Introduction to Rheology of complex fluids
Brief Lecture Notes

Linear Viscoelasticity
Contents

- Introductory Lecture
- Simple Flows
- Material functions & Rheological Characterization
- Experimental Observations
- Generalized Newtonian Fluids
- Generalized Linear viscoelastic Fluids
- Nonlinear Constitutive Models
Maxwell Model

- Constitutive modelling is the art and science of finding appropriate tensorial expressions for the stress as a function of the deformation to match observed material behavior.

- The Maxwell model is empirical (like Newton’s and Hooke’s laws) and its validity depends on how well it predicts material behavior.
Maxwell Model

Differential approach, based on “additivity” ideas of elasticity, which hold for small deformations

Viscoelastic Material

$t >> 1$

Viscous fluid
no memory of past events

$t << 1$

Elastic Solid
Remembers where it was at $t_o$

Hook’s Law for elastic solids
Valid for infinitesimally small displacements

$\tau(t) = G \gamma(t_o, t)$

Newton’s Law for viscous fluids
Valid for arbitrarily large displacement gradients

$\tau(t) = \eta \dot{\gamma}(t)$
Maxwell Model

\[
\begin{align*}
\dot{\gamma}_{xy}(t) &= \frac{\partial}{\partial t} \gamma_{xy}(t_0, t) \\
\gamma_{xy}(t_0, t) &= \int_{t_0}^{t} \dot{\gamma}_{xy}(t')dt'
\end{align*}
\]

Use of Spring (elastic behavior) and dashpot (fluid behavior) in series.

Initial State: No Force Imposed

Final State: Force, \( f \), resist to the displacement

The (small) displacements can be added

The total displacement is:

\[ d_{total} = d_{spring} + d_{dashpot} \]

When the resistances are in parallel, the Kelvin-Voigt model is derived.

Maxwell model combines the viscous and the elastic behavior in series.
Maxwell Model

The force on the spring:

\[ f = G_{sp} d_{spring} \]

The force on the dashpot:

\[ f = \mu \frac{d(d_{dash})}{dt} \]

The total Displacement

\[ d_{total} = d_{spring} + d_{dashpot} \]

\[ \frac{d(d_{total})}{dt} = \frac{d(d_{spring})}{dt} + \frac{d(d_{dashpot})}{dt} \]

\[ \frac{d(d_{total})}{dt} = \frac{1}{G_{sp}} \frac{df}{dt} + \frac{1}{\mu} f \]

\[ f + \frac{\mu}{G_{sp}} \frac{df}{dt} = \mu \frac{d(d_{total})}{dt} \]
Maxwell Model

For all stress comp

Two parameters

Relaxation Time

Zero-Shear Viscosity

Is this generalization correct?
Integral form of Maxwell Model

Addition of contributions of past events with “fading” memory to predict the stress at the current time:

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

Two parameters

\[ \lambda = \frac{\eta_0}{G_0} \quad \text{Relaxation Time} \]

\[ \eta_0 \quad \text{Zero-Shear Viscosity} \]

The stress at time t depends on the rate of strain at time t and the rate of strain at all past times t' with a weighting factor that decays exponentially (backwards) in time.

OR

The history of strain at all past times

\[
\left\{ \left( \frac{\eta_0}{\lambda^2} \right) e^{-(t-t')/\lambda} \right\}
\]

(Fading) Memory function
Maxwell Model Predictions in Rheological Flows
Simple Shear Flow

**Kinematics**

\[ \nu(y, t) = \dot{\gamma}(t) y e_x \]

\[ \ddot{\gamma}(t) = \dot{\gamma}_o = \text{constant} \]

**Material Properties**

\[ \eta \equiv \frac{\tau_{yx}}{\dot{\gamma}_o} \]

\[ \Psi_1 \equiv \frac{\tau_{xx} - \tau_{yy}}{\dot{\gamma}_o^2} \]

\[ \Psi_2 \equiv \frac{\tau_{yy} - \tau_{zz}}{\dot{\gamma}_o^2} \]
Steady Shear Flow

\[ \tau + \frac{\eta_o}{G_o} \frac{\partial \tau}{\partial t} = \eta_o \dot{\gamma} \]

Constitutive Model

\[ \tau = \eta_o \dot{\gamma} \]

\[ \eta \equiv \frac{\tau_{yx}}{\dot{\gamma}_o} = \eta_o \]

\[ \Psi_1 \equiv \frac{\tau_{xx} - \tau_{yy}}{\dot{\gamma}_o^2} = 0 \]

\[ \Psi_2 \equiv \frac{\tau_{yy} - \tau_{zz}}{\dot{\gamma}_o^2} = 0 \]

Cannot Predict Shear Thinning

Cannot Predict Normal Stresses
Start up of Simple Shear Flow

Kinematics

\[ \nu(y,t) = \dot{\gamma}(t) ye_x \]

\[ \dot{\gamma}(t) = \dot{\gamma}_o H(t) \]

Material Properties

\[ \eta^+ \equiv \frac{\tau_{yx}}{\dot{\gamma}_o} \]

\[ \Psi_1^+ \equiv \frac{\tau_{xx} - \tau_{yy}}{\dot{\gamma}_o^2} \]

\[ \Psi_2^+ \equiv \frac{\tau_{yy} - \tau_{zz}}{\dot{\gamma}_o^2} \]

Unidirectional Flow

\[ \dot{\gamma} = \begin{pmatrix} 0 & \dot{\gamma}(t) & 0 \\ \dot{\gamma}(t) & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \]
Start up of Simple Shear Flow

Constitutive Model

\[ \tau_{xx} + \frac{\eta_o}{G_o} \frac{\partial \tau_{xx}}{\partial t} = \eta_o \dot{\gamma}_{xx} = 0 \]

\[ \tau_{yy} + \frac{\eta_o}{G_o} \frac{\partial \tau_{yy}}{\partial t} = \eta_o \dot{\gamma}_{yy} = 0 \]

\[ \tau_{zz} + \frac{\eta_o}{G_o} \frac{\partial \tau_{zz}}{\partial t} = \eta_o \dot{\gamma}_{zz} = 0 \]

\[ \tau_{yx} + \frac{\eta_o}{G_o} \frac{\partial \tau_{yx}}{\partial t} = \eta_o \dot{\gamma}_{xy} H(t) \]

\[ \tau_{yx}(t) = \int_{-\infty}^{t} \left( \frac{\eta_o}{\lambda} \right) e^{-(t-t')/\lambda} \dot{\gamma}_{o} H(t') dt' = \left( \frac{\eta_o}{\lambda} \right) \dot{\gamma}_{o} \int_{0}^{t} e^{-(t-t')/\lambda} H(t') dt' \]

\[ = \left( \frac{\eta_o}{\lambda} \right) \dot{\gamma}_{o} \int_{0}^{t} e^{-(t-t')/\lambda} dt' = \left( \frac{\eta_o}{\lambda} \right) \dot{\gamma}_{o} \int_{-t/\lambda}^{0} e^{u} \lambda du = \eta_o \dot{\gamma}_{o} e^{0} \int_{-t/\lambda}^{0} = \eta_o \dot{\gamma}_{o} (1 - e^{-t/\lambda}) \]
Start up of Simple Shear Flow

\[ \tau_{yx}(t) = \eta_0 \gamma_o (1 - e^{-t/\lambda}) \]

\[ \eta^+ \equiv \frac{\tau_{yx}}{\gamma_o} = \eta_o (1 - \exp(-t/\lambda)) \]

It can predict the gradual increase of shear stress

\[ \Psi_1^+ \equiv \frac{\tau_{xx} - \tau_{yy}}{\dot{\gamma}_o^2} = 0 \quad \Psi_2^+ \equiv \frac{\tau_{yy} - \tau_{zz}}{\dot{\gamma}_o^2} = 0 \]

Cannot Predict Normal Stresses
Step strain Test

Kinematics

\[ \nu(y,t) = \dot{\gamma}(t) y e_x \]

\[ \dot{\gamma}(t) = \lim_{\varepsilon \to 0} \begin{cases} 
0 & t < 0 \\
\dot{\gamma}_o, & 0 \leq t < \varepsilon \\
0 & t \geq \varepsilon 
\end{cases} = \dot{\gamma}_o \delta^+(t) \]

\[ \dot{\gamma}_o \varepsilon = \text{constant} = \gamma_o \]

Material Properties

\[ G(t, \gamma_o) \equiv \frac{\tau_{yx}}{\gamma_o} \]
\[ G_{\Psi_1} \equiv \frac{\tau_{xx} - \tau_{yy}}{\gamma_o^2} \]
\[ G_{\Psi_2} \equiv \frac{\tau_{yy} - \tau_{zz}}{\gamma_o^2} \]

Relaxation Modulus
Step strain Test

\[ \tau(t = 0) = 0 \]

\[ \tau + \frac{\eta_o}{G_o} \frac{\partial \tau}{\partial t} = \eta_o \dot{\gamma} \]

\[ \tau_{xx} + \frac{\eta_o}{G_o} \frac{\partial \tau_{xx}}{\partial t} = \eta_o \dot{\gamma}_{xx} = 0 \]

\[ \tau_{yy} + \frac{\eta_o}{G_o} \frac{\partial \tau_{yy}}{\partial t} = \eta_o \dot{\gamma}_{yy} = 0 \]

\[ \tau_{zz} + \frac{\eta_o}{G_o} \frac{\partial \tau_{zz}}{\partial t} = \eta_o \dot{\gamma}_{zz} = 0 \]

\[ \tau_{yx} + \frac{\eta_o}{G_o} \frac{\partial \tau_{yx}}{\partial t} = \eta_o \dot{\gamma}_o \delta^+(t) \]

\[ \tau_{yx}(t) = \int_{-\infty}^{t} \left( \frac{\eta_o}{\lambda} \right) e^{-(t-t')/\lambda} \dot{\gamma}_o \delta(t') \, dt' = \left( \frac{\eta_o}{\lambda} \right) \dot{\gamma}_o \int_{0}^{t} e^{-(t-t')/\lambda} \delta(t') \, dt' = \left( \frac{\eta_o}{\lambda} \right) \dot{\gamma}_o e^{-t/\lambda} \]
Step strain Test

\[ \tau_{yx}(t) = \frac{\eta_o}{\lambda} \dot{\gamma}_o e^{-t/\lambda} \]

\[ G(t) = \frac{\tau_{yx}}{\gamma_o} = \frac{\eta_o}{\lambda} \exp(-t/\lambda) \]

Predicts realistic behavior for the Relaxation Modulus

\[ G_o = G(t = 0) \]

\[ G_{\Psi_1} \equiv \frac{\tau_{xx} - \tau_{yy}}{\gamma_o^2} = 0 \quad G_{\Psi_2} \equiv \frac{\tau_{yy} - \tau_{zz}}{\gamma_o^2} = 0 \]

Cannot Predict Normal Stresses
Relaxation Modulus

Linear Scale

Log- Scale
Relaxation Modulus

Comparison with Experiments for polystyrene solution, $M_w = 10^6$, again points to the need for model improvement

\[ G_o = \frac{\eta_o}{\lambda} = 2,500 \text{Pa} \]
\[ \lambda = 150 \text{s} \]
Generalized Maxwell model for multiple relaxation times
Superposition of Maxwell Models with different relaxation times $\lambda_1 > \lambda_2 > \ldots \lambda_N$

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

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

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

$$-\int_{-\infty}^{t} \sum_{k=1}^{N} \left[ \left( \frac{\eta_k}{\lambda_k^2} \right) e^{-(t-t')/\lambda_k} \right] \gamma(t,t') \, dt'$$

2N unknowns $\{\eta_k, \lambda_k\}$
Steady Simple & Step Shear

**Steady Simple Shear**

\[ \eta \equiv \frac{\tau_{yx}}{\dot{\gamma}_o} = \sum_{k=1}^{N} \eta_k \]

Cannot predict shear thinning.

**Step Shear**

\[ G(t) \equiv \sum_{k=1}^{N} \frac{\eta_k}{\lambda_k} \exp(-t / \lambda_k) \]

\[ G_{\Psi_1} \equiv \frac{\tau_{xx} - \tau_{yy}}{\dot{\gamma}_o^2} = 0 \]

\[ G_{\Psi_2} \equiv \frac{\tau_{yy} - \tau_{zz}}{\dot{\gamma}_o^2} = 0 \]

Cannot predict normal stresses.

Can describe relaxation for more extended periods of time.
Comparison with Experiments

Adding four Maxwell modes improves linear data
Kinematics
\[ y(t) = \dot{\gamma}(t) y e_x \]
\[ \dot{\gamma}(t) = \dot{\gamma}_o \cos(\omega t) \quad ; \quad \gamma_o = \dot{\gamma}_o / \omega \]

Material Properties
\[ \tau_{yx}(\gamma_o, t) \]
\[ \gamma_o \]
\[ G'(\omega) = \frac{\tau_o}{\dot{\gamma}_o} \cos(\delta) \quad \quad G''(\omega) = \frac{\tau_o}{\dot{\gamma}_o} \sin(\delta) \]
SAOS

Predictions of GMM

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

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

\[ 
G''(\omega) = \sum_{k=1}^{N} \frac{\eta_k \omega}{1 + (\lambda_k \omega)^2} 
\]
SAOS prediction of the Maxwell model for a single relaxation time
Comparison with experiments of GMM for multiple relaxation times (5 modes)

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

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

\[ \begin{array}{ccc}
  k & \lambda_k(s) & g_k(kPa) \\
  1 & 2.3E-3 & 16 \\
  2 & 3.0E-4 & 140 \\
  3 & 3.0E-5 & 90 \\
  4 & 3.0E-6 & 400 \\
  5 & 3.0E-7 & 4000 \\
\end{array} \]
General linear viscoelastic model
Consider a sequence of small deformations where their response is linear.

For the 1st deformation the stress is:

\[ \tau_{yx}(t) = G(t-t_1) \delta y_{yx}(t_1) \quad t_1 < t < t_2 \]

For the 2nd deformation the stress is:

\[ \tau_{yx}(t) = G(t-t_1) \delta y_{yx}(t_1) + G(t-t_2) \delta y_{yx}(t_2) \quad t_2 < t < t_3 \]

After N deformations:

\[ \tau_{yx}(t) = \sum_{i=1}^{N} G(t-t_i) \delta y_{yx}(t_i) \quad t_N < t \]
Continuum Consideration:

\[ \tau_{yx}(t) = \int_0^t G(t-t') \, d\gamma_{yx}(t') \]

Change of Variables

\[ d\gamma_{yx}(t') = \dot{\gamma}_{yx}(t') \, dt' \]

In practice

\[ \tau_{yx}(t) = \int_{-\infty}^t G(t-t') \, \dot{\gamma}_{yx}(t') \, dt' \]

It reminds us that we have to take into account the history of the material.
General linear viscoelastic model

Has factorized structure: Nature of fluid * Nature of flow, $\gamma$, $\dot{\gamma}$

For all stress components:

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

$G(t-t')$ : Relaxation Modulus

$M(t-t') = \partial G(t-t') / \partial t'$ : Memory Function

In practice:

$$
\tau(t) = \int_{0}^{t} G(t-t') \dot{\gamma}(t') dt'
$$
Steady Shear Flow

Kinematics

\[ \nu(y, t) = \dot{\gamma}(t) y e_x \]

\[ \dot{\gamma}(t) = \dot{\gamma}_o = \text{constant} \]

Material Properties

\[ \eta \equiv \frac{\tau_{yx}}{\dot{\gamma}_o} \quad \Psi_1 \equiv \frac{\tau_{xx} - \tau_{yy}}{\dot{\gamma}_o^2} \quad \Psi_2 \equiv \frac{\tau_{yy} - \tau_{zz}}{\dot{\gamma}_o^2} \]
Steady Shear Flow

Constitutive Relation

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

\[ \tau_{yy}(t) = \int_{-\infty}^{t} G(t-t') \dot{\gamma}_{yx}(t') dt' \]

\[ \tau_{ii}(t) = 0 \]

\[ \Psi_1 \equiv \frac{\tau_{xx} - \tau_{yy}}{\dot{\gamma}_o^2} = 0 \]

\[ \Psi_2 \equiv \frac{\tau_{yy} - \tau_{zz}}{\dot{\gamma}_o^2} = 0 \]

Cannot predict normal stresses
Steady Shear Flow

Constitutive Relation

\[ \tau_{yx}(t) = \int_{-\infty}^{t} G(t - t') \dot{\gamma}_{yx}(t') dt' \]

With change of variables

\[ s = t - t' \quad ds = d(t - t') = -dt' \]
\[ t' = -\infty \Rightarrow s = \infty \quad t' = t \Rightarrow s = 0 \]

Thus:

\[ \tau_{yx}(t) = \dot{\gamma}_o \int_{0}^{\infty} G(s) ds \]

The viscosity is:

\[ \eta \equiv \frac{\tau_{yx}}{\dot{\gamma}_o} = \int_{0}^{\infty} G(s) ds \rightarrow \eta_o \]

In the LVE
Uniaxial Elongation

Kinematics
\[ \dot{\gamma} = \nabla \mathbf{v} + (\nabla \mathbf{v})^T = 2 \dot{\varepsilon}_o \begin{pmatrix} -1/2 & 0 & 0 \\ 0 & -1/2 & 0 \\ 0 & 0 & 1 \end{pmatrix} \]

Constitutive Model
\[ \tau(t) = \int_{-\infty}^{t} G(t-t') \dot{\gamma}(t')dt' \]

With change of variables
\[ s = t - t' \quad \implies \quad ds = d(t-t') = -dt' \]
\[ t' = -\infty \implies s = \infty \quad \text{and} \quad t' = t \implies s = 0 \]

\[ \tau(s + t') = 2 \dot{\varepsilon}_o \int_0^s G(s) \begin{pmatrix} -1/2 & 0 & 0 \\ 0 & -1/2 & 0 \\ 0 & 0 & 1 \end{pmatrix} ds \]

Extensional Stress
\[ \tau_E = \tau_{zz} - \tau_{xx} \]
Start-up of Steady Shear

**Kinematics**

\[ \nu(y, t) = \dot{\gamma}(t) ye_x \]

\[ \dot{\gamma}(t) = \dot{\gamma}_o H(t) \]

**Material Properties**

\[ \eta^+ = \frac{\tau_{yx}}{\dot{\gamma}_o} \]

\[ \Psi_1^+ = \frac{\tau_{xx} - \tau_{yy}}{\dot{\gamma}_o^2} \]

\[ \Psi_2^+ = \frac{\tau_{yy} - \tau_{zz}}{\dot{\gamma}_o^2} \]

**Stress Growth Coefficient**

\[ \dot{\gamma} = \begin{pmatrix} 0 & \dot{\gamma}(t) & 0 \\ \dot{\gamma}(t) & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \]
**Start-up of Steady Shear**

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

Constitutive Model

\[ \tau_{yx}(t) = \int_{-\infty}^{t} G(t-t') \dot{\gamma}_{yx}(t') dt' \]

\[ \tau_{ii}(t) = 0 \]

\[ \Psi_1^+ \equiv \frac{\tau_{xx} - \tau_{yy}}{\dot{\gamma}_o^2} = 0 \quad \Psi_2^+ \equiv \frac{\tau_{yy} - \tau_{zz}}{\dot{\gamma}_o^2} = 0 \]

Cannot predict normal stresses
Start-up of Steady Shear

**Constitutive Model**

\[ \tau_{yx}(t) = \int_{-\infty}^{t} G(t-t') \dot{\gamma}_{yx}(t') dt' \]

Thus:

\[ \tau_{yx}(t) = \dot{\gamma}_o \int_{0}^{t} G(s) \, ds \]

The viscosity is:

\[ \eta^+ \equiv \frac{\tau_{yx}}{\dot{\gamma}_o} = \int_{0}^{t} G(s) \, ds \]

With change of variables

\[ s = t - t' \quad \Rightarrow \quad ds = d(t-t') = -dt' \]

\[ t' = 0 \Rightarrow s = t \quad \quad t' = t \Rightarrow s = 0 \]

\[ \tau_{yx}(t) = \dot{\gamma}_o \int_{0}^{t} G(s) \, ds \]
Cessation of Steady Shear

Kinematics

\[ \nu(y, t) = \dot{\gamma}(t) y e_x \]

\[ \dot{\gamma}(t) = \gamma_0 H(-t) \]

Material Properties

\[ \eta^- \equiv \frac{\tau_{yx}}{\gamma_0} \quad \Psi_1^- \equiv \frac{\tau_{xx} - \tau_{yy}}{\gamma_0^2} \quad \Psi_2^- \equiv \frac{\tau_{yy} - \tau_{zz}}{\gamma_0^2} \]

Stress cessation Coefficient

Unidirectional Flow
Cessation of Steady Shear

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

Constitutive Model

\[ \tau_{yx}(t) = \int_{-\infty}^{t} G(t - t') \dot{\gamma}_{yx}(t') dt' \]

\[ \tau_{ii}(t) = 0 \]

\[ \Psi_{1}^{-} \equiv \frac{\tau_{xx} - \tau_{yy}}{\dot{\gamma}_o^2} = 0 \quad \Psi_{2}^{-} \equiv \frac{\tau_{yy} - \tau_{zz}}{\dot{\gamma}_o^2} = 0 \]

Cannot predict normal stresses
Cessation of Steady Shear

Constitutive Model

\[ \tau_{yx}(t) = \int_{-\infty}^{t} G(t-t') \dot{\gamma}_{yx}(t') dt' \]

With Change of Variables

\[ s = t - t' \]
\[ ds = d(t - t') = -dt' \]
\[ t' = -\infty \implies s = \infty \]
\[ t' = t \implies s = 0 \]

Hence:

\[ \tau_{yx}(t) = \dot{\gamma}_o \int_{t}^{\infty} G(s) ds \]

The viscosity is

\[ \eta^- \equiv \frac{\tau_{yx}}{\dot{\gamma}_o} = \int_{t}^{\infty} G(s) ds \]
The Linear Viscoelastic Model

Differential form of the Maxwell model

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

Integral form of the Maxwell model

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

Generalized Maxwell model (N-Modes)

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

General Viscoelastic Model
Pros & Cons of GLVE Models

Pros

• The first set of constitutive relations with “memory”
• Can predict SAOS & Step Change Flows well
• Easy Calculations
• Can approximate start-up and cessation flows

Cons

• Predict Constant shear viscosity (no shear thinning, small strain rates).
• Assume that strains can be added (small strains)
• Like in generalized Newtonian models, stresses are proportional to strain rates. Hence they cannot predict Normal Stresses in shear flow.
• Their predictions are not frame-invariant!
**Frame Invariance**

The rotating coordinate system is related to the Cartesian one via:

\[
\begin{align*}
\bar{x} &= (x - x_o) \cos(Wt) + (y - y_o) \sin(Wt) \\
\bar{y} &= -(x - x_o) \sin(Wt) + (y - y_o) \cos(Wt)
\end{align*}
\]

Constant velocity is applied on the upper plate of a Couette device:

\[
\bar{u}_x = \dot{\gamma} y, \quad \text{where} \quad \dot{\gamma} \neq 1
\]

The rate of strain tensor based on the observer xyz-system is:

\[
\dot{\gamma} = \begin{pmatrix}
-\sin(2Wt) & \cos(2Wt) & 0 \\
\cos(2Wt) & \sin(2Wt) & 0 \\
0 & 0 & 0
\end{pmatrix}
\]

The integral form of the GLVM stress tensor is

\[
\tau = -\int_0^\infty G(s) \dot{\gamma} ds = -\dot{\gamma} \int_0^\infty G(s) \begin{pmatrix}
-\sin(2W(t - s)) & \cos(2W(t - s)) & 0 \\
\cos(2W(t - s)) & \sin(2W(t - s)) & 0 \\
0 & 0 & 0
\end{pmatrix} ds
\]
Remarks and conclusions

- The stress tensor depends on the rotation velocity of the moving coordinate system!!!

- The zero-shear viscosity for \( t=0 \) is:

\[
\tau_{xy} = -\eta_0 \dot{\gamma} = -\dot{\gamma} \int_0^\infty G(s) \cos(2Ws) ds \Rightarrow \eta_0 = \int_0^\infty G(s) \cos(2Ws) ds
\]

Hence, it depends on the angular velocity!!!

- Also, elastic materials are analyzed under the Lagrangian framework. Cause? The generalization of Maxwell’s equation to the tensorial form.

Thus, for viscoelastic materials, which are partially elastic, we need a better mathematical description to study them in the Eulerian framework.

Solution?

Objective time derivatives
SAOS

Kinematics
\[ v(y,t) = \dot{\gamma}(t) y e_x \]
\[ \dot{\gamma}(t) = \dot{\gamma}_o \cos(\omega t) \quad ; \quad \gamma_o = \dot{\gamma}_o / \omega \]

Material Properties
\[ \frac{\tau_{yx}(\gamma_o, t)}{\dot{\gamma}_o} = G' \sin(\omega t) + G'' \cos(\omega t) \]

Storage Modulus
\[ G'(\omega) = \frac{\tau_o}{\dot{\gamma}_o} \cos(\delta) \]

Loss Modulus
\[ G''(\omega) = \frac{\tau_o}{\dot{\gamma}_o} \sin(\delta) \]
SAOS

GVLE Predictions

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

\[ G'(\omega) = \omega \int_{0}^{\omega} G(s) \sin(\omega s) ds \]

\[ G''(\omega) = \omega \int_{0}^{\omega} G(s) \cos(\omega s) ds \]

\[ J_s^0 = \lim_{\omega \to 0} \left( \frac{G'(\omega)}{(G''(\omega))^2} \right) \]

Compliance in Steady Flow
SAOS

\[ \eta_0 = \lim_{\omega \to 0} \left( \frac{G''(\omega)}{\omega} \right) = \lim_{\omega \to 0} (\eta'(\omega)) \]

\[ \eta_0 = \frac{2}{\pi} \int_{-\infty}^{\infty} \frac{G'(\omega)}{\omega} d(\ln(\omega)) \]

\[ G_N^o = \frac{2}{\pi} \int_{-\infty}^{\infty} G''(\omega) d(\ln(\omega)) \]

\[ A_G \equiv \lim_{\omega \to 0} \left( \frac{G'(\omega)}{\omega^2} \right) = \int_{0}^{\infty} G(s)sds \]

\[ A_G \equiv J_s^o \eta_o^2 \]
SAOS

Proof that:

\[ A_G \equiv J_s^o \eta_o^2 \]

\[
A_G \equiv \lim_{\omega \to 0} \left( \frac{G'(\omega)}{\omega^2} \right) = \int_0^\infty G(s)sds
\]

\[
\lim_{\omega \to 0} (\sin(\omega s)) = \omega s
\]

\[
G'(\omega) = \omega \int_0^\infty G(s) \sin(\omega s)ds
\]

\[
A_G \equiv \lim_{\omega \to 0} \left( \frac{G'(\omega)}{\omega^2} \right) = \lim_{\omega \to 0} \left( \frac{\omega \int_0^\infty G(s) \sin(\omega s)ds}{\omega^2} \right) = \lim_{\omega \to 0} \left( \frac{\omega \int_0^\infty G(s)\omega ds}{\omega^2} \right) = \int_0^\infty G(s)ds
\]

\[
J_s^o = \lim_{\omega \to 0} \left( \frac{G'(\omega)}{\left(G''(\omega)\right)^2} \right) = \frac{1}{\eta_o^2} \int_0^\infty G(s)s(s)
\]

\[ A_G \equiv J_s^o \eta_o^2 \]
SAOS

Plateau Modulus
Integration of the loss modulus

\[ G^o_N = \frac{2}{\pi} \int_{-\infty}^{\infty} G''(\omega)d(ln(\omega)) \]
Creep Test

Kinematics

\[ \dot{\gamma}_{yx}(t) y e_x \]

Material Properties

\[ J(t, \tau_o) = \frac{\gamma_{yx}(0,t)}{\tau_o} \]

\[ J_r(t', \tau_o) = \frac{\gamma_r(t')}{\tau_o} \]

Shear Compliance

Recoverable Compliance

In linear viscoelasticity \( J \) is independent of \( \tau_o \) (cm\(^2\)/dyn)
Creep Test

Compliance in steady state gives a modulus of the final stored elastic energy

\[ J(t, \tau_0) = J_s^o + \frac{t}{\eta_o} \]

Boltzmann superposition results

\[ \eta_o = \int_0^\infty G(s) \, ds \]

\[ J_s^o = \frac{1}{\eta_o^2} \int_0^\infty G(s) \, ds = \frac{\int_0^\infty G(s) \, ds}{\left[ \int_0^\infty G(s) \, ds \right]^2} \]

\[ J_s^o = \frac{1}{\eta_o^2} \int_{-\infty}^\infty G(s) \, s^2 \, d(\ln(s)) \]
Relaxation Modulus

Comparison with Experiments for the determination of the relaxation time

**Maxwell Model**

\[ G(t) = G_o \exp(-t / \lambda) \]

The function \( tG(t) \) reaches its max value when \( t = \lambda \)

t\( G(t) \) for polybutylene of high molecular weight \( M_w=940,000 \) and zero dispersity in the length of macromolecular chains. The continuous line depicts the predictions of the Maxwell model.