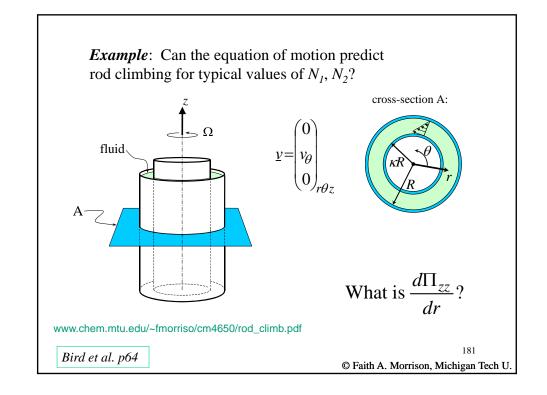
Viscoelastic - solution of polyacrylamide in glycerin

179

© Faith A. Morrison, Michigan Tech U.

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





What's next?

Shear-free (elongational, extensional)

Shear

 $\underline{v} = \begin{pmatrix} \underline{\dot{\varsigma}(t)} x_2 \\ 0 \\ 0 \end{pmatrix}_{123}$

Even with just these 2 (or 4) standard flows, we can still generate an *infinite* number of flows by varying $\dot{\varphi}(t)$ and $\dot{\varepsilon}(t)$.

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

Elongational flow: b=0, $\dot{\varepsilon}(t) > 0$ Biaxial stretching: b=0, $\dot{\varepsilon}(t) < 0$ Planar elongation: b=1, $\dot{\varepsilon}(t) > 0$

182

© Faith A. Morrison, Michigan Tech U.

We seek to quantify the behavior of non-Newtonian fluids

Procedure:

- 1. Choose a flow type (shear or a type of elongation).
- 2. Specify $\dot{\zeta}(t)$ or $\dot{\varepsilon}(t)$ as appropriate.
- 3. Impose the flow on a fluid of interest.
- 4. Measure stresses.

 $\begin{array}{ccc} & \text{shear} & \tau_{21}, N_1, N_2 \\ \text{elongation} & \tau_{33} - \tau_{11}, \tau_{22} - \tau_{11} \end{array}$

5. Report stresses in terms of material functions.

6a. Compare measured material functions with predictions of these material functions (from proposed constitutive equations).

7a. Choose the most appropriate constitutive equation for use in numerical modeling.

6b. Compare measured material functions with those measured on other materials.

7a. Draw conclusions on the likely properties of the unknown material based on the comparison.

183