CM4650 Polymer Rheology

Just-in-time

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What exactly do we observe when we subject non-Newtonian fluids to deformation?

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Part II-A. Continuum versus molecular modeling

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What exactly do we observe when we subject non-Newtonian fluids to deformation?

Rheology uses a sort of an ASTM or ISO-like technical standards approach to organize observations:

1. *Choose a standard flow (shear or elongation)*
2. *Choose a set of flow kinematics (the speed and time-profile of the specific test)*
3. *Measure specified quantities (related to stress or deformation)*
4. *Report a standardized function (material function)*

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What exactly do we observe when we subject non-Newtonian fluids to deformation?

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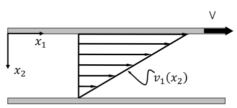
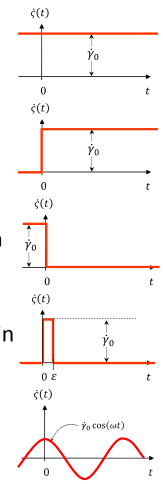
Standard flow	$\dot{\varsigma}(t) =$ Standard kinematics	What do we observe?
Shear	a) Steady b) Start-up c) Cessation d) Step-strain e) SAOS*	Shear Material Functions

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





(*SAOS=small-amplitude oscillatory shear)

What exactly do we observe when we subject non-Newtonian fluids to deformation?

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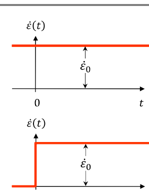
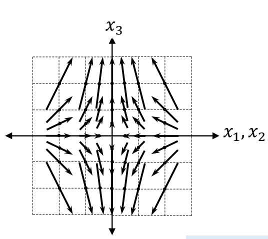
Standard flow	$\dot{\varepsilon}(t) =$ Standard kinematics	What do we observe?
Elongation	a) Steady b) Start-up	Elongation Material Functions

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



(etc.)



Note: the Society of Rheology convention has flow in the 1-direction rather than the 3-direction.

What exactly do we observe when we subject non-Newtonian fluids to deformation?

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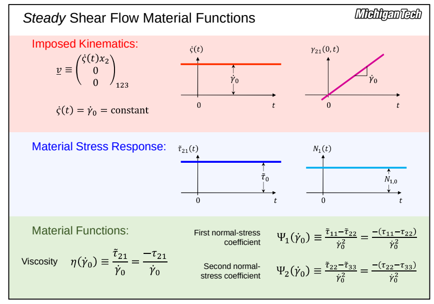
Material Functions

Summarized on "recipe cards"



- Vocabulary (framework) of material comparison
- Used to characterize a material as Newtonian vs. non-Newtonian

Newtonian	Non-Newtonian
$\eta = \mu = \text{constant}$	$\eta = \eta(\dot{\gamma})$
$\Psi_1 = \Psi_2 = 0$	$\Psi_1 \neq 0; \Psi_2 \neq 0$
$G' = 0$	$G', G'' \neq 0$
etc.	etc.

What exactly do we observe when we subject non-Newtonian fluids to deformation?

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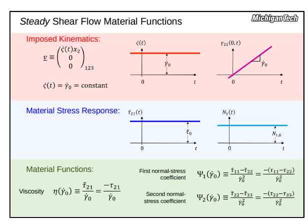

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$G' = 0$	$G', G'' \neq 0$
etc.	etc.

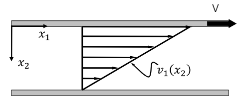
- Within non-Newtonian fluids, used to further categorize materials

  Cross-linked rubber: $G' = G_0 = \text{constant}$
  Entangled melt: characteristic $G'(\omega), G''(\omega)$ shapes
  Shear thinning, shear thickening melt: characteristic $\eta(\dot{\gamma})$
  Branched polymer: characteristic $G'(\omega), G''(\omega)$ shapes

Part II-A. Continuum versus molecular modeling

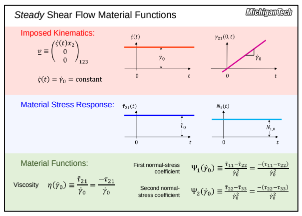
Shear Material Functions

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

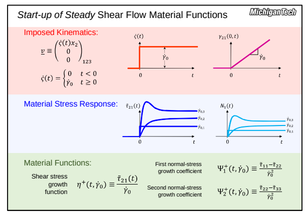


"Recipe cards"

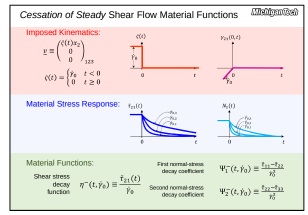
a) Steady



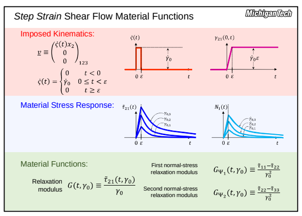
b) Start-up



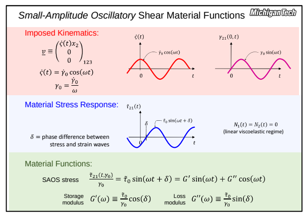
c) Cessation



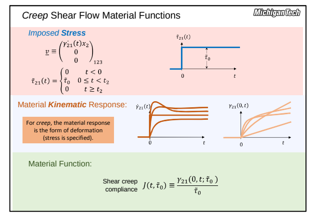
d) Step strain



e) SAOS



f) Creep



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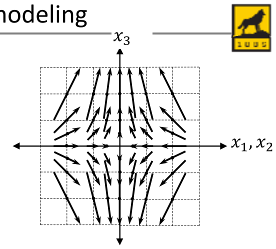
Part II-A. Continuum versus molecular modeling

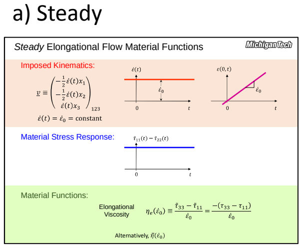
Elongation Material Functions

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

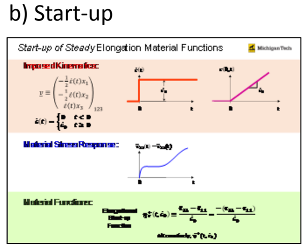


"Recipe cards"

a) Steady



b) Start-up



c) Cessation

(currently unobservable)

d) Step strain

(exists, but less often discussed)

e) SAOE

(exists, but easily converted to SAOS so is redundant)

f) Creep

(exists)

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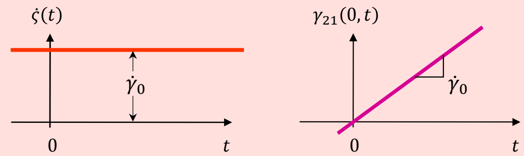
Steady Shear Flow Material Functions

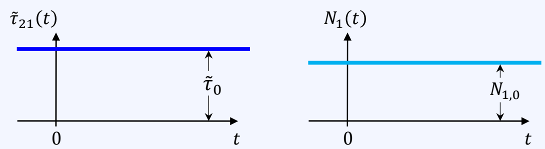
Imposed Kinematics:

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

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



Material Stress Response:



Material Functions:

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

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

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

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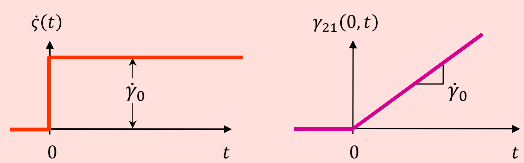
Start-up of Steady Shear Flow Material Functions

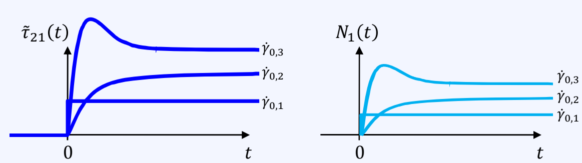
Imposed Kinematics:

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

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



Material Stress Response:



Material Functions:

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

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

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

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Cessation of Steady Shear Flow Material Functions

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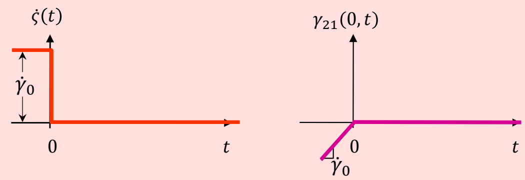
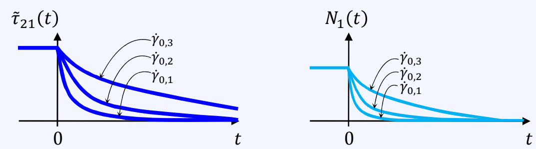
Imposed Kinematics:

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

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



Material Stress Response:



Material Functions:

Shear stress decay function

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

First normal-stress decay coefficient

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

Second normal-stress decay coefficient

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

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Step Strain Shear Flow Material Functions

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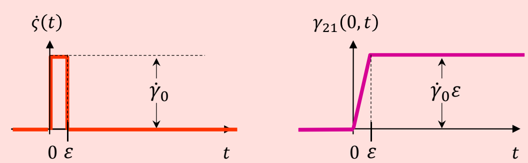
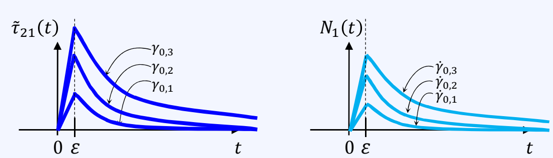
Imposed Kinematics:

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

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



Material Stress Response:



Material Functions:

Relaxation modulus

$$G(t,\gamma_0) \equiv \frac{\tilde{\tau}_{21}(t,\gamma_0)}{\gamma_0} = \frac{-\tau_{21}(t,\gamma_0)}{\gamma_0}$$

First normal-stress relaxation modulus

$$G_{\Psi_1}(t,\gamma_0) \equiv \frac{\tilde{\tau}_{11} - \tilde{\tau}_{22}}{\gamma_0^2}$$

Second normal-stress relaxation modulus

$$G_{\Psi_2}(t,\gamma_0) \equiv \frac{\tilde{\tau}_{22} - \tilde{\tau}_{33}}{\gamma_0^2}$$

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Small-Amplitude Oscillatory Shear Material Functions

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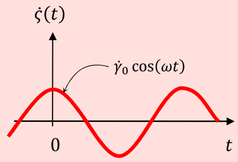
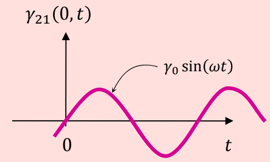
Imposed Kinematics:

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

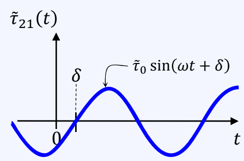
$$\dot{\varsigma}(t) = \dot{\gamma}_0 \cos(\omega t)$$

$$\gamma_0 = \frac{\dot{\gamma}_0}{\omega}$$





Material Stress Response:



δ = phase difference between stress and strain waves

$N_1(t) = N_2(t) = 0$
(linear viscoelastic regime)

Material Functions:

SAOS stress $$\frac{\tilde{\tau}_{21}(t,\gamma_0)}{\gamma_0} = \frac{-\tau_{21}(t,\gamma_0)}{\gamma_0} = \tilde{\tau}_0 \sin(\omega t + \delta) = G' \sin(\omega t) + G'' \cos(\omega t)$$

Storage modulus $$G'(\omega) \equiv \frac{\tilde{\tau}_0}{\gamma_0}\cos(\delta)$$

Loss modulus $$G''(\omega) \equiv \frac{\tilde{\tau}_0}{\gamma_0}\sin(\delta)$$

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Creep Shear Flow Material Functions

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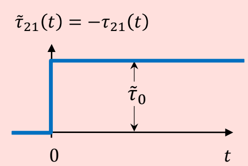
Imposed Stress

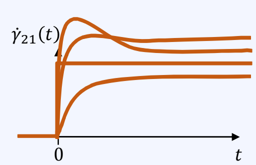
$$\underline{v} \equiv \begin{pmatrix} \dot{\gamma}_{21}(t)x_2 \\ 0 \\ 0 \end{pmatrix}_{123}$$

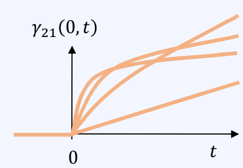
$$\tilde{\tau}_{21}(t) = -\tau_{21}(t) = \begin{cases} 0 & t < 0 \\ \tilde{\tau}_0 & 0 \le t < t_2 \\ 0 & t \ge t_2 \end{cases}$$



Material *Kinematic* Response:

For *creep*, the material response is the form of deformation (stress is specified).





Material Function:

Shear creep compliance $$J(t,\tilde{\tau}_0) \equiv \frac{\gamma_{21}(0,t;\tilde{\tau}_0)}{\tilde{\tau}_0}$$

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Steady Elongational Flow Material Functions

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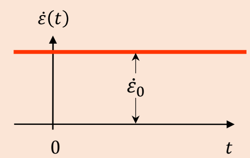
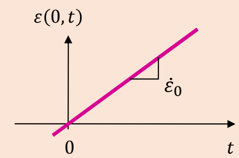
Imposed Kinematics:

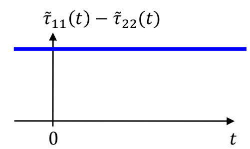
$$\underline{v} \equiv \begin{pmatrix} -\frac{1}{2}\dot{\varepsilon}(t)x_1 \\ -\frac{1}{2}\dot{\varepsilon}(t)x_2 \\ \dot{\varepsilon}(t)x_3 \end{pmatrix}_{123}$$

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





Material Stress Response:



Material Functions:

Elongational Viscosity $\quad \eta_e(\dot{\varepsilon}_0) \equiv \dfrac{\tilde{\tau}_{33} - \tilde{\tau}_{11}}{\dot{\varepsilon}_0} = \dfrac{-(\tau_{33} - \tau_{11})}{\dot{\varepsilon}_0}$

Alternatively, $\bar{\eta}(\dot{\varepsilon}_0)$

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Start-up of Steady Elongation Material Functions

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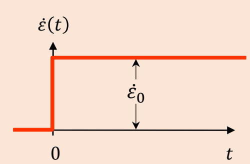
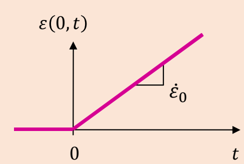
Imposed Kinematics:

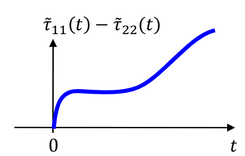
$$\underline{v} \equiv \begin{pmatrix} -\frac{1}{2}\dot{\varepsilon}(t)x_1 \\ -\frac{1}{2}\dot{\varepsilon}(t)x_2 \\ \dot{\varepsilon}(t)x_3 \end{pmatrix}_{123}$$

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





Material Stress Response:



Material Functions:

Elongational Start-up Function $\quad \eta_e^+(t, \dot{\varepsilon}_0) \equiv \dfrac{\tilde{\tau}_{33} - \tilde{\tau}_{11}}{\dot{\varepsilon}_0} = \dfrac{-(\tau_{33} - \tau_{11})}{\dot{\varepsilon}_0}$

Alternatively, $\bar{\eta}^+(t, \dot{\varepsilon}_0)$

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What exactly do we observe when we subject non-Newtonian fluids to deformation?

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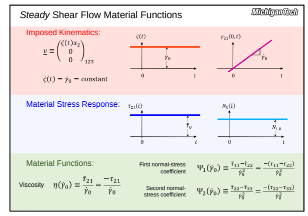
Summary

Rheological Material Functions



- Are the answer to the question *"What exactly do we observe when we subject non-Newtonian fluids to deformation?"*
- Are based on continuum view
- Provide a framework/vocabulary of comparison
- Help to categorize and organize observed material responses

Material Functions do not:

- Identify a material conclusively
- Tell us the form of $\underline{\underline{\tau}}(\underline{v})$

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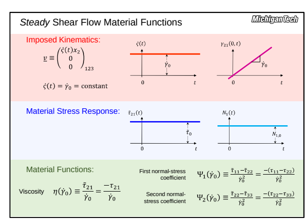
Summary

Rheological Material Functions



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Cannot conclusively identify, but can classify and can be used to assess proposed models

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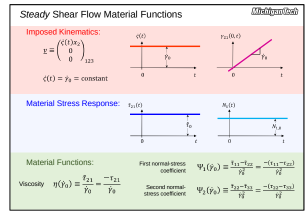
Rheological Material Functions



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Cannot conclusively identify, but can classify and can be used to assess proposed models

Except for Newtonian fluids, the structure of the model for stress is not known $\underline{\underline{\tau}}(\underline{v}) = ?$, and remains a mystery

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Back to the book

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