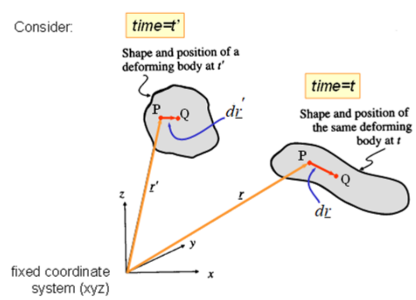
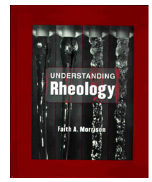
Chapter 9: Advanced Constitutive Models

Michigan Tech
CM4650
Polymer Rheology

We desire a strain tensor that accurately captures large-strain deformation without being affected by rigid-body rotation.





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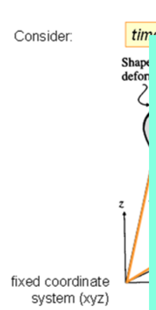
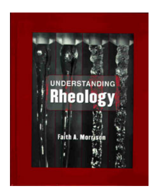


WARNING:
There is *way more* to this than we can cover



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Advanced Constitutive Modeling – Chapter 9

We have learned that the GLVE is a **good** model for:

- Deformations at low rates
- Deformation to low strains (linear regime)

The GLVE does **not** work for the *nonlinear* regime, due to the problem of lack of **frame invariance**.

Fluids with Memory – Chapter 8

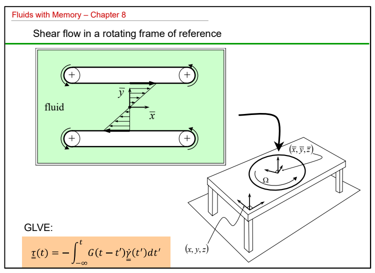
Summary: *Generalized Linear-Viscoelastic Constitutive Equations*

PRO:
- A first constitutive equation with memory
- Can match SAOS, step-strain data very well
- Captures start-up/cessation effects
- Simple to calculate with
- Can be used to calculate the LVE spectrum

CON:
- Fails to predict shear normal stresses
- Fails to predict shear-thinning/thickening
- Only valid at small strains, small rates
- **Not frame-invariant**

GLVE:

$$\underline{\underline{\tau}}(t) = -\int_{-\infty}^{t} G(t-t')\dot{\underline{\underline{\gamma}}}(t')dt'$$

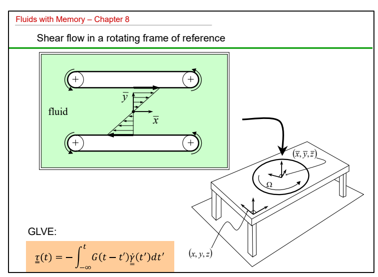


Turntable problem

Advanced Constitutive Modeling – Chapter 9

Strain-related issues?

⇒ perhaps the problem with the GLVE model is associated with how strain is mathematically described.



The question then becomes, how is strain mathematically described in the GLVE Model?

$$\underline{\underline{\tau}}(t) = -\int_{-\infty}^{t} G(t-t')\dot{\underline{\underline{\gamma}}}(t')dt'$$

strain rate

What is the strain measure that is used in the GLVE model?

$$\underline{\underline{\tau}}(t) = -\int_{-\infty}^{t} G(t-t')\dot{\underline{\underline{\gamma}}}(t')dt'$$

strain rate

(use integration by parts;
see hand calculations)

Generalized Linear-Viscoelastic Model:
(strain version)

$$\underline{\underline{\tau}}(t) = +\int_{-\infty}^{t} M(t-t')\underline{\underline{\gamma}}(t,t')dt'$$

The infinitesimal strain tensor is the strain measure of the GLVE

$$M(t-t') \equiv \frac{\partial G(t-t')}{\partial t'}$$

memory function

Infinitesimal Strain Tensor

$$\underline{\underline{\gamma}}(t,t') = \int_{t}^{t'} \underline{\underline{\gamma}}(t'')dt''$$

Turns out:

It is the use of the *infinitesimal strain tensor* as the strain measure that causes the frame-variance in the GLVE model.

We have seen the infinitesimal strain tensor before: when we first defined strain (when we discussed material functions).

Infinitesimal strain tensor $\underline{\underline{\gamma}} \equiv \nabla \underline{u} + (\nabla \underline{u})^T$

When formally developed, $\underline{\underline{\gamma}}(t,t')$ is related to the displacement function, $\underline{u}(t,t')$.

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

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

What is strain? Summary (from Ch5)

Strain is our measure of deformation (change of shape)

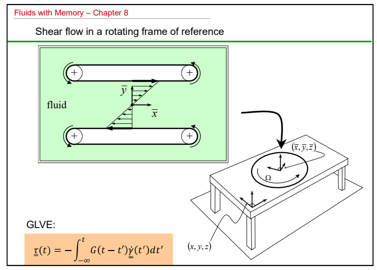
For shear flow (steady or unsteady):

$\gamma_{21}(t_1,t_2) = \int_{t_1}^{t_2} \dot{\gamma}_{21}(t')dt'$	**Strain** is the integral of strain rate	*Strain accumulates as the flow progresses*
$\frac{d\gamma_{21}}{dt} = \dot{\gamma}_{21}(t)$ Deformation rate	The **time derivative of strain** is the strain rate	*The strain rate is the rate of instantaneous shape change*

Applying this to each component of $\underline{\underline{\dot{\gamma}}}$ and generalizing to all flows:

Infinitesimal strain tensor $\underline{\underline{\gamma}} \equiv \nabla \underline{u} + (\nabla \underline{u})^T$

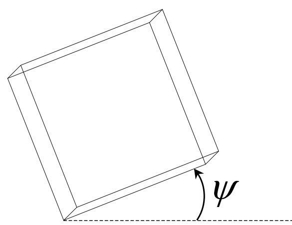
In addition to the turntable example, another "flow" we can use to test the GLVE model is **rigid body rotation** (no strain).



Turntable problem

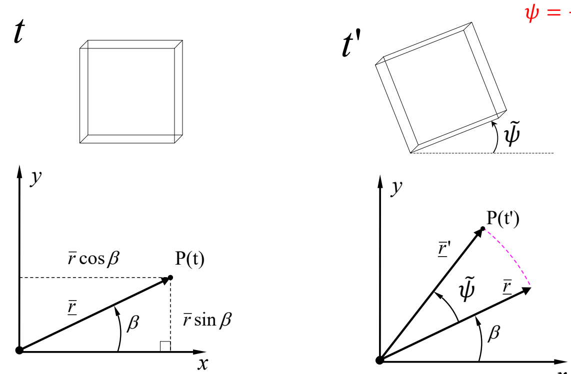
Counter clockwise rigid body rotation **(no strain)**.

No strain should produce **no stress**.



No stress is generated when a fluid is rotated CCW through $\tilde{\psi}$ (from position at time t to position at time t', **what does the GLVE predict**?

(Warning: later, we are going to consider CCW rotation from t' to t through an angle $\psi = -\tilde{\psi}$; see Table 9.3)



- calculate the infinitesimal strain tensor for rigid body rotation
- use the strain-evident version of the GLVE

(note: we need $\underline{\underline{\gamma}}(t,t')$ in the GLVE)

What does the GLVE Predict for CCW Rigid-Body Rotation around the *z*-axis from t to t'?

$$\underline{r} = \begin{pmatrix} x \\ y \\ z \end{pmatrix}_{xyz} \quad \underline{r}' = \begin{pmatrix} x' \\ y' \\ z' \end{pmatrix}_{xyz}$$

$$\underline{u}(t,t') = \underline{r}' - \underline{r}$$

$$\underline{\underline{\gamma}}(t,t') = \nabla \underline{u} + (\nabla \underline{u})^T$$

(see book for details)

What does the GLVE Predict for CCW Rigid-Body Rotation around the *z*-axis from t to t'?

From geometry

$$y = \bar{r}\sin\beta$$
$$x = \bar{r}\cos\beta$$

From trigonometry

$$\begin{aligned} y' &= \bar{r}\sin(\beta+\tilde{\psi}) = \bar{r}(\sin\beta\cos\tilde{\psi} + \sin\tilde{\psi}\cos\beta) \\ &= y\cos\tilde{\psi} + x\sin\tilde{\psi} \\ x' &= \bar{r}\cos(\beta+\tilde{\psi}) = \bar{r}(\cos\beta\cos\tilde{\psi} - \sin\beta\sin\tilde{\psi}) \\ &= x\cos\tilde{\psi} - y\sin\tilde{\psi} \\ z &= z' \end{aligned}$$

From definitions of $\underline{u}$ and $\underline{\underline{\gamma}}$

$$\underline{u} = \underline{\bar{r}}' - \underline{\bar{r}} = \begin{pmatrix} x\cos\tilde{\psi} - y\sin\tilde{\psi} - x \\ y\cos\tilde{\psi} + x\sin\tilde{\psi} - y \\ 0 \end{pmatrix}_{xyz}$$

$$\underline{\underline{\gamma}}(t,t') = \nabla \underline{u} + (\nabla \underline{u})^T =$$

GLVE Prediction for CCW Rigid-Body Rotation
around the z-axis from t to t':

$$\underline{\underline{\tau}}(t) = + \int_{-\infty}^{t} M(t-t') \begin{pmatrix} 2(\cos\tilde{\psi} - 1) & 0 & 0 \\ 0 & 2(\cos\tilde{\psi} - 1) & 0 \\ 0 & 0 & 0 \end{pmatrix}_{xyz} dt'$$

GLVE Prediction for CCW Rigid-Body Rotation
around the z-axis from t to t':

WRONG

$$\underline{\underline{\tau}}(t) = + \int_{-\infty}^{t} M(t-t') \xcancel{\begin{pmatrix} 2(\cos\tilde{\psi} - 1) & 0 & 0 \\ 0 & 2(\cos\tilde{\psi} - 1) & 0 \\ 0 & 0 & 0 \end{pmatrix}_{xyz}} dt'$$

Stress depends on angle of rotation!

Why does GLVE make this erroneous prediction?

$$\underline{\underline{\gamma}}(t,t') = \nabla \underline{u}(t,t') + \left[\nabla \underline{u}(t,t')\right]^T$$

$$\underline{u}(t,t') = \underline{r}(t') - \underline{r}(t)$$

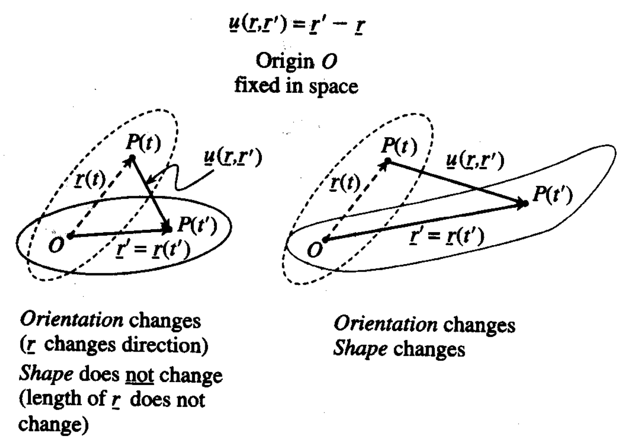
Because this vector, while accounting for deformation, ***also accounts for changes in orientation***.

Advanced Constitutive Modeling – Chapter 9

$$\underline{\underline{\gamma}}(t,t') = \nabla \underline{u}(t,t') + \left[\nabla \underline{u}(t,t')\right]^T$$

$$\underline{u}(t,t') = \underline{r}(t') - \underline{r}(t)$$

Accounts for changes in shape and orientation.



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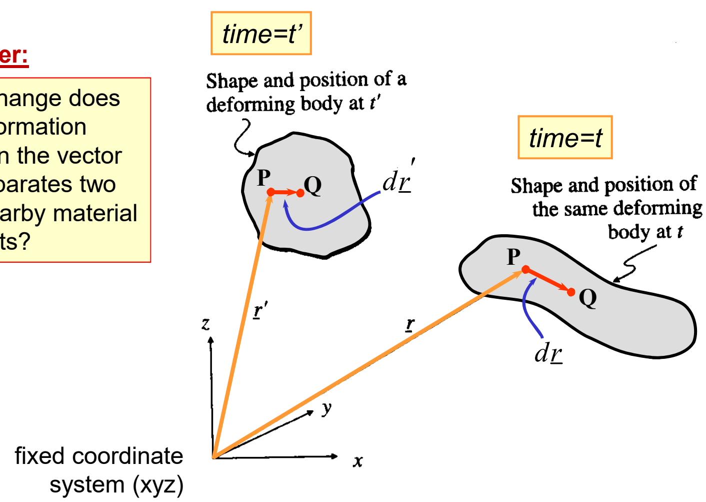
Advanced Constitutive Modeling – Chapter 9

We desire a strain tensor that accurately captures large-strain deformation without being affected by **translation** and **rotation**.

Consider:

What change does the deformation cause in the vector that separates two very nearby material elements?



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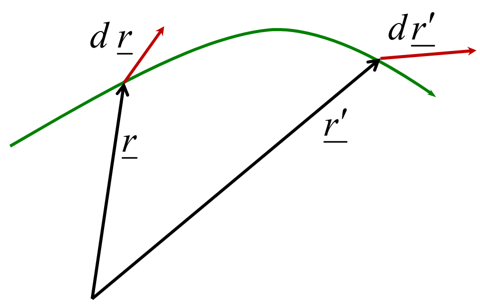
How does $d\underline{r}$ map to $d\underline{r}'$ along a particle path?

Define change-of-shape tensors that rely on relative location of two nearby particles

$\underline{r}$ particle label (reference time t)

$\underline{r}'$ location at time t' of the particle labeled $\underline{r}$

Particle position at t'
$\underline{r}'$ is a function of past position, $r' = f(\underline{r})$



$$\underline{r}' = \begin{pmatrix} x' \\ y' \\ z' \end{pmatrix}_{xyz} = f(\underline{r})$$

$$df = \begin{pmatrix} dx' \\ dy' \\ dz' \end{pmatrix}_{xyz} = ?$$

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We can relate dr' to dr using the chain rule.

$$\underline{r}' = \begin{pmatrix} x' \\ y' \\ z' \end{pmatrix}_{xyz} = f(x, y, z)$$

$$dx' = ?$$
$$dy' = ?$$
$$dz' = ?$$

(see text)

$$dx' = \frac{\partial x'}{\partial x}dx + \frac{\partial x'}{\partial y}dy + \frac{\partial x'}{\partial z}dz$$

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Combine answers from 3 directions:

$$\begin{pmatrix} dx' & dy' & dz' \end{pmatrix}_{xyz} = \begin{pmatrix} dx & dy & dz \end{pmatrix}_{xyz} \begin{pmatrix} \frac{\partial x'}{\partial x} & \frac{\partial y'}{\partial x} & \frac{\partial z'}{\partial x} \\ \frac{\partial x'}{\partial y} & \frac{\partial y'}{\partial y} & \frac{\partial z'}{\partial y} \\ \frac{\partial x'}{\partial z} & \frac{\partial y'}{\partial z} & \frac{\partial z'}{\partial z} \end{pmatrix}_{xyz}$$

$$d\underline{r}' = d\underline{r} \cdot \underline{\underline{F}}$$

Deformation-gradient tensor

$$\underline{\underline{F}}(t,t') \equiv \begin{pmatrix} \frac{\partial x'}{\partial x} & \frac{\partial y'}{\partial x} & \frac{\partial z'}{\partial x} \\ \frac{\partial x'}{\partial y} & \frac{\partial y'}{\partial y} & \frac{\partial z'}{\partial y} \\ \frac{\partial x'}{\partial z} & \frac{\partial y'}{\partial z} & \frac{\partial z'}{\partial z} \end{pmatrix}_{xyz} = \frac{\partial \underline{r}'}{\partial \underline{r}} = \frac{\partial r_i'}{\partial r_p} \hat{e}_p \hat{e}_i$$

In Einstein notation:
$\underline{r}' = r_i' \hat{e}_i$
$r_1' = x', r_2' = y', r_2' = z'$

We can calculate F^{-1} as follows:

Define: $\underline{\underline{F}}^{-1} \cdot \underline{\underline{F}} = \underline{\underline{I}}$

Then use: $d\underline{r}' = d\underline{r} \cdot \underline{\underline{F}}$

$\Rightarrow ?$

$$d\underline{r}' = d\underline{r} \cdot \underline{\underline{F}}$$
$$d\underline{r}' \cdot \underline{\underline{F}}^{-1} = d\underline{r} \cdot \underline{\underline{F}} \cdot \underline{\underline{F}}^{-1}$$
$$d\underline{r}' \cdot \underline{\underline{F}}^{-1} = d\underline{r}$$

Deformation-gradient tensor

$$d\underline{r}' = d\underline{r}\cdot\underline{\underline{F}}$$

$$\underline{\underline{F}}(t,t') \equiv \begin{pmatrix} \frac{\partial x'}{\partial x} & \frac{\partial y'}{\partial x} & \frac{\partial z'}{\partial x} \\ \frac{\partial x'}{\partial y} & \frac{\partial y'}{\partial y} & \frac{\partial z'}{\partial y} \\ \frac{\partial x'}{\partial z} & \frac{\partial y'}{\partial z} & \frac{\partial z'}{\partial z} \end{pmatrix}_{xyz} = \frac{\partial \underline{r}'}{\partial \underline{r}} = \frac{\partial r_i'}{\partial r_p}\hat{e}_p\hat{e}_i$$

Inverse deformation-gradient tensor

$$d\underline{r} = d\underline{r}'\cdot\underline{\underline{F}}^{-1}$$

$$\underline{\underline{F}}^{-1}(t',t) \equiv \begin{pmatrix} \frac{\partial x}{\partial x'} & \frac{\partial y}{\partial x'} & \frac{\partial z}{\partial x'} \\ \frac{\partial x}{\partial y'} & \frac{\partial y}{\partial y'} & \frac{\partial z}{\partial y'} \\ \frac{\partial x}{\partial z'} & \frac{\partial y}{\partial z'} & \frac{\partial z}{\partial z'} \end{pmatrix}_{xyz} = \frac{\partial \underline{r}}{\partial \underline{r}'} = \frac{\partial r_m}{\partial r_j'}\hat{e}_j\hat{e}_m$$

These strain measures get rid of the **translation** problem.

We desire a strain tensor that accurately captures large-strain deformation without being affected by **translation** and **rotation**.

$\nabla\underline{u}$, $\underline{\underline{\gamma}}$: These strain measures include translation, deformation and orientation

$\underline{\underline{F}}$, $\underline{\underline{F}}^{-1}$: These strain measures include deformation and orientation

We can separate the deformation and orientation information in $\underline{\underline{F}}$ and $\underline{\underline{F}}^{-1}$ using a technique called *polar decomposition*.

(en.wikipedia.org/wiki/Polar_decomposition)

Polar Decomposition Theorem

(en.wikipedia.org/wiki/Polar_decomposition)

Any tensor for which an inverse exists has two unique decompositions:

$$\underline{\underline{A}} = \underline{\underline{R}} \cdot \underline{\underline{U}}$$
$$\underline{\underline{A}} = \underline{\underline{V}} \cdot \underline{\underline{R}}$$

Pure rotation tensor

$\underline{\underline{U}} = (\underline{\underline{A}}^T \cdot \underline{\underline{A}})^{1/2}$ Right stretch tensor

$\underline{\underline{R}}^{-1} = \underline{\underline{R}}^T$ Orthogonal tensor

$\underline{\underline{V}} = (\underline{\underline{A}} \cdot \underline{\underline{A}}^T)^{1/2}$ Left stretch tensor

$\underline{\underline{U}}, \underline{\underline{V}}$ symmetric, nonsingular tensors

$$\underline{\underline{R}} = \underline{\underline{A}} \cdot (\underline{\underline{A}}^T \cdot \underline{\underline{A}})^{-1/2} = \underline{\underline{A}} \cdot \underline{\underline{U}}^{-1}$$

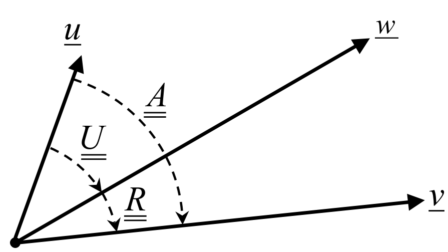
EXAMPLE: Calculate the right stretch tensor and rotation tensor for a given tensor. Calculate the angle through which $\underline{\underline{R}}$ rotates the vector $\underline{u}$.

$$\underline{\underline{A}} = \begin{pmatrix} 1 & 0 & 2 \\ 0 & 3 & 2 \\ 2 & 0 & 0 \end{pmatrix}_{xyz} \qquad \underline{u} = \begin{pmatrix} 1 \\ 2 \\ 1 \end{pmatrix}_{xyz}$$

$$\underline{\underline{A}} = \underline{\underline{R}} \cdot \underline{\underline{U}}$$
$$\underline{\underline{A}} \cdot \underline{u} = \underline{\underline{R}} \cdot \underbrace{\underline{\underline{U}} \cdot \underline{u}}_{\underline{w}}$$

Pure rotation

All the stretch; some of the rotation



We have partially isolated the effect of rotation through polar decomposition.

pure rotation tensor

left stretch tensor

$$\underline{\underline{A}} = \underline{\underline{R}} \cdot \underline{\underline{U}} = \underline{\underline{V}} \cdot \underline{\underline{R}}$$

right stretch tensor

original (strain) tensor

We can further isolate stretch from rotation by considering the *eigenvectors* of $\underline{\underline{U}}$ and $\underline{\underline{V}}$.

$$\underline{\underline{A}} = \underline{\underline{R}} \cdot \underline{\underline{U}}$$
$$\underline{\underline{A}} = \underline{\underline{V}} \cdot \underline{\underline{R}}$$

eigenvectors

$$\underline{\underline{U}} \cdot \hat{\xi}_k = \lambda_k \hat{\xi}_k$$

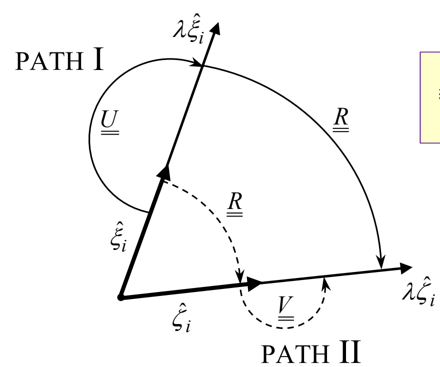
$$\underline{\underline{V}} \cdot \hat{\zeta}_j = \nu_j \hat{\zeta}_j$$

eigenvalues

Physical Interpretation

$$\underline{\underline{A}} = \underline{\underline{R}} \cdot \underline{\underline{U}}$$
$$\underline{\underline{A}} \cdot \underline{\xi_k} = \underline{\underline{R}} \cdot \underline{\underline{U}} \cdot \underline{\xi_k}$$
$$= \underline{\underline{R}} \cdot \underbrace{\lambda_k \underline{\xi_k}}_{\text{Pure stretch}}$$

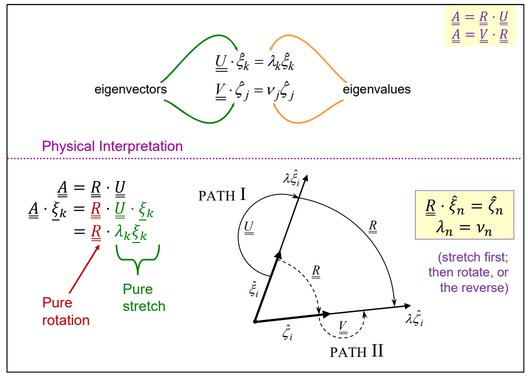
Pure rotation



$$\underline{\underline{R}} \cdot \hat{\xi}_n = \hat{\zeta}_n$$
$$\lambda_n = \nu_n$$

(stretch first; then rotate, or the reverse)

Advanced Constitutive Modeling – Polar Decomposition



Omitting the details, the idea is:

- $\underline{\underline{F}}, \underline{\underline{F}}^{-1}$ are **plausible strain measures** (*translation* has been eliminated, but they contain *rotation*)
- **Eliminate *rotation*** by decomposing $\underline{\underline{F}}, \underline{\underline{F}}^{-1}$ into pure stretch tensors using polar decomposition

$$\underline{\underline{U}} = (\underline{\underline{A}}^T \cdot \underline{\underline{A}})^{1/2}$$
$$\underline{\underline{V}} = (\underline{\underline{A}} \cdot \underline{\underline{A}}^T)^{1/2}$$

Advanced Constitutive Modeling – Polar Decomposition

$\underline{\underline{A}} = \underline{\underline{R}} \cdot \underline{\underline{U}}$
$\underline{\underline{A}} = \underline{\underline{V}} \cdot \underline{\underline{R}}$

Finite Strain Tensors

$$\underline{\underline{U}} = (\underline{\underline{A}}^T \cdot \underline{\underline{A}})^{1/2}$$
$$\underline{\underline{V}} = (\underline{\underline{A}} \cdot \underline{\underline{A}}^T)^{1/2}$$

$\underline{\underline{A}}$	$\underline{\underline{V}}^2$	$\underline{\underline{U}}^2$
$\underline{\underline{F}}$	$\underline{\underline{F}} \cdot \underline{\underline{F}}^T$	$\underline{\underline{F}}^T \cdot \underline{\underline{F}}$
$\underline{\underline{F}}^T$	$\underline{\underline{F}}^T \cdot \underline{\underline{F}}$	$\underline{\underline{F}} \cdot \underline{\underline{F}}^T$
$\underline{\underline{F}}^{-1}$	$\underline{\underline{F}}^{-1} \cdot (\underline{\underline{F}}^{-1})^T$	$(\underline{\underline{F}}^{-1})^T \cdot \underline{\underline{F}}^{-1}$
$(\underline{\underline{F}}^{-1})^T$	$(\underline{\underline{F}}^{-1})^T \cdot \underline{\underline{F}}^{-1}$	$\underline{\underline{F}}^{-1} \cdot (\underline{\underline{F}}^{-1})^T$

proposed deformation tensors; contain stretch and rotation; **$\underline{\underline{V}}$ and $\underline{\underline{U}}$ are symmetric**

proposed deformation tensors; contain stretch of eigenvectors, **BUT NO ROTATION**

Cauchy tensor	$\underline{\underline{C}} \equiv \underline{\underline{F}} \cdot \underline{\underline{F}}^T$
Finger tensor	$\underline{\underline{C}}^{-1} \equiv (\underline{\underline{F}}^{-1})^T \cdot \underline{\underline{F}}^{-1}$

Now we can construct new constitutive equations using the new strain measures:

Replace: $\underline{\underline{\gamma}}(t,t')$ with: $-\underline{\underline{C}}(t',t)$

(we use the negative so that at small strains we recover $\underline{\underline{\gamma}}(t,t')$, like in the GLVE)

Finite Strain Hooke's Law of elastic solids:

$$\underline{\underline{\tau}}(t) = +G\underline{\underline{C}}^{-1}(t,0)$$

Finite Strain Maxwell Model:

$$\underline{\underline{\tau}}(t) = -\int_{-\infty}^{t} \frac{\eta_0}{\lambda^2} e^{\frac{-(t-t\prime)}{\lambda}} \underline{\underline{C}}^{-1}(t',t)\,dt'$$

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Now we can construct new constitutive equations using the new strain measures:

Replace: $\underline{\underline{\gamma}}(t,t')$ with: $-\underline{\underline{C}}(t',t)$

Finite Strain Hooke's Law of elastic solids:

$$\underline{\underline{\tau}}(t) = +G\underline{\underline{C}}^{-1}(t,0)$$

Time to take these out for a spin

Finite Strain Maxwell Model:

$$\underline{\underline{\tau}}(t) = -\int_{-\infty}^{t} \frac{\eta_0}{\lambda^2} e^{\frac{-(t-t\prime)}{\lambda}} \underline{\underline{C}}^{-1}(t',t)\,dt'$$

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EXAMPLE: Calculate stress predicted in rigid-body rotation (around z through a counter-clockwise angle ψ) by a finite-strain Hooke's law.

$$\underline{\underline{\tau}}(t) = +G\underline{\underline{C}}^{-1}(t,0)$$

(this didn't work when the infinitesimal strain tensor $\underline{\underline{\gamma}}(t,t')$ was used)

EXAMPLE: Calculate stress predicted in rigid-body rotation (around z through a counter-clockwise angle ψ) by a finite-strain Hooke's law.

$$\underline{\underline{\tau}}(t) = +G\underline{\underline{C}}^{-1}(t,0)$$

Usual solution steps:
1. Begin with kinematics of the flow
2. Calculate the needed tensor elements ($\underline{\underline{\dot{\gamma}}}$ before, $\underline{\underline{C}}^{-1}$ now)
3. Calculate the stress
4. Calculate functions that rely on stress (material functions)

EXAMPLE: Calculate stress predicted in rigid-body rotation (around z through a counter-clockwise angle ψ) by a finite-strain Hooke's law.

$$\underline{\underline{\tau}}(t) = +G\underline{\underline{C}}^{-1}(t,0)$$

Usually, start with
$\underline{v}, \dot{\varsigma}(t)$ or $\dot{\varepsilon}(t), \rightarrow \dot{\underline{\underline{\gamma}}}$ …

Usual solution steps:
1. Begin with **kinematics** of the flow
2. Calculate the needed tensor elements ($\dot{\underline{\underline{\gamma}}}$ before, $\underline{\underline{C}}^{-1}$ now)
3. Calculate the stress
4. Calculate functions that rely on stress (material functions)

Our old constitutive equations were $\dot{\underline{\underline{\gamma}}}$-based:

$$\underline{\underline{\tau}}(t) = -\mu\dot{\underline{\underline{\gamma}}}(t)$$
$$\underline{\underline{\tau}}(t) = -\eta\dot{\underline{\underline{\gamma}}}(t)$$
$$\underline{\underline{\tau}}(t) = -\int_{-\infty}^{t} \frac{\eta_0}{\lambda} e^{\frac{-(t-t')}{\lambda}} \dot{\underline{\underline{\gamma}}}(t')dt'$$
$$\underline{\underline{\tau}}(t) = -\int_{-\infty}^{t} G(t-t')\dot{\underline{\underline{\gamma}}}(t')dt'$$
$$etc.$$

And our "recipe cards" were, therefore, $\dot{\underline{\underline{\gamma}}}$-based
…

Steady Shear Flow Material Functions

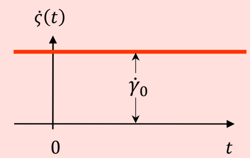
Michigan Tech

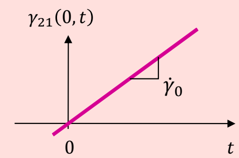
Traditional "recipe card"

Imposed Kinematics:

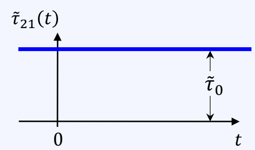
$$\underline{v} \equiv \begin{pmatrix} \dot{\varsigma}(t)x_2 \\ 0 \\ 0 \end{pmatrix}_{123}$$

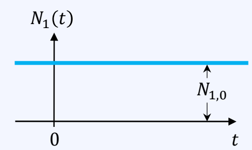
$$\dot{\varsigma}(t) = \dot{\gamma}_0 = \text{constant}$$





Material Stress Response:





Material Functions:

Viscosity $\quad \eta(\dot{\gamma}_0) \equiv \dfrac{\tilde{\tau}_{21}}{\dot{\gamma}_0} = \dfrac{-\tau_{21}}{\dot{\gamma}_0}$

First normal-stress coefficient $\quad \Psi_1(\dot{\gamma}_0) \equiv \dfrac{\tilde{\tau}_{11}-\tilde{\tau}_{22}}{\dot{\gamma}_0^2} = \dfrac{-(\tau_{11}-\tau_{22})}{\dot{\gamma}_0^2}$

Second normal-stress coefficient $\quad \Psi_2(\dot{\gamma}_0) \equiv \dfrac{\tilde{\tau}_{22}-\tilde{\tau}_{33}}{\dot{\gamma}_0^2} = \dfrac{-(\tau_{22}-\tau_{33})}{\dot{\gamma}_0^2}$

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Our NEW constitutive equations are strain-based, $\underline{\underline{\gamma}}(t,t'), \underline{\underline{C}}^{-1}(t',t),$ etc.:

$$\underline{\underline{\tau}}(t) = -G_0 \underline{\underline{\gamma}}(0,t) \qquad \underline{\underline{\tau}}(t) = +G_0 \underline{\underline{C}}^{-1}(t,0)$$

$$\underline{\underline{\tau}}(t) = +\int_{-\infty}^{t} \frac{\eta_0}{\lambda^2} e^{\frac{-(t-t')}{\lambda}} \underline{\underline{\gamma}}(t,t')dt' \qquad \underline{\underline{\tau}}(t) = -\int_{-\infty}^{t} \frac{\eta_0}{\lambda^2} e^{\frac{-(t-t')}{\lambda}} \underline{\underline{C}}^{-1}(t',t)dt'$$

$$\underline{\underline{\tau}}(t) = +\int_{-\infty}^{t} \frac{\partial G(t-t')}{\partial t'} \underline{\underline{\gamma}}(t,t')dt' \qquad \underline{\underline{\tau}}(t) = -\int_{-\infty}^{t} \frac{\partial G(t-t')}{\partial t'} \underline{\underline{C}}^{-1}(t',t)dt'$$

$$etc. \qquad etc.$$

Our recipe cards must now be deformation-based, $\underline{r}, \underline{r}'$ ...

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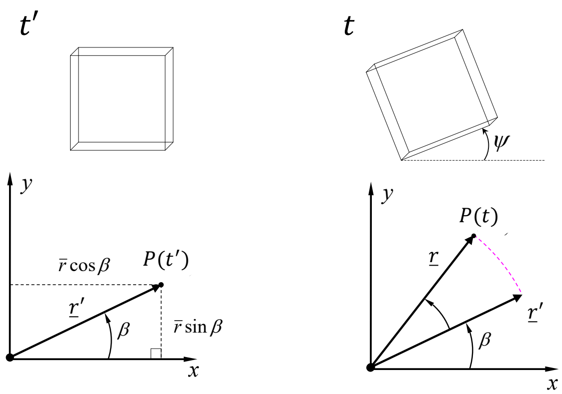
What is the Finger Tensor $\underline{\underline{C}}^{-1}(t',t)$ in CCW Rigid Body Rotation from t' to t through an angle ψ?



Strain Tensor Prediction for CCW Rigid-Body Rotation around the *z*-axis from t' to t:

$$x' = \bar{r}\cos\beta$$
$$y' = \bar{r}\sin\beta$$

From geometry

From trigonometry

$$x = \bar{r}\cos(\beta+\psi) = \bar{r}(\cos\beta\cos\psi - \sin\beta\sin\psi)$$
$$= x'\cos\psi - y'\sin\psi$$

$$y = \bar{r}\sin(\beta+\psi) = \bar{r}(\sin\beta\cos\psi + \sin\psi\cos\beta)$$
$$= y'\cos\psi + x'\sin\psi$$

$$z = z'$$

From definition:

$$\underline{\underline{F}}^{-1}(t',t) = \frac{\partial \underline{r}}{\partial \underline{r}'} =$$

…

Strain Tensor Prediction for CCW Rigid-Body Rotation around the z-axis from t' to t:

$$\underline{\underline{F}}^{-1}(t',t) = \frac{\partial \underline{r}}{\partial \underline{r}'} = \begin{pmatrix} \cos\psi & \sin\psi & 0 \\ -\sin\psi & \cos\psi & 0 \\ 0 & 0 & 1 \end{pmatrix}_{xyz}$$

(matches answer in Table 9.3)

NOTE: caption definition of ψ is in error

$$\underline{\underline{C}}^{-1}(t',t) = (\underline{\underline{F}}^{-1})^T \cdot \underline{\underline{F}}^{-1}$$

CCW Rigid Body Rotation "Material Functions"

Strain-centered "recipe card"

Imposed Kinematics:

$\underline{v} = 0$ *(in a coordinate system with origin within the fluid)*

$$\underline{r}' = \begin{pmatrix} x' \\ y' \\ z' \end{pmatrix}_{xyz} \qquad \underline{r} = \begin{pmatrix} x \\ y \\ z \end{pmatrix}_{xyz} = \begin{pmatrix} x'\cos\psi - y'\sin\psi \\ y'\cos\psi + x'\sin\psi \\ z' \end{pmatrix}_{xyz}$$

$$\underline{\underline{F}}^{-1}(t',t) = \frac{\partial \underline{r}}{\partial \underline{r}'} = \begin{pmatrix} \cos\psi & \sin\psi & 0 \\ -\sin\psi & \cos\psi & 0 \\ 0 & 0 & 1 \end{pmatrix}_{xyz} \qquad \underline{\underline{C}}^{-1}(t',t) = \underline{\underline{I}}$$

$$\underline{\underline{\tau}} = unchanged$$

(no deformation
⇒ no stress)

EXAMPLE: Calculate stress predicted in shear by a finite-strain Hooke's law. Compare with experimental results.

$$\underline{\underline{\tau}}(t) = +G\underline{\underline{C}}^{-1}(t,0)$$

Steady Shear Flow Material Functions

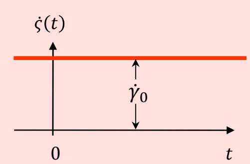
Michigan Tech

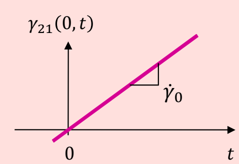
Traditional "recipe card"

Imposed Kinematics:

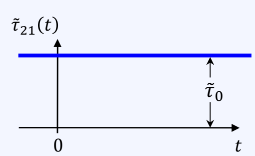
$$\underline{v} \equiv \begin{pmatrix} \dot{\varsigma}(t)x_2 \\ 0 \\ 0 \end{pmatrix}_{123}$$

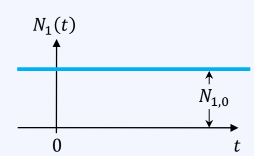
$$\dot{\varsigma}(t) = \dot{\gamma}_0 = \text{constant}$$





Material Stress Response:





Material Functions:

Viscosity $\eta(\dot{\gamma}_0) \equiv \frac{\tilde{\tau}_{21}}{\dot{\gamma}_0} = \frac{-\tau_{21}}{\dot{\gamma}_0}$

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

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

Steady Shear Flow Material Functions

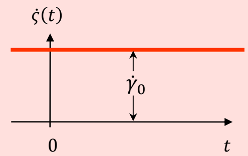
Michigan Tech

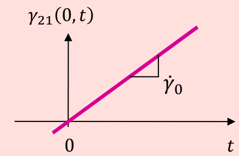
Strain-centered "recipe card"

Imposed Kinematics:

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

$$\dot{\varsigma}(t) = \dot{\gamma}_0 = \text{constant}$$





$$\underline{r}' = \begin{pmatrix} x' \\ y' \\ z' \end{pmatrix}_{123} \qquad \underline{r} = \begin{pmatrix} x \\ y \\ z \end{pmatrix}_{123} = \begin{pmatrix} x' + \dot{\gamma}_0 (t - t') \\ y' \\ z' \end{pmatrix}_{123}$$

$$\underline{\underline{F}}^{-1}(t',t) = \begin{pmatrix} 1 & 0 & 0 \\ \gamma & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}_{123} \qquad \underline{\underline{C}}^{-1}(t',t) = \begin{pmatrix} 1+\gamma^2 & \gamma & 0 \\ \gamma & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}_{123} \qquad \gamma = \dot{\gamma}_0 (t - t')$$

Material Functions:

Viscosity $\eta(\dot{\gamma}_0) \equiv \frac{\tilde{\tau}_{21}}{\dot{\gamma}_0} = \frac{-\tau_{21}}{\dot{\gamma}_0}$

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

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

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Advanced Constitutive Modeling – Chapter 9

EXAMPLE: Calculate stress predicted in <u>shear</u> by a finite-strain Hooke's law. Compare with experimental results.

From shear kinematics:

$$\left\{ \begin{array}{l} \underline{\underline{C}}^{-1}(t',t) = \begin{pmatrix} 1+\gamma^2 & \gamma & 0 \\ \gamma & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}_{123} \\ \gamma = \gamma(t',t) = \dot{\gamma}_0 (t - t') \end{array} \right.$$

$$\underline{\underline{\tau}}(t) = +G_0 \underline{\underline{C}}^{-1}(t,0)$$

$$\underline{\underline{\tau}}(t) = G_0 \begin{pmatrix} 1 + \dot{\gamma}_0^2 t^2 & -\dot{\gamma}_0 t & 0 \\ -\dot{\gamma}_0 t & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}_{123}$$

(recall sign convention on stress)

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EXAMPLE: Calculate stress predicted in <u>shear</u> by a finite-strain Hooke's law. Compare with experimental results.

NOTE: *for the first time we have predicted **nonzero normal stresses** in shear.*

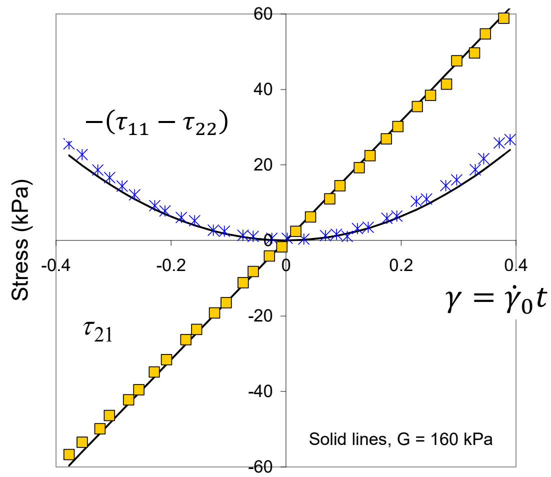

Figure 9.6, p. 325 DeGroot; solid rubber

tensor	shear in 1-direction with gradient in 2-direction	uniaxial elongation in 3-direction	ccw rotation around $\hat{e}_3$
$\underline{\underline{F}}(t,t')$	$\begin{pmatrix} 1 & 0 & 0 \\ -\gamma & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}_{123}$	$\begin{pmatrix} e^{\frac{\epsilon}{2}} & 0 & 0 \\ 0 & e^{\frac{\epsilon}{2}} & 0 \\ 0 & 0 & e^{-\epsilon} \end{pmatrix}_{123}$	$\begin{pmatrix} \cos\psi & -\sin\psi & 0 \\ \sin\psi & \cos\psi & 0 \\ 0 & 0 & 1 \end{pmatrix}_{123}$
$\underline{\underline{F}}^{-1}(t',t)$	$\begin{pmatrix} 1 & 0 & 0 \\ \gamma & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}_{123}$	$\begin{pmatrix} e^{-\frac{\epsilon}{2}} & 0 & 0 \\ 0 & e^{-\frac{\epsilon}{2}} & 0 \\ 0 & 0 & e^{\epsilon} \end{pmatrix}_{123}$	$\begin{pmatrix} \cos\psi & \sin\psi & 0 \\ -\sin\psi & \cos\psi & 0 \\ 0 & 0 & 1 \end{pmatrix}_{123}$
$\underline{\underline{C}}(t,t')$	$\begin{pmatrix} 1 & -\gamma & 0 \\ -\gamma & 1+\gamma^2 & 0 \\ 0 & 0 & 1 \end{pmatrix}_{123}$	$\begin{pmatrix} e^{\epsilon} & 0 & 0 \\ 0 & e^{\epsilon} & 0 \\ 0 & 0 & e^{-2\epsilon} \end{pmatrix}_{123}$	$\underline{\underline{I}}$
$\underline{\underline{C}}^{-1}(t',t)$	$\begin{pmatrix} 1+\gamma^2 & \gamma & 0 \\ \gamma & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}_{123}$	$\begin{pmatrix} e^{-\epsilon} & 0 & 0 \\ 0 & e^{-\epsilon} & 0 \\ 0 & 0 & e^{2\epsilon} \end{pmatrix}_{123}$	$\underline{\underline{I}}$
$\underline{\underline{\gamma}}^{[0]}(t,t')$	$\begin{pmatrix} 0 & -\gamma & 0 \\ -\gamma & \gamma^2 & 0 \\ 0 & 0 & 1 \end{pmatrix}_{123}$	$\begin{pmatrix} e^{\epsilon}-1 & 0 & 0 \\ 0 & e^{\epsilon}-1 & 0 \\ 0 & 0 & e^{-2\epsilon}-1 \end{pmatrix}_{123}$	$\underline{\underline{0}}$
$\underline{\underline{\gamma}}_{[0]}(t,t')$	$\begin{pmatrix} -\gamma^2 & \gamma & 0 \\ \gamma & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}_{123}$	$\begin{pmatrix} e^{-\epsilon}-1 & 0 & 0 \\ 0 & e^{-\epsilon}-1 & 0 \\ 0 & 0 & e^{2\epsilon}-1 \end{pmatrix}_{123}$	$\underline{\underline{0}}$

Table 9.3 has strain tensors for standard flows

(Note there is a typo in the definition of ψ in the caption of Table 9.3; there is says from $\underline{r}$ to $\underline{r}'$, which is backwards.)

$$\gamma = \gamma(t',t) = \int_{t'}^{t} \dot{\varsigma}(t'')dt''$$

$$\epsilon = \epsilon(t',t) = \int_{t'}^{t} \dot{\epsilon}(t'')dt''$$

ψ is the angle from $\underline{r}'$ to $\underline{r}$ in ccw rotation around $\hat{e}_z$

This is correct

Now, let's fix the Maxwell model.

Integral GLVE model (rate version):

$$\underline{\underline{\tau}}(t) = -\int_{-\infty}^{t} G(t-t')\dot{\underline{\underline{\gamma}}}(\boldsymbol{t'})dt'$$

Integral GLVE model (strain version):

$$\underline{\underline{\tau}} = +\int_{-\infty}^{t} M(t-t')\underline{\underline{\gamma}}(\boldsymbol{t'},\boldsymbol{t})dt'$$

$$M(t-t') \equiv \frac{\partial G(t-t')}{\partial t'}$$

Integral Maxwell model (strain version):

$$\underline{\underline{\tau}} = +\int_{-\infty}^{t} \underbrace{\left[\frac{\eta_0}{\lambda^2}e^{-\frac{(t-t')}{\lambda}}\right]}_{M(t-t')}\underline{\underline{\gamma}}(t',t)dt'$$

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Lodge model

Integral Maxwell model (**strain** version):

$$\underline{\underline{\tau}} = +\int_{-\infty}^{t} \left[\frac{\eta_0}{\lambda^2}e^{-\frac{(t-t')}{\lambda}}\right]\underline{\underline{\gamma}}(t',t)dt'$$

substitute (-Finger tensor) for infinitesimal strain tensor $-\underline{\underline{C}}^{-1}(t',t)$

Lodge Model:

$$\underline{\underline{\tau}}(t) = -\int_{-\infty}^{t} \left[\frac{\eta_0}{\lambda^2}e^{-\frac{(t-t')}{\lambda}}\right]\underline{\underline{C}}^{-1}(t',t)dt'$$

What does it predict?

A finite-strain, viscoelastic constitutive equation

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EXAMPLE: Calculate the material functions of steady shear flow for the Lodge model.

Lodge Model: $\underline{\underline{\tau}}(t) = -\int_{-\infty}^{t} \left[\frac{\eta_0}{\lambda^2} e^{-\frac{(t-t')}{\lambda}} \right] \underline{\underline{C}}^{-1}(t',t)dt'$

EXAMPLE: Calculate the material functions of steady shear flow for the Lodge model.

Lodge Model: $\underline{\underline{\tau}}(t) = -\int_{-\infty}^{t} \left[\frac{\eta_0}{\lambda^2} e^{-\frac{(t-t')}{\lambda}} \right] \underline{\underline{C}}^{-1}(t',t)dt'$

You try.

Steady Shear Flow Material Functions

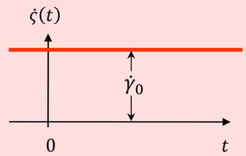
Michigan Tech

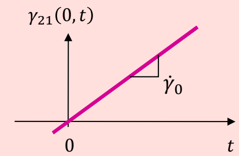
Strain-centered "recipe card"

Imposed Kinematics:

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

$$\dot{\varsigma}(t) = \dot{\gamma}_0 = \text{constant}$$





$$\underline{r}' = \begin{pmatrix} x' \\ y' \\ z' \end{pmatrix}_{123} \qquad \underline{r} = \begin{pmatrix} x \\ y \\ z \end{pmatrix}_{123} = \begin{pmatrix} x' + \dot{\gamma}_0 (t - t') \\ y' \\ z' \end{pmatrix}_{123}$$

$$\underline{\underline{F}}^{-1}(t',t) = \begin{pmatrix} 1 & 0 & 0 \\ \gamma & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}_{123} \qquad \underline{\underline{C}}^{-1}(t',t) = \begin{pmatrix} 1+\gamma^2 & \gamma & 0 \\ \gamma & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}_{123} \qquad \gamma = \dot{\gamma}_0 (t - t')$$

Material Functions:

Viscosity $$\eta(\dot{\gamma}_0) \equiv \frac{\tilde{\tau}_{21}}{\dot{\gamma}_0} = \frac{-\tau_{21}}{\dot{\gamma}_0}$$

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

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

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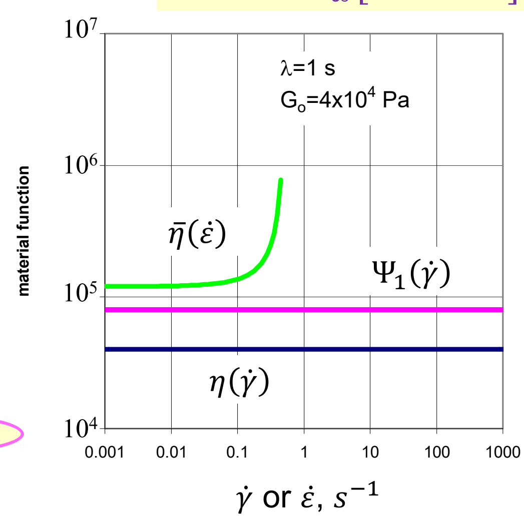
Advanced Constitutive Modeling – Chapter 9

Lodge model

$$\underline{\underline{\tau}}(t) = -\int_{-\infty}^{t} \left[\frac{\eta_0}{\lambda^2} e^{-\frac{(t-t')}{\lambda}} \right] \underline{\underline{C}}^{-1}(t',t)\, dt'$$



Lodge Model Report card:

- η does not shear thin
- Ψ_1 is not zero!
- $\Psi_2 = 0$

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Start-up of Steady Shear Flow Material Functions

Michigan Tech

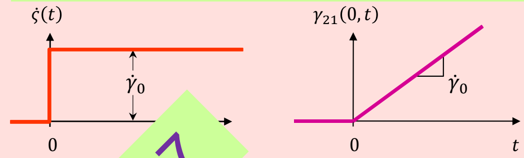
Needs to become a Strain-centric "recipe card"

Homework 7

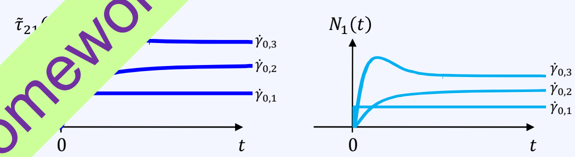
Imposed Kinematics:

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

$$\dot{\varsigma}(t) = \begin{cases} 0 & t < 0 \\ \dot{\gamma}_0 & t \geq 0 \end{cases}$$



Material Stress Response:



Material Functions:

Shear stress growth function
$$\eta^+(t,\dot{\gamma}_0) \equiv \frac{\tilde{\tau}_{21}(t)}{\dot{\gamma}_0} = \frac{-\tau_{21}(t)}{\dot{\gamma}_0}$$

First normal-stress growth coefficient
$$\Psi_1^+(t,\dot{\gamma}_0) \equiv \frac{\tilde{\tau}_{11} - \tilde{\tau}_{22}}{\dot{\gamma}_0^2}$$

Second normal-stress growth coefficient
$$\Psi_2^+(t,\dot{\gamma}_0) \equiv \frac{\tilde{\tau}_{22} - \tilde{\tau}_{33}}{\dot{\gamma}_0^2}$$

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Cessation of Steady Shear Flow Material Functions

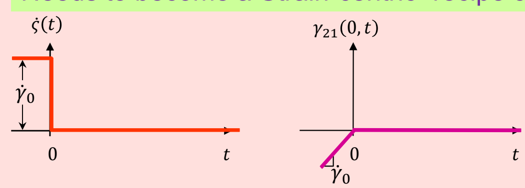
Michigan Tech

Needs to become a Strain-centric "recipe card"

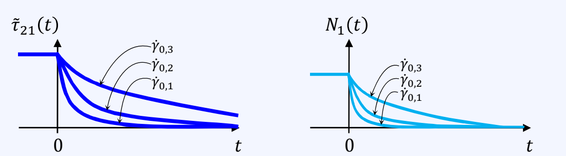
Imposed Kinematics:

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

$$\dot{\varsigma}(t) = \begin{cases} \dot{\gamma}_0 & t < 0 \\ 0 & t \geq 0 \end{cases}$$



Material Stress Response:



Material Functions:

Shear stress decay function
$$\eta^-(t,\dot{\gamma}_0) \equiv \frac{\tilde{\tau}_{21}(t)}{\dot{\gamma}_0} = \frac{-\tau_{21}(t)}{\dot{\gamma}_0}$$

First normal-stress decay coefficient
$$\Psi_1^-(t,\dot{\gamma}_0) \equiv \frac{\tilde{\tau}_{11} - \tilde{\tau}_{22}}{\dot{\gamma}_0^2}$$

Second normal-stress decay coefficient
$$\Psi_2^-(t,\dot{\gamma}_0) \equiv \frac{\tilde{\tau}_{22} - \tilde{\tau}_{33}}{\dot{\gamma}_0^2}$$

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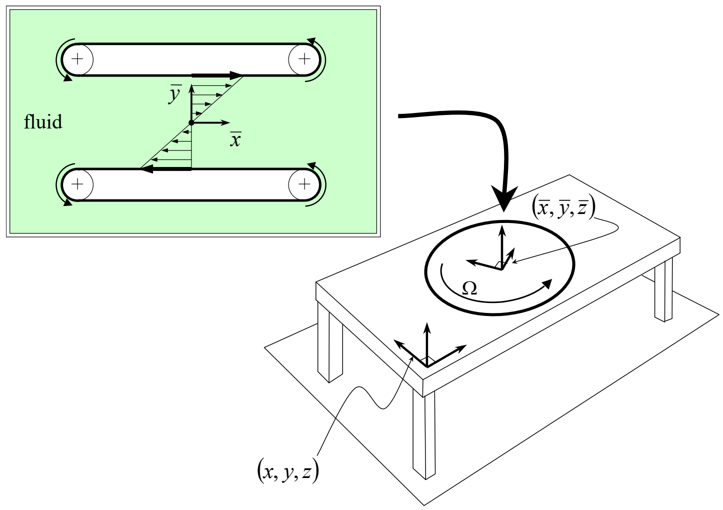
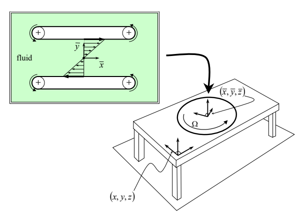
EXAMPLE: Does the Lodge model pass the test of objectivity posed by the turntable example? (remember, the GLVE failed this test)



Turntable Example: Lodge Model



$$\underline{\underline{\tau}}(t) = -\int_{-\infty}^{t} \left[\frac{\eta_0}{\lambda^2} e^{-\frac{(t-t')}{\lambda}} \right] \underline{\underline{C}}^{-1}(t', t)\, dt'$$

$$\underline{\underline{F}}^{-1}(t', t) \equiv \frac{\partial \underline{r}}{\partial \underline{r}'} = \frac{\partial r_m}{\partial r_j'} \hat{e}_j \hat{e}_m = \begin{pmatrix} \frac{\partial x}{\partial x'} & \frac{\partial y}{\partial x'} & \frac{\partial z}{\partial x'} \\ \frac{\partial x}{\partial y'} & \frac{\partial y}{\partial y'} & \frac{\partial z}{\partial y'} \\ \frac{\partial x}{\partial z'} & \frac{\partial y}{\partial z'} & \frac{\partial z}{\partial z'} \end{pmatrix}_{xyz}$$

$$\underline{r} = \begin{pmatrix} \bar{x} \\ \bar{y} \\ \bar{z} \end{pmatrix}_{xyz} = \begin{pmatrix} \bar{x}' + \dot{\gamma}_0 (t - t') \bar{y}' \\ \bar{y}' \\ \bar{z}' \end{pmatrix}_{xyz}$$

Deformation in shear flow (strain)

$$\underline{r}(t_{ref}) = \begin{pmatrix} x_1(t_{ref}) \\ x_2(t_{ref}) \\ x_3(t_{ref}) \end{pmatrix}_{123} \qquad \gamma_{21}(t_{ref},t) \equiv \frac{\partial u_1}{\partial x_2}$$ **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**

Turntable Example

Lodge Model: $\underline{\underline{\tau}}(t) = -\int_{-\infty}^{t} \left[\frac{\eta_0}{\lambda^2} e^{-\frac{(t-t')}{\lambda}}\right] \underline{\underline{C}}^{-1}(t',t)\,dt'$

$$\underline{\underline{C}}^{-1} = \begin{pmatrix} 1+\gamma^2 & \gamma & 0 \\ \gamma & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}_{\overline{xyz}}$$

Lodge prediction: rotating frame

$$\boxed{\underline{\underline{\tau}} = -\int_{-\infty}^{t} \frac{\eta_0}{\lambda^2} e^{-\frac{(t-t')}{\lambda}} \begin{pmatrix} 1+\gamma^2 & \gamma & 0 \\ \gamma & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}_{\overline{xyz}} dt'}$$

Lodge turntable - from stationary frame

$$\underline{r} = \begin{pmatrix} x \\ y \\ z \end{pmatrix}_{xyz} = \begin{pmatrix} x_0 + (y' - y_0)\left[-SC' + CS' + CC'\gamma\right] + (x' - x_0)\left[SS' + CC' - CS'\gamma\right] \\ y_0 + (y' - y_0)\left[C'C + S'S + SC'\gamma\right] + (x' - x_0)\left[-CS' + SC' - SS'\gamma\right] \\ z' \end{pmatrix}_{xyz}$$

Now, calculate $\underline{\underline{F}}^{-1}$ and $\underline{\underline{C}}^{-1}$.

$$S = \sin \Omega t$$
$$S' = \sin \Omega t'$$
$$C = \cos \Omega t$$
$$C' = \cos \Omega t'$$
$$\gamma = \dot{\gamma}_0 (t - t')$$

$$\underline{\underline{F}}^{-1}(t',t) \equiv \frac{\partial \underline{r}}{\partial \underline{r}'} = \frac{\partial r_m}{\partial r_j'} \hat{e}_j \hat{e}_m = \begin{pmatrix} \frac{\partial x}{\partial x'} & \frac{\partial y}{\partial x'} & \frac{\partial z}{\partial x'} \\ \frac{\partial x}{\partial y'} & \frac{\partial y}{\partial y'} & \frac{\partial z}{\partial y'} \\ \frac{\partial x}{\partial z'} & \frac{\partial y}{\partial z'} & \frac{\partial z}{\partial z'} \end{pmatrix}_{xyz}$$

$$\underline{\underline{C}}^{-1} \equiv \left(\underline{\underline{F}}^{-1}\right)^T \cdot \underline{\underline{F}}^{-1}$$

http://pages.mtu.edu/~fmorriso/cm4650/Lodge_turntable.pdf

Result:

$$\underline{\underline{C}}^{-1}(t',t) = \begin{pmatrix} 1 - 2CS\gamma + C^2\gamma^2 & (C^2 - S^2)\gamma + SC\gamma^2 & 0 \\ (C^2 - S^2)\gamma + SC\gamma^2 & 1 + 2CS\gamma + S^2\gamma^2 & 0 \\ 0 & 0 & 1 \end{pmatrix}_{xyz}$$

Lodge Model prediction in stationary frame:

$$\underline{\underline{\tau}} = -\int_{-\infty}^{t} \frac{\eta_0}{\lambda^2} e^{-\frac{(t-t')}{\lambda}} \begin{pmatrix} 1 - 2CS\gamma + C^2\gamma^2 & (C^2 - S^2)\gamma + SC\gamma^2 & 0 \\ (C^2 - S^2)\gamma + SC\gamma^2 & 1 + 2CS\gamma + S^2\gamma^2 & 0 \\ 0 & 0 & 1 \end{pmatrix}_{xyz} dt'$$

$$S = \sin \Omega t \qquad C = \cos \Omega t$$
$$S' = \sin \Omega t' \qquad C' = \cos \Omega t'$$
$$\gamma = \dot{\gamma}_0 (t - t')$$

To compare to previous result, must consider shear coordinate system, e.g. $t = 0$

Lodge prediction: stationary frame, t=0

$$\underline{\underline{\tau}} = -\int_{-\infty}^{t} \frac{\eta_0}{\lambda^2} e^{-\frac{(t-t')}{\lambda}} \begin{pmatrix} 1+\gamma^2 & \gamma & 0 \\ \gamma & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}_{\underline{xyz}} dt'$$

IDENTICAL

Lodge prediction: rotating frame

$$\underline{\underline{\tau}} = -\int_{-\infty}^{t} \frac{\eta_0}{\lambda^2} e^{-\frac{(t-t')}{\lambda}} \begin{pmatrix} 1+\gamma^2 & \gamma & 0 \\ \gamma & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}_{\underline{xyz}} dt'$$

Lodge Model (Maxwell with Finger strain tensor) passes test of objectivity! ✓

What is the differential form of the Lodge model?

Lodge Model: $$\underline{\underline{\tau}}(t) = -\int_{-\infty}^{t} \left[\frac{\eta_0}{\lambda^2} e^{-\frac{(t-t')}{\lambda}}\right] \underline{\underline{C}}^{-1}(t',t)dt'$$

$$\frac{d\underline{\underline{\tau}}(t)}{dt} = ?$$

$$\frac{d\underline{\underline{C}}^{-1}}{dt} = ?$$

(see discussion in text…)

Differential Lodge Equation
(Upper-Convected Maxwell Model)

$$\underline{\underline{\tau}} + \lambda\left[\frac{\partial \underline{\underline{\tau}}}{\partial t} + \underline{v}\cdot\nabla\underline{\underline{\tau}} - (\nabla\underline{v})^T\cdot\underline{\underline{\tau}} - \underline{\underline{\tau}}\cdot\nabla\underline{v}\right] = -\eta_0\dot{\underline{\underline{\gamma}}}$$

$$\boxed{\underline{\underline{\tau}} + \lambda\overset{\triangledown}{\underline{\underline{\tau}}} = -\eta_0\dot{\underline{\underline{\gamma}}}}$$

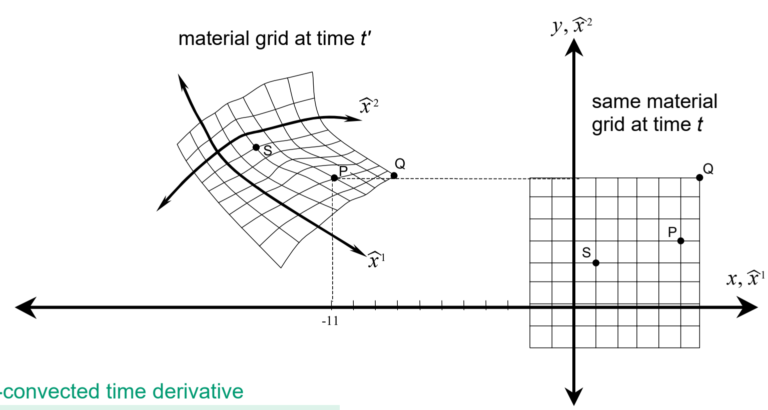
Upper-Convected Maxwell Model

$$\overset{\triangledown}{\underline{\underline{\tau}}} \equiv \frac{D\underline{\underline{\tau}}}{Dt} - (\nabla\underline{v})^T\cdot\underline{\underline{\tau}} - \underline{\underline{\tau}}\cdot\nabla\underline{v}$$

Looks like the Maxwell model, but with a new type of time derivative. We call it the upper-convected time derivative.

$$\frac{D\underline{\underline{\tau}}}{Dt} \equiv \left[\frac{\partial \underline{\underline{\tau}}}{\partial t} + \underline{v}\cdot\nabla\underline{\underline{\tau}}\right]$$

The *Upper-Convected time derivative* can be understood to be the time derivative calculated in a coordinate system that is translating and deforming with the fluid (see section 9.3).



upper-convected time derivative

$$\overset{\triangledown}{\underline{\underline{\tau}}} \equiv \frac{D\underline{\underline{\tau}}}{Dt} - (\nabla\underline{v})^T\cdot\underline{\underline{\tau}} - \underline{\underline{\tau}}\cdot\nabla\underline{v}$$

Other Convected Derivatives

Upper-convected time derivative

$$\overset{\triangledown}{\underline{\underline{\tau}}} \equiv \frac{D\underline{\underline{\tau}}}{Dt} - (\nabla\underline{v})^T \cdot \underline{\underline{\tau}} - \underline{\underline{\tau}} \cdot \nabla\underline{v}$$

Lower-convected time derivative

$$\overset{\vartriangle}{\underline{\underline{\tau}}} \equiv \frac{D\underline{\underline{\tau}}}{Dt} + \nabla\underline{v} \cdot \underline{\underline{\tau}} + \underline{\underline{\tau}} \cdot (\nabla\underline{v})^T$$

Corotational time derivative

$$\overset{\circ}{\underline{\underline{\tau}}} \equiv \frac{D\underline{\underline{\tau}}}{Dt} + \frac{1}{2}\left(\underline{\underline{\omega}} \cdot \underline{\underline{\tau}} + \underline{\underline{\tau}} \cdot \underline{\underline{\omega}}\right)$$

$$\underline{\underline{\omega}} \equiv \nabla\underline{v} - (\nabla\underline{v})^T$$

The vorticity vector

Lodge Model:
(upper-convected Maxwell)

$$\underline{\underline{\tau}}(t) = -\int_{-\infty}^{t} \left[\frac{\eta_0}{\lambda^2} e^{-\frac{(t-t')}{\lambda}}\right] \underline{\underline{C}}^{-1}(t',t)dt'$$

Cauchy-Maxwell Model:
(lower-convected Maxwell)

$$\underline{\underline{\tau}}(t) = +\int_{-\infty}^{t} \left[\frac{\eta_0}{\lambda^2} e^{-\frac{(t-t')}{\lambda}}\right] \underline{\underline{C}}(t,t')dt'$$

Lodge Rubberlike Liquid Model:

$$\underline{\underline{\tau}}(t) = -\int_{-\infty}^{t} M(t-t')\underline{\underline{C}}^{-1}(t',t)dt'$$

Lodge Model:
(upper-convected Maxwell)

$$\underline{\underline{\tau}}(t) = -\int_{-\infty}^{t} \left[\frac{\eta_0}{\lambda^2} e^{-\frac{(t-t')}{\lambda}}\right] \underline{\underline{C}}^{-1}(t',t)dt'$$

(fix Maxwell with the Finger tensor)

Cauchy-Maxwell Model:
(lower-convected Maxwell)

$$\underline{\underline{\tau}}(t) = +\int_{-\infty}^{t} \left[\frac{\eta_0}{\lambda^2} e^{-\frac{(t-t')}{\lambda}}\right] \underline{\underline{C}}(t,t')dt'$$

(fix Maxwell with the Cauchy tensor)

Lodge Rubberlike Liquid Model:

$$\underline{\underline{\tau}}(t) = -\int_{-\infty}^{t} M(t-t')\underline{\underline{C}}^{-1}(t',t)dt'$$

(fix GLVE with the Finger tensor)

Advanced Constitutive Modeling – Chapter 9

Lodge Model:
(upper-convected Maxwell)

$$\underline{\underline{\tau}}(t) = -\int_{-\infty}^{t} \left[\frac{\eta_0}{\lambda^2} e^{-\frac{(t-t')}{\lambda}}\right] \underline{\underline{C}}^{-1}(t',t)dt'$$

(fix Maxwell with the Finger tensor)

Time to take them out for a spin!

(fix GLVE with the Finger tensor)

Advanced Constitutive Modeling – Appendix D

Lodge Equation (UCM)

TABLE D.2
Predictions of Lodge Equation or Upper Convected Maxwell Model in Shear and Extensional Flows

1. *Shear*		
Startup	$\eta^+(t,\dot\gamma)$	$\eta_0\left(1-e^{-\frac{t}{\lambda}}\right)$
	$\Psi_1^+(t,\dot\gamma)$	$2\eta_0\lambda\left[1-e^{\frac{-t}{\lambda}}\left(1+\frac{t}{\lambda}\right)\right]$
	$\Psi_2^+(t,\dot\gamma)$	0
Steady	$\eta(\dot\gamma)$	$\eta_0 \equiv G_0\lambda$
	$\Psi_1(\dot\gamma)$	$2G_0\lambda^2 = 2\eta_0\lambda$
	$\Psi_2(\dot\gamma)$	0
Cessation	$\eta^-(t,\dot\gamma)$	$\eta_0 e^{\frac{-t}{\lambda}}$
	$\Psi_1^-(t,\dot\gamma)$	$2\lambda\eta_0 e^{\frac{-t}{\lambda}}$
	$\Psi_2^-(t,\dot\gamma)$	0
Step shear strain	$G(t,\gamma_0)$	$G_0 e^{-\frac{t}{\lambda}}$
	$G_{\Psi_1}(t,\gamma_0)$	$G_0 e^{-\frac{t}{\lambda}}$
	$G_{\Psi_2}(t,\gamma_0)$	0
2. *Extension*		
Startup Uniaxial ($b=0, \dot\epsilon_0>0$) or biaxial ($b=0, \dot\epsilon_0<0$)	$\bar\eta^+(t,\dot\epsilon_0)$ or $\bar\eta_B^+(t,\dot\epsilon_0)$	$\frac{\eta_0}{\mathcal{AB}}\left(3-2\mathcal{B}e^{-\frac{t\mathcal{A}}{\lambda}}-\mathcal{A}e^{-\frac{t\mathcal{B}}{\lambda}}\right)$ $\mathcal{A}=1-2\dot\epsilon_0\lambda$ $\mathcal{B}=1+\dot\epsilon_0\lambda$
Planar ($b=1, \dot\epsilon_0>0$)	$\bar\eta_{P_1}^+(t,\dot\epsilon_0)$	$\frac{2\eta_0}{\mathcal{AC}}\left(2-\mathcal{A}e^{-\frac{\mathcal{C}t}{\lambda}}-\mathcal{C}e^{-\frac{\mathcal{A}t}{\lambda}}\right)$ $\mathcal{A}=1-2\dot\epsilon_0\lambda$ $\mathcal{C}=1+2\dot\epsilon_0\lambda$
	$\bar\eta_{P_2}^+(t,\dot\epsilon_0)$	$\frac{2\eta_0}{\mathcal{C}}\left(1-e^{-\frac{\mathcal{C}t}{\lambda}}\right)$
Steady Uniaxial ($b=0, \dot\epsilon_0>0$) or biaxial ($b=0, \dot\epsilon_0<0$)	$\bar\eta(\dot\epsilon_0)$ or $\bar\eta_B(\dot\epsilon_0)$	$\frac{3\eta_0}{(1-2\lambda\dot\epsilon_0)(1+\lambda\dot\epsilon_0)}=\frac{3\eta_0}{\mathcal{AB}}$
Planar ($b=1, \dot\epsilon_0>0$)	$\bar\eta_{P_1}(\dot\epsilon_0)$	$\frac{4\eta_0}{1-4\dot\epsilon_0^2\lambda^2}=\frac{4\eta_0}{\mathcal{AC}}$
	$\bar\eta_{P_2}(\dot\epsilon_0)$	$\frac{2\eta_0}{1+2\dot\epsilon_0\lambda}=\frac{2\eta_0}{\mathcal{C}}$

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Advanced Constitutive Modeling – Appendix D

Cauchy-Maxwell Equation (LCM)

TABLE D.3
Predictions of Cauchy–Maxwell Equation or Lower Convected Maxwell Model in Shear and Extensional Flows

1. *Shear*		
Startup	$\eta^+(t,\dot\gamma)$	$\eta_0\left(1-e^{-\frac{t}{\lambda}}\right)$
	$\Psi_1^+(t,\dot\gamma)$	$2\eta_0\lambda\left[1-e^{\frac{t}{\lambda}}\left(1+\frac{t}{\lambda}\right)\right]$
	$\Psi_2^+(t,\dot\gamma)$	$-\Psi_1^+$
Steady	$\eta(\dot\gamma)$	$\eta_0 \equiv G_0\lambda$
	$\Psi_1(\dot\gamma)$	$2G_0\lambda^2 = 2\eta_0\lambda$
	$\Psi_2(\dot\gamma)$	$-\Psi_1$
Cessation	$\eta^-(t,\dot\gamma)$	$\eta_0 e^{\frac{-t}{\lambda}}$
	$\Psi_1^-(t,\dot\gamma)$	$2\lambda\eta_0 e^{\frac{-t}{\lambda}}$
	$\Psi_2^-(t,\dot\gamma)$	$-\Psi_1^-$
Step shear strain	$G(t,\gamma_0)$	$G_0 e^{-\frac{t}{\lambda}}$
	$G_{\Psi_1}(t,\gamma_0)$	$G_0 e^{-\frac{t}{\lambda}}$
	$G_{\Psi_2}(t,\gamma_0)$	$-G_{\Psi_1}$
2. *Extension*		
Startup Uniaxial ($b=0, \dot\epsilon_0>0$) or biaxial ($b=0, \dot\epsilon_0<0$)	$\bar\eta^+(t,\dot\epsilon_0)$ or $\bar\eta_B^+(t,\dot\epsilon_0)$	$\frac{\eta_0}{\mathcal{CD}}\left(3-2\mathcal{D}e^{-\frac{t\mathcal{C}}{\lambda}}-\mathcal{C}e^{-\frac{t\mathcal{D}}{\lambda}}\right)$ $\mathcal{C}=1+2\dot\epsilon_0\lambda$ $\mathcal{D}=1-\dot\epsilon_0\lambda$
Planar ($b=1, \dot\epsilon_0>0$)	$\bar\eta_{P_1}^+(t,\dot\epsilon_0)$	$\frac{-2\eta_0}{\mathcal{AC}}\left(2-\mathcal{A}e^{-\frac{\mathcal{C}t}{\lambda}}-\mathcal{C}e^{-\frac{\mathcal{A}t}{\lambda}}\right)$ $\mathcal{A}=1-2\dot\epsilon_0\lambda$
	$\bar\eta_{P_2}^+(t,\dot\epsilon_0)$	$\frac{-2\eta_0}{\mathcal{A}}\left(1-e^{-\frac{\mathcal{A}t}{\lambda}}\right)$
Steady Uniaxial ($b=0, \dot\epsilon_0>0$) or biaxial ($b=0, \dot\epsilon_0<0$)	$\bar\eta(\dot\epsilon_0)$ or $\bar\eta_B(\dot\epsilon_0)$	$\frac{3\eta_0}{(1+2\lambda\dot\epsilon_0)(1-\lambda\dot\epsilon_0)}=\frac{3\eta_0}{\mathcal{CD}}$
Planar ($b=1, \dot\epsilon_0>0$)	$\bar\eta_{P_1}(\dot\epsilon_0)$	$\frac{-4\eta_0}{1-4\dot\epsilon_0^2\lambda^2}=\frac{-4\eta_0}{\mathcal{AC}}$
	$\bar\eta_{P_2}(\dot\epsilon_0)$	$\frac{-2\eta_0}{1-2\dot\epsilon_0\lambda}=\frac{-2\eta_0}{\mathcal{A}}$

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SUMMARY:
Approaches to finite-strain constitutive equations

Non-objective time derivative

replace with $\overset{\nabla}{\underline{\underline{\tau}}}, \overset{\triangle}{\underline{\underline{\tau}}}$, or other, objective, time derivatives

equivalent

differential Maxwell model

$$\underline{\underline{\tau}}(t) + \lambda \frac{\partial \underline{\underline{\tau}}}{\partial t} = -\eta_0 \dot{\underline{\underline{\gamma}}}$$

integral Maxwell model

$$\underline{\underline{\tau}}(t) = \int_{-\infty}^{t} \left[\frac{\eta_0}{\lambda^2} e^{-\frac{(t-t')}{\lambda}} \right] \underline{\underline{\gamma}}(t,t')\, dt'$$

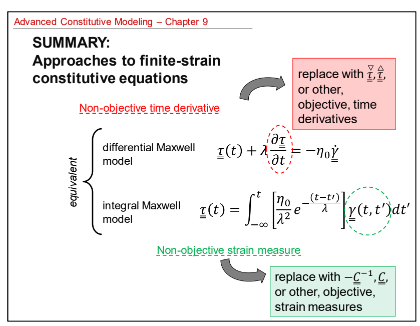
Non-objective strain measure

replace with $-\underline{\underline{C}}^{-1}, \underline{\underline{C}}$, or other, objective, strain measures

Methods of Improving Constitutive Equations

We have seen **two techniques** to generate finite-strain constitutive equations from the *Maxwell equation*.

- *Fix the time derivative*
- *Fix the strain measure*



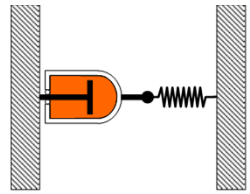
We can also change the form of the basic equation.

- *linear modifications*
- *non-linear modifications*

We can also change the form of the basic equation.

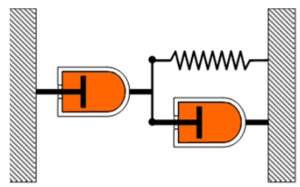
Maxwell Model - Mechanical Analog

$$\tau_{21}(t) + \lambda \frac{\partial \tau_{21}}{\partial t} = -\eta_0 \dot{\gamma}_{21}$$



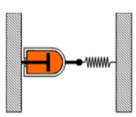
Jeffreys Model - Mechanical Analog

$$\tau_{21}(t) + \lambda_1 \frac{\partial \tau_{21}}{\partial t} = -\eta_0 \left(\dot{\gamma}_{21} + \lambda_2 \frac{\partial \dot{\gamma}_{21}}{\partial t} \right)$$



Other Constitutive Approaches

We can also change the form of the basic equation.

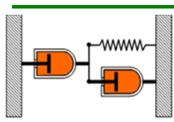


Simple **Maxwell** Model, shear flow only

$$\tau_{21}(t) + \lambda \frac{\partial \tau_{21}}{\partial t} = -\eta_0 \dot{\gamma}_{21}$$

Upper-Convected **Maxwell** Model, general flow

$$\underline{\underline{\tau}}(t) + \lambda \overset{\nabla}{\underline{\underline{\tau}}} = -\eta_0 \dot{\underline{\underline{\gamma}}}$$



Simple **Jeffreys** Model, shear flow only

retardation time

$$\tau_{21}(t) + \lambda_1 \frac{\partial \tau_{21}}{\partial t} = -\eta_0 \left(\dot{\gamma}_{21} + \lambda_2 \frac{\partial \dot{\gamma}_{21}}{\partial t} \right)$$

Upper-Convected **Jeffreys** Model, general flow (Oldroyd B Fluid)

$$\underline{\underline{\tau}}(t) + \lambda_1 \overset{\nabla}{\underline{\underline{\tau}}} = -\eta_0 \left(\dot{\underline{\underline{\gamma}}} + \lambda_2 \overset{\nabla}{\dot{\underline{\underline{\gamma}}}} \right)$$

We can also change the form of the basic equation.

Non-linear modifications of the Maxwell Model

White-Metzner Model
(brute force shear thinning)

$$\underline{\underline{\tau}}(t) + \frac{\eta(\dot{\gamma})}{G_0}\overset{\triangledown}{\underline{\underline{\tau}}} = -\eta(\dot{\gamma})\underline{\underline{\dot{\gamma}}}$$

Oldroyd 8-Constant Model: comprehensive continuum mechanics

$$\underline{\underline{\tau}}(t) + \lambda_1\overset{\triangledown}{\underline{\underline{\tau}}} + \frac{1}{2}(\lambda_1 - \mu_1)\left(\underline{\underline{\dot{\gamma}}}\cdot\underline{\underline{\tau}} + \underline{\underline{\tau}}\cdot\underline{\underline{\dot{\gamma}}}\right) + \frac{1}{2}\mu_0(tr\ \underline{\underline{\tau}})\underline{\underline{\dot{\gamma}}} + \frac{1}{2}\nu_1\left(\underline{\underline{\tau}}:\underline{\underline{\dot{\gamma}}}\right)\underline{\underline{I}}$$
$$= -\eta_0\left(\underline{\underline{\dot{\gamma}}} + \lambda_2\overset{\triangledown}{\underline{\underline{\dot{\gamma}}}} + (\lambda_2 - \mu_2)\left(\underline{\underline{\dot{\gamma}}}\cdot\underline{\underline{\dot{\gamma}}}\right) + \frac{1}{2}\nu_2\left(\underline{\underline{\dot{\gamma}}}:\underline{\underline{\dot{\gamma}}}\right)\underline{\underline{I}}\right)$$

The Oldroyd 8-constant contains many other constitutive equations as special cases.

UCM

UCM + terms = UCJ

We can also change the form of the basic equation.

The Oldroyd 8-Constant model contains all terms *linear* in stress tensor and at most *quadratic* in rate-of-deformation tensor that are also consistent with frame invariance.

$$\underline{\underline{\tau}}(t) + \lambda_1\overset{\triangledown}{\underline{\underline{\tau}}} + \frac{1}{2}(\lambda_1 - \mu_1)\left(\underline{\underline{\dot{\gamma}}}\cdot\underline{\underline{\tau}} + \underline{\underline{\tau}}\cdot\underline{\underline{\dot{\gamma}}}\right) + \frac{1}{2}\mu_0(tr\ \underline{\underline{\tau}})\underline{\underline{\dot{\gamma}}} + \frac{1}{2}\nu_1\left(\underline{\underline{\tau}}:\underline{\underline{\dot{\gamma}}}\right)\underline{\underline{I}}$$
$$= -\eta_0\left(\underline{\underline{\dot{\gamma}}} + \lambda_2\overset{\triangledown}{\underline{\underline{\dot{\gamma}}}} + (\lambda_2 - \mu_2)\left(\underline{\underline{\dot{\gamma}}}\cdot\underline{\underline{\dot{\gamma}}}\right) + \frac{1}{2}\nu_2\left(\underline{\underline{\dot{\gamma}}}:\underline{\underline{\dot{\gamma}}}\right)\underline{\underline{I}}\right)$$

Giesekus Model

$$\underline{\underline{\tau}}(t) + \lambda\overset{\triangledown}{\underline{\underline{\tau}}} + \underbrace{\frac{\alpha\lambda}{\eta_0}}_{\text{quadratic in stress}}\underline{\underline{\tau}}:\underline{\underline{\tau}} = -\eta_0\underline{\underline{\dot{\gamma}}}$$

The only way to choose among these nonlinear models is to compare predictions.

Advanced Constitutive Modeling – Appendix D

We can also change the form of the basic equation.

White-Metzner

TABLE D.5
Predictions of White–Metzner Equation in Shear and Extensional Flows [26]*

1. *Shear*			
	Startup	$\eta^+(t,\dot\gamma)$	$\eta(\dot\gamma)\left(1-e^{-\frac{t}{\lambda(\dot\gamma)}}\right)$
		$\Psi_1^+(t,\dot\gamma)$	$2\eta(\dot\gamma)\lambda(\dot\gamma)\left[1-e^{-\frac{t}{\lambda(\dot\gamma)}}\left(1+\frac{t}{\lambda(\dot\gamma)}\right)\right]$
		$\Psi_2^+(t,\dot\gamma)$	0
	Steady	$\eta(\dot\gamma)$	$\eta(\dot\gamma)$
		$\Psi_1(\dot\gamma)$	$2\eta(\dot\gamma)\lambda(\dot\gamma)$
		$\Psi_2(\dot\gamma)$	0
2. *Extension*			
	Steady		
	Uniaxial ($b=0$, $\dot\epsilon_0>0$) or biaxial ($b=0$, $\dot\epsilon_0<0$)	$\bar\eta(\dot\epsilon_0)$ or $\bar\eta_B(\dot\epsilon_0)$	$\frac{3\eta(\dot\gamma)}{[1-2\lambda(\dot\gamma)\dot\epsilon_0][1+\lambda(\dot\gamma)\dot\epsilon_0]}=\frac{3\eta(\dot\gamma)}{\mathcal{A}(\dot\gamma)\mathcal{B}(\dot\gamma)}$; $\mathcal{A}(\dot\gamma)=1-2\dot\epsilon_0\lambda(\dot\gamma)$; $\mathcal{B}(\dot\gamma)=1+\dot\epsilon_0\lambda(\dot\gamma)$
	Planar ($b=1$, $\dot\epsilon_0>0$)	$\bar\eta_{P_1}(\dot\epsilon_0)$	$\frac{4\eta(\dot\gamma)}{1-4\dot\epsilon_0^2\lambda(\dot\gamma)^2}=\frac{4\eta(\dot\gamma)}{\mathcal{A}(\dot\gamma)C(\dot\gamma)}$; $\mathcal{A}(\dot\gamma)=1-2\dot\epsilon_0\lambda(\dot\gamma)$; $C(\dot\gamma)=1+2\dot\epsilon_0\lambda(\dot\gamma)$
		$\bar\eta_{P_2}(\dot\epsilon_0)$	$\frac{2\eta(\dot\gamma)}{1+2\dot\epsilon_0\lambda(\dot\gamma)}=\frac{2\eta(\dot\gamma)}{C(\dot\gamma)}$

*$\lambda(\dot\gamma)=\eta(\dot\gamma)/G_0$ and $\dot\gamma=|\underline{\underline{\dot\gamma}}|$.

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Advanced Constitutive Modeling – Appendix D

Oldroyd B (Convected Jeffreys)

TABLE D.4
Predictions of Oldroyd B or Convected Jeffreys Model in Shear and Extensional Flows [26]

1. *Shear*			
	Startup	$\eta^+(t,\dot\gamma)$	$\eta_0\left[\frac{\lambda_2}{\lambda_1}+\left(1-\frac{\lambda_2}{\lambda_1}\right)\left(1-e^{-\frac{t}{\lambda_1}}\right)\right]$
		$\Psi_1^+(t,\dot\gamma)$	$2\eta_0(\lambda_1-\lambda_2)\left[1-e^{-\frac{t}{\lambda_1}}\left(1+\frac{t}{\lambda_1}\right)\right]$
		$\Psi_2^+(t,\dot\gamma)$	0
	Steady	$\eta(\dot\gamma)$	η_0
		$\Psi_1(\dot\gamma)$	$2\eta_0(\lambda_1-\lambda_2)$
		$\Psi_2(\dot\gamma)$	0
	Cessation	$\eta^-(t,\dot\gamma)$	$\eta_0\left(1-\frac{\lambda_2}{\lambda_1}\right)e^{-\frac{t}{\lambda_1}}$
		$\Psi_1^-(t,\dot\gamma)$	$2\eta_0(\lambda_1-\lambda_2)e^{-\frac{t}{\lambda_1}}$
		$\Psi_2^-(t,\dot\gamma)$	0
	SAOS	$G'(\omega)$	$\eta_0\frac{(\lambda_1-\lambda_2)\omega^2}{1+\lambda_1^2\omega^2}$
		$G''(\omega)$	$\eta_0\omega\frac{1+\lambda_1\lambda_2\omega^2}{1+\lambda_1^2\omega^2}$
2. *Extension*			
	Startup		
	Uniaxial ($b=0$, $\dot\epsilon_0>0$) or biaxial ($b=0$, $\dot\epsilon_0<0$)	$\bar\eta^+(t,\dot\epsilon_0)$ or $\bar\eta_B^+(t,\dot\epsilon_0)$	$3\eta_0\frac{\lambda_2}{\lambda_1}+\frac{\eta_0}{\mathcal{A}\mathcal{B}}\left(1-\frac{\lambda_2}{\lambda_1}\right)\left(3-2\mathcal{B}e^{-\frac{t\mathcal{A}}{\lambda_1}}-\mathcal{A}e^{-\frac{t\mathcal{B}}{\lambda_1}}\right)$; $\mathcal{A}=1-2\dot\epsilon_0\lambda_1$; $\mathcal{B}=1+\dot\epsilon_0\lambda_1$
	Planar ($b=1$, $\dot\epsilon_0>0$)	$\bar\eta_{P_1}^+(t,\dot\epsilon_0)$	$4\eta_0\frac{\lambda_2}{\lambda_1}+\frac{2\eta_0}{\mathcal{A}C}\left(1-\frac{\lambda_2}{\lambda_1}\right)\left(2-\mathcal{A}e^{-\frac{Ct}{\lambda_1}}-Ce^{-\frac{\mathcal{A}t}{\lambda_1}}\right)$; $\mathcal{A}=1-2\dot\epsilon_0\lambda_1$; $C=1+2\dot\epsilon_0\lambda_1$
		$\bar\eta_{P_2}^+(t,\dot\epsilon_0)$	$2\eta_0\frac{\lambda_2}{\lambda_1}+\frac{2\eta_0}{C}\left(1-\frac{\lambda_2}{\lambda_1}\right)\left(1-e^{-\frac{Ct}{\lambda_1}}\right)$
	Steady		
	Uniaxial ($b=0$, $\dot\epsilon_0>0$) or biaxial ($b=0$, $\dot\epsilon_0<0$)	$\bar\eta(\dot\epsilon_0)$ or $\bar\eta_B(\dot\epsilon_0)$	$3\eta_0\left(\frac{\lambda_2}{\lambda_1}+\frac{1-\frac{\lambda_2}{\lambda_1}}{\mathcal{A}\mathcal{B}}\right)$
	Planar ($b=1$, $\dot\epsilon_0>0$)	$\bar\eta_{P_1}(\dot\epsilon_0)$	$4\eta_0\left(\frac{\lambda_2}{\lambda_1}+\frac{1-\frac{\lambda_2}{\lambda_1}}{\mathcal{A}C}\right)$
		$\bar\eta_{P_2}(\dot\epsilon_0)$	$2\eta_0\left(\frac{\lambda_2}{\lambda_1}+\frac{1-\frac{\lambda_2}{\lambda_1}}{C}\right)$

We can also change the form of the basic equation.

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Advanced Constitutive Modeling – Chapter 9

We can also change the form of the basic equation.

We can also **modify integral models** to add non-linearity and thus produce new constitutive equations.

Factorized Rivlin-Sawyers Model

$$\underline{\underline{\tau}}(t) = +\int_{-\infty}^{t} M(t-t')\left(\Phi_2(I_1,I_2)\underline{\underline{C}} - \Phi_1(I_1,I_2)\underline{\underline{C}}^{-1}\right)dt'$$

Factorized K-BKZ Model

$$\underline{\underline{\tau}}(t) = +\int_{-\infty}^{t} M(t-t')\left(2\frac{\partial U}{\partial I_2}\underline{\underline{C}} - 2\frac{\partial U}{\partial I_1}\underline{\underline{C}}^{-1}\right)dt'$$

I_1, I_2 are the invariants of the Finger or Cauchy strain tensors (these are related).

Again, the only way to choose among these nonlinear models is to compare predictions
(see R. G. Larson, Constitutive Equations for Polymer Melts).

Advanced Constitutive Modeling – Appendix D

We can also change the form of the basic equation.

Factorized Rivlin-Sawyers

TABLE D.6
Predictions of Factorized Rivlin–Sawyers Model in Shear and Extensional Flows [26]

1. *Shear*		
Steady	$\eta(\dot\gamma)$	$\int_0^\infty M(s)s(\Phi_1+\Phi_2)\,ds$
	$\Psi_1(\dot\gamma)$	$\int_0^\infty M(s)s^2(\Phi_1+\Phi_2)\,ds$
	$\Psi_2(\dot\gamma)$	$-\int_0^\infty M(s)s^2\Phi_2\,ds$
SAOS	$G'(\omega)$	$\int_0^\infty M(s)(1-\cos\omega s)\,ds$
	$G''(\omega)$	$\int_0^\infty M(s)\sin\omega s\,ds$
2. *Extension*		
Steady		
Uniaxial ($b=0, \dot\epsilon_0>0$) or biaxial ($b=0, \dot\epsilon_0<0$)	$\bar\eta(\dot\epsilon_0)$ or $\bar\eta_B(\dot\epsilon_0)$	$\frac{1}{\dot\epsilon_0}\int_0^\infty M(s)\left[\Phi_1\left(e^{2\dot\epsilon_0 s}-e^{-\dot\epsilon_0 s}\right)+\Phi_2\left(e^{\dot\epsilon_0 s}-e^{-2\dot\epsilon_0 s}\right)\right]ds$
Planar ($b=1, \dot\epsilon_0>0$)	$\bar\eta_{P_1}(\dot\epsilon_0)$	$\frac{1}{\dot\epsilon_0}\int_0^\infty M(s)\left[\Phi_1\left(e^{2\dot\epsilon_0 s}-e^{-2\dot\epsilon_0 s}\right)+\Phi_2\left(e^{2\dot\epsilon_0 s}-e^{-2\dot\epsilon_0 s}\right)\right]ds$
	$\bar\eta_{P_2}(\dot\epsilon_0)$	$\frac{1}{\dot\epsilon_0}\int_0^\infty M(s)\left[\left(\Phi_1 e^{-\dot\epsilon_0 s}+\Phi_2 e^{\dot\epsilon_0 s}\right)\left(e^{\dot\epsilon_0 s}-e^{-\dot\epsilon_0 s}\right)\right]ds$

Choosing Constitutive Equations

We have fixed all the obvious flaws in our constitutive equations, and now we have too many choices!

We could make predictions and compare with experimental data, but some of the models (Rivlin Sawyer, K-BKZ) have undefined functions that must be specified.

How to proceed? *We need some guidance.*

All along we have taken a *continuum-mechanics approach*. We have run that course all the way through. Now we must go back and seek some insight from molecular ideas of relaxation and polymer dynamics.

Some of what we have learned from Continuum Modeling

- We can model **linear viscoelasticity**. The GMM does a good job; there is no reason to play around with springs and dashpots to improve linear viscoelasticity
- We can model **shear normal stresses**. The kind of deformation described by the Finger tensor (affine motion) gives a first normal stress difference and zero second-normal stress; the kind of deformation described by the Cauchy tensor gives both stress differences, but too much N_2.
- We can model **shear thinning**. But only by brute force (GNF, White-Metzner)
- We can model **elongational flows**. But we predict singularities that do not appear to be present.
- **Frame-Invariance** is important. Calculations outside the linear viscoelastic regime are incorrect if the equations are not properly frame invariant.
- **Thinking in terms of strain** is an advantage. When we think only in terms of rate, we can only model Newtonian fluids.
- **Looking for contradictions** when stretching a model to its limits is productive.
- **Continuum models do not give molecular insight**. We can fit continuum models and obtain material functions (viscosity, relaxation times) but we cannot predict these functions for new, related materials

Advanced Constitutive Modeling – Chapter 9

It's time for a new approach.

Molecular Constitutive Modeling

- Begin with a picture (model) of the kind of material that interests you
- Derive how stress is produced by deformation of that picture
- Write the stress as a function of deformation (constitutive equation)

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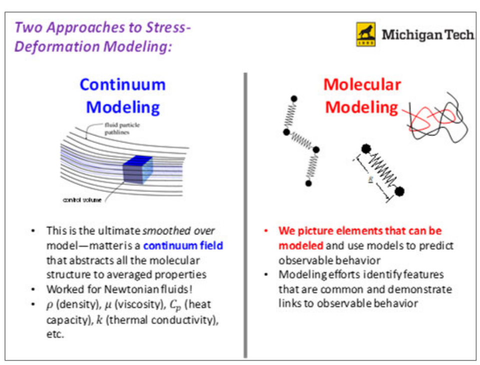
second half Molecular

Chapter 9: Advanced ~~Constitutive~~ Models



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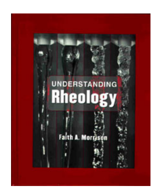
Polymer Rheology



Professor Faith A. Morrison
Department of Chemical Engineering
Michigan Technological University

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Advanced Constitutive Modeling – Molecular modeling

At the beginning of the course we started with materials . . .

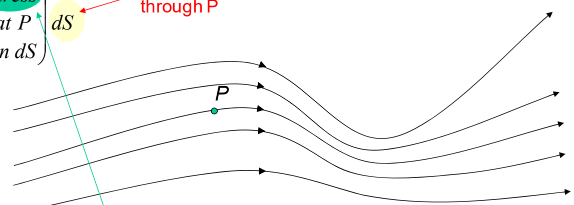
Chapter 3: Newtonian Fluid Mechanics Polymer Rheology

Molecular Forces (contact) – this is the tough one

$$\underline{f} = \begin{pmatrix} stress \\ at\ P \\ on\ dS \end{pmatrix} dS$$

the force on that surface

choose a surface through P



We need an expression for the state of **stress** at an arbitrary point P in a flow.

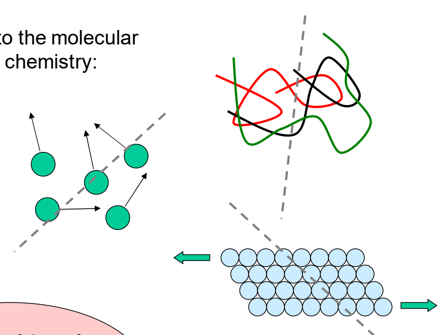
Advanced Constitutive Modeling – Molecular modeling

At the beginning of the course we started with materials . . .

At that time we wanted to avoid specifying much about our materials.

Molecular Forces *(continued)*

Think back to the molecular picture from chemistry:



The specifics of these forces, connections, and interactions must be captured by the molecular forces term that we seek.

Advanced Constitutive Modeling – Molecular modeling

At the beginning of the course . . .we turned to continuum mechanics.

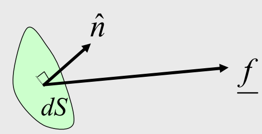
Molecular Forces *(continued)*

•We will concentrate on **expressing the molecular forces** mathematically;

•We leave to later the task of relating the resulting mathematical expression to experimental observations.

First, choose a surface:

•arbitrary shape
•small



$$\begin{pmatrix} stress \\ at\ P \\ on\ dS \end{pmatrix} dS = \underline{f}$$

What is *f* ?

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Advanced Constitutive Modeling – Molecular modeling

At the beginning of the course . . .we turned to continuum mechanics.

Molecular Forces *(continued)*

Assembling the force vector:

$$\begin{aligned} \underline{f} = dS\ \hat{n} \cdot \big[& \Pi_{11}\hat{e}_1\hat{e}_1 + \Pi_{21}\hat{e}_2\hat{e}_1 + \Pi_{31}\hat{e}_3\hat{e}_1 \\ & + \Pi_{12}\hat{e}_1\hat{e}_2 + \Pi_{22}\hat{e}_2\hat{e}_2 + \Pi_{32}\hat{e}_3\hat{e}_2 \\ & + \Pi_{13}\hat{e}_1\hat{e}_3 + \Pi_{23}\hat{e}_2\hat{e}_3 + \Pi_{33}\hat{e}_3\hat{e}_3 \big] \\ = dS\ \hat{n} \cdot & \sum_{p=1}^{3}\sum_{m=1}^{3} \Pi_{pm}\hat{e}_p\hat{e}_m \\ = dS\ \hat{n} \cdot & \Pi_{pm}\hat{e}_p\hat{e}_m \end{aligned}$$

$$\boxed{\underline{f} = dS\ \hat{n} \cdot \underline{\underline{\Pi}}}$$

Total stress tensor
(molecular stresses)

We swept all molecular contact forces into the stress tensor.

Now, we seek to calculate molecular contact forces directly from a molecular picture.

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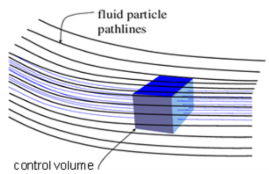
Two Approaches to Stress-Deformation Modeling:

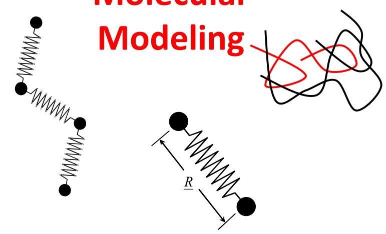
Michigan Tech

Continuum Modeling



- This is the ultimate *smoothed over* model—matter is a **continuum field** that abstracts all the molecular structure to averaged properties
- Worked for Newtonian fluids!
- ρ (density), μ (viscosity), C_p (heat capacity), k (thermal conductivity), etc.

Molecular Modeling



- **We picture elements that can be modeled** and use models to predict observable behavior
- Modeling efforts identify features that are common and demonstrate links to observable behavior

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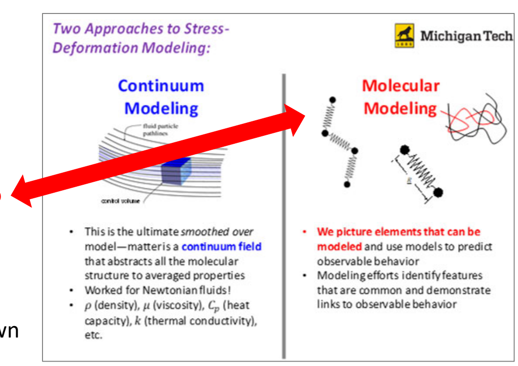
Advanced Molecular Modeling in Rheology (Chapter 9, 2nd half)

Restart:

Molecular Modeling?



- Start with a **specific material** (known chemistry, structure)
- Postulate a **dominant physics** that produces an observed behavior
- See if it's **TRUE**
- Use model to **address engineering, technology, end-use questions**

3/4/2020 90

Advanced Constitutive Modeling – Molecular modeling

Long-Chain **Polymer** Constitutive Modeling

molecular tension force on arbitrary surface

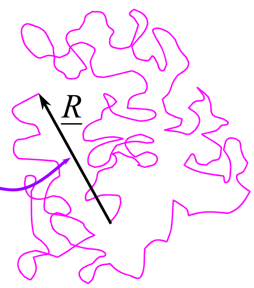
$$\tilde{\underline{f}} = dA\,\hat{n}\cdot(-\underline{\underline{\tau}})$$

stress tensor

We now attempt to calculate molecular forces by considering molecular models.

Polymer Dynamics

end-to-end vector, $\underline{R}$



Long-chain polymers may be modeled as random walks.

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Advanced Constitutive Modeling – Molecular modeling

Long-Chain **Polymer** Constitutive Modeling

molecular tension force on arbitrary surface

$$\tilde{\underline{f}} = dA\,\hat{n}\cdot(-\underline{\underline{\tau}})$$

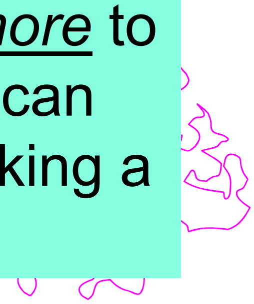
stress tensor

We n
mole
mole

Polyme

WARNING:

There is ***way*** ***more*** to this than we can cover; we're taking a ***tour*** only



may be modeled as random walks.

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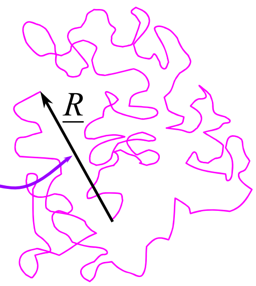
Advanced Constitutive Modeling – Molecular modeling

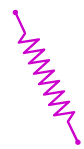
Polymer coil responds to deformation

A polymer chain adopts the most random configuration at equilibrium.

end-to-end vector, $\underline{R}$



When deformed, the chain tries to recover that most random configuration, giving rise to a spring-like restoring force.



spring of equilibrium length and orientation $\underline{R}$

We will model the chain dynamics with a random walk.

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Advanced Constitutive Modeling – Molecular modeling

Gaussian Springs (random walk)

Equilibrium configuration distribution function - probability a walk of N steps of length a has end-to-end distance $\underline{R}$

$$\psi_0(\underline{R}) = \left(\frac{\beta}{\sqrt{\pi}}\right)^3 e^{-\beta^2 \underline{R}\cdot\underline{R}}$$

$$\beta = \frac{3}{2Na^2}$$

From an entropy calculation of the work needed to extend a random walk, we can calculate the force needed to deform a the polymer coil

$$\underline{f} = \frac{3kT}{Na^2}\underline{R}$$

If we can relate **this force**, the force to extend the spring, to the force on an arbitrary surface, we can predict rheological properties

molecular tension force on arbitrary surface

$$\underline{\tilde{f}} = -dA\,\hat{n}\cdot\underline{\underline{\tau}}$$

stress tensor

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Advanced Constitutive Modeling – Molecular modeling

Molecular force generated by deforming chain

$$\underset{\sim}{\tilde{f}} = \begin{pmatrix}\text{Tension} \\ \text{force on } dA\end{pmatrix} = \iiint \underbrace{\begin{pmatrix}\text{Force on surface} \\ dA \text{ due to chains} \\ \text{of ETE } \underline{R}\end{pmatrix}}$$

$$\begin{pmatrix}\text{Probability} \\ \text{chain of ETE } \underline{R} \\ \text{crosses surface} \\ \text{dA}\end{pmatrix}\begin{pmatrix}\text{Probability} \\ \text{chain has ETE} \\ \underline{R}\end{pmatrix}\begin{pmatrix}\text{Force exerted} \\ \text{by chain w/} \\ \text{ETE } \underline{R}\end{pmatrix}$$

$(\hat{n}\cdot\underline{R})\nu^{\frac{1}{3}}$

(see next slide)

$\psi(\underline{R})dR_1 dR_2 dR_3$

$$\underline{f} = \frac{3kT}{Na^2}\underline{R}$$

ν = number of polymer chains per unit volume

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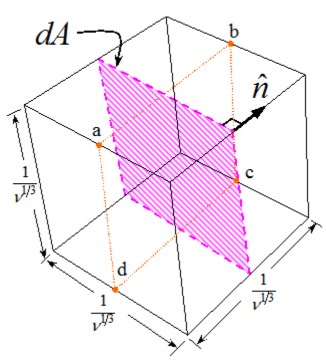
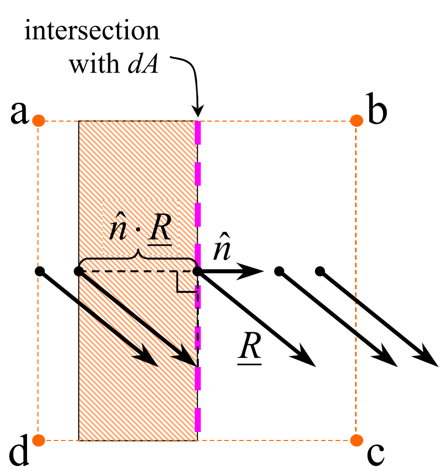
Advanced Constitutive Modeling – Molecular modeling



Probability chain of ETE $\underline{R}$ crosses surface dA



$$\begin{pmatrix}\text{Probability} \\ \text{chain of ETE } \underline{R} \\ \text{crosses surface} \\ \text{dA}\end{pmatrix} = \frac{(\hat{n}\cdot\underline{R})\left(\nu^{-\frac{1}{3}}\right)\left(\nu^{-\frac{1}{3}}\right)}{\left(\nu^{-1/3}\right)^3}$$

1/ν = volume per polymer chain

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Molecular force generated by deforming chain

$$\boxed{\underset{\sim}{\tilde{f}} = \frac{3kT\nu^{\frac{1}{3}}}{Na^2}\left(\hat{n}\cdot\langle \underline{R}\cdot\underline{R}\rangle\right)}$$

$$\langle \underline{R}\cdot\underline{R}\rangle \equiv \iiint \underline{R}\cdot\underline{R}\,\psi(\underline{R})dR_1 dR_2 dR_3$$

BUT, from before . . .

$$\boxed{\underline{\tilde{f}} = -dA\,\hat{n}\cdot\underline{\underline{\tau}}}$$

molecular tension force on arbitrary surface in terms of $\underline{\underline{\tau}}$

Comparing these two we conclude,

$$\boxed{\underline{\underline{\tau}} = -\frac{3kT\nu}{Na^2}\langle \underline{R}\cdot\underline{R}\rangle}$$

$$(dA = \nu^{-\frac{2}{3}})$$

Molecular force generated by deforming chain

How can we convert this equation,

$$\boxed{\underline{\underline{\tau}} = -\frac{3kT\nu}{Na^2}\langle \underline{R}\cdot\underline{R}\rangle}$$

Molecular stress in a fluid generated by a deforming chain

which relates molecular ETE vector and stress, into a constitutive equation, which relates stress and deformation?

*We need an **idea** that connects ETE vector motion to macroscopic deformation of a polymer network or melt.*

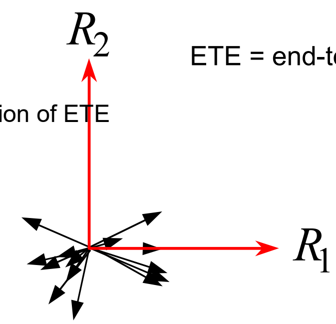
a "model"

Advanced Constitutive Modeling – Molecular modeling

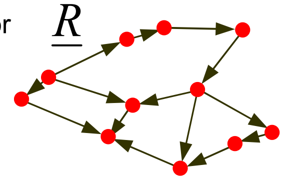
Elastic (Crosslinked) Solid

Between every two crosslinks there is a polymer strand that follows a random walk of *N* steps of length *a.*

Distribution of ETE vectors



ETE = end-to-end vector $\underline{R}$



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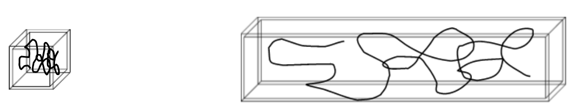
Advanced Constitutive Modeling – Molecular modeling

Affine motion

How can we relate changes in end-to-end vector to macroscopic deformation?

AN ANSWER: **affine-motion** assumption: the macroscopic dimension changes are proportional to the microscopic dimension changes

before *after*



There is no internal slippage of polymer chains: deformation with length scale.

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Consider a general elongational deformation:

Inverse deformation gradient tensor, $\underline{\underline{F}}^{-1}$

$$\underline{\underline{F}}^{-1} = \begin{pmatrix} \lambda_1 & 0 & 0 \\ 0 & \lambda_2 & 0 \\ 0 & 0 & \lambda_3 \end{pmatrix}_{123}$$

For affine motion we can relate the components of the initial and final *ETE* vectors as,

"ETE"="end-to-end"

ETE after

$$\lambda_1 = \frac{R_1}{R_1'} \qquad \lambda_2 = \frac{R_2}{R_2'} \qquad \lambda_3 = \frac{R_3}{R_3'}$$

ETE before

$$\underline{R}(t) = \begin{pmatrix} \lambda_1 R_1' \\ \lambda_2 R_2' \\ \lambda_3 R_3' \end{pmatrix}_{123}$$

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We are attempting to calculate the stress tensor with this equation:

$$\underline{\underline{\tau}} = -\frac{3kT\nu}{Na^2}\langle \underline{R}\cdot\underline{R}\rangle$$

$$\langle \underline{R}\cdot\underline{R}\rangle \equiv \iiint \underline{R}\cdot\underline{R}\,\psi(\underline{R})\,dR_1 dR_2 dR_3$$

$$\underline{R}(t) = \begin{pmatrix} \lambda_1 R_1' \\ \lambda_2 R_2' \\ \lambda_3 R_3' \end{pmatrix}_{123}$$

But, where do we get this?

Configuration distribution function

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Probability chain has ETE between $\underline{R}$ and $\underline{R}+d\underline{R}$: $\psi(\underline{R})dR_1 dR_2 dR_3$

Configuration distribution function

Equilibrium configuration distribution function:

$$\psi_0(\underline{R}) = \left(\frac{\beta}{\sqrt{\pi}}\right)^3 e^{-\beta^2 \underline{R}'\cdot\underline{R}'}$$

$$\beta = \frac{3}{2Na^2}$$

But, if the deformation is **affine**, then the number of ETE vectors between $\underline{R}$ and $\underline{R}+d\underline{R}$ at time t is equal to the number of vectors with ETE between $\underline{R}'$ and $\underline{R}'+d\underline{R}'$ at t'

Conclusion: $\psi(\underline{R}) = \psi_0(\underline{R}') = \left(\frac{\beta}{\sqrt{\pi}}\right)^3 e^{-\beta^2 \underline{R}'\cdot\underline{R}'}$

Now we are ready to calculate the stress tensor.

$$\underline{\underline{\tau}} = -\frac{3kT\nu}{Na^2}\left\langle \underline{R}\cdot\underline{R}\right\rangle$$

$$\left\langle \underline{R}\cdot\underline{R}\right\rangle \equiv \iiint \underline{R}\cdot\underline{R}\,\psi(\underline{R})dR_1 dR_2 dR_3$$

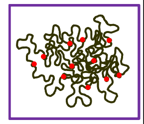
$$R_i' = \frac{R_i}{\lambda_i}$$

$$\underline{R}(t) = \begin{pmatrix} \lambda_1 R_1' \\ \lambda_2 R_2' \\ \lambda_3 R_3' \end{pmatrix}_{123}$$

$$\psi(\underline{R}) = \psi_0(\underline{R}') = \left(\frac{\beta}{\sqrt{\pi}}\right)^3 e^{-\beta^2 \underline{R}'\cdot\underline{R}'}$$

(much algebra omitted; solved in Problem 9.57)

Final solution: $\underline{\underline{\tau}} = -\nu kT\lambda_i^2 \hat{e}_i\hat{e}_i$



Final solution for stress: $\underline{\underline{\tau}} = -\nu kT \lambda_i^2 \hat{e}_i \hat{e}_i = -\nu kT \begin{pmatrix} \lambda_1^2 & 0 & 0 \\ 0 & \lambda_2^2 & 0 \\ 0 & 0 & \lambda_3^2 \end{pmatrix}_{123}$

Compare this solution with the Finger strain tensor for this flow.

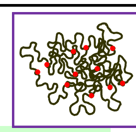
$$\underline{\underline{C}}^{-1}(t',t) = \left(\underline{\underline{F}}^{-1}\right)^T \cdot \underline{\underline{F}}^{-1} = \begin{pmatrix} \lambda_1^2 & 0 & 0 \\ 0 & \lambda_2^2 & 0 \\ 0 & 0 & \lambda_3^2 \end{pmatrix}_{123}$$

Affine motion

$$\underline{\underline{\tau}} = -\nu kT \underline{\underline{C}}^{-1}$$

Since the Finger tensor for **any** deformation may be written in diagonal form (symmetric tensor) our derivation is valid for all deformations.

Which is the same as the finite-strain Hooke's law discussed earlier, with $G = \nu kT$.



What about polymer melts?

Non permanent crosslinks

Green-Tobolsky **Temporary** Network Model

The model:

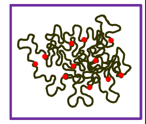
- ν junction points per unit volume = constant
- ETE vectors have finite lifetimes
- when old junctions die, new ones are born
- newly born ETE vectors adopt the equilibrium distribution ψ_0

Use a statistical approach:

$$\left(\begin{array}{c} \text{Probability per unit} \\ \text{time that strand dies} \\ \text{and is reborn at} \\ \text{equilibrium} \end{array} \right) \equiv \frac{1}{\lambda}$$

$$\left(\begin{array}{c} \text{Probability that strand} \\ \text{retains same ETE from t' to} \\ \text{t (survival probability)} \end{array} \right) \equiv P_{t',t}$$

Advanced Constitutive Modeling – Molecular modeling



What is the probability that a strand retains the same ETE vector between t' and $t' + \Delta t$?

$$P_{t',t+\Delta t} = \left(\text{Probability that strand retains same ETE from } t' \text{ to } t \text{ (survival probability)} \right) \left(\text{Probability that strand does not die over interval } \Delta t \right)$$

$$P_{t',t+\Delta t} = P_{t',t}\left(1 - \frac{1}{\lambda}\Delta t\right)$$

$$\frac{dP_{t',t}}{dt} = -\frac{1}{\lambda} P_{t',t}$$

$$\ln P_{t',t} = -\frac{t}{\lambda} + C_1$$

$$\boxed{P_{t',t} = e^{-\frac{(t-t')}{\lambda}}}$$

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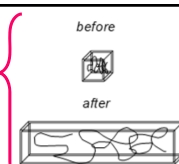
Advanced Constitutive Modeling – Molecular modeling

The contribution to the stress tensor of the individual strands can be calculated from,

Affine motion



$$\left(\text{Stress at } t \text{ from strands born between } t' \text{ and } t' + dt' \right) = \left(\text{Probability that strand is born between } t' \text{ and } t' + dt' \right) \left(\text{Probability that a strand survives from } t' \text{ to } t \right) \left(\text{Stress generated by an affinely deforming strand between } t' \text{ and } t \right)$$

$$d\underline{\underline{\tau}} = \left[\frac{1}{\lambda} dt'\right]\left[e^{-\frac{(t-t')}{\lambda}}\right]\left[-G\underline{\underline{C}}^{-1}(t',t)\right]$$

Green-Tobolsky temporary network mode (Lodge model)

$$\underline{\underline{\tau}}(t) = -\int_{-\infty}^{t} \left[\frac{G}{\lambda} e^{-\frac{(t-t')}{\lambda}}\right] \underline{\underline{C}}^{-1}(t',t)\,dt'$$

$$G = \frac{\eta_0}{\lambda}$$

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Oh no, back where we started!

$$\underline{\underline{\tau}}(t) = -\int_{-\infty}^{t} \left[\frac{G}{\lambda} e^{-\frac{(t-t')}{\lambda}}\right] \underline{\underline{C}}^{-1}(t',t)dt'$$

NO!

Green-Tobolsky temporary network mode (Lodge model)

We now know that affine motion of strands with equal birth and death rates gives a model with no shear-thinning, no second-normal stress difference.

To model shear-thinning, N_2, etc., therefore, we must add something else to our physical picture, e.g.,

- Anisotropic drag
- **nonaffine** motion of various types

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Anisotropic drag - Giesekus

In a system undergoing deformation, the surroundings of a given molecule will be anisotropic; this will result in the drag on any given molecule being anisotropic too.

Starting with the dumbbell model (gives UCM), replace $\frac{8kt\beta^2}{\zeta}$ with an anisotropic mobility tensor $\underline{\underline{B}}/\lambda$. Assume also that the anisotropy in $\underline{\underline{B}}$ is proportional to the anisotropy in $\underline{\underline{\tau}}$.

$$\underline{\underline{B}} - \underline{\underline{I}} = \frac{\alpha}{G}\underline{\underline{\tau}}$$

Giesekus Model $\underline{\underline{\tau}}(t) + \lambda \overset{\triangledown}{\underline{\underline{\tau}}} + \frac{\alpha\lambda}{\eta_0}\underline{\underline{\tau}} : \underline{\underline{\tau}} = -\eta_0 \dot{\underline{\underline{\gamma}}}$

see Larson, *Constitutive Equations for Polymer Melts*, Butterworths, 1988

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Constitutive equations incorporating **non-affine** motion include:

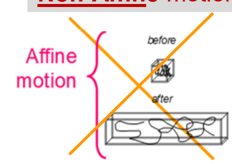
Gordon and Schowalter: "strands of polymer **slip** with respect to the deformation of the macroscopic continuum"; see Larson, p130 (this model has problems in step-shear strains)

strand slippage

$$\underline{\underline{\tau}} \equiv \frac{D\underline{\underline{\tau}}}{Dt} - (\nabla \underline{v})^T \cdot \underline{\underline{\tau}} - \underline{\underline{\tau}} \cdot \nabla \underline{v} + \frac{\xi}{2}\left(\underline{\underline{\tau}} \cdot \dot{\underline{\underline{\gamma}}} + \dot{\underline{\underline{\gamma}}} \cdot \underline{\underline{\tau}}\right)$$

- Phan-Thien/Tanner
- Johnson-Segalman

Non-Affine motion



Larson: uses **non-affine** motion that is a generalization of the motion in the Doi Edwards model; see Larson, Chapter 5

Wagner: uses irreversible **non-affine** motion; see Larson, Chapter 5

see Larson, *Constitutive Equations for Polymer Melts*, Butterworths, 1988

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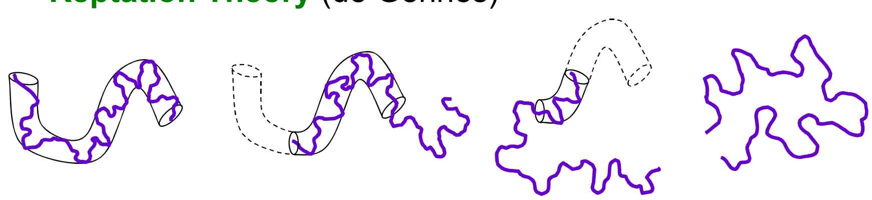
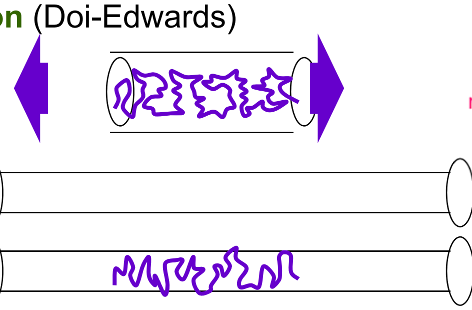
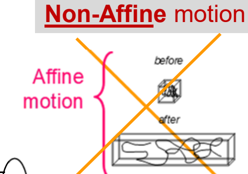
Reptation Theory (de Gennes)



Retraction (Doi-Edwards)



Non-Affine motion



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Advanced Constitutive Modeling – Molecular modeling

Step shear strain - *strain dependence*

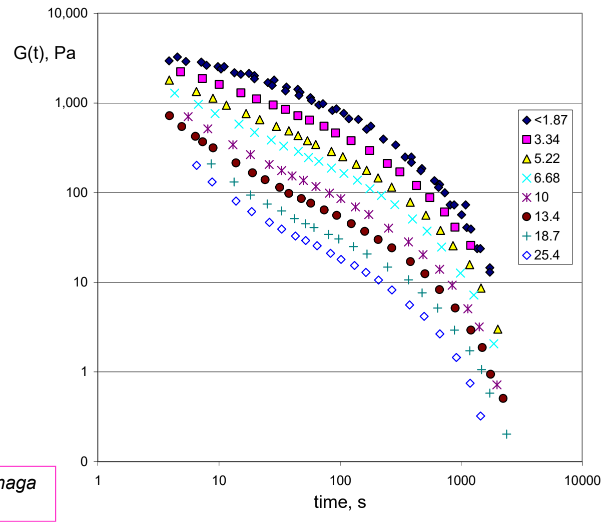

Figure 6.57, p. 212 Einaga et al.; PS soln

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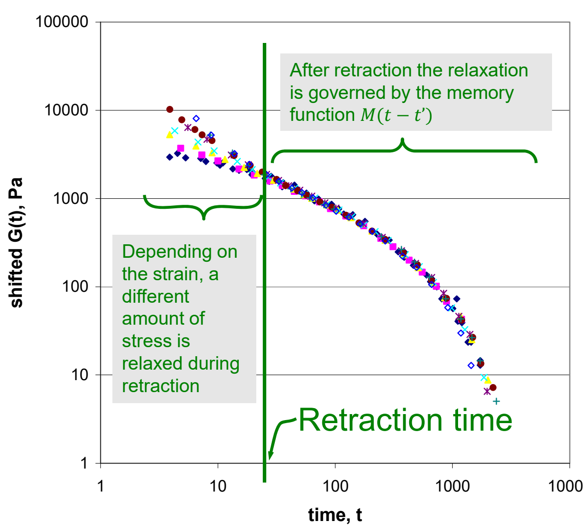
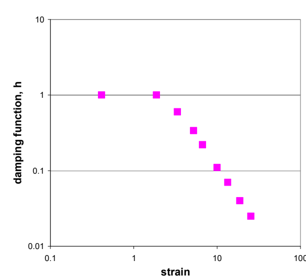
Advanced Constitutive Modeling – Molecular modeling

Step shear strain - **Damping Function**





The Doi-Edwards model does a good job of predicting the damping function, $h(\gamma)$ (see Larson p108)

Figure 6.58, p. 213 Einaga et al.; PS soln

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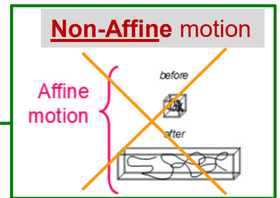
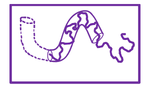
Advanced Constitutive Modeling – Molecular modeling

Doi-Edwards Model

Predicts a strain measure





$$\underline{\underline{\tau}} = -\int_{-\infty}^{t} M(t-t')\underline{\underline{Q}}(t',t)\,dt'$$

$$\underline{\underline{Q}}(t',t) = \frac{1}{4\pi}\int_0^{2\pi}\int_0^{\pi} 5\left(\frac{\hat{u}'\cdot\underline{\underline{F}}^{-1}\,\hat{u}'\cdot\underline{\underline{F}}^{-1}}{\left|\hat{u}'\cdot\underline{\underline{F}}^{-1}\right|^2}\right)\sin\theta\,d\theta d\phi$$

Predicts a memory function

$$M(t-t') = \sum_{i\ odd}\frac{G_i}{\lambda_i}e^{-\frac{t-t'}{\lambda_i}} \qquad G_i = \frac{8G_N^0}{\pi^2 i^2} \qquad \lambda_i = \frac{\lambda_1}{i^2}$$

(Factorized K-BKZ type)

Predicts a relaxation time distribution

$\hat{u}' =$ unit vector that gives orientation of strands at time *t'*

M. Doi and S. Edwards J. Chem Soc. Faraday Trans II 74, 1818 (1978); ibid 74 560, 918 (1978); ibid 75, 32 (1979); ibid 75, 38 (1979)

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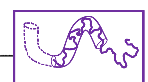
Advanced Constitutive Modeling – Molecular modeling

Doi-Edwards Model
Steady Shear
SAOS

M. Doi and S. Edwards J. Chem Soc. Faraday Trans II 75, 38 (1979)



$\frac{\Psi_1}{\Psi_{1,0}}$ $\frac{\Psi_2}{\Psi_{2,0}}$

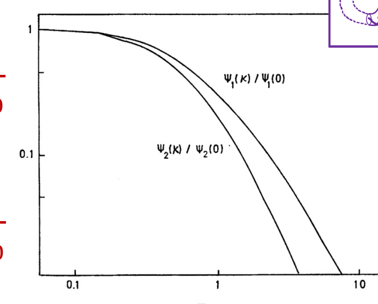


FIG. 5.—First and the second normal stress coefficients $\psi_1(\kappa)$ and $\psi_2(\kappa)$ in steady shear flow. [Note that $\psi_2(0) < 0$, so that $\psi_2(\kappa) < 0$].

$\frac{\eta^*}{\eta_0}$ $\frac{\eta}{\eta_0}$ $\frac{\eta'}{\eta_0}$

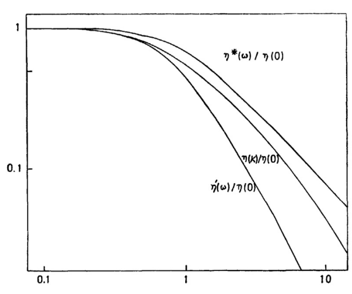


FIG. 3.—Non-linear viscosity $\eta(\kappa)$ in steady state, the modulus, $|\eta^*(\omega)|$, and the real part, $\eta'(\omega)$ of the linear dynamic viscosity. All quantities are normalized by the steady state viscosity at zero shear rate, $\eta(0)$.

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Advanced Constitutive Modeling
– Molecular modeling

Doi-Edwards Model
Shear Start Up

M. Doi and S. Edwards J. Chem Soc. Faraday Trans II 75, 38 (1979)

$$\frac{\tau_{21}(t)}{\tau_{21,\infty}}$$

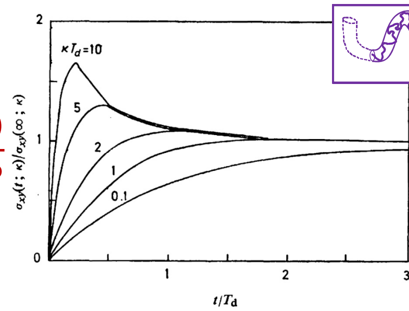
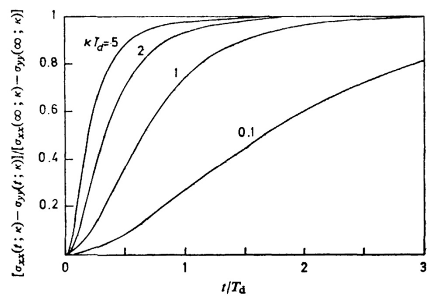


Fig. 6.—Shear stress when a shear flow is started at $t = 0$ with shear rate κ.



$$\frac{N_1(t)}{N_{1,\infty}(t)}$$

Fig. 7.—Growth of the first normal stress component when a shear flow is started at $t = 0$ with shear rate κ.

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Advanced Constitutive Modeling
– Molecular modeling

Doi-Edwards Model
Steady Elongation
Elongation Startup

M. Doi and S. Edwards J. Chem Soc. Faraday Trans II 75, 38 (1979)

Elongation growth stress difference

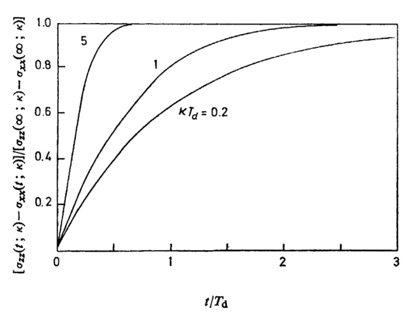

Fig. 13.—Growth of stress when an elongational flow is started at $t = 0$.

$$\frac{\bar{\eta}}{\bar{\eta}_0}$$

$$\frac{3\eta(\dot{\gamma})}{\bar{\eta}_0}$$

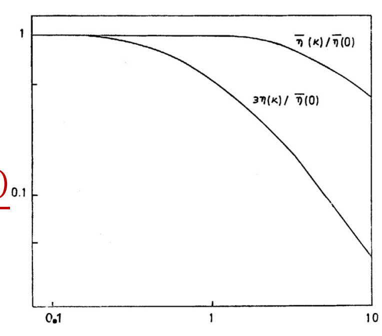

Fig. 12.—Steady elongational viscosity $\bar{\eta}(\kappa)$ and the steady shear viscosity $3\eta(\kappa)$. Both are normalized by $\bar{\eta}(0) = 3\eta(0)$.

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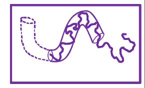
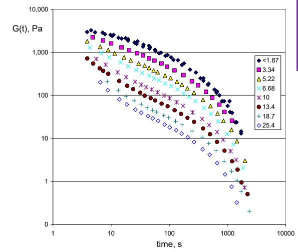
Advanced Constitutive Modeling – Molecular modeling

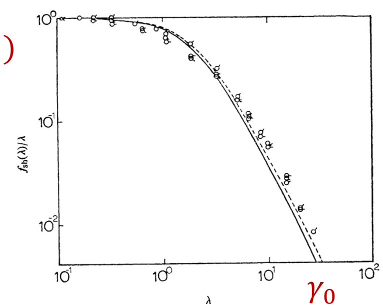




Doi-Edwards Model Large-Amplitude Step Shear

M. Doi and S. Edwards J. Chem Soc. Faraday Trans II 74, 1802 (1979)

$h(\gamma_0)$



γ_0

FIG. 6.—Strain dependent part of the stress relaxation function for simple shear [eqn (6.7)]. Circles, observed values [after ref. (11): sample, polystyrene solution in diethyl phthalate; molecular weight, 3×10^6; concentration, 0.166 g cm^{-3}, 0.221 g cm^{-3}, 0.275 g cm^{-3}]. Solid curve, eqn (6.8). Broken curve, eqn (7.4). In the ideal gaussian rubber f_{sh}/λ is constant.

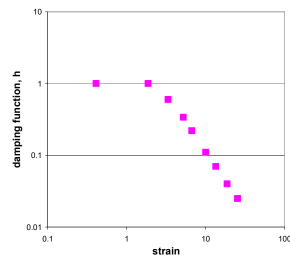
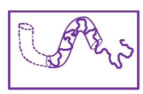


Figure 6.58, p. 213 Einaga et al.; PS soln

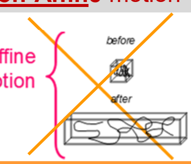
Advanced Constitutive Modeling – Molecular modeling

Doi-Edwards Model



Non-Affine motion

Affine motion



Correctly predicts:

- Ratio of $\frac{\Psi_1}{\Psi_2}$
- shape of start-up curves
- shape of $h(\gamma_0)$(nonlinear step strain, damping function)
- Predicts $\eta_0 = AM^3$
- !!!! shear thinning of $\eta(\dot{\gamma}), \Psi_1(\dot{\gamma})$
- tension-thinning elongational viscosity $\eta_e(\dot{\varepsilon})$

Tentatively conclude: shear thinning is an issue of **non-affine motion**

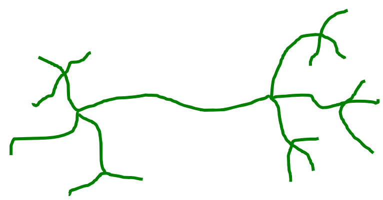
Fails to predict:

- $\eta_0 = AM^{3.4}$
- shape of shear thinning of $\eta(\dot{\gamma}), \Psi_1(\dot{\gamma})$
- reversing flows
- Elongational strain hardening (branched polymers)

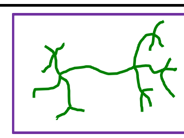
Advanced Models

Long-chain branched polymers

Pom-Pom Model (McLeish and Larson, *JOR* 42 81, 1998)
Extended Pom-Pom (Verbeeten, Peters, and Baaijens, *JOR* 45 823, 2001)



- Single backbone with multiple branches
- Backbone can readily be stretched in an extensional flow, producing strain hardening
- In shear startup, backbone stretches only temporarily, and eventually collapses, producing strain softening
- Based on reptation ideas; two decoupled equations, one for orientation, one for stretch; separate relaxation times for orientation and stretch)



Extended Pom-Pom (Verbeeten, Peters, and Baaijens, *JOR* 45 823, 2001)

Predicts elongational strain hardening

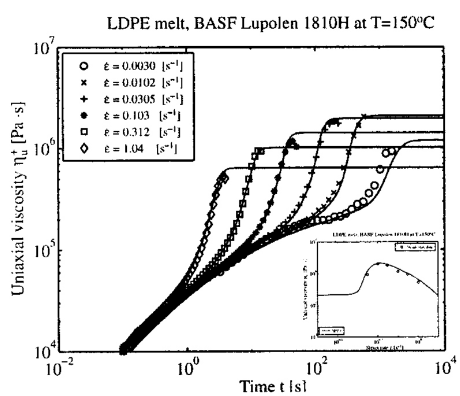
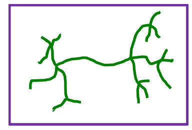


FIG. 5. Transient and quasisteady state (*inset*) uniaxial elongational viscosity η_u of the XPP model for Lupolen 1810H melt at $T = 150\,°C$. $\nu_i = 2/q_i$, $\varepsilon = 0.0030, 0.0102, 0.0305, 0.103, 0.312, 1.04\ s^{-1}$.



Extended Pom-Pom (Verbeeten, Peters, and Baaijens, *JOR* 45 823, 2001)

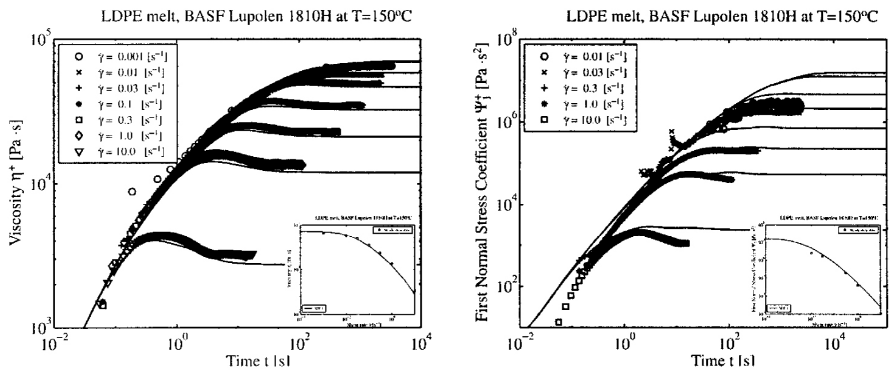


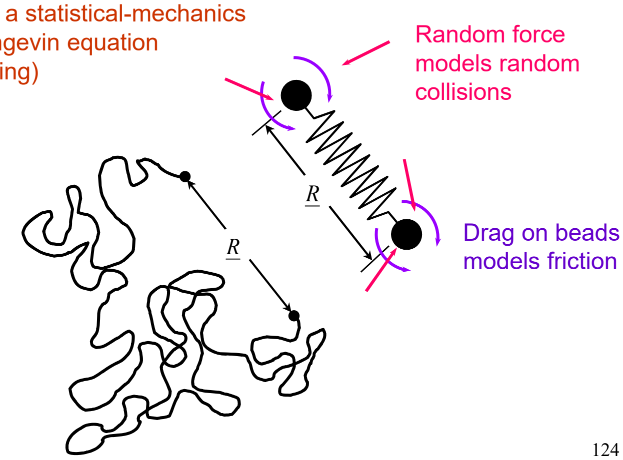
FIG. 8. Transient and steady state (*inset*) shear viscosity η (*left*) and first normal stress coefficient Ψ_1 (*right*) of the XPP model for Lupolen 1810H melt at $T = 150\,°C$. $\nu_i = 2/q_i$. $\gamma = 0.001, 0.01, 0.03, 0.1, 0.3, 1, 10\ s^{-1}$.

What about polymer solutions?

•Dilute solutions: chains do not interact
•collisions with solvent molecules are modeled stochastically
•calculate $\psi(R)$ by a statistical-mechanics solution to the Langevin equation (ensemble averaging)

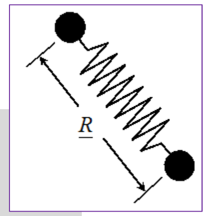
Elastic Dumbbell Model

W. Kuhn, 1934



Advanced Constitutive Modeling – Molecular modeling

Elastic Dumbbell Model



Continuum modeling
Momentum balance on a control volume (Navier-Stokes Equation)

$$\rho\left(\frac{\partial \underline{v}}{\partial t}+\underline{v}\cdot\nabla\underline{v}\right)=-\nabla p+\mu\nabla^2\underline{v}+\rho\underline{g}$$

Inertia = surface + body

Mixed Continuum/Stochastic modeling (Langevin Equation)
Momentum balance on a discrete body (mass *m*, velocity $\underline{u}$)
In a fluid continuum (velocity field $\underline{v}$)

$$m\left(\frac{d\underline{u}}{dt}\right)=-\zeta\left(\underline{u}-\underline{R}\cdot\nabla\underline{v}\right)-4kT\beta^2\underline{R}+\underline{A}$$

Inertia = drag + spring + random (Brownian)

Construct an ensemble of dumbbells and seek the probability of a given ETE at *t*

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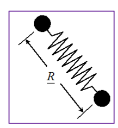
Advanced Constitutive Modeling – Molecular modeling

Elastic Dumbbell Model



Construct an ensemble of dumbbells and seek the probability of a given ETE at *t*

Langevin Equation

$$m\left(\frac{d\underline{u}}{dt}\right)=-\zeta\left(\underline{u}-\underline{R}\cdot\nabla\underline{v}\right)-4kT\beta^2\underline{R}+\underline{A}$$

To solve, (see Larson pp41-45). Consider an ensemble of dumbbells and seek the probability ψ that a dumbbell has an ETE R at a given time t. The equation for ψ is the Smoluchowski equation:

$$\frac{\partial\psi}{\partial t}+\frac{\partial}{\partial\underline{R}}\cdot\left[\underline{R}\cdot\nabla\underline{v}\,\psi-\frac{4kT\beta^2}{\zeta}\underline{R}\,\psi-\frac{2kT}{\zeta}\frac{\partial\psi}{\partial\underline{R}}\right]=0$$

We can calculate stress from: $\underline{\underline{\tau}}=-\frac{3kT\nu}{Na^2}\iiint\underline{R}\cdot\underline{R}\,\psi(\underline{R})dR_1dR_2dR_3$

If we multiply the Smoluchowski equation by $\underline{R}\cdot\underline{R}$ and integrate over $\underline{R}$ space, we obtain an expression for $\underline{\underline{\tau}}$ (i.e. the constitutive equation for this model)

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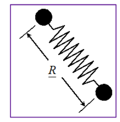
Advanced Constitutive Modeling – Molecular modeling



Integration yields:

see Larson, *Constitutive Equations for Polymer Melts*, Butterworths, 1988

Elastic dumbbell model

$$\underline{\underline{\tau}} + \lambda \overset{\nabla}{\underline{\underline{\tau}}} = -\eta_0 \underline{\underline{\dot{\gamma}}}$$

Upper-Convected Maxwell Model!

(same as temporary netrowk model)

Two different models give the same constitutive equation (because stress only depends on the second moment of ψ, not on details of ψ)

$$G = \nu kT$$

number of dumbbells/volume

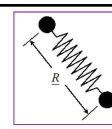
$$\lambda = \frac{\zeta}{8kT\beta^2}$$

bead friction factor

$$\beta^2 \equiv \frac{3}{2Na^2}$$

from random walk

Advanced Constitutive Modeling – Molecular modeling



Elastic Dumbbell Model for Dilute Polymer Solutions

$$\underline{\underline{\tau}}_p + \lambda \overset{\nabla}{\underline{\underline{\tau}}}_p = -\eta_0 \underline{\underline{\dot{\gamma}}}$$

Polymer contribution

$$\underline{\underline{\tau}}_s = -\eta_s \underline{\underline{\dot{\gamma}}}$$

Solvent contribution

$$\underline{\underline{\tau}} = \underline{\underline{\tau}}_p + \underline{\underline{\tau}}_s$$

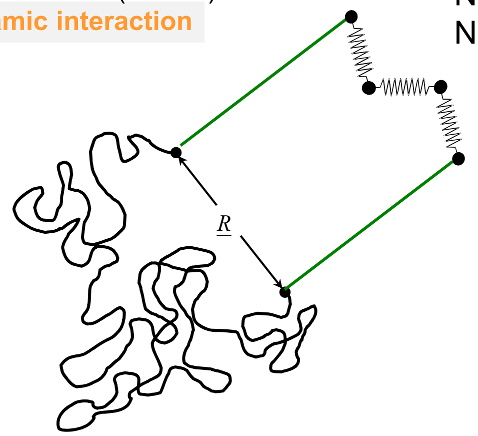
Dumbbell Model (Oldroyd B)

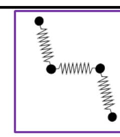
See problem 9.49

see Larson, *Constitutive Equations for Polymer Melts*, Butterworths, 1988

Rouse Model

- Multimodal bead-spring model
- Springs represent different sub-molecules
- Drag localized on beads (Stokes)
- No hydrodynamic interaction





Rouse Model

see Larson, *Constitutive Equations for Polymer Melts*, Butterworths, 1988

- Rouse wrote the Langevin equation for each spring. Each spring's equation is coupled to its neighbor springs which produces a matrix of equations to solve.

Langevin Equation

$$m\left(\frac{d\underline{u}}{dt}\right) = -\zeta\left(\underline{u} - \underline{R}\cdot\nabla\underline{v}\right) - 4kT\beta^2\underline{R} + \underline{A}$$

- Rouse found a way to diagonalize the matrix of the averaged Langevin equations; this allowed him to find a Smoluchowski equation for each transformed "mode" $\underline{\tilde{R}}_i$ of the Rouse chain
- Each Smoluchowski equation gives a UCM for each of the modes $\underline{\tilde{R}}_i$

$$\underline{\underline{\tau}} = \sum_{i=1}^{N} \underline{\underline{\tau}}_i \qquad G = \nu kT$$

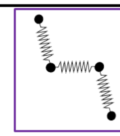
$$\underline{\underline{\tau}}_i + \lambda \overset{\nabla}{\underline{\underline{\tau}}}_i = -G\underline{\underline{I}} \qquad \lambda_i = \frac{\zeta}{16kT\beta^2 \sin^2(i\pi/2(N+1))}$$

Rouse Model for polymer solutions (multi-mode UCM)

Advanced Constitutive Modeling – Molecular modeling

Zimm Model

see Larson, *Constitutive Equations for Polymer Melts*, Butterworths, 1988

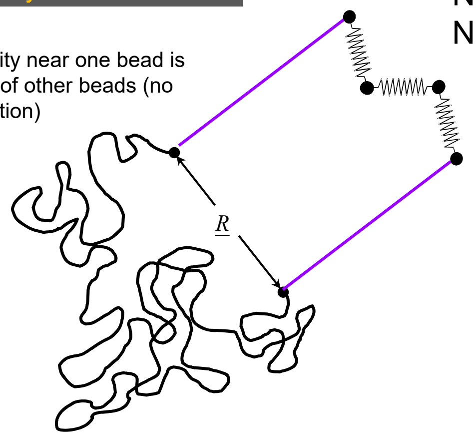


- Multimodal bead-spring model
- Springs represent different sub-molecules
- Drag localized on beads (Stokes)
- Dominant hydrodynamic interaction

N+1beads
N springs

Rouse: solvent velocity near one bead is unaffected by motion of other beads (no hydrodynamic interaction)

Zimm: dominant hydrodynamic interaction)



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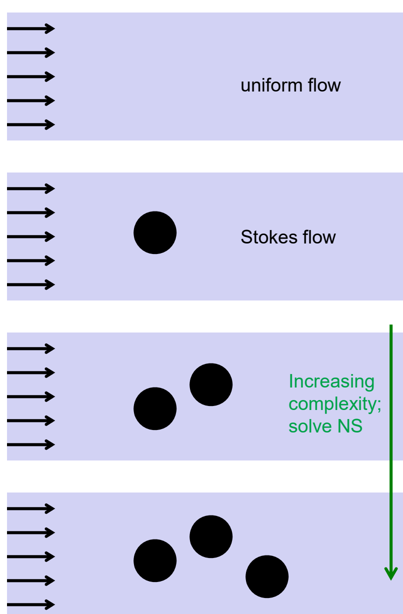
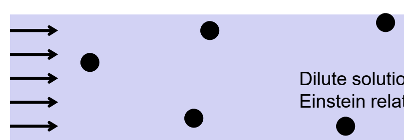
Advanced Constitutive Modeling – Molecular modeling

What about suspensions?

(Mewis and Wagner, *Colloidal Suspension Rheology*, Cambridge 2012)



. . .

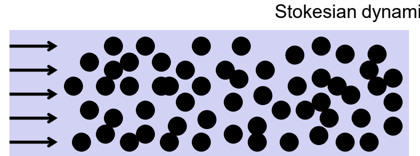


Dilute solution
Einstein relation

$$\eta = \eta_m (1 + 2.5\phi)$$

. . .

Concentrated suspensions
Stokesian dynamics



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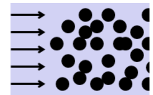
Advanced Constitutive Modeling – Suspensions

Stokesian Dynamics

Brady and Bossis, *Ann. Rev. Fluid Mech*, 20 111 1988
Wagner and Brady, *Phys. Today* 2009, p27



Langevin Equation for Dumbbells

$$m\left(\frac{d\underline{u}}{dt}\right) = -\zeta\left(\underline{u} - \underline{R}\cdot\nabla\underline{v}\right) - 4kT\beta^2\,\underline{R} + \underline{A}$$

Inertia = drag + spring + random (Brownian)

Another Langevin Equation
Stokesian Dynamics for Concentrated Suspensions

$$\underline{\underline{M}}\cdot\frac{d\underline{U}}{dt} = \underline{F}_{hydrodynamic} + \underline{F}_{particle} + \underline{F}_{Brownian}$$

Hydrodynamic = everything the suspending fluid is doing (including drag)
Particle = interparticle forces, gravity (including spring forces)
Brownian = random thermal events

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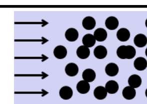
Advanced Constitutive Modeling – Suspensions

Stokesian Dynamics

Brady and Bossis, *Ann. Rev. Fluid Mech*, 20 111 1988

Spanning clusters increase viscosity



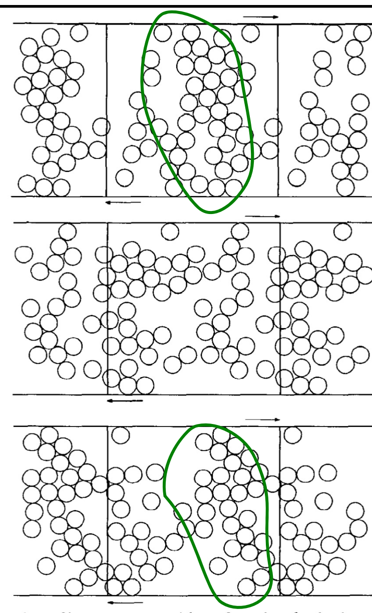


Figure 14 Snapshots of instantaneous particle configurations for the sheared suspension of Figure 13. The sequence (from top to bottom) corresponds in time to that indicated by the arrows in Figure 13. These arrows correspond to the maxima and minima of the viscosity fluctuations. Both the top and bottom frames show the presence of a spanning cluster—a connected path from one wall to the other—and give rise to large viscosities. In the middle frame, no spanning cluster is present and the viscosity is relatively low.

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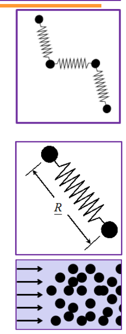
Advanced Constitutive Modeling – Molecular modeling

Summary



Molecular models may lead to familiar constitutive equations

- •Rubber-elasticity theory = Finite-strain Hooke's law model
- •Green-Tobolsky temporary network theory = Lodge equation (UCM)
- •Reptation theory = K-BKZ type equation
- •Elastic dumbbell model for polymer solutions = Oldroyd B equation

Model parameters have greater meaning when connected to a molecular model

- •$G = \nu kT$
- •G_i, λ_i specified by model

Molecular models are essential to narrowing down the choices available in the continuum-based models (e.g. K-BKZ, Rivlin-Sawyers, etc.)

As always, the proof is in the prediction.

see Larson, esp. Ch 7

Modeling may lead directly to information sought (without ever calculating the stress tensor)

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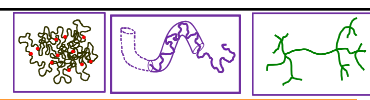
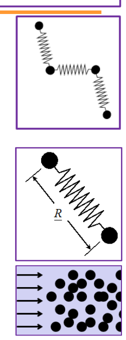
Advanced Constitutive Modeling – Molecular modeling



Summary



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Caution: correct stress predictions do not imply that the molecular model is correct

Stress is proportional to the second moment of $\psi(R)$, but different functions may have the same second moments.

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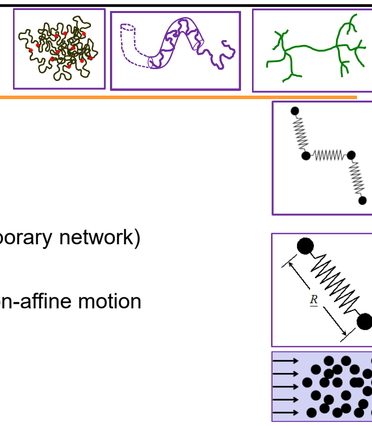
Summary



Materials Discussed

- Elastic solids
- Linear polymer melts with affine motion (temporary network)
- Linear polymer melts with anisotropic drag
- Linear polymer melts with various types of non-affine motion
  - Chain slip
  - Reptation
- Branched melts (pom-pom)
- Polymer solutions
- Suspensions

Resources

R. G. Larson, Constitutive Equations for Polymer Melts
R. G. Larson, The Structure and Rheology of Complex Fljuids
J. Mewis and N. Wagner, Colloidal Suspension Rheology

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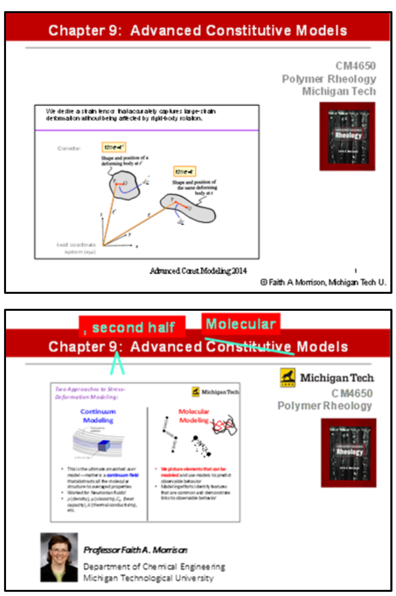
Done with Advanced Constitutive Models



Let's move on to Rheometry

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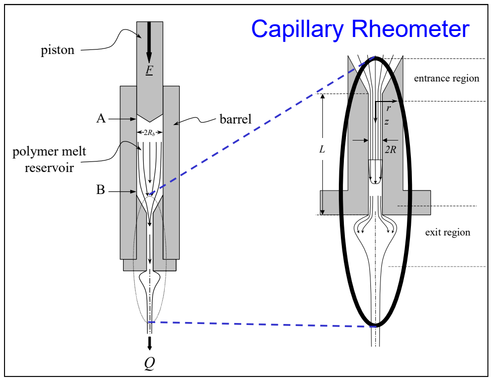
Chapter 10: Rheometry



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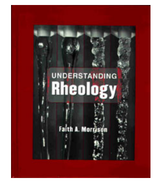
Polymer Rheology



Professor Faith A. Morrison

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Michigan Technological University

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