

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

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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

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

Cauchy Momentum Equation

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

Non-Newtonian constitutive equation

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Rheological Behavior of Fluids – Non-Newtonian

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

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Cauchy Momentum Equation

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

Non-Newtonian constitutive equation

This is the missing piece

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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

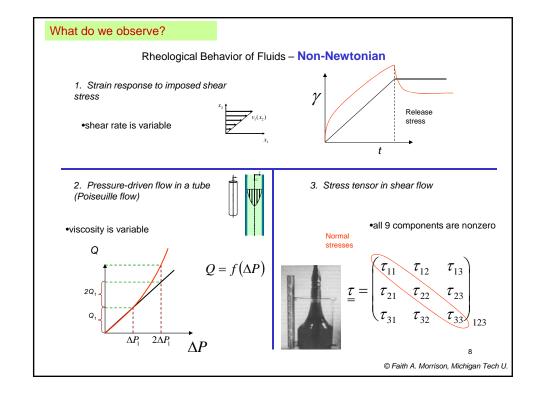
Chapter 9: Advanced

New Constitutive Equations

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

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What do we observe? Rheological Behavior of Fluids - Newtonian 1. Strain response to imposed shear stress $\dot{\gamma} = \frac{d\gamma}{d\gamma} = \text{constant}$ •shear rate is constant 2. Pressure-driven flow in 3. Stress tensor in shear a tube (Poiseuille flow) flow •only two components are viscosity is constant nonzero Q =constant ΔP © Faith A. Morrison, Michigan Tech U.

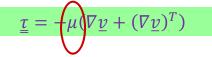


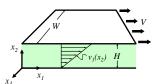
- We have observations that some materials are not like Newtonian fluids.
- How can we be systematic about developing new, unknown models for these materials?

Need measurements

For Newtonian fluids, measurements were **easy**:

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





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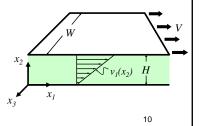
Non-Newtonian Constitutive Equations

Need measurements

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

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

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



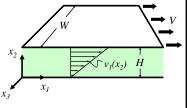
Need measurements

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

We know we need to make measurements to know more,

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

 $\tau = ???$



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Non-Newtonian Constitutive Equations



Need measurements

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

We know we need to make measurements to know more,

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- Four non-zero stresses even 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 <u>functions</u> in $\underline{\tau}(\underline{v})$

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

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!

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What should we do?

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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

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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

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Non-Newtonian Constitutive Equations

What should we do?

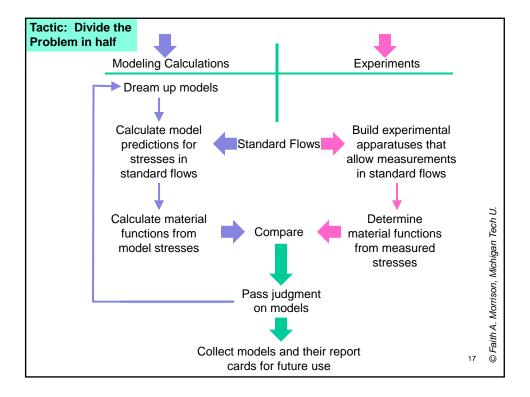
- 1. Pick a small number of simple flows Chapter 4: Standard flows
 - Standardize the flows
 - · Make them easy to calculate with
 - Make them easy to produce in the lab
- 2. Make calculations
- 3. Make measurements
- 4. Try to deduce $\underline{\tau}(\underline{v})$

Chapter 5: Material Functions Chapter 6: Experimental Data

Chapter 6: Experimental Data

Chapter 7: GNF Chapter 8: GLVE Chapter 9: Advanced

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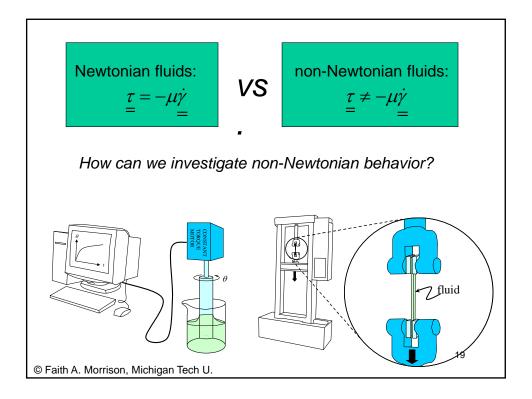
<u>Standard flows</u> – choose a velocity field (not an apparatus or a procedure)

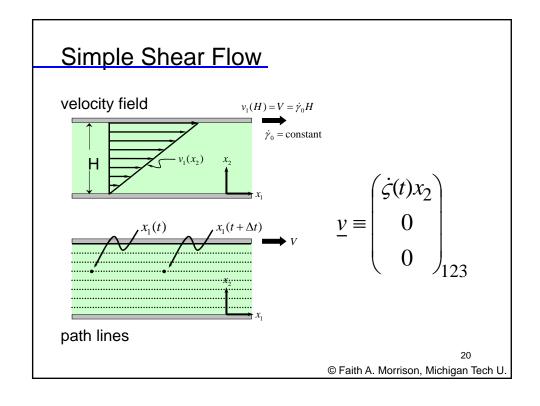
- •For model predictions, calculations are straightforward
- •For experiments, design can be optimized for accuracy and fluid variety

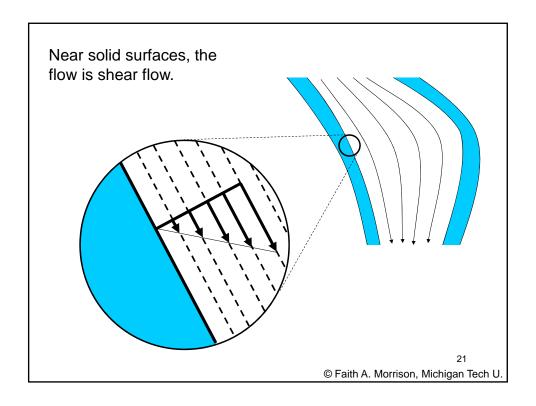
<u>Material functions</u> – choose a common vocabulary of stress and kinematics to report results

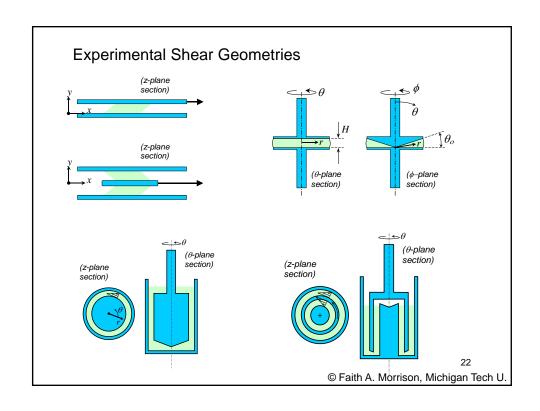
- •Make it easier to compare model/experiment
- •Record an "inventory" of fluid behavior (expertise)

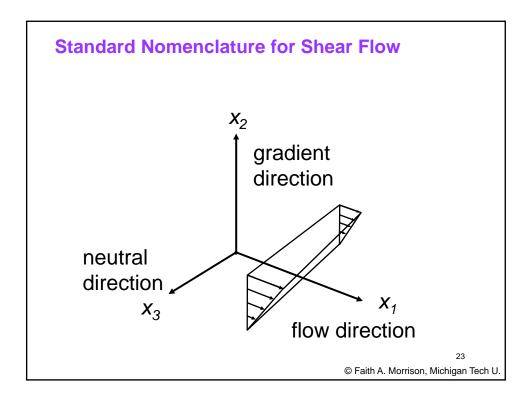
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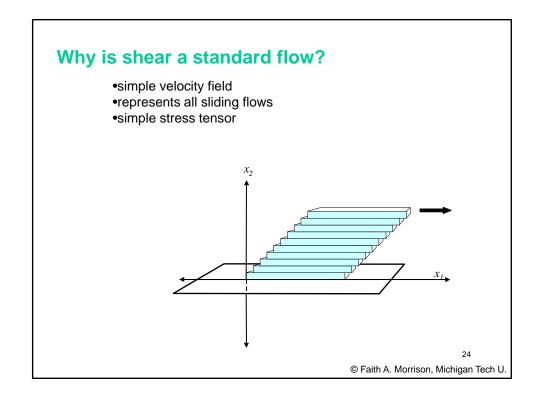


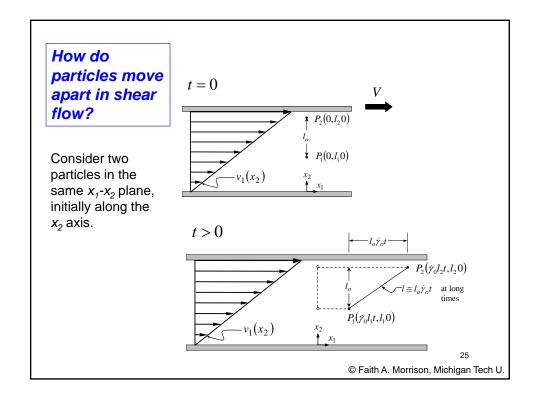


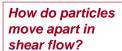












Consider two particles in the same x_1 - x_2 plane, initially along the x_2 axis $(x_1$ =0).

$$\underline{v} = \begin{pmatrix} \gamma_0 x_2 \\ 0 \\ 0 \end{pmatrix}_{123}$$

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

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

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

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

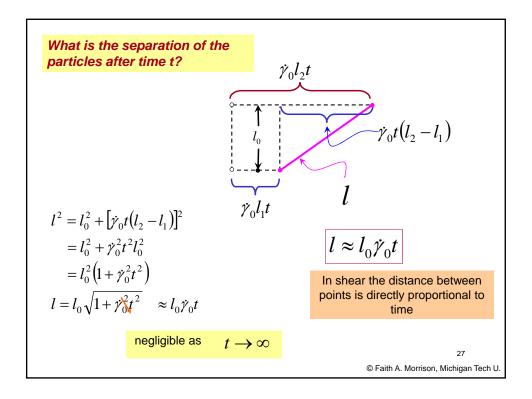
The initial x_1 position of each particle is x_1 =0. After t seconds, the two particles are at the following positions:

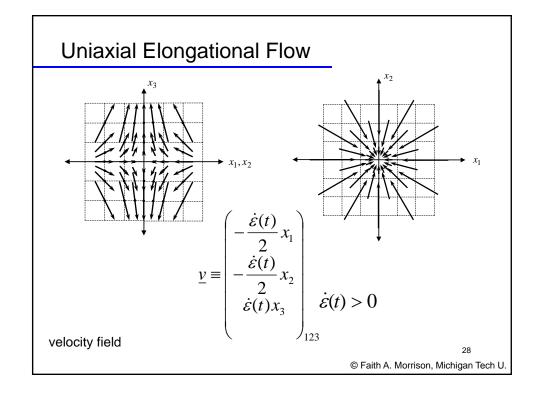
$$P_1(t): \quad x_1 = \dot{\gamma}_0 l_1 t$$

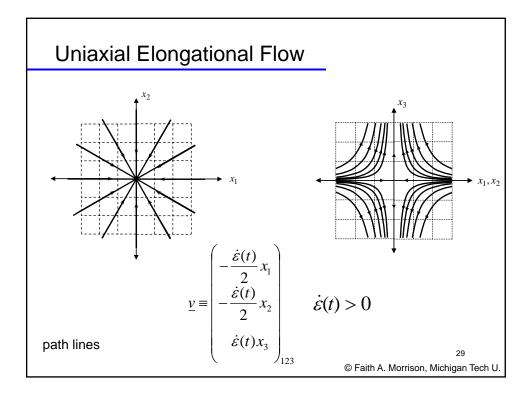
$$P_2(t): \quad x_1 = \frac{\dot{\gamma}_0 l_2 t}{2}$$

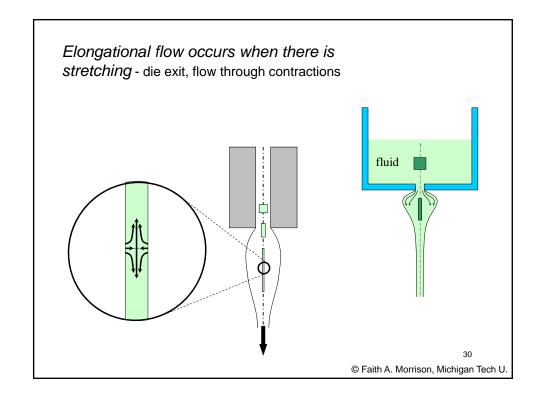
$$location = initial + \left(\frac{length}{time}\right) \left(\frac{time}{time}\right)$$

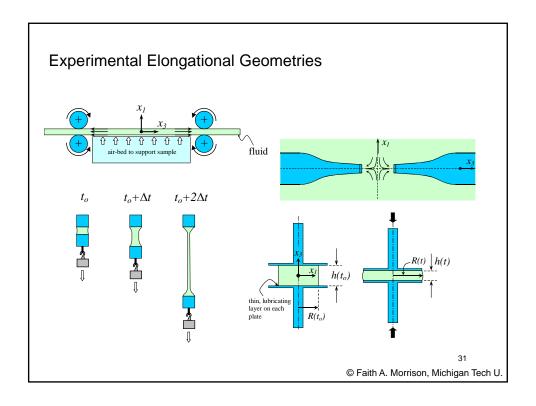
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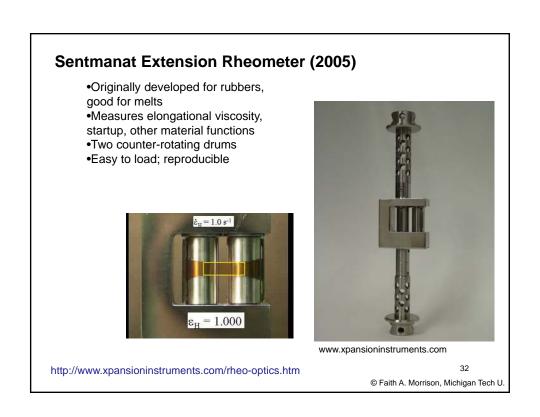


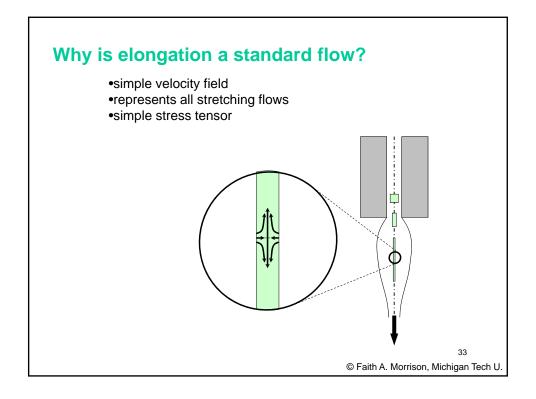


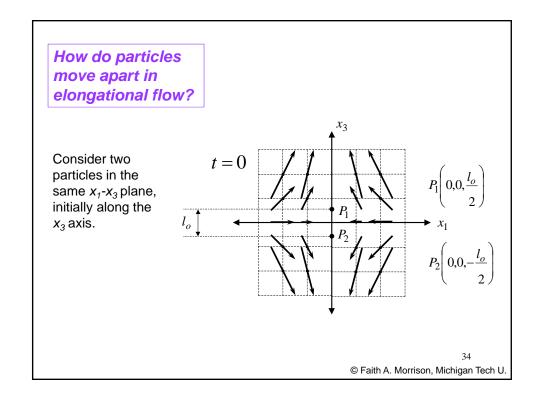












How do particles move apart in elongational flow?

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

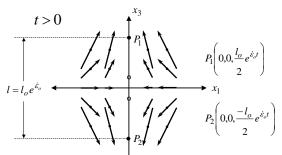
$$x_1 = 0$$

$$x_2 = 0$$

$$x_3 \text{ varies}$$

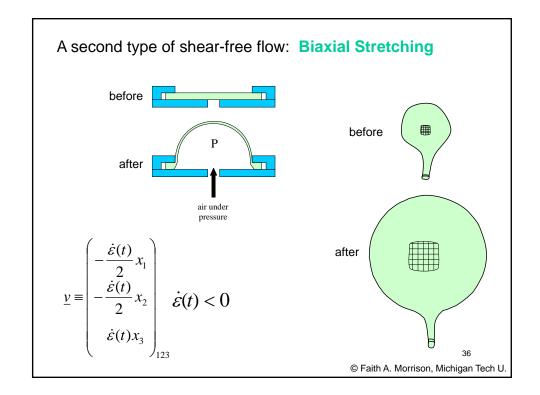
$$\underline{v} = \begin{pmatrix} -\frac{\dot{\varepsilon}_0}{2} x_1 \\ -\frac{\dot{\varepsilon}_0}{2} x_2 \\ \dot{\varepsilon}_0 x_3 \end{pmatrix}_{123} = \begin{pmatrix} 0 \\ 0 \\ \dot{\varepsilon}_0 x_3 \end{pmatrix}_{123}$$

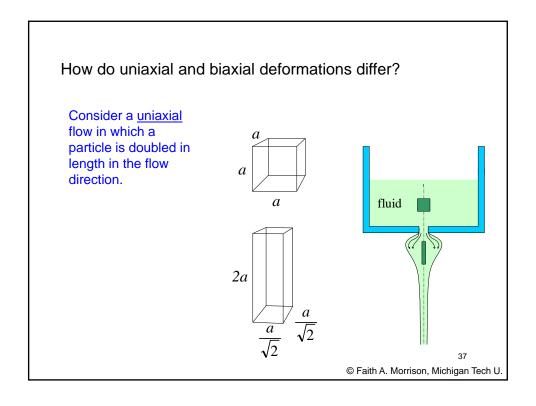
$$v_{3} = \frac{dx_{3}}{dt} = \dot{\varepsilon}_{0}x_{3}$$
$$\frac{dx_{3}}{x_{3}} = \dot{\varepsilon}_{0}dt$$
$$\ln x_{3} = \dot{\varepsilon}_{0}t + C_{1}$$
$$x_{3} = x_{3}(0)e^{\dot{\varepsilon}_{0}t}$$

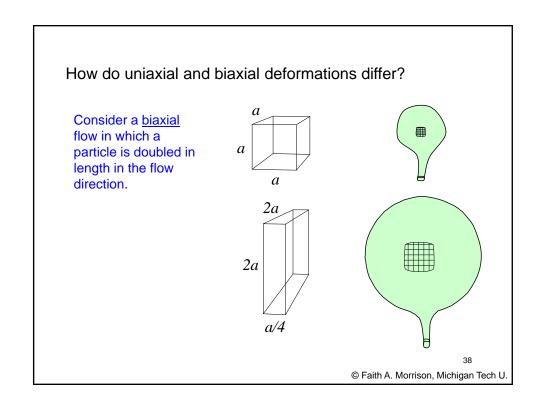


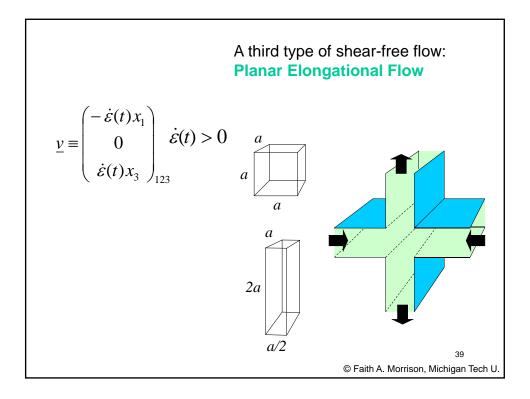
 $l = l_0 e^{\dot{\varepsilon}_0 t}$

Particles move apart exponentially fast.









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, $\dot{\mathcal{E}}(t) > 0$

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

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

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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.

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In general:

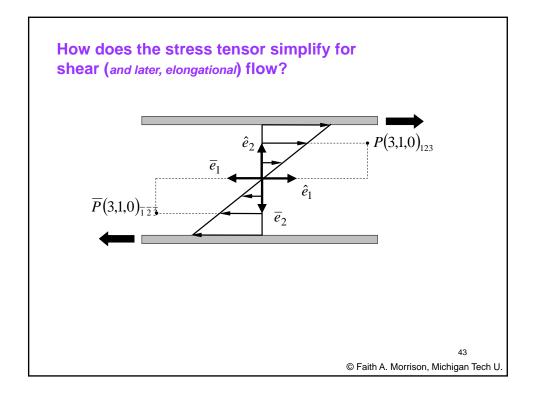
$$\underline{\underline{\tau}} = \begin{pmatrix} \tau_{11} & \tau_{12} & \tau_{13} \\ \tau_{21} & \tau_{22} & \tau_{23} \\ \tau_{31} & \tau_{32} & \tau_{33} \end{pmatrix}_{123}$$

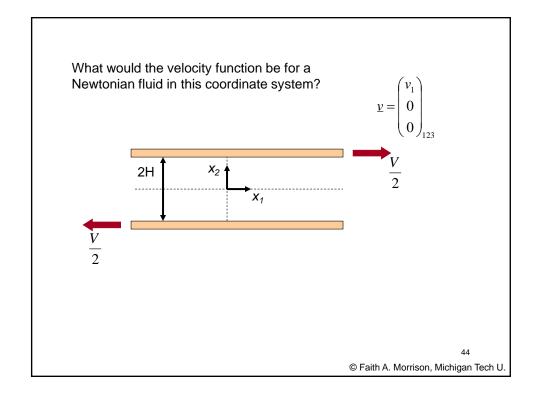
But the stress tensor is <u>symmetric</u> – leaving 6 independent stress components.

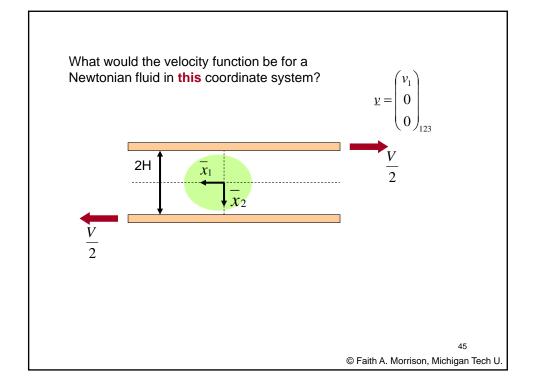
Can we choose a flow to use in which there are fewer than 6 independent stress components?

Yes we can – symmetric flows

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Vectors are independent of coordinate system, but <u>in general</u> 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, <u>however</u>:

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

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$$v = \begin{pmatrix} \frac{V}{2H} x_2 \\ 0 \\ 0 \\ 0 \end{pmatrix}_{123} = \begin{pmatrix} \frac{V}{2H} x_2 \\ 0 \\ 0 \\ 0 \end{pmatrix}_{\bar{1}\bar{2}\bar{3}} x_1$$

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 <u>WILL</u> 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.

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

This is an unusual circumstance only true for the particular coordinate systems chosen.

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

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

$$\begin{aligned} \hat{e}_1 &= -\bar{e}_1 \\ \hat{e}_2 &= -\bar{e}_2 \\ \hat{e}_3 &= \bar{e}_3 \end{aligned}$$

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

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

(now, substitute from previous slide and simplify)

You try.

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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 $\tau_{21} = \tau_{12}$).

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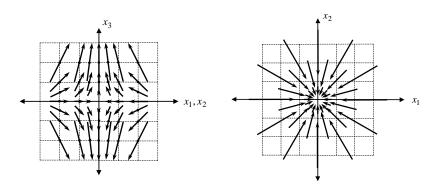
Summary:

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.

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How does the stress tensor simplify for elongational flow?



There is 180° of symmetry around all three coordinate axes.

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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.

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Standard Flows Summary

Choose velocity field:

Symmetry alone implies: (no constitutive equation needed yet)

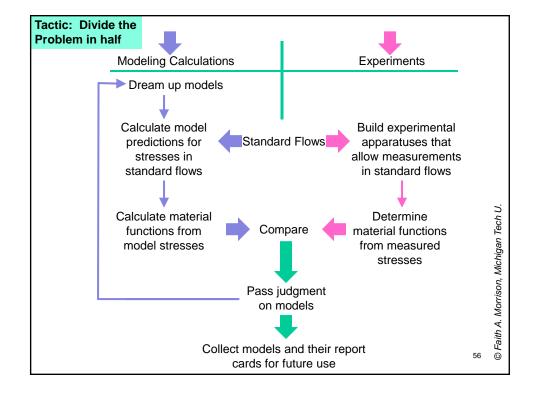
$$\underline{v} = \begin{pmatrix} \dot{\varsigma}(t)x_2 \\ 0 \\ 0 \end{pmatrix}_{123}$$

$$\equiv \begin{pmatrix} \zeta(t)x_2 \\ 0 \\ 0 \end{pmatrix}_{123} \qquad \qquad \tau = \begin{pmatrix} \tau_{11} & \tau_{12} & 0 \\ \tau_{21} & \tau_{22} & 0 \\ 0 & 0 & \tau_{33} \end{pmatrix}$$

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

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

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

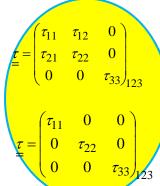


Choose velocity field: Symmetry alone implies: (no constitutive equation needed yet)

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

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

Next, build and assume this



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Measure and

predict this

One final comment on measuring stresses. . .

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

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

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

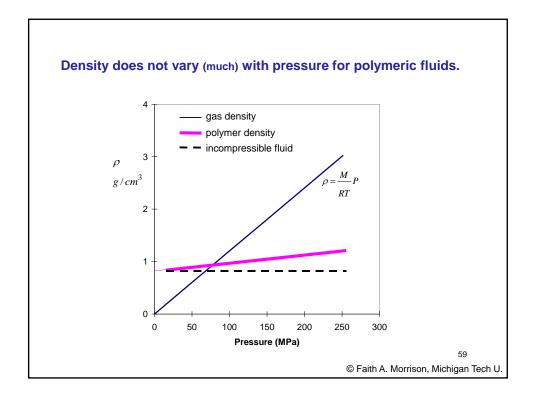
Compressible fluids:

$$= \frac{nRT}{V}$$
 Get p from measurements of T and V .

Incompressible fluids:



•



For incompressible fluids it is not possible to separate p from t_{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

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

We do not need t_{ii} directly to solve for velocities

Solution? Normal stress differences

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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

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

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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

 $\tau_{21} (N_1, N_2) \\ \tau_{21} (N_1, N_2) \\ \text{differences} \\ \text{real?}$

In elongational flow, two stress quantities are measured

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

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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

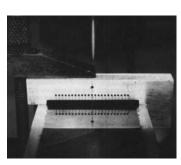
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Bird, et al., <u>Dynamics of Polymeric Fluids</u>, vol. 1, Wiley, 1987, Figure 2.3-1 page 63. (DPL)

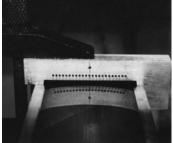
Second normal stress effects: inclined openchannel flow

 $\tau_{22} - \tau_{33} > 0$

Extra tension in the 2-direction pulls down the free surface where dv_1/dx_2 is greatest (see DPL p65).



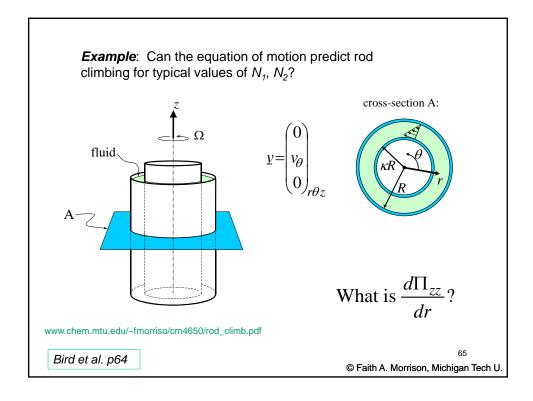
Newtonian - glycerin



Viscoelastic - 1% soln of polyethylene oxide in water

 $N_2 \sim -N_1/10$

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





Shear

Shear-free (elongational, extensional)

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

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

$$\underline{v} = \begin{pmatrix} -\frac{1}{2} \dot{\varepsilon}(t)(1+b)x_1 \\ -\frac{1}{2} \dot{\varepsilon}(t)(1-b)x_2 \\ \dot{\varepsilon}(t)x_3 \end{pmatrix}_{122}$$

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

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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.

