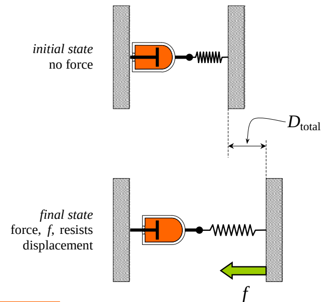
Chapter 8: Memory Effects: GLVE

CM4650
Polymer Rheology
Michigan Tech

Maxwell's model combines viscous and elastic responses in series

Spring (elastic) and dashpot (viscous) in series:



Displacements are additive:

$$D_{total} = D_{spring} + D_{dashpot}$$

40

Fluids with Memory - Chapter 8

We seek a constitutive equation that includes memory effects.

$$\underline{\underline{\tau}}(t) = f(\underline{\underline{\dot{\gamma}}}, I_{\underline{\underline{\dot{\gamma}}}}, II_{\underline{\underline{\dot{\gamma}}}}, III_{\underline{\underline{\dot{\gamma}}}}, \text{material information})$$

calculates the stress at a particular time, *t*

2 equations so far:

$$\underline{\underline{\tau}}(t) = -\mu \underline{\underline{\dot{\gamma}}}(t)$$

$$\underline{\underline{\tau}}(t) = -\eta(\dot{\gamma})\underline{\underline{\dot{\gamma}}}(t) \qquad \dot{\gamma} = \left|\underline{\underline{\dot{\gamma}}}\right|$$

So far, stress at *t* depends on rate-of-deformation **at *t* only**

41

Current Constitutive Equations

Newtonian $\underline{\underline{\tau}}(t) = -\mu \underline{\underline{\dot{\gamma}}}(t)$

Generalized Newtonian $\underline{\underline{\tau}}(t) = -\eta(\dot{\gamma})\underline{\underline{\dot{\gamma}}}(t)$ $\dot{\gamma} = \left|\underline{\underline{\dot{\gamma}}}\right|$

Neither can predict:

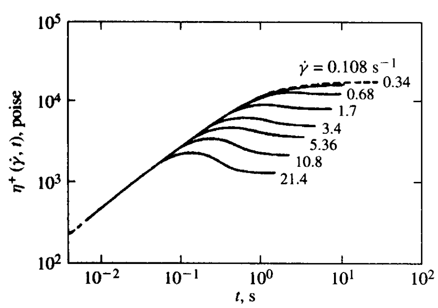
- •Shear normal stresses - *this will be wrong so long as we use constitutive equations proportional to* $\underline{\underline{\dot{\gamma}}}$
- •stress transients in shear (startup, cessation) - *this flaw seems to be related to omitting fluid memory*

We will try to fix this now; we will address the first point when we discuss advanced constitutive equations

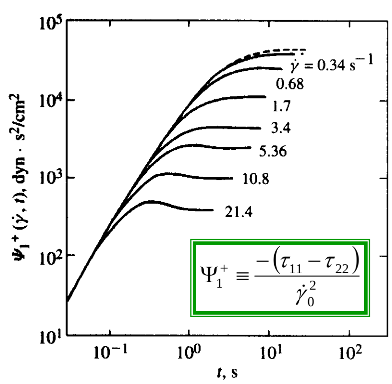
42

Startup of Steady Shearing

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



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

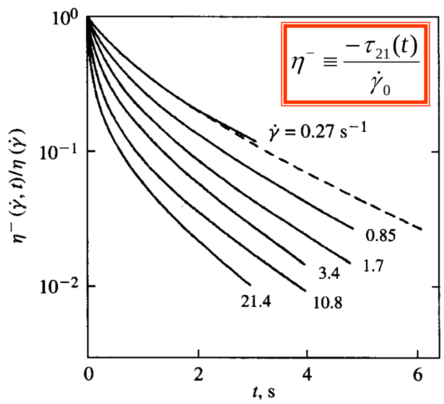


Figures 6.49, 6.50, p. 208 Menezes and Graessley, PB soln

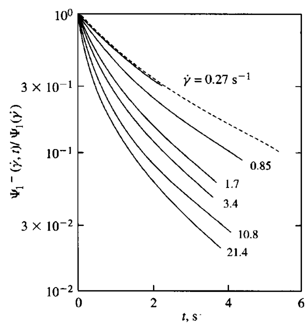
43

Cessation of Steady Shearing

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



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



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

Figures 6.51, 6.52, p. 209 Menezes and Graessley, PB soln

44

How can we incorporate time-dependent effects?

First we explore a simple memory fluid.

Let's construct a new constitutive equation that remembers the stress at a time t_0 seconds ago

$$-\underline{\underline{\tau}}(t) = \tilde{\eta}\,\underline{\underline{\dot{\gamma}}}(t) + (0.8\tilde{\eta})\,\underline{\underline{\dot{\gamma}}}(t - t_0)$$

Newtonian contribution

contribution from fluid memory

This is the rate-of-deformation tensor t_0 seconds before time t

$\tilde{\eta}$ is a constant parameter of the model

45

What does this model predict?

Steady shear

$\eta = ?$

$\Psi_1 = ?$

$\Psi_2 = ?$

Shear start-up

$\eta^+(t) = ?$

$\Psi_1^+(t) = ?$

$\Psi_2^+(t) = ?$

46

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

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

47

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

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

48

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

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

Second normal-stress decay function

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

49

Predictions of the simple memory fluid

$$-\underline{\underline{\tau}}(t)=\tilde{\eta}\,\underline{\underline{\dot{\gamma}}}(t)+(0.8\tilde{\eta})\,\underline{\underline{\dot{\gamma}}}(t-t_0)$$

Steady shear

$$\eta = 1.8\tilde{\eta}$$

$$\Psi_1=\Psi_2=0$$

The steady viscosity reflects contributions from what is currently happening and contributions from what happened t_0 seconds ago.

Shear start-up

$$\eta^+(t)=\begin{cases}0 & t<0\\ \tilde{\eta} & 0\le t\le t_0\\ 1.8\tilde{\eta} & t\ge t_0\end{cases}$$

$$\Psi_1^+(t)=\Psi_2^+(t)=0$$

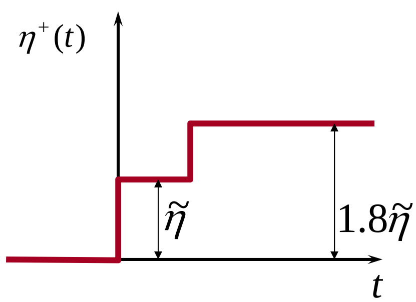
50

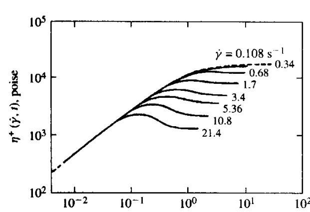
Predictions of the simple memory fluid

Shear start-up

$$\eta^+(t)=\begin{cases}0 & t<0\\ \tilde{\eta} & 0\le t\le t_0\\ 1.8\tilde{\eta} & t\ge t_0\end{cases}$$

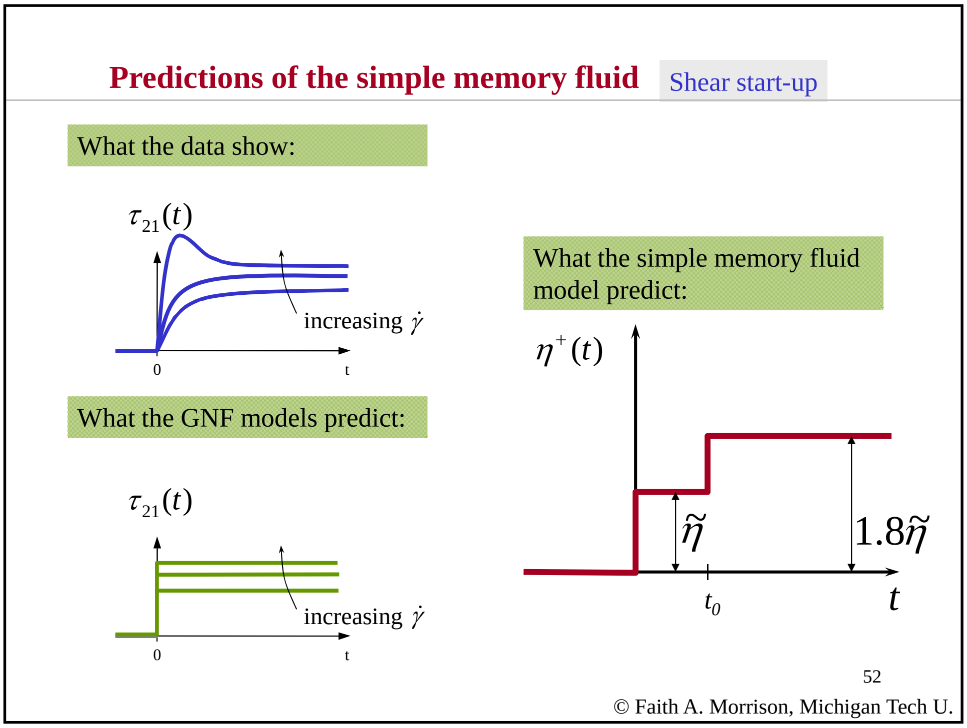
$$\Psi_1^+(t)=\Psi_2^+(t)=0$$

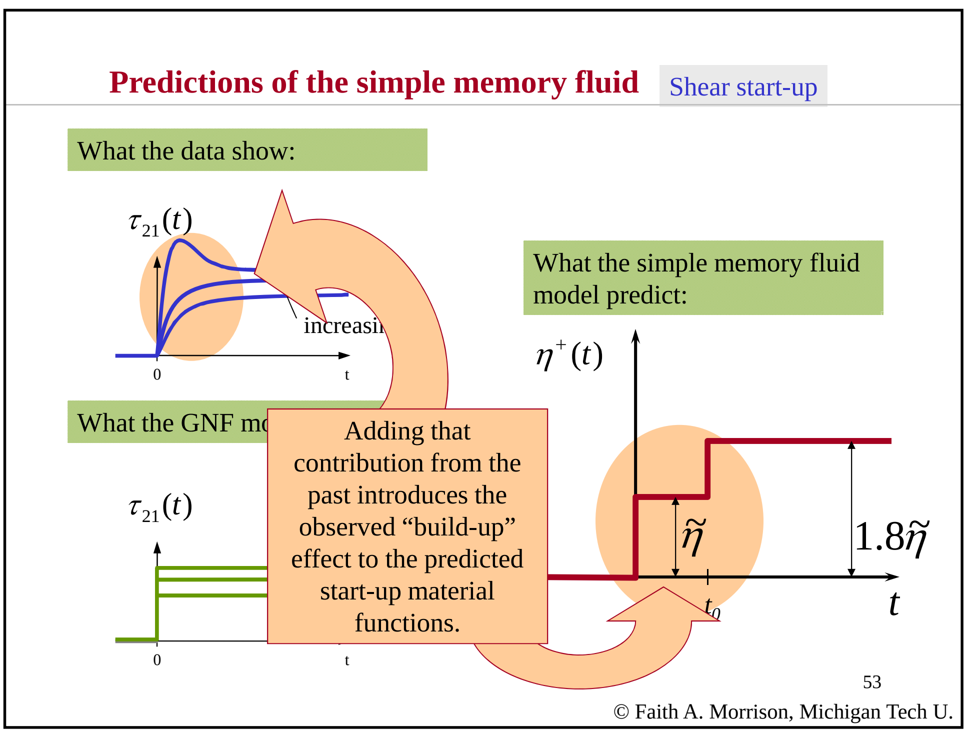




Figures 6.49, 6.50, p. 208 Menezes and Graessley, PB soln

51


Predictions of the simple memory fluid
Shear start-up
What the data show:
$\tau_{21}(t)$
increasing $\dot{\gamma}$
0
t
What the GNF models predict:
$\tau_{21}(t)$
increasing $\dot{\gamma}$
0
t
What the simple memory fluid model predict:
$\eta^+(t)$
$\tilde{\eta}$
$1.8\tilde{\eta}$
t_0
t
52
© Faith A. Morrison, Michigan Tech U.


Predictions of the simple memory fluid
Shear start-up
What the data show:
$\tau_{21}(t)$
0
t
What the GNF mo
$\tau_{21}(t)$
0
t
Adding that contribution from the past introduces the observed "build-up" effect to the predicted start-up material functions.
What the simple memory fluid model predict:
$\eta^+(t)$
$\tilde{\eta}$
$1.8\tilde{\eta}$
t
53
© Faith A. Morrison, Michigan Tech U.

We can make the stress rise smoother by adding more fading memory terms.

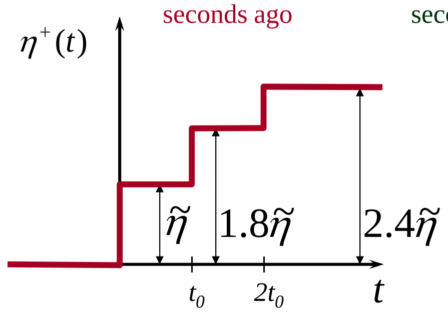
The memory is fading

$$-\underline{\underline{\tau}}(t) = \tilde{\eta}\,\dot{\underline{\underline{\gamma}}}(t) + (0.8\tilde{\eta})\,\dot{\underline{\underline{\gamma}}}(t-t_0) + (0.6\tilde{\eta})\,\dot{\underline{\underline{\gamma}}}(t-2t_0)$$

Newtonian contribution

contribution from t_0 seconds ago

contribution from $2t_0$ seconds ago

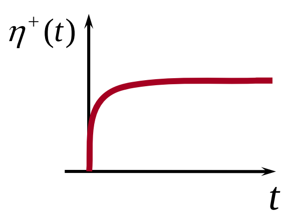


The fit can be made to be perfectly smooth by using a sum of exponentially decaying terms as the weighting functions.

$$-\underline{\underline{\tau}}(t) = \tilde{\eta}\Big[\dot{\underline{\underline{\gamma}}}(t) + (0.37)\,\dot{\underline{\underline{\gamma}}}(t-t_0) + (0.14)\,\dot{\underline{\underline{\gamma}}}(t-2t_0) + (0.05)\,\dot{\underline{\underline{\gamma}}}(t-3t_0) + \dots\Big]$$

$$= -\tilde{\eta}\sum_{p=0}^{\infty} e^{-pt_0/\lambda}\,\dot{\underline{\underline{\gamma}}}(t-pt_0)$$

$\frac{pt_0}{\lambda}$	$e^{-pt_0/\lambda}$
0	1.00
1	0.37
2	0.14
3	0.05
4	0.02



(t_0/λ scales the decay)

New model:

$$-\underline{\underline{\tau}}(t)=\tilde{\eta}\sum_{p=0}^{\infty}e^{-pt_0/\lambda}\,\underline{\underline{\dot{\gamma}}}(t-pt_0)$$

This sum can be rewritten as an integral.

$$I=\int_a^b f(x)dx \equiv \lim_{N\rightarrow\infty}\left[\sum_{i=1}^{N} f(a+i\Delta x)\Delta x\right], \qquad \Delta x=\frac{b-a}{N}$$

$a \rightarrow t$

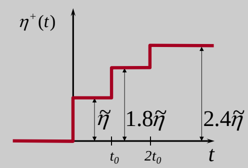
$x \rightarrow -t'$

$\Delta x \rightarrow -\Delta t'$

$i\Delta x \rightarrow -pt_0 = -p\Delta t'$

$f(a+i\Delta x) \rightarrow e^{-p\Delta t'}\,\underline{\underline{\dot{\gamma}}}(t-p\Delta t')$

(Actually, it takes a bit of renormalizing to make this transformation actually work.)



In the current formulation, η^+ grows as N goes to infinity.

56

With proper reformulation, we obtain:

Maxwell Model (integral version)

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

Two parameters:

Zero-shear viscosity η_0 – gives the value of the steady shear viscosity

Relaxation time λ - quantifies how fast memory fades

Steps to here:
- Add information about past deformations
- Make memory fade

57

We've seen that including terms that invoke past deformations (fluid memory) can improve the constitutive predictions we make.

This same class of models can be derived in differential form, beginning with the idea of combining viscous and elastic effects.

58

The Maxwell Models

The basic Maxwell model is based on the observation that at long times viscoelastic materials behave like Newtonian liquids, while at short times they behave like elastic solids.

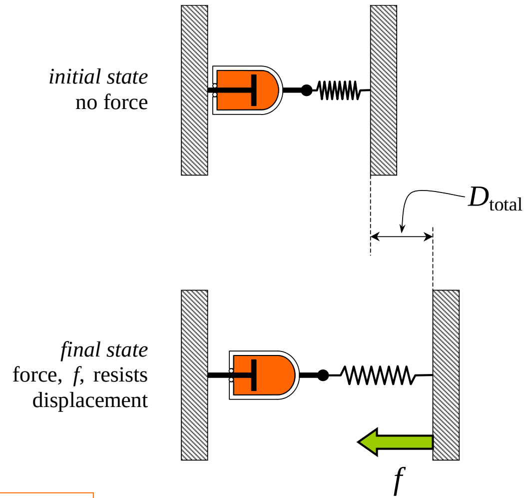
Hooke's Law for elastic solids $\tau_{21} = -G\gamma_{21}$

Newton's Law for viscous liquids $\tau_{21} = -\eta\dot{\gamma}_{21}$

59

Maxwell's model combines viscous and elastic responses in series

Spring (elastic) and dashpot (viscous) in series:



Displacements are additive:

$$D_{total} = D_{spring} + D_{dashpot}$$

60

In the spring: $f = -G_{sp} D_{spring}$

In the dashpot: $f = -\mu \dfrac{dD_{dash}}{dt}$

$$D_{total} = D_{spring} + D_{dash}$$

$$\frac{dD_{total}}{dt} = \frac{dD_{spring}}{dt} + \frac{dD_{dash}}{dt}$$

$$= -\frac{1}{G_{sp}}\frac{df}{dt} - \frac{1}{\mu} f$$

$$f + \frac{\mu}{G_{sp}}\frac{df}{dt} = -\mu \frac{dD_{total}}{dt}$$

61

$$f+\frac{\mu}{G_{sp}}\frac{df}{dt}=-\mu\frac{dD_{total}}{dt}$$

By analogy:

$$\tau_{21}+\frac{\eta_0}{G}\frac{\partial\tau_{21}}{\partial t}=-\eta_0\dot{\gamma}_{21}\quad \text{shear}$$

$$\underline{\underline{\tau}}+\frac{\eta_0}{G}\frac{\partial\underline{\underline{\tau}}}{\partial t}=-\eta_0\underline{\underline{\dot{\gamma}}}\quad \text{all flows}$$

Two parameter model: $\lambda=\frac{\eta_0}{G}$ *Relaxation time*

η_0 *Viscosity*

62

The Maxwell Model

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

Two parameter model: $\lambda=\frac{\eta_0}{G}$ *Relaxation time*

η_0 *Viscosity*

63

How does the Maxwell model behave at steady state? For short time deformations?

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

64

Example: Solve the Maxwell Model for an expression explicit in the stress tensor

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

First-order, linear differential equations:

$$\frac{dy}{dx} + y\,a(x) + b(x) = 0$$

Integrating function, *u(x)*

$$u(x) = e^{\int a(x')dx'}$$

Maxwell Model (integral version)

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

We arrived at this equation following **two different** paths:

- Add up fading contributions of past deformations
- Add viscous and elastic effects in series

67

What are the predictions of the Maxwell model?

Need to check the predictions to see if
what we have done is worth keeping.

Predictions:

- •Steady shear
- •Steady elongation
- •Start-up of steady shear
- •Step shear strain
- •Small-amplitude oscillatory shear

68

What are the predictions of the Maxwell model?

Need to check the predictions to see if
what we have done is worth keeping.

Predictions:

- •Steady shear
- •Steady elongation
- •Start-up of steady shear
- •Step shear strain
- •Small-amplitude oscillatory shear

69

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

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

Predictions of the (single-mode) Maxwell Model

$$\underline{\underline{\tau}} + \frac{\eta_0}{G}\frac{\partial \underline{\underline{\tau}}}{\partial t} = -\eta_0 \underline{\underline{\dot{\gamma}}} \qquad \underline{\underline{\tau}}(t) = -\int_{-\infty}^{t} \left(\frac{\eta_0}{\lambda}\right) e^{-(t-t')/\lambda}\, \underline{\underline{\dot{\gamma}}}(t')\, dt'$$

Steady shear	$\eta = \eta_0$ $\Psi_1 = \Psi_2 = 0$	Fails to predict shear normal stresses. Fails to predict shear-thinning.
Steady elongation	$\bar{\eta} = 3\eta_0$	Trouton's rule

Steady shear viscosity and first normal stress coefficient

BOGER FLUIDS

There are some systems with a constant viscosity but still start-up effects.

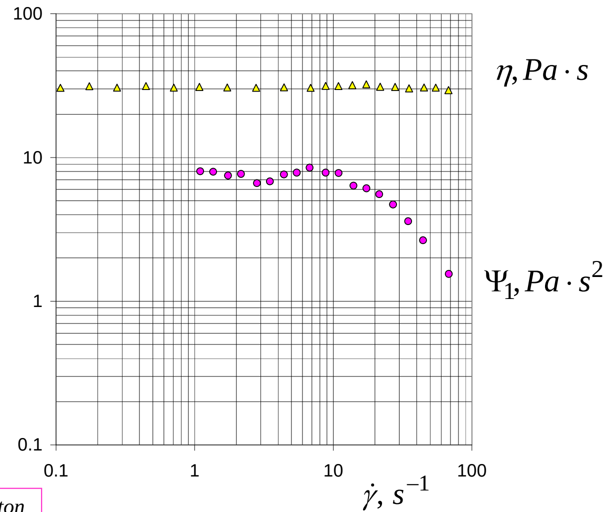


Figure 6.5, p. 173 Binnington and Boger; PIB soln

72

Steady shear viscosity and first and ***second*** normal stress coefficient

BOGER FLUIDS

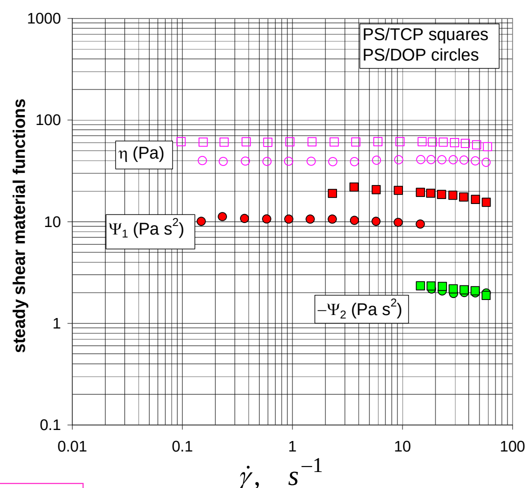


Figure 6.6, p. 174 Magda et al.; PS solns

73

Step Shear Strain Material Functions

Kinematics:

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

$$\dot{\gamma}_0 \varepsilon = \text{constant} = \gamma_0$$

Material Functions:

$$G(t,\gamma_0) \equiv \frac{-\tau_{21}(t,\gamma_0)}{\gamma_0}$$

Relaxation modulus

First normal-stress relaxation modulus

$$G_{\Psi_1} \equiv \frac{-(\tau_{11} - \tau_{22})}{\gamma_0^2}$$

Second normal-stress relaxation modulus

$$G_{\Psi_2} \equiv \frac{-(\tau_{22} - \tau_{33})}{\gamma_0^2}$$

74

Predictions of the (single-mode) Maxwell Model

$$\underline{\underline{\tau}} + \frac{\eta_0}{G}\frac{\partial \underline{\underline{\tau}}}{\partial t} = -\eta_0 \dot{\underline{\underline{\gamma}}} \qquad \underline{\underline{\tau}}(t) = -\int_{-\infty}^{t} \left(\frac{\eta_0}{\lambda}\right) e^{-(t-t')/\lambda}\, \dot{\underline{\underline{\gamma}}}(t')\, dt'$$

Shear start-up

$$\eta^+(t) = \eta_0\left(1 - e^{-t/\lambda}\right)$$

$$\Psi_1^+(t) = \Psi_2^+(t) = 0$$

Does predict a gradual build-up of stresses on start-up.

Step shear strain

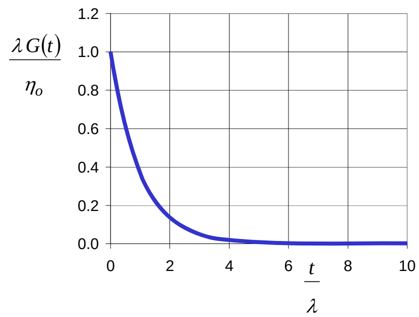
$$G(t) = \frac{\eta_0}{\lambda} e^{-t/\lambda}$$

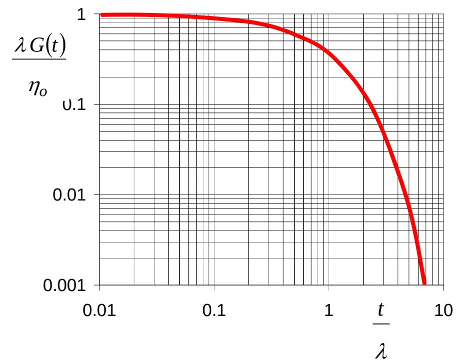
$$G_{\Psi 1} = G_{\Psi 2} = 0$$

Does predict a reasonable relaxation function in step strain (but no normal stresses again).

75

Step-Shear-Strain Material Function *G(t)* for Maxwell Model





76

Comparison to experimental data

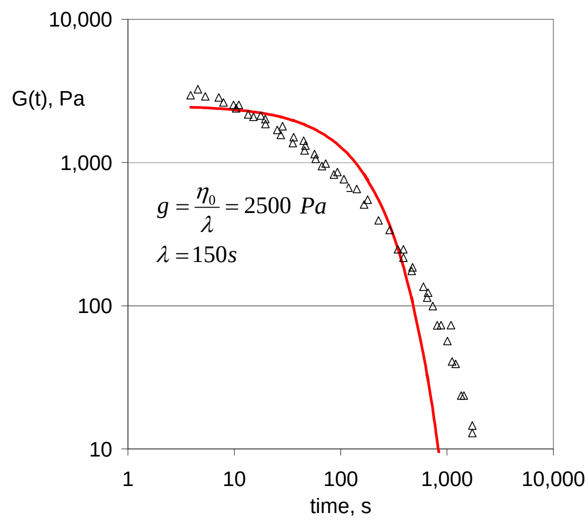


Figure 8.4, p. 274 data from Einaga et al., PS 20% soln in chlorinated diphenyl

77

We can improve this fit by adjusting the Maxwell model to allow multiple relaxation modes

$$\underline{\underline{\tau}}_{(k)} = -\int_{-\infty}^{t} \left(\frac{\eta_k}{\lambda_k}\right) e^{-(t-t')/\lambda_k} \dot{\underline{\underline{\gamma}}}(t')\, dt'$$

$$\underline{\underline{\tau}}(t) = \sum_{k=1}^{N} \underline{\underline{\tau}}_{(k)}$$

Generalized Maxwell Model

$$\underline{\underline{\tau}} = -\int_{-\infty}^{t} \left[\sum_{k=1}^{3} \frac{\eta_k}{\lambda_k} e^{-(t-t')/\lambda_k} \right] \dot{\underline{\underline{\gamma}}}(t')\, dt'$$

2N parameters (can fit *anything*)

78

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

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

79

Step Shear Strain Material Functions

Kinematics:

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

$$\dot{\varsigma}(t) = \lim_{\varepsilon \to 0} \begin{cases} 0 & t < 0 \\ \dot{\gamma} & 0 \le t < \varepsilon \\ 0 & t \ge \varepsilon \end{cases}$$

$$\dot{\gamma}\varepsilon = \text{constant} = \gamma_0$$

Material Functions:

$$G(t, \gamma_0) \equiv \frac{-\tau_{21}(t, \gamma_0)}{\gamma_0}$$

Relaxation modulus

First normal-stress relaxation modulus

$$G_{\Psi_1} \equiv \frac{-(\tau_{11} - \tau_{22})}{\gamma_0^2}$$

Second normal-stress relaxation modulus

$$G_{\Psi_2} \equiv \frac{-(\tau_{22} - \tau_{33})}{\gamma_0^2}$$

80

Predictions of the Generalized Maxwell Model

$$\underline{\underline{\tau}} = -\int_{-\infty}^{t} \left[\sum_{k=1}^{3} \frac{\eta_k}{\lambda_k} e^{-(t-t')/\lambda_k} \right] \underline{\underline{\dot{\gamma}}}(t')\, dt'$$

Steady shear

$$\eta = \sum_{k=1}^{N} \eta_k$$

$$\Psi_1 = \Psi_2 = 0$$

Fails to predict shear normal stresses

Fails to predict shear-thinning

Step shear strain

$$G(t) = \sum_{k=1}^{N} \frac{\eta_k}{\lambda_k} e^{-t/\lambda_k}$$

$$G_{\Psi 1} = G_{\Psi 2} = 0$$

This function can fit ***any*** observed data; note that the GMM does not predict shear normal stresses.

81

Fitting G(t) to Generalized Maxwell Model

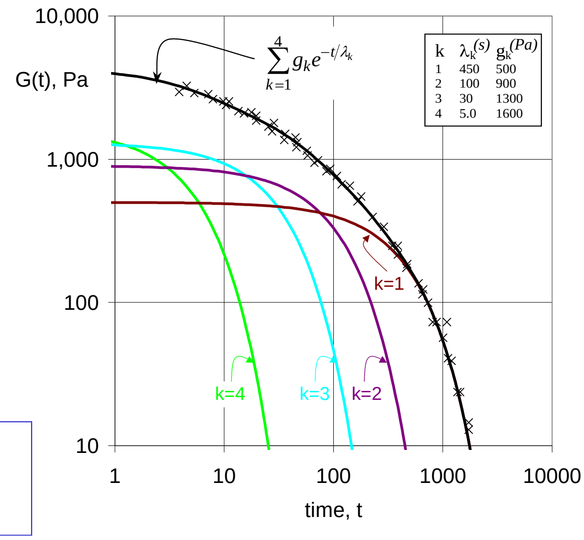


Figure 8.4, p. 274 data from Einaga et al., PS 20% soln in chlorinated diphenyl

82

The Linear-Viscoelastic Models

Differential Maxwell (one mode):

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

Integral Maxwell (one mode):

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

Generalized Maxwell model (N modes):

$$\underline{\underline{\tau}} = -\int_{-\infty}^{t} \left[\sum_{k=1}^{N} \frac{\eta_k}{\lambda_k} e^{-\frac{(t-t')}{\lambda_k}} \right] \dot{\underline{\underline{\gamma}}}(t')\,dt'$$

83

The Linear-Viscoelastic Models

Differential Maxwell (one mode):

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

Integral Maxwell (one mode):

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

Generalized Maxwell model (N modes):

$$\underline{\underline{\tau}} = -\int_{-\infty}^{t} \left[\sum_{k=1}^{N} \frac{\eta_k}{\lambda_k} e^{-\frac{(t-t')}{\lambda_k}} \right] \dot{\underline{\underline{\gamma}}}(t')\, dt'$$

Since the term in brackets is just the predicted relaxation modulus *G(t)*, we can write an even more ***general linear viscoelastic model*** by leaving this function unspecified.

84

The Linear-Viscoelastic Models

Differential Maxwell (one mode):

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

Integral Maxwell (one mode):

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

Generalized Maxwell model (N modes):

$$\underline{\underline{\tau}} = -\int_{-\infty}^{t} \left[\sum_{k=1}^{N} \frac{\eta_k}{\lambda_k} e^{-\frac{(t-t')}{\lambda_k}} \right] \dot{\underline{\underline{\gamma}}}(t')\, dt'$$

Generalized Linear-Viscoelastic Model:

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

85

Small-Amplitude Oscillatory Shear Material Functions

Kinematics:

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

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

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

Material Functions:

$$\frac{-\tau_{21}(t, \gamma_0)}{\gamma_0} = G' \sin \omega t + G'' \cos \omega t$$

$$G'(\omega) \equiv \frac{\tau_0}{\gamma_0} \cos \delta$$

Storage modulus

(δ is the phase difference between stress and strain)

$$G''(\omega) \equiv \frac{\tau_0}{\gamma_0} \sin \delta$$

Loss modulus

86

Predictions of the Generalized Maxwell Model (GMM) and Generalized Linear-Viscoelastic Model (GLVE)

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

$$\underline{\underline{\tau}} = -\int_{-\infty}^{t} \left[\sum_{k=1}^{3} \frac{\eta_k}{\lambda_k} e^{-(t-t')/\lambda_k} \right] \underline{\underline{\dot{\gamma}}}(t') \, dt'$$

Small-amplitude oscillatory shear

GLVE

$$G'(\omega) = \omega \int_0^\infty G(s) \cos \omega s \, ds$$

$$G''(\omega) = \omega \int_0^\infty G(s) \sin \omega s \, ds$$

GMM

$$G'(\omega) = \sum_{k=1}^{N} \frac{\eta_k \lambda_k \omega^2}{1 + (\lambda_k \omega)^2}$$

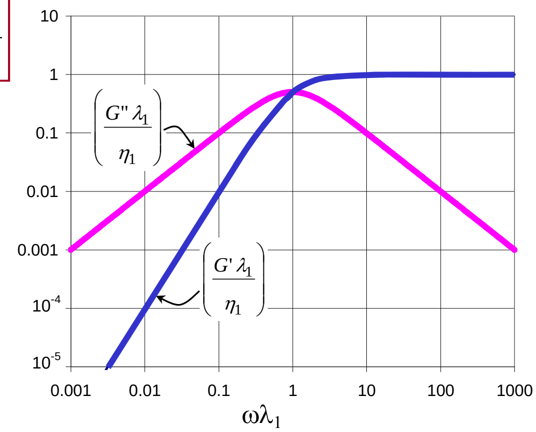
$$G''(\omega) = \sum_{k=1}^{N} \frac{\eta_k \omega}{1 + (\lambda_k \omega)^2}$$

87

Predictions of (single-mode) Maxwell Model in SAOS

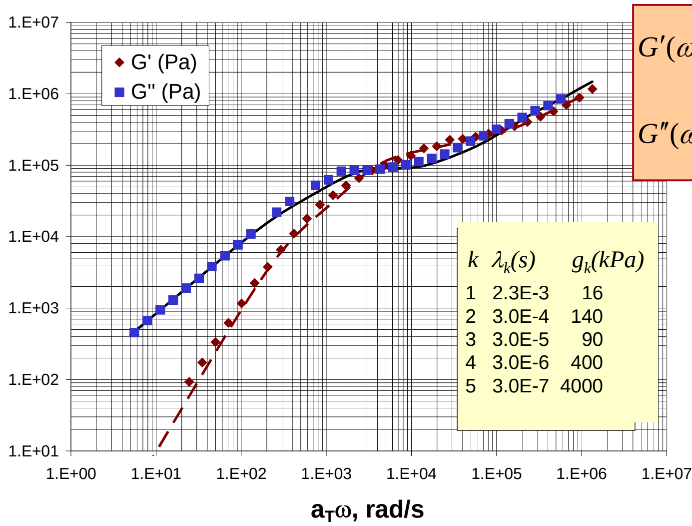
$$G'(\omega) = \frac{g_1 \lambda_1^2 \omega^2}{1+(\lambda_1\omega)^2} = \frac{\eta_1 \lambda_1 \omega^2}{1+(\lambda_1\omega)^2}$$

$$G''(\omega) = \frac{g_1 \lambda_1 \omega}{1+(\lambda_1\omega)^2} = \frac{\eta_1 \omega}{1+(\lambda_1\omega)^2}$$



88

Predictions of (multi-mode) Maxwell Model in SAOS



k	$\lambda_k(s)$	$g_k(kPa)$
1	2.3E-3	16
2	3.0E-4	140
3	3.0E-5	90
4	3.0E-6	400
5	3.0E-7	4000

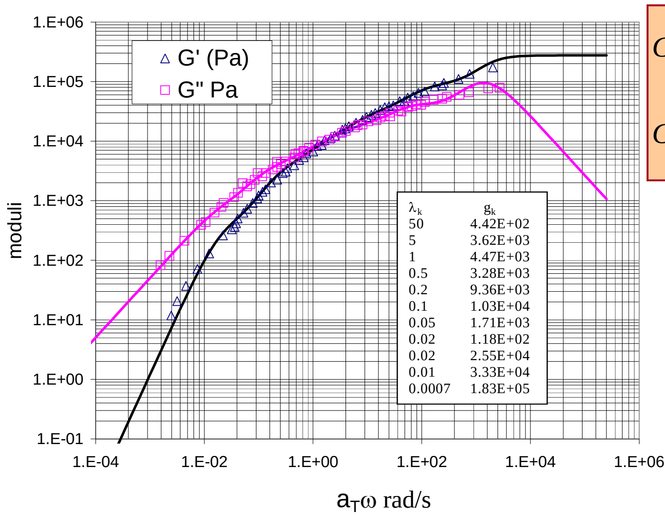
$$G'(\omega) = \sum_{k=1}^{N} \frac{\eta_k \lambda_k \omega^2}{1+(\lambda_k\omega)^2}$$

$$G''(\omega) = \sum_{k=1}^{N} \frac{\eta_k \omega}{1+(\lambda_k\omega)^2}$$

Figure 8.8, p. 284 data from Vinogradov, PS melt

89

Predictions of (multi-mode) Maxwell Model in SAOS



$$G'(\omega)=\sum_{k=1}^{N}\frac{\eta_k\lambda_k\omega^2}{1+(\lambda_k\omega)^2}$$

$$G''(\omega)=\sum_{k=1}^{N}\frac{\eta_k\omega}{1+(\lambda_k\omega)^2}$$

Figure 8.10, p. 286 data from Laun, PE melt

90

Limitations of the GLVE Models

•Predicts constant shear viscosity

•Only valid in regime where strain is additive (small-strain, low rates)

•All stresses are proportional to the deformation-rate tensor; thus shear normal stresses cannot be predicted

•Cannot describe flows with a superposed rigid rotation (as we will now discuss; see Morrison p296)

91

Steady shear viscosity and first and ***second*** normal stress coefficient

BOGER FLUIDS

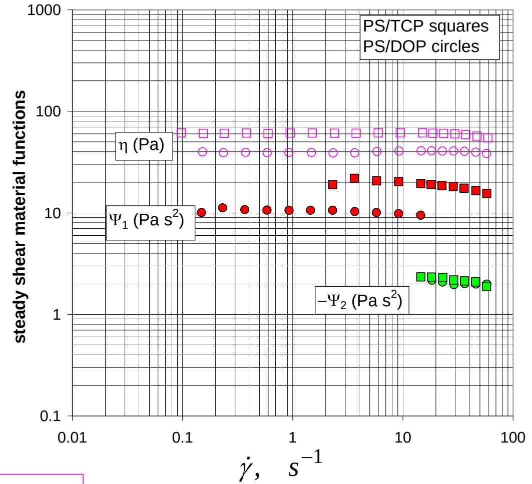
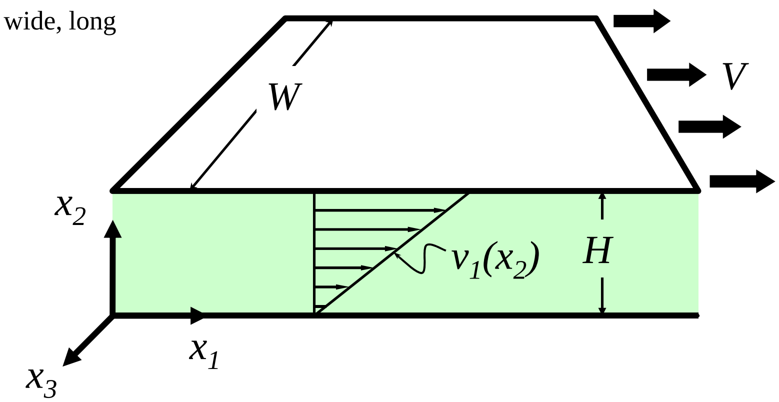


Figure 6.6, p. 174 Magda et al.; PS solns

92

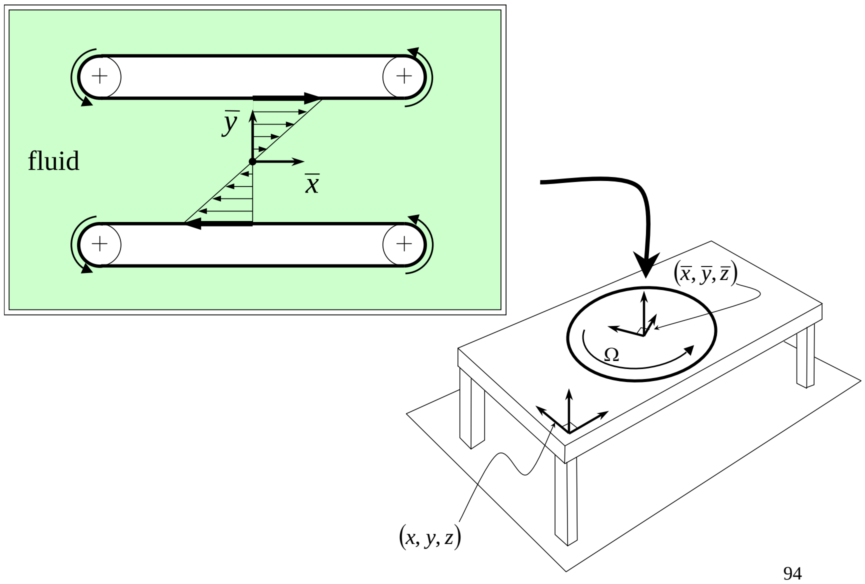
EXAMPLE: Drag flow of a Generalized Linear-Viscoelastic fluid between infinite parallel plates

- steady state
- incompressible fluid
- infinitely wide, long



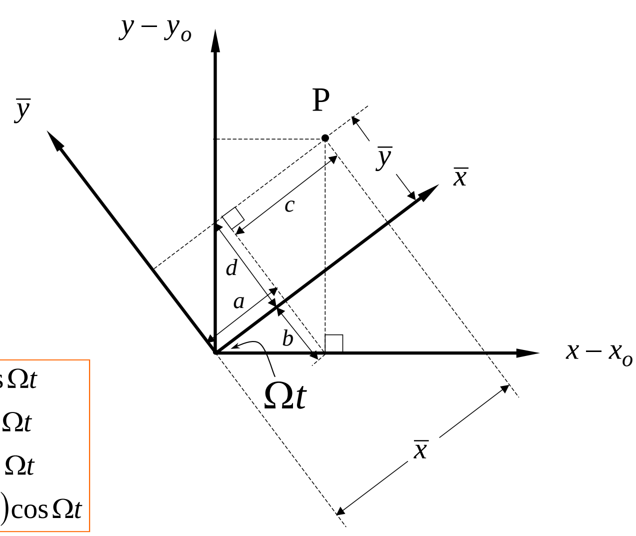
93

Shear flow in a rotating frame of reference



94

Shear flow in a rotating frame of reference



$$a = (x - x_o)\cos \Omega t$$
$$b = (x - x_o)\sin \Omega t$$
$$c = (y - y_o)\sin \Omega t$$
$$d + b = (y - y_o)\cos \Omega t$$

95

Summary: *Generalized Linear-Viscoelastic Constitutive Equations*

PRO:

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

CON:

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

96