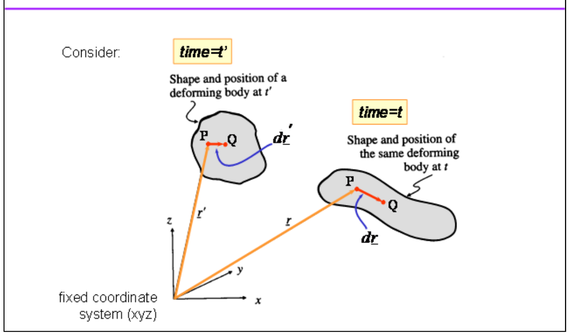
Chapter 9: Advanced Constitutive Models

CM4650
Polymer Rheology
Michigan Tech

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



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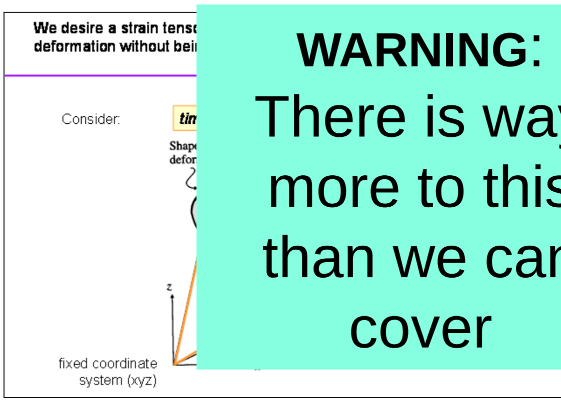

WARNING:
There is way more to this than we can cover

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Advanced Constitutive Modeling

Generalized Linear-Viscoelastic Model:

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

strain-rate tensor

Good only for small strains, small strain-rates

To develop constitutive equations for large strain, large strain-rate flows, the strain and strain history are important.

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

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

(use integration by parts;
see hand calculations)

Generalized Linear-Viscoelastic Model: (strain version)

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

infinitesimal strain tensor

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

memory function

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 $\underline{\underline{\gamma}} \equiv \nabla \underline{u} + \left(\nabla \underline{u}\right)^T$

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

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

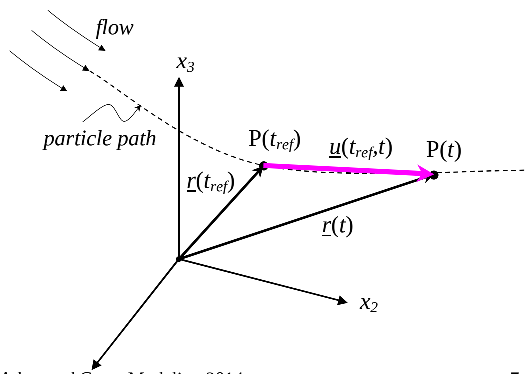
Strain in Shear Flow

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

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

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

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



Deformation in shear flow (strain)

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

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

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

Displacement function in shear

Deformation in shear flow (strain)

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

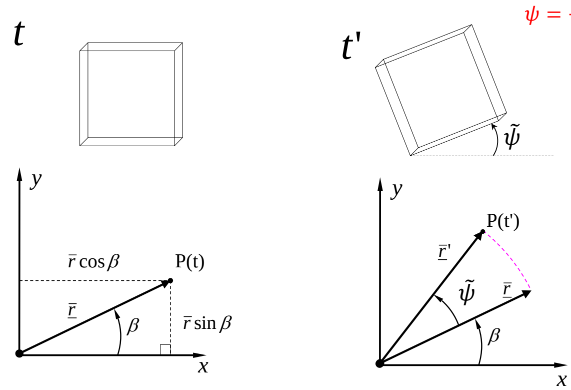
$$\nabla \underline{u} = \begin{pmatrix} 0 & 0 & 0 \\ (t-t_{ref})\dot{\gamma}_0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}_{123}$$

$$\underline{\underline{\gamma}} = \nabla \underline{u} + (\nabla \underline{u})^T = \begin{pmatrix} 0 & (t-t_{ref})\dot{\gamma}_0 & 0 \\ (t-t_{ref})\dot{\gamma}_0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}_{123}$$

Infinitesimal strain tensor in shear

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'?

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

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

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

You try.

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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

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

From definition

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

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

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

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

Stress depends on angle of rotation!

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

Why does GLVE make this erroneous prediction?

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

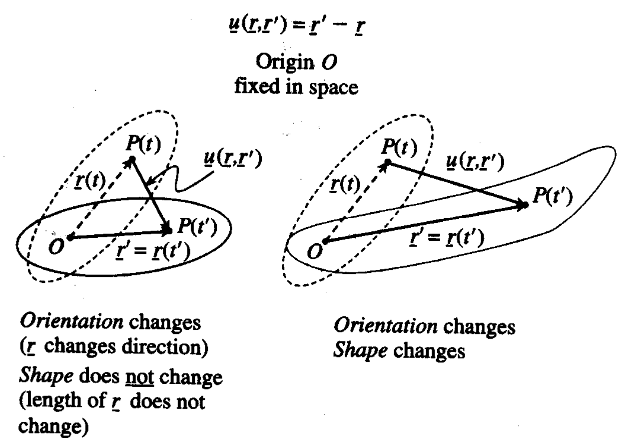
$$\underline{u}(t,t') = \underline{r}(t') - \underline{r}(t)$$

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

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

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

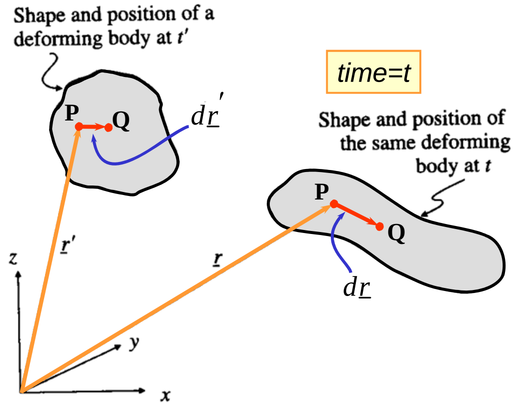
Accounts for changes in shape and orientation.



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

Consider: *time=t'*

time=t



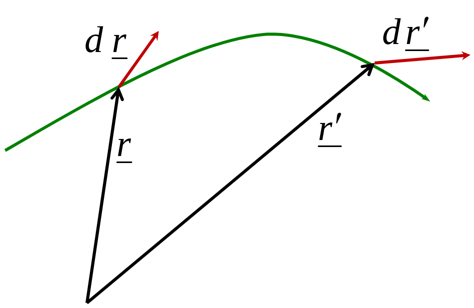
fixed coordinate system (xyz)

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 $\underline{r}$



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

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

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

(chain rule)

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

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

Deformation-gradient tensor

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

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

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

$\Rightarrow ?$

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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

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

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

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

$$\left.\begin{array}{c}\nabla \underline{u}\\ \underline{\underline{\gamma}}\\ \underline{\underline{F}}\\ \underline{\underline{F}}^{-1}\end{array}\right\}$$

All these strain measures include both 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*.

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Polar Decomposition Theorem

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

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

Pure rotation tensor

$$\underline{\underline{U}} = \left(\underline{\underline{A}}^T \cdot \underline{\underline{A}}\right)^{\frac{1}{2}}$$

$$\underline{\underline{V}} = \left(\underline{\underline{A}} \cdot \underline{\underline{A}}^T\right)^{\frac{1}{2}}$$

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

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

Orthogonal tensor

$\underline{\underline{U}}, \underline{\underline{V}}$

Symmetric, nonsingular tensors

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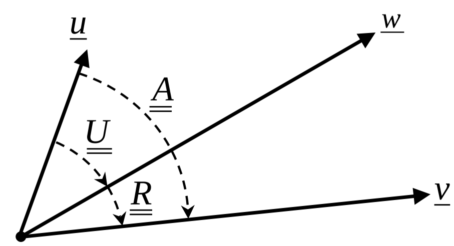
EXAMPLE: Calculate the right stretch tensor and rotation tensor for a given tensor. Calculate the angle through which $\underline{\underline{R}}$ rotates the vector $\underline{u}$.

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



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

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

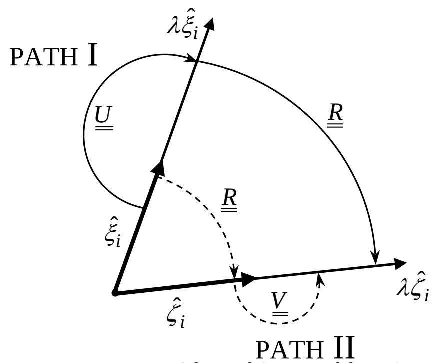
We can further isolate stretch from rotation by considering the *eigenvectors* of $\underline{\underline{U}}$ and $\underline{\underline{V}}$.

eigenvectors / eigenvalues

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

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

Physical Interpretation



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

$$\lambda_n = \nu_n$$

Finite Strain Tensors

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

proposed deformation tensors; contain stretch and rotation

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

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

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

Finite Strain Hooke's Law of elastic solids:

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

(Reference time is 0)

Finite Strain Maxwell Model:

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

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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:

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

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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
$\underline{v}, \varsigma(t)$ *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)

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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 ...

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Traditional "recipe card"

Steady Shear Flow Material Functions

Kinematics:

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

Material Functions:

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

Viscosity

First normal-stress coefficient

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

Second normal-stress coefficient

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

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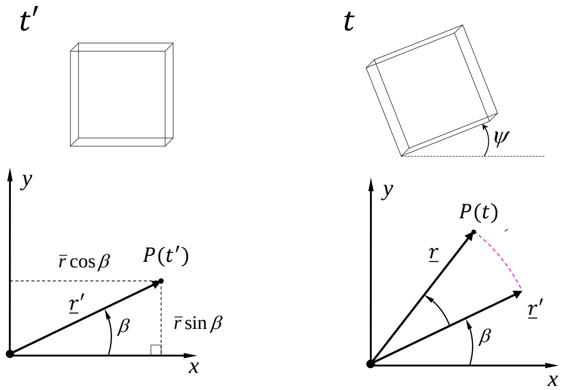
What is the Finger Tensor $\underline{\underline{C}}^{-1}(t',t)$ in CCW Rigid Body Rotation from t' to t through an angle ψ?



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

From geometry

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

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; caption definition of ψ is in error)

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

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Strain-centric "recipe card"

CCW Rigid Body Rotation "Material Functions"

Kinematics:

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

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

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

Material Functions:

There is no such thing since it's not a *flow*! (no deformation)

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

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

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

Traditional "recipe card"

Steady Shear Flow Material Functions

Kinematics:

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

Material Functions:

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

Viscosity

First normal-stress coefficient

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

Second normal-stress coefficient

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

Strain-centric "recipe card"

Steady Shear Flow Material Functions

Kinematics:

$$\underline{v} \equiv \begin{pmatrix} \dot{\varsigma}(t)x_2 \\ 0 \\ 0 \end{pmatrix}_{123} \qquad \dot{\varsigma}(t) = \gamma_0 = \text{constant}$$

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

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

Material Functions:

Viscosity	First normal-stress coefficient	Second normal-stress coefficient
$\eta \equiv \frac{-\tau_{21}}{\dot{\gamma}_0}$	$\Psi_1 \equiv \frac{-(\tau_{11}-\tau_{22})}{\dot{\gamma}_0^2}$	$\Psi_2 \equiv \frac{-(\tau_{22}-\tau_{33})}{\dot{\gamma}_0^2}$

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

From shear kinematics:

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

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

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

(recall sign convention on stress)

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

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

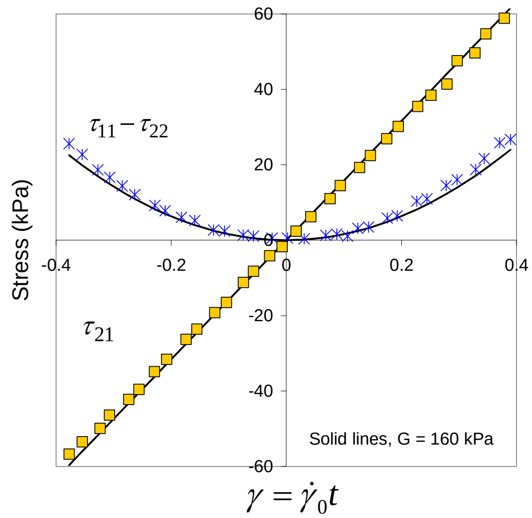

Figure 9.6, p. 325 DeGroot; solid rubber

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

TABLE D.1
Comparison of Nomenclature for Strain Tensors Used in the Literature

Name	This Text	Larson [138]	DPL [26]	Macosko [162]	Middleman [179]
Stress tensor	$\underline{\underline{\Pi}} = \underline{\underline{\tau}} + p\underline{\underline{I}}$	$-\underline{\underline{T}} = -\underline{\underline{\sigma}} + p\underline{\underline{I}}$	$\underline{\underline{\Pi}} = \underline{\underline{\tau}} + p\underline{\underline{I}}$	$-\underline{\underline{T}} = -\underline{\underline{\tau}} + p\underline{\underline{I}}$	$-\underline{\underline{T}} = -\underline{\underline{\tau}} + p\underline{\underline{I}}$
Gradient of a vector	$\nabla \underline{w} = \frac{\partial w_p}{\partial x_k}\hat{e}_k\hat{e}_p$	$\nabla \underline{w} = \frac{\partial w_p}{\partial x_k}\hat{e}_k\hat{e}_p$	$\nabla \underline{w} = \frac{\partial w_p}{\partial x_k}\hat{e}_k\hat{e}_p$	$\bar{\nabla} \underline{w} = \frac{\partial w_p}{\partial x_k}\hat{e}_p\hat{e}_k$	$\bar{\nabla} \underline{w} = \frac{\partial w_p}{\partial x_k}\hat{e}_p\hat{e}_k$
Deformation-gradient tensor	$\underline{\underline{F}}$	$\underline{\underline{F}}$	$\underline{\underline{\Delta}}^T$	$(\underline{\underline{F}}^{-1})^T$	—
Inverse deformation-gradient tensor	$\underline{\underline{F}}^{-1}$	$\underline{\underline{F}}^{-1}$	$\underline{\underline{E}}^T$	$\underline{\underline{F}}^T$	—
Cauchy tensor	$\underline{\underline{C}}$	$\underline{\underline{C}}$	$\underline{\underline{B}}^{-1}$	$\underline{\underline{B}}^{-1}$	—
Finger tensor	$\underline{\underline{C}}^{-1}$	$\underline{\underline{C}}^{-1}$	$\underline{\underline{B}}$	$\underline{\underline{B}}$	—
Finite strain based on Cauchy	$\underline{\underline{\gamma}}^{[0]}$	$\underline{\underline{C}} - \underline{\underline{I}}$	$\underline{\underline{\gamma}}^{[0]}$	$\underline{\underline{B}}^{-1} - \underline{\underline{I}}$	—
Finite strain based on Finger	$\underline{\underline{\gamma}}_{[0]}$	$\underline{\underline{I}} - \underline{\underline{C}}^{-1}$	$\underline{\underline{\gamma}}_{[0]}$	$-\underline{\underline{E}}$	—
Rate-of-strain tensor	$\dot{\underline{\underline{\gamma}}}$	$2\underline{\underline{D}}$	$\dot{\underline{\underline{\gamma}}}$	$2\underline{\underline{D}}$	$\underline{\underline{\Delta}}$
Green tensor	$\underline{\underline{F}}^{-1} \cdot (\underline{\underline{F}}^{-1})^T$	$\underline{\underline{F}}^{-1} \cdot (\underline{\underline{F}}^{-1})^T$	$\underline{\underline{E}}^T \cdot \underline{\underline{E}}$	$\underline{\underline{C}}$	—

Now, let's fix the Maxwell model.

Integral Maxwell model (rate version):

$$\underline{\underline{\tau}} = -\int_{-\infty}^{t} \frac{\eta_0}{\lambda} e^{-\frac{(t-t')}{\lambda}} \dot{\underline{\underline{\gamma}}}(t')\, dt'$$

GLVE model (strain version):

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

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

Integral Maxwell model (strain version):

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

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

what does it predict?

A finite-strain, viscoelastic constitutive equation

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

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

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

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

You try.

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Strain-centric "recipe card"

Steady Shear Flow Material Functions

Kinematics:

$$\underline{v} \equiv \begin{pmatrix} \dot{\varsigma}(t) x_2 \\ 0 \\ 0 \end{pmatrix}_{123} \qquad \dot{\varsigma}(t) = \gamma_0 = \text{constant}$$

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

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

Material Functions:

Viscosity	First normal-stress coefficient	Second normal-stress coefficient
$\eta \equiv \frac{-\tau_{21}}{\dot{\gamma}_0}$	$\Psi_1 \equiv \frac{-(\tau_{11} - \tau_{22})}{\dot{\gamma}_0^2}$	$\Psi_2 \equiv \frac{-(\tau_{22} - \tau_{33})}{\dot{\gamma}_0^2}$

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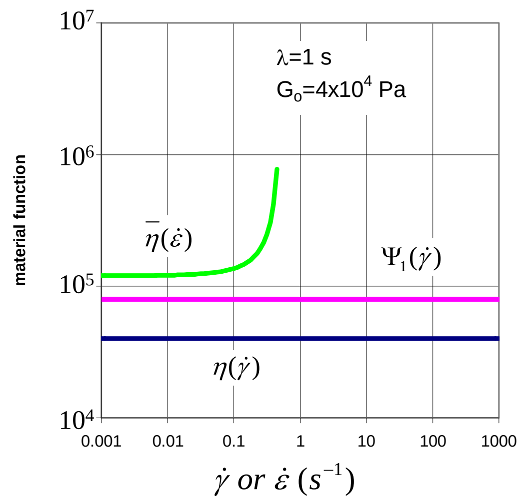
Lodge model



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Needs to become a Strain-centric "recipe card"

Start-up of Steady Shear Flow Material Functions

Kinematics:

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

Material Functions:

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

Shear stress growth function

First normal-stress growth function

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

Second normal-stress growth function

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

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Needs to become a Strain-centric "recipe card"

Cessation of Steady Shear Flow Material Functions

Kinematics:

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

Material Functions:

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

Shear stress decay function

First normal-stress decay function

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

Second normal-stress decay function

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

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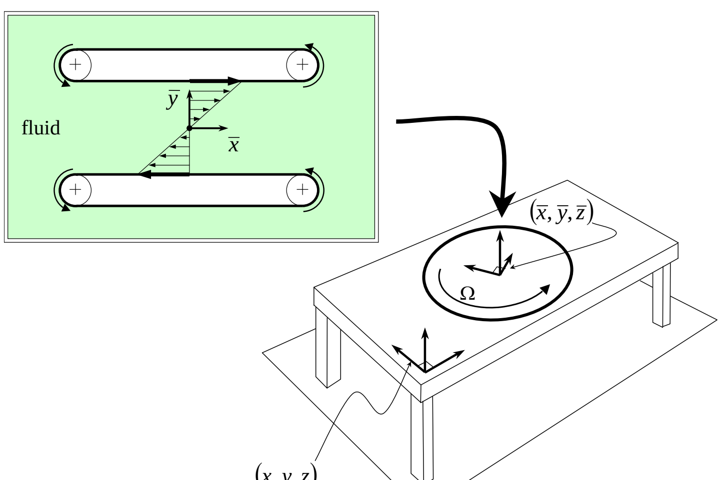
EXAMPLE: Does the Lodge model pass the test of objectivity posed by the turntable example? (remember, the GLVE failed this test)



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Turntable Example

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

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

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

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

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

Lodge prediction: rotating frame

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

Lodge turntable - from stationary frame

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

$S = \sin\Omega t$

$S' = \sin\Omega t'$

$C = \cos\Omega t$

$C' = \cos\Omega t'$

$\gamma = \dot{\gamma}_0(t-t')$

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

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

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

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 (Maxwell with Finger strain tensor) passes test of objectivity

What is the differential form of the Lodge model?

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

$$\frac{d\underline{\underline{\tau}}}{dt} = ?$$

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

(Homework)

EXAMPLE: What is $\frac{\partial \underline{\underline{F}}^{-1}}{\partial t}$?

We can answer by writing the definition of the deformation gradient tensor in Einstein notation. We will also need the chain rule of differentiation.

(after this, use Table 9.1)

Aside: Why did we use $-\underline{\underline{C}}^{-1}(t',t)$ in the Lodge model?

EXAMPLE: What is $\underline{\underline{C}}^{-1}(t,t)$?

EXAMPLE: Define: $\underline{\underline{\gamma}}^{[0]}(t,t') \equiv \underline{\underline{C}} - \underline{\underline{I}}$ What is this strain tensor in the limit of small strains?

Hint: $\nabla \underline{u} = \frac{\partial(\underline{r}' - \underline{r})}{\partial r}$

EXAMPLE: Define: $\underline{\underline{\gamma}}_{[0]}(t,t') \equiv \underline{\underline{I}} - \underline{\underline{C}}^{-1}$ What is this strain tensor in the limit of small strains?

Hint: $\nabla' \underline{u} = \frac{\partial(\underline{r}' - \underline{r})}{\partial r'}$

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(Differential Lodge Equation, continued)

$$\underline{\underline{\tau}} + \lambda \overset{\triangledown}{\underline{\underline{\tau}}} = -\frac{\eta_0}{\lambda} \underline{\underline{I}}$$

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

If we define: $\tilde{\underline{\underline{\tau}}} = \underline{\underline{\tau}} + \frac{\eta_0}{\lambda} \underline{\underline{I}}$ (does not affect practical predictions since only normal stress differences can be measured)

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Note on the total derivative/substantial derivative:

$$\frac{d\underline{\underline{\tau}}(t,x_1,x_2,x_3)}{dt} = \frac{\partial \underline{\underline{\tau}}}{\partial t} + \frac{\partial \underline{\underline{\tau}}}{\partial x_1}\frac{\partial x_1}{\partial t} + \frac{\partial \underline{\underline{\tau}}}{\partial x_2}\frac{\partial x_2}{\partial t} + \frac{\partial \underline{\underline{\tau}}}{\partial x_3}\frac{\partial x_3}{\partial t}$$

$$\frac{d\underline{\underline{\tau}}}{dt} = \frac{\partial \underline{\underline{\tau}}}{\partial t} + \sum_{m=1}^{3} \frac{\partial \underline{\underline{\tau}}}{\partial x_m}\frac{\partial x_m}{\partial t}$$

If the path along which we are taking the derivative is a particle path *(which we have already assumed when conceiving the deformation gradient tensors)*, then

$$\frac{d\underline{\underline{\tau}}}{dt} = \left(\frac{\partial \underline{\underline{\tau}}}{\partial t} + \sum_{m=1}^{3} \frac{\partial \underline{\underline{\tau}}}{\partial x_m} v_m\right) = \left(\frac{\partial \underline{\underline{\tau}}}{\partial t} + \underline{v}\cdot\nabla\underline{\underline{\tau}}\right) = \frac{D\underline{\underline{\tau}}}{Dt}$$

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Differential Lodge Equation (Upper Convected Maxwell Model)

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

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

upper-convected time derivative

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

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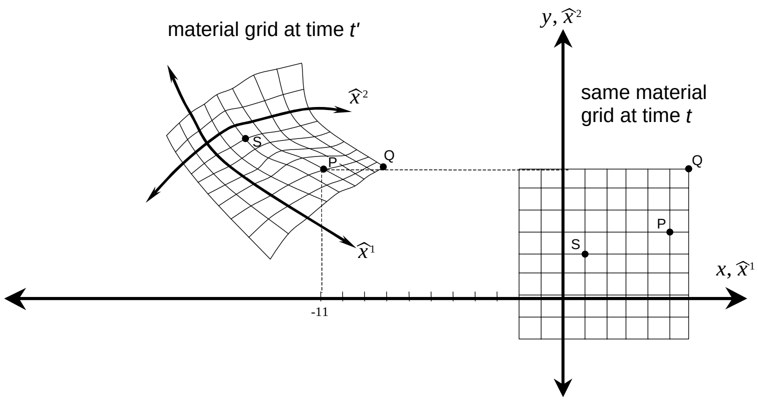
The *Upper-Convected time derivative* can be understood to be the time derivative calculated in a coordinate system that is translating and deforming with the fluid (see section 9.3).



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

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

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

Lodge Model:
(upper-convected Maxwell)

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

Cauchy-Maxwell Model:
(lower-convected Maxwell)

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

Lodge Rubberlike Liquid Model:

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

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	$\eta(\dot\gamma)$	$\eta_0 = G_0\lambda$
	$\Psi_1(\dot\gamma)$	$2G_0\lambda^2 = 2\eta_0\lambda$
	$\Psi_2(\dot\gamma)$	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 $\bar\eta_B^+(t,\dot\epsilon_0)$	$\frac{\eta_0}{\mathcal{A}\mathcal{B}}\left(3-2\mathcal{B}e^{-\frac{\mathcal{A}t}{\lambda}}-\mathcal{A}e^{-\frac{\mathcal{B}t}{\lambda}}\right)$; $\mathcal{A}=1-2\dot\epsilon_0\lambda$; $\mathcal{B}=1+\dot\epsilon_0\lambda$
Planar ($b=1, \dot\epsilon_0>0$)	$\bar\eta_{P_1}^+(t,\dot\epsilon_0)$	$\frac{2\eta_0}{\mathcal{A}C}\left(2-\mathcal{A}e^{-\frac{Ct}{\lambda}}-Ce^{-\frac{\mathcal{A}t}{\lambda}}\right)$; $\mathcal{A}=1-2\dot\epsilon_0\lambda$; $C=1+2\dot\epsilon_0\lambda$
	$\bar\eta_{P_2}^+(t,\dot\epsilon_0)$	$\frac{2\eta_0}{C}\left(1-e^{-\frac{Ct}{\lambda}}\right)$
Steady		
Uniaxial ($b=0, \dot\epsilon_0>0$) or biaxial ($b=0, \dot\epsilon_0<0$)	$\bar\eta(\dot\epsilon_0)$ or $\bar\eta_B(\dot\epsilon_0)$	$\frac{3\eta_0}{(1-2\lambda\dot\epsilon_0)(1+\lambda\dot\epsilon_0)} = \frac{3\eta_0}{\mathcal{A}\mathcal{B}}$
Planar ($b=1, \dot\epsilon_0>0$)	$\bar\eta_{P_1}(\dot\epsilon_0)$	$\frac{4\eta_0}{1-4\dot\epsilon_0^2\lambda^2} = \frac{4\eta_0}{\mathcal{A}C}$
	$\bar\eta_{P_2}(\dot\epsilon_0)$	$\frac{2\eta_0}{1+2\dot\epsilon_0\lambda} = \frac{2\eta_0}{C}$

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	$\eta(\dot\gamma)$	$\eta_0=G_0\lambda$
	$\Psi_1(\dot\gamma)$	$2G_0\lambda^2=2\eta_0\lambda$
	$\Psi_2(\dot\gamma)$	$-\Psi_1$
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	$G(t,\gamma_0)$	$G_0e^{-\frac{t}{\lambda}}$
	$G_{\Psi_1}(t,\gamma_0)$	$G_0e^{-\frac{t}{\lambda}}$
	$G_{\Psi_2}(t,\gamma_0)$	$-G_{\Psi_1}$
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 $\bar\eta_B^+(t,\dot\epsilon_0)$	$\frac{\eta_0}{\mathcal{C}\mathcal{D}}\left(3-2\mathcal{D}e^{-\frac{\mathcal{C}t}{\lambda}}-\mathcal{C}e^{-\frac{\mathcal{D}t}{\lambda}}\right)$; $\mathcal{C}=1+2\dot\epsilon_0\lambda$, $\mathcal{D}=1-\dot\epsilon_0\lambda$
Planar ($b=1,\dot\epsilon_0>0$)	$\bar\eta_{P_1}^+(t,\dot\epsilon_0)$	$\frac{-2\eta_0}{\mathcal{A}\mathcal{C}}\left(2-\mathcal{A}e^{-\frac{\mathcal{C}t}{\lambda}}-\mathcal{C}e^{-\frac{\mathcal{A}t}{\lambda}}\right)$; $\mathcal{A}=1-2\dot\epsilon_0\lambda$
	$\bar\eta_{P_2}^+(t,\dot\epsilon_0)$	$\frac{-2\eta_0}{\mathcal{A}}\left(1-e^{-\frac{\mathcal{A}t}{\lambda}}\right)$
Steady		
Uniaxial ($b=0,\dot\epsilon_0>0$) or biaxial ($b=0,\dot\epsilon_0<0$)	$\bar\eta(\dot\epsilon_0)$ or $\bar\eta_B(\dot\epsilon_0)$	$\frac{3\eta_0}{(1+2\lambda\dot\epsilon_0)(1-\lambda\dot\epsilon_0)}=\frac{3\eta_0}{\mathcal{C}\mathcal{D}}$
Planar ($b=1,\dot\epsilon_0>0$)	$\bar\eta_{P_1}(\dot\epsilon_0)$	$\frac{-4\eta_0}{1-4\dot\epsilon_0^2\lambda^2}=\frac{-4\eta_0}{\mathcal{A}\mathcal{C}}$
	$\bar\eta_{P_2}(\dot\epsilon_0)$	$\frac{-2\eta_0}{1-2\dot\epsilon_0\lambda}=\frac{-2\eta_0}{\mathcal{A}}$

Approaches to finite-strain constitutive equations

non-objective time derivative

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

equivalent

differential Maxwell model

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

integral Maxwell model

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

non-objective strain measure

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

Methods of Improving Constitutive Equations

Maxwell Model

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

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

We can improve with new time derivatives or new strain measures.

We can also change the basic equation:

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

Other Constitutive Approaches

Simple Maxwell Model, shear

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

Upper-Convected Maxwell Model, general

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

---

retardation time

Simple Jeffreys Model, shear

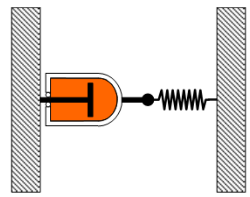
$$\tau_{21} + \lambda_1 \frac{\partial \tau_{21}}{\partial t} = -\eta_0 \left(\dot{\gamma}_{21} + \lambda_2 \frac{\partial \dot{\gamma}_{21}}{\partial t} \right)$$

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

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

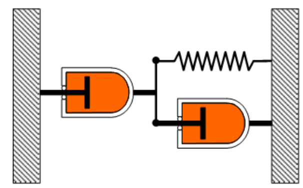
Maxwell Model - Mechanical Analog

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



Jeffreys Model - Mechanical Analog

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



Unfortunately, this change only modifies G(t-t');
the Jeffreys Model is a GLVE model

Simple Jeffreys Model (not frame-invariant) $\underline{\underline{\tau}} + \lambda_1 \frac{\partial \underline{\underline{\tau}}}{\partial t} = -\eta_0 \left(\underline{\underline{\dot{\gamma}}} + \lambda_2 \frac{\partial \underline{\underline{\dot{\gamma}}}}{\partial t} \right)$

Now, solving for τ_{21} explicitly we obtain,

$$\underline{\underline{\tau}}(t) = -\int_{-\infty}^{t} \underbrace{\left[\frac{\eta_0}{\lambda_1} \left(1 - \frac{\lambda_2}{\lambda_1} \right) e^{-\frac{t-t'}{\lambda_1}} + \frac{2\eta_0 \lambda_2}{\lambda_1} \delta(t-t') \right]}_{G(t-t')} \underline{\underline{\dot{\gamma}}}(t')dt'$$

Other linear modifications of the Maxwell model motivated by springs and dashpots in series and parallel modify G(t-t') but do not otherwise introduce new behavior.

(Might as well use the Generalized Maxwell model)

Non-linear modifications of the Maxwell Model

White-Metzner Model

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

Oldroyd 8-Constant Model

$$\underline{\underline{\tau}} + \lambda_1 \overset{\triangledown}{\underline{\underline{\tau}}} + \frac{1}{2}(\lambda_1 - \mu_1)\left(\underline{\underline{\dot{\gamma}}}\cdot\underline{\underline{\tau}} + \underline{\underline{\tau}}\cdot\underline{\underline{\dot{\gamma}}}\right) + \frac{1}{2}\mu_0\left(\mathrm{tr}\,\underline{\underline{\tau}}\right)\underline{\underline{\dot{\gamma}}} + \frac{1}{2}\nu_1\left(\underline{\underline{\tau}}:\underline{\underline{\dot{\gamma}}}\right)\underline{\underline{I}}$$

$$= -\eta_0\left(\underline{\underline{\dot{\gamma}}} + \lambda_2 \overset{\triangledown}{\underline{\underline{\dot{\gamma}}}} + (\lambda_2 - \mu_2)\left(\underline{\underline{\dot{\gamma}}}:\underline{\underline{\dot{\gamma}}}\right) + \frac{1}{2}\nu_2\left(\underline{\underline{\dot{\gamma}}}:\underline{\underline{\dot{\gamma}}}\right)\underline{\underline{I}}\right)$$

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

UCM

UCM + terms = UCJ

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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 ($b = 1, \dot{\epsilon}_0 > 0$)	$\bar{\eta}_{P_1}(\dot{\epsilon}_0)$	$\frac{4\eta(\dot{\gamma})}{1-4\dot{\epsilon}_0^2\lambda(\dot{\gamma})^2} = \frac{4\eta(\dot{\gamma})}{\mathcal{A}(\dot{\gamma})\mathcal{C}(\dot{\gamma})}$; $\mathcal{A}(\dot{\gamma}) = 1 - 2\dot{\epsilon}_0\lambda(\dot{\gamma})$; $\mathcal{C}(\dot{\gamma}) = 1 + 2\dot{\epsilon}_0\lambda(\dot{\gamma})$
	$\bar{\eta}_{P_2}(\dot{\epsilon}_0)$	$\frac{2\eta(\dot{\gamma})}{1+2\dot{\epsilon}_0\lambda(\dot{\gamma})} = \frac{2\eta(\dot{\gamma})}{\mathcal{C}(\dot{\gamma})}$

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

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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 ($b=1,\dot\epsilon_0>0$)	$\bar\eta_{P_1}^+(t,\dot\epsilon_0)$	$4\eta_0\frac{\lambda_2}{\lambda_1}+\frac{2\eta_0}{\mathcal{A}\mathcal{C}}\left(1-\frac{\lambda_2}{\lambda_1}\right)\left(2-\mathcal{A}e^{-\frac{t\mathcal{C}}{\lambda_1}}-\mathcal{C}e^{-\frac{t\mathcal{A}}{\lambda_1}}\right)$; $\mathcal{A}=1-2\dot\epsilon_0\lambda_1$, $\mathcal{C}=1+2\dot\epsilon_0\lambda_1$
	$\bar\eta_{P_2}^+(t,\dot\epsilon_0)$	$2\eta_0\frac{\lambda_2}{\lambda_1}+\frac{2\eta_0}{\mathcal{C}}\left(1-\frac{\lambda_2}{\lambda_1}\right)\left(1-e^{-\frac{t\mathcal{C}}{\lambda_1}}\right)$
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 ($b=1,\dot\epsilon_0>0$)	$\bar\eta_{P_1}(\dot\epsilon_0)$	$4\eta_0\left(\frac{\lambda_2}{\lambda_1}+\frac{1-\frac{\lambda_2}{\lambda_1}}{\mathcal{A}\mathcal{C}}\right)$
		$2\eta_0\left(\frac{\lambda_2}{\lambda_1}+\frac{1-\frac{\lambda_2}{\lambda_1}}{\mathcal{C}}\right)$

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.

$$\underline{\underline{\tau}}+\lambda_1\overset{\nabla}{\underline{\underline{\tau}}}+\frac{1}{2}(\lambda_1-\mu_1)\left(\dot{\underline{\underline{\gamma}}}\cdot\underline{\underline{\tau}}+\underline{\underline{\tau}}\cdot\dot{\underline{\underline{\gamma}}}\right)+\frac{1}{2}\mu_0\left(\mathrm{tr}\,\underline{\underline{\tau}}\right)\dot{\underline{\underline{\gamma}}}+\frac{1}{2}\nu_1\left(\underline{\underline{\tau}}:\dot{\underline{\underline{\gamma}}}\right)\underline{\underline{I}}$$

$$=-\eta_0\left(\dot{\underline{\underline{\gamma}}}+\lambda_2\overset{\nabla}{\dot{\underline{\underline{\gamma}}}}+(\lambda_2-\mu_2)\left(\dot{\underline{\underline{\gamma}}}:\dot{\underline{\underline{\gamma}}}\right)+\frac{1}{2}\nu_2\left(\dot{\underline{\underline{\gamma}}}:\dot{\underline{\underline{\gamma}}}\right)\underline{\underline{I}}\right)$$

Giesekus Model

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

quadratic
in stress

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

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).

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.

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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 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 second.
- 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

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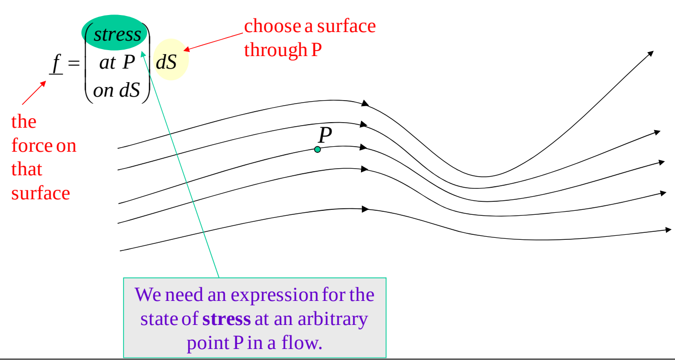
Molecular Constitutive Modeling

- •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)

At the beginning of the course . . .

Chapter 3: Newtonian Fluid Mechanics Polymer Rheology

Molecular Forces (contact) – this is the tough one

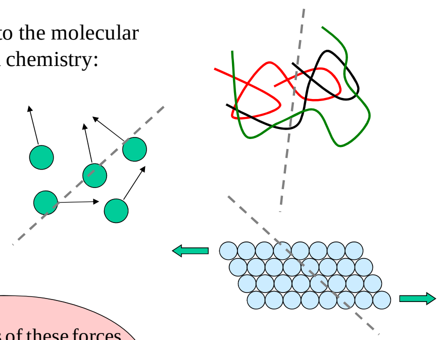


At the beginning of the course . . .

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.

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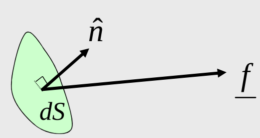
At the beginning of the course . . .

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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At the beginning of the course . . .

Molecular Forces *(continued)*

Assembling the force vector:

$$\underline{f} = dS\ \hat{n}\cdot\big[\Pi_{11}\hat{e}_1\hat{e}_1 + \Pi_{21}\hat{e}_2\hat{e}_1 + \Pi_{31}\hat{e}_3\hat{e}_1 + \Pi_{12}\hat{e}_1\hat{e}_2 + \Pi_{22}\hat{e}_2\hat{e}_2 + \Pi_{32}\hat{e}_3\hat{e}_2 + \Pi_{13}\hat{e}_1\hat{e}_3 + \Pi_{23}\hat{e}_2\hat{e}_3 + \Pi_{33}\hat{e}_3\hat{e}_3\big]$$

$$= dS\ \hat{n}\cdot\sum_{p=1}^{3}\sum_{m=1}^{3}\Pi_{pm}\hat{e}_p\hat{e}_m$$

$$= dS\ \hat{n}\cdot\Pi_{pm}\hat{e}_p\hat{e}_m$$

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

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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Long-Chain Polymer Constitutive Modeling

molecular tension force on arbitrary surface

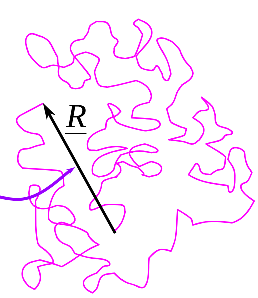
$$\underline{\tilde{f}} = dA\ \hat{n}\cdot(-\underline{\underline{\tau}})$$

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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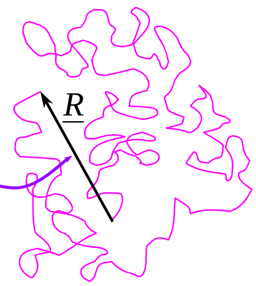
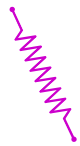
Polymer coil responds to deformation

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.

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

Molecular force generated by deforming chain

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

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

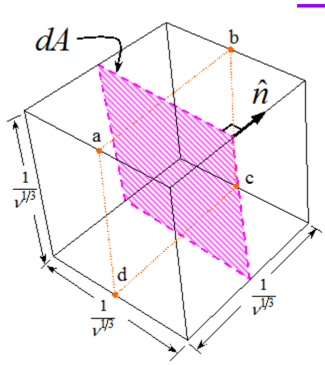
$(\hat{n}\cdot\underline{R})\nu^{\frac{1}{3}}$ (see next slide)

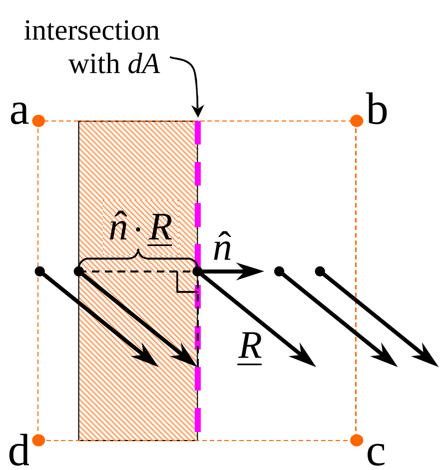
$\psi(\underline{R})dR_1 dR_2 dR_3$

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

ν = number of polymer chains per unit volume

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

Molecular force generated by deforming chain

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

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

BUT, from before . . .

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

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

Comparing these two we conclude,

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

Molecular force generated by deforming chain

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How can we convert this equation,

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

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

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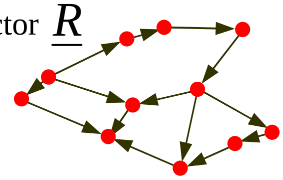
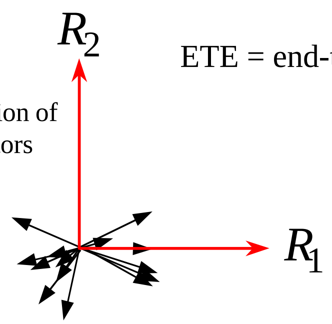
Elastic (Crosslinked) Solid

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

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



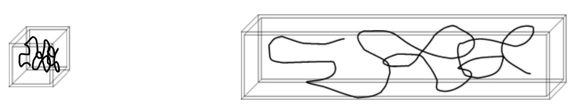
Distribution of ETE vectors



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

AN ANSWER: <u>affine-motion</u> assumption: the macroscopic dimension changes are proportional to the microscopic dimension changes

before *after*



Consider a general elongational deformation:

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

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

ETE after

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

ETE before

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

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

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

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

But, where do we get this?

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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.

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

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

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

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

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

(much algebra omitted; solved in Problem 9.57)

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

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.

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

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

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

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

- 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

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

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

What is the probability that a strand retains the same ETE vector between *t'* and *t'*+*Δt*?

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

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

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

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

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

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

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

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

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

Green-Tobolsky temporary network mode (Lodge model)

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Oh no, back where we started!

NO!

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

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

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 $\frac{\underline{\underline{B}}}{\lambda}$. 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 $$\underline{\underline{\tau}} + \lambda \overset{\nabla}{\underline{\underline{\tau}}} + \frac{\alpha\lambda}{\eta_0}\underline{\underline{\tau}} : \underline{\underline{\tau}} = -\eta_0 \dot{\underline{\underline{\gamma}}}$$

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

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

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

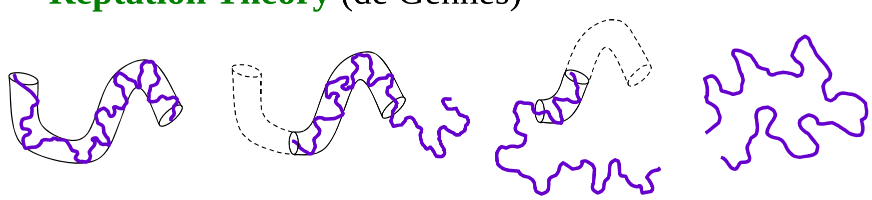
- Phan-Thien/Tanner
- Johnson-Segalman

Larson: uses nonaffine motion that is a generalization of the motion in the Doi Edwards model; see Larson, Chapter 5

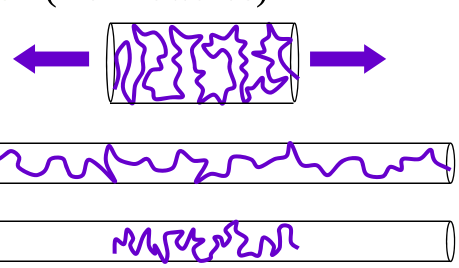
Wagner: uses irreversible nonaffine motion; see Larson, Chapter 5

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

Reptation Theory (de Gennes)



Retraction (Doi-Edwards)



Non-affine motion

Step shear strain - *strain dependence*

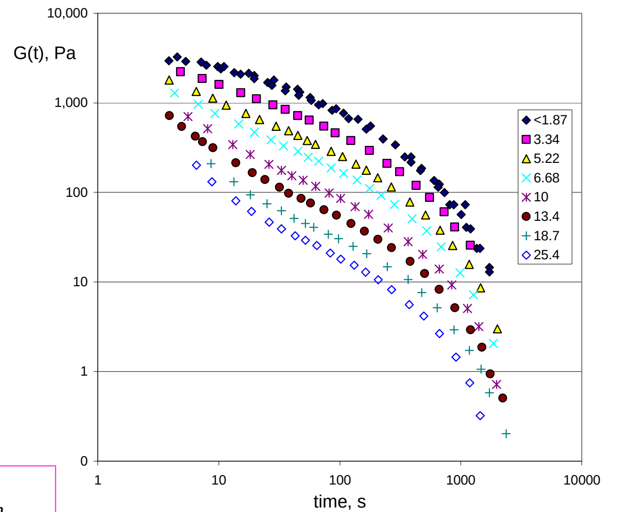
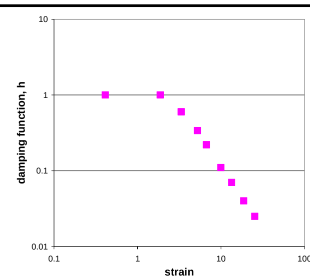
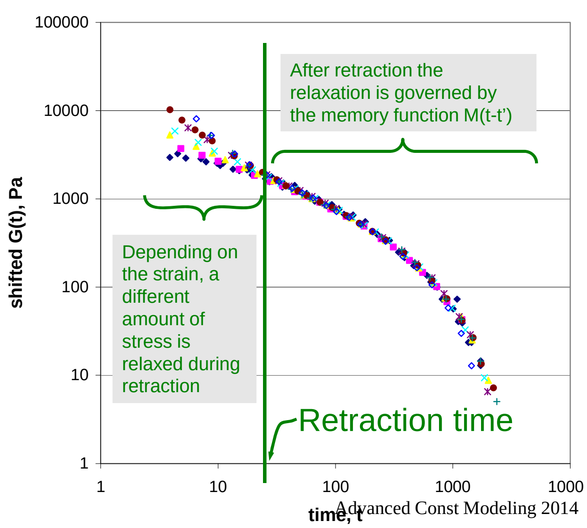


Figure 6.57, p. 212
Einaga et al.; PS soln

Step shear strain - **Damping Function**





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

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

Doi-Edwards Model

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

Predicts a strain measure

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

Predicts a relaxation time distribution

Predicts a memory function

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

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

(Factorized K-BKZ type)

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)

Doi-Edwards Model
Steady Shear
SAOS

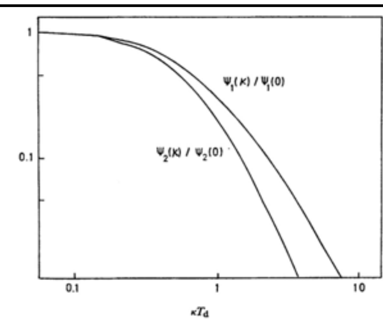


FIG. 5.—First and the second normal stress coefficients $\psi_1(\kappa)$ and $\psi_2(\kappa)$ in steady shear flow. [Note that $\psi_2(0) < 0$, so that $\psi_2(\kappa) < 0$].

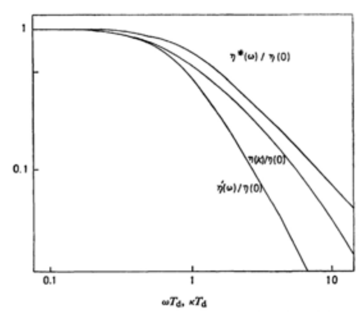


FIG. 3.—Non-linear viscosity $\eta(\kappa)$ in steady state, the modulus, $|\eta^*(\omega)|$, and the real part, $\eta'(\omega)$ of the linear dynamic viscosity. All quantities are normalized by the steady state viscosity at zero shear rate, $\eta(0)$.

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

Doi-Edwards Model
Shear Start Up

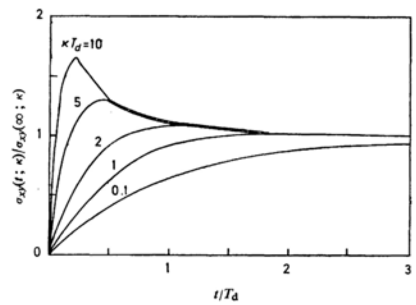


FIG. 6.—Shear stress when a shear flow is started at $t = 0$ with shear rate κ.

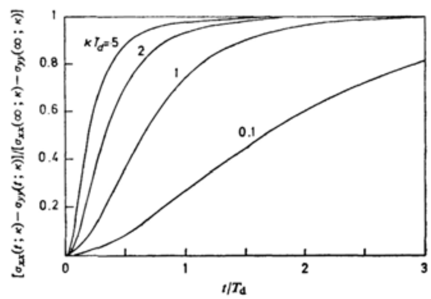


FIG. 7.—Growth of the first normal stress component when a shear flow is started at $t = 0$ with shear rate κ.

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

Doi-Edwards Model
Steady Elongation
Elongation Startup

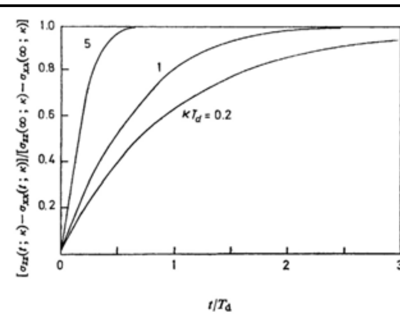


FIG. 13.—Growth of stress when an elongational flow is started at $t = 0$.

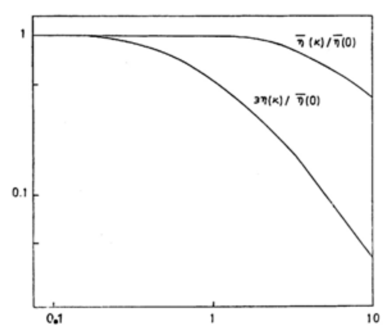


FIG. 12.—Steady elongational viscosity $\bar{\eta}(\kappa)$ and the steady shear viscosity $3\eta(\kappa)$. Both are normalized by $\bar{\eta}(0) = 3\eta(0)$.

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

Doi-Edwards Model
Large-Amplitude Step Shear

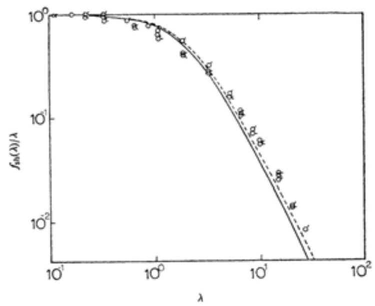


FIG. 6.—Strain dependent part of the stress relaxation function for simple shear [eqn (6.7)]. Circles, observed values [after ref. (11): sample, polystyrene solution in diethyl phthalate; molecular weight, 3×10^6; concentration, ◌ 0.166 g cm^{-3}, ○ 0.221 g cm^{-3}, ◌ 0.275 g cm^{-3}]. Solid curve, eqn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

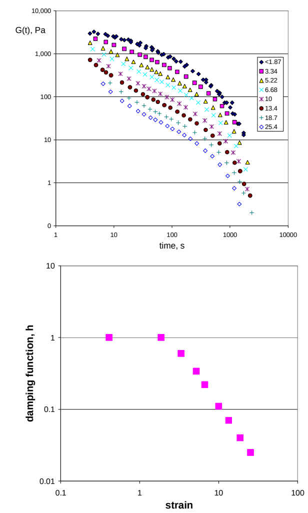


Figure 6.58, p. 213 Einaga et al.; PS soln

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

Doi-Edwards Model

Correctly predicts:

- Ratio of Ψ_1/Ψ_2
- shape of start-up curves
- shape of $h(\gamma_0)$ (nonlinear step strain, damping function)
- predicts $\eta = AM^3$
- !!!! shear thinning of η, Ψ_1
- tension-thinning elongational viscosity

Fails to predict:

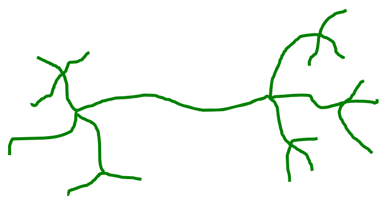
- $\eta = AM^{3.4}$
- shape of shear thinning of η, Ψ_1
- reversing flows
- Elongational strain hardening (branched polymers)

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

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)

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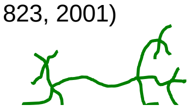
Extended Pom-Pom (Verbeeten, Peters, and Baaijens, *JOR* 45 823, 2001)



Predicts elongational strain hardening

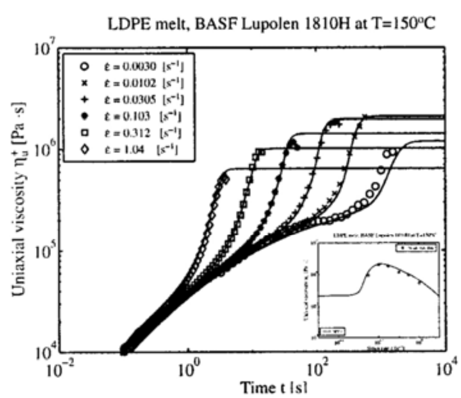


FIG. 5. Transient and quasisteady state (*inset*) uniaxial elongational viscosity η_u of the XPP model for Lupolen 1810H melt at $T = 150\,°C$. $\nu_i = 2/q_i$, $\varepsilon = 0.0030,\ 0.0102,\ 0.0305,\ 0.103,\ 0.312,\ 1.04\ s^{-1}$.

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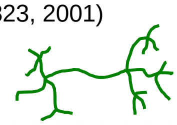
Extended Pom-Pom (Verbeeten, Peters, and Baaijens, *JOR* 45 823, 2001)



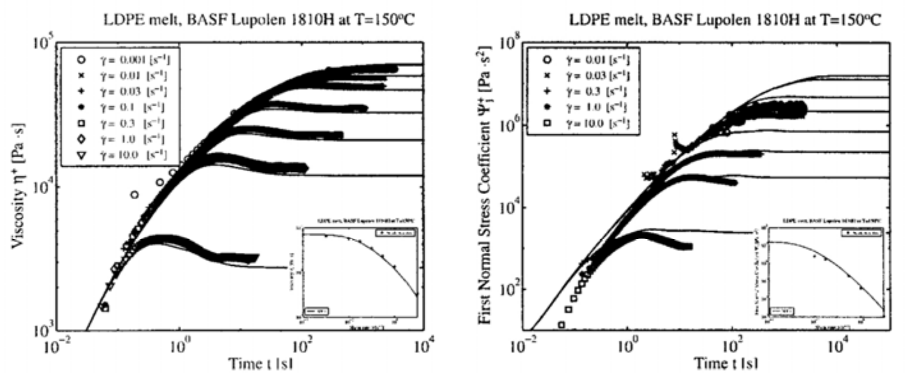


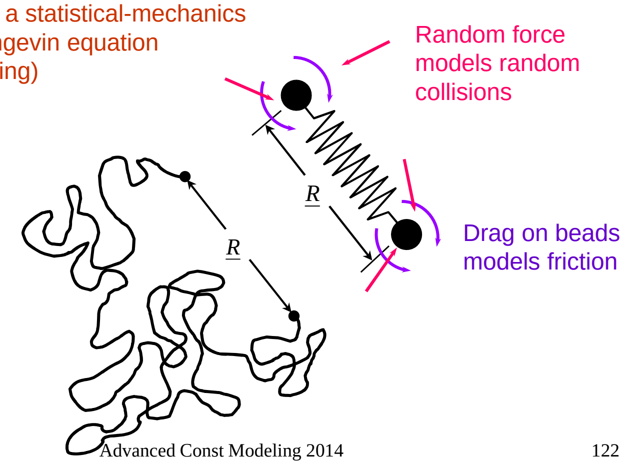
FIG. 8. Transient and steady state (*inset*) shear viscosity η (*left*) and first normal stress coefficient Ψ_1 (*right*) of the XPP model for Lupolen 1810H melt at $T = 150\,°\mathrm{C}$. $\nu_i = 2/q_i$. $\gamma = 0.001, 0.01, 0.03, 0.1, 0.3, 1, 10\ \mathrm{s}^{-1}$.

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



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*

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)

Integration yields:

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

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

Upper-Convected Maxwell 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

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Elastic Dumbbell Model for Dilute Polymer Solutions

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

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

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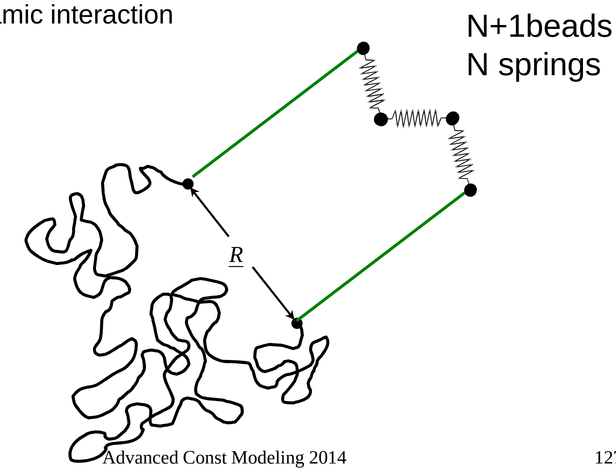
Rouse Model

- 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)

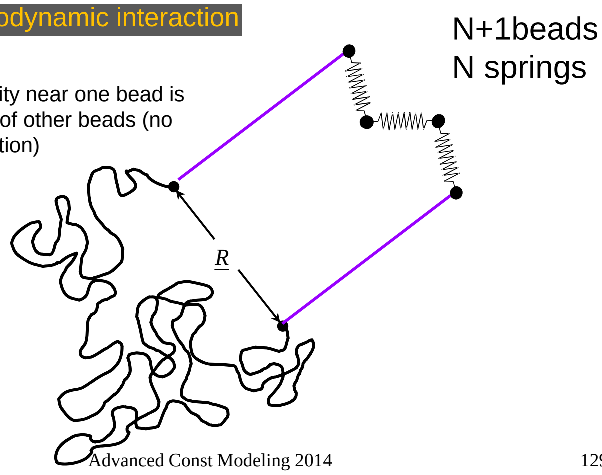
Zimm Model

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

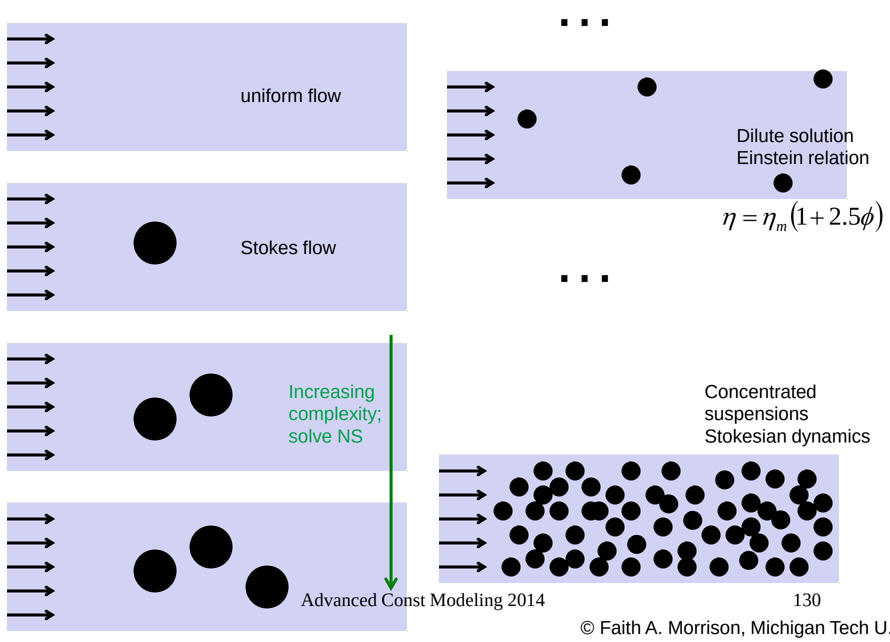
Rouse: solvent velocity near one bead is unaffected by motion of other beads (no hydrodynamic interaction)

Zimm: dominant hydrodynamic interaction)



What about suspensions?

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



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

Stokesian Dynamics

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

Stokesian Dynamics

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

Spanning clusters increase viscosity

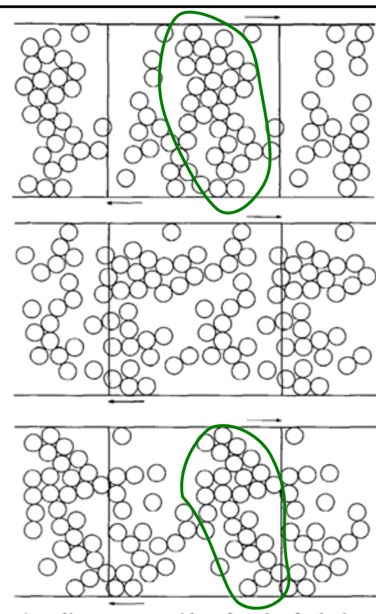


Figure 14 Snapshots of instantaneous particle configurations for the sheared suspension of Figure 13. The sequence (from top to bottom) corresponds in time to that indicated by the arrows in Figure 13. These arrows correspond to the maxima and minima of the viscosity fluctuations. Both the top and bottom 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.

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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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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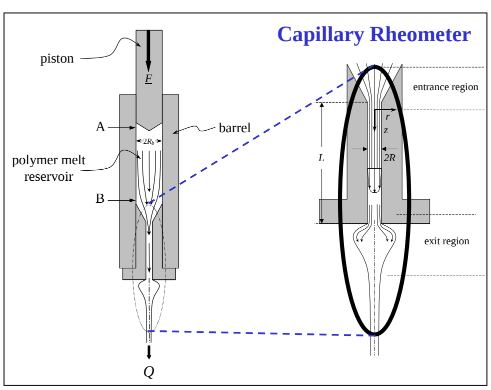
Chapter 10: Rheometry

CM4650
Polymer Rheology
Michigan Tech



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