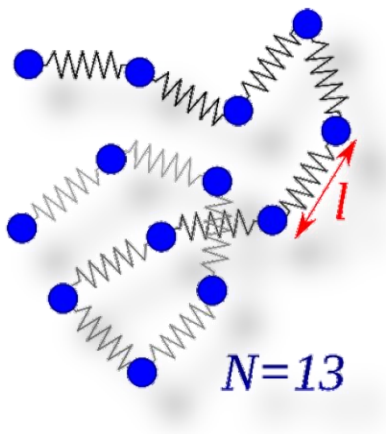
Introduction to Rheology of complex fluids
Brief Lecture Notes

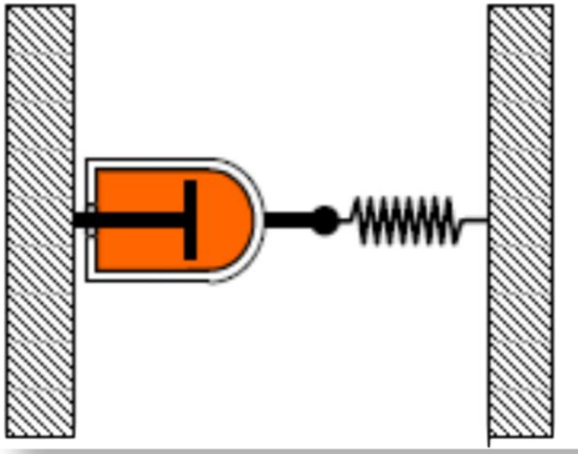
Linear Viscoelasticity

UNIVERSITY OF PATRAS
Department Of Chemical Engineering
ChemEngUP

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

UNIVERSITY OF PATRAS
Department Of Chemical Engineering
ChemEngUP

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

$$\underline{\underline{\tau}}(t) = G\underline{\underline{\gamma}}(t_o, t)$$

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

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

UNIVERSITY OF PATRAS
Department Of Chemical Engineering
ChemEngUP

Maxwell Model

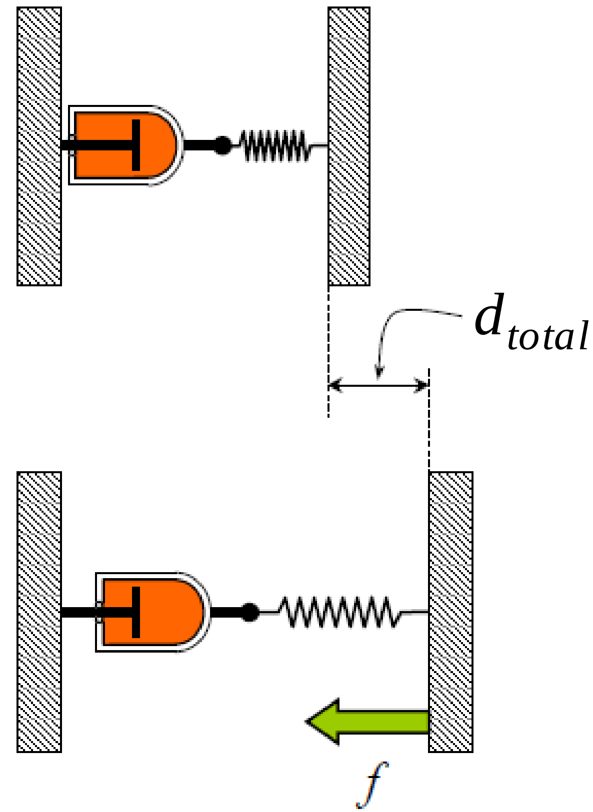
$$\begin{cases} \dot{\gamma}_{xy}(t) = \dfrac{\partial}{\partial t}\gamma_{xy}(t_o,t) \\ \gamma_{xy}(t_o,t) = \int_{t_o}^{t} \dot{\gamma}_{xy}(t')dt' \end{cases}$$

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

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: $$d_{total} = d_{sping} + d_{dashpot}$$

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

Maxwell Model

The force on the spring:

$$f = G_{sp} d_{spring}$$

The force on the dashpot:

$$f = \mu \frac{d\left(d_{dash}\right)}{dt}$$

The total Displacement

$$d_{total} = d_{sping} + d_{dashpot}$$

$$\frac{d\left(d_{total}\right)}{dt} = \frac{d\left(d_{sping}\right)}{dt} + \frac{d\left(d_{dashpot}\right)}{dt}$$

$$\frac{d\left(d_{total}\right)}{dt} = \frac{1}{G_{sp}} \frac{df}{dt} + \frac{1}{\mu} f$$

$$f + \frac{\mu}{G_{sp}} \frac{df}{dt} = \mu \frac{d\left(d_{total}\right)}{dt}$$

Maxwell Model

$$f+\frac{\mu}{G_{sp}}\frac{df}{dt}=\mu\frac{d\left(d_{total}\right)}{dt}$$

In Shear

$$\tau_{yx}+\frac{\eta_o}{G_o}\frac{\partial\tau_{yx}}{\partial t}=\eta_o\dot{\gamma}_{yx}$$

G_o Relaxation Modulus

For all stress comp

$$\underline{\underline{\tau}}+\frac{\eta_o}{G_o}\frac{\partial\underline{\underline{\tau}}}{\partial t}=\eta_o\underline{\underline{\dot{\gamma}}}$$

Two parameters

$\lambda=\frac{\eta_o}{G_o}$ Relaxation Time

η_o 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:

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

$$- \int_{-\infty}^{t} \left\{ \left(\frac{\eta_o}{\lambda^2} \right) e^{-(t-t')/\lambda} \right\} \underline{\underline{\gamma}}(t,t')dt'$$

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

Two parameters

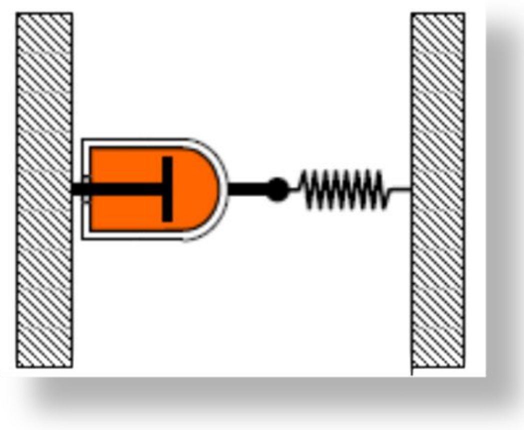
$$\lambda = \frac{\eta_o}{G_o}$$ Relaxation Time

η_o Zero-Shear Viscosity

$$\left\{ \left(\frac{\eta_o}{\lambda^2} \right) e^{-(t-t')/\lambda} \right\}$$

(Fading) Memory function

UNIVERSITY OF PATRAS
Department Of Chemical Engineering
ChemEngUP



Maxwell Model Predictions in Rheological Flows

UNIVERSITY OF PATRAS
Department Of Chemical Engineering
ChemEngUP

Simple Shear Flow

Kinematics

$$\underline{v}(y,t) = \dot{\varsigma}(t)\, y\, \underline{e}_x$$

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

Material Properties

$$\eta \equiv \frac{\tau_{yx}}{\dot{\gamma}_o} \qquad \Psi_1 \equiv \frac{\tau_{xx} - \tau_{yy}}{\dot{\gamma}_o^2} \qquad \Psi_2 \equiv \frac{\tau_{yy} - \tau_{zz}}{\dot{\gamma}_o^2}$$

Steady Shear Flow

$$\underline{\underline{\tau}} + \frac{\eta_o}{G_o}\underbrace{\frac{\partial \underline{\underline{\tau}}}{\partial t}}_{\underline{\underline{0}}} = \eta_o \underline{\underline{\dot{\gamma}}} \Rightarrow \underline{\underline{\tau}} = \eta_o \underline{\underline{\dot{\gamma}}}$$

Constitutive Model

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

Cannot Predict Shear Thinning

$$\Psi_1 \equiv \frac{\tau_{xx} - \tau_{yy}}{\dot{\gamma}_o^2} = 0 \qquad \Psi_2 \equiv \frac{\tau_{yy} - \tau_{zz}}{\dot{\gamma}_o^2} = 0$$

Cannot Predict Normal Stresses

Start up of Simple Shear Flow

Kinematics

$$\underline{v}(y,t) = \dot{\varsigma}(t) y \underline{e}_x$$

$$\dot{\varsigma}(t) = \dot{\gamma}_o H(t)$$

Unidirectional Flow

$$\underline{\underline{\dot{\gamma}}} = \begin{pmatrix} 0 & \dot{\varsigma}(t) & 0 \\ \dot{\varsigma}(t) & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

Material Properties

$$\eta^+ \equiv \frac{\tau_{yx}}{\dot{\gamma}_o} \qquad \Psi_1^+ \equiv \frac{\tau_{xx} - \tau_{yy}}{\dot{\gamma}_o^2} \qquad \Psi_2^+ \equiv \frac{\tau_{yy} - \tau_{zz}}{\dot{\gamma}_o^2}$$

UNIVERSITY OF PATRAS
Department Of Chemical Engineering
ChemEngUP

Start up of Simple Shear Flow

$$\underline{\underline{\tau}} + \frac{\eta_o}{G_o}\frac{\partial \underline{\underline{\tau}}}{\partial t} = \eta_o \underline{\underline{\dot{\gamma}}}$$

$$\underline{\underline{\tau}}(t=0)=0$$

Constitutive Model

$$\tau_{xx} + \frac{\eta_o}{G_o}\frac{\partial \tau_{xx}}{\partial t} = \eta_o \dot{\gamma}_{xx} = 0 \quad \Rightarrow \quad \tau_{xx}=0$$

$$\tau_{yy} + \frac{\eta_o}{G_o}\frac{\partial \tau_{yy}}{\partial t} = \eta_o \dot{\gamma}_{yy} = 0 \quad \Rightarrow \quad \tau_{yy}=0$$

$$\tau_{zz} + \frac{\eta_o}{G_o}\frac{\partial \tau_{zz}}{\partial t} = \eta_o \dot{\gamma}_{zz} = 0 \quad \Rightarrow \quad \tau_{zz}=0$$

$$\tau_{yx} + \frac{\eta_o}{G_o}\frac{\partial \tau_{yx}}{\partial t} = \eta_o \dot{\gamma}_o H(t)$$

$$\tau_{yx}(t) = \int_{-\infty}^{t}\left(\frac{\eta_o}{\lambda}\right)e^{-(t-t')/\lambda}\dot{\gamma}_o H(t')dt' = \left(\frac{\eta_o}{\lambda}\right)\dot{\gamma}_o \int_0^t e^{-(t-t')/\lambda} H(t')dt'$$

$$= \left(\frac{\eta_o}{\lambda}\right)\dot{\gamma}_o \int_0^t e^{-(t-t')/\lambda}dt' \overset{u=-\frac{t-t'}{\lambda}}{=} \left(\frac{\eta_o}{\lambda}\right)\dot{\gamma}_o \int_{-t/\lambda}^{0} e^{u}\lambda du = \eta_o\dot{\gamma}_o e^{u}\Big|_{-t/\lambda}^{0} = \eta_o\dot{\gamma}_o\left(1-e^{-t/\lambda}\right)$$

Start up of Simple Shear Flow

$$\tau_{yx}(t) = \eta_o \dot{\gamma}_o (1 - e^{-t/\lambda})$$

$$\eta^+ \equiv \frac{\tau_{yx}}{\dot{\gamma}_o} = \eta_o (1 - \exp(-t/\lambda))$$

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

UNIVERSITY OF PATRAS Department Of Chemical Engineering ChemEngUP

Step strain Test

Kinematics

$$\underline{v}(y,t)=\dot{\varsigma}(t)y\underline{e}_x$$

Unidirectional Flow

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

$$\dot{\gamma}_o\varepsilon=\text{constant}=\gamma_o$$

Material Properties

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

Relaxation Modulus

Step strain Test

$$\underline{\underline{\tau}} + \frac{\eta_o}{G_o}\frac{\partial \underline{\underline{\tau}}}{\partial t} = \eta_o \underline{\underline{\dot{\gamma}}}$$

$$\underline{\underline{\tau}}(t=0) = 0$$

$$\left\{\begin{aligned}
&\tau_{xx} + \frac{\eta_o}{G_o}\frac{\partial \tau_{xx}}{\partial t} = \eta_o \underbrace{\dot{\gamma}_{xx}}_{0} = 0 \\
&\tau_{yy} + \frac{\eta_o}{G_o}\frac{\partial \tau_{yy}}{\partial t} = \eta_o \underbrace{\dot{\gamma}_{yy}}_{0} = 0 \\
&\tau_{zz} + \frac{\eta_o}{G_o}\frac{\partial \tau_{zz}}{\partial t} = \eta_o \underbrace{\dot{\gamma}_{zz}}_{0} = 0 \\
&\tau_{yx} + \frac{\eta_o}{G_o}\frac{\partial \tau_{yx}}{\partial t} = \eta_o \dot{\gamma}_o \delta^+(t)
\end{aligned}\right.$$

$$\tau_{xx} = 0$$

$$\tau_{yy} = 0$$

$$\tau_{zz} = 0$$

$$\tau_{yx}(t) = \int_{-\infty}^{t}\left(\frac{\eta_o}{\lambda}\right)e^{-(t-t')/\lambda}\dot{\gamma}_o\delta(t')dt' = \left(\frac{\eta_o}{\lambda}\right)\dot{\gamma}_o\int_0^t e^{-(t-t')/\lambda}\delta(t')dt' = \left(\frac{\eta_o}{\lambda}\right)\dot{\gamma}_o e^{-t/\lambda}$$

University of Patras – Department Of Chemical Engineering – ChemEngUP

Step strain Test

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

$$G(t) \equiv \frac{\tau_{yx}}{\gamma_o} = \underbrace{\frac{\eta_o}{\lambda}}_{G_o} \exp(-t/\lambda)$$

Predicts realistic behavior
for the Relaxation Modulus

$$G_o = G(t=0)$$

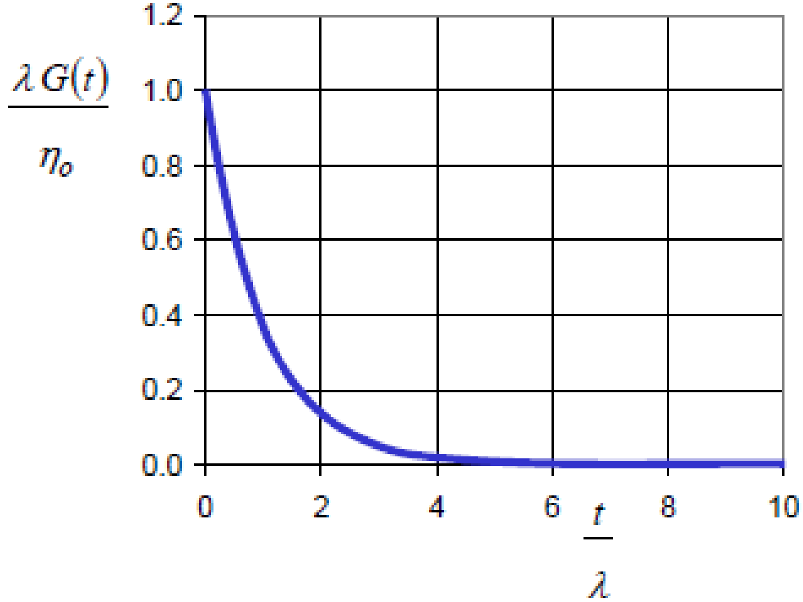
$$G_{\Psi_1} \equiv \frac{\tau_{xx} - \tau_{yy}}{\gamma_o^2} = 0 \qquad G_{\Psi_2} \equiv \frac{\tau_{yy} - \tau_{zz}}{\gamma_o^2} = 0$$

Cannot Predict
Normal Stresses

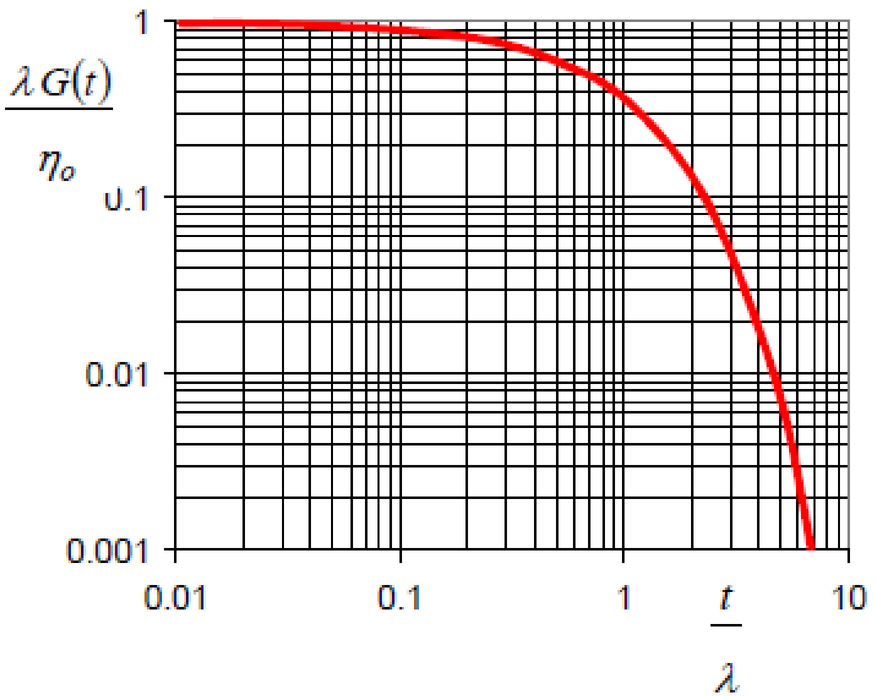
UNIVERSITY OF PATRAS
Department
Of Chemical
Engineering
ChemEngUP

Relaxation Modulus

Linear Scale

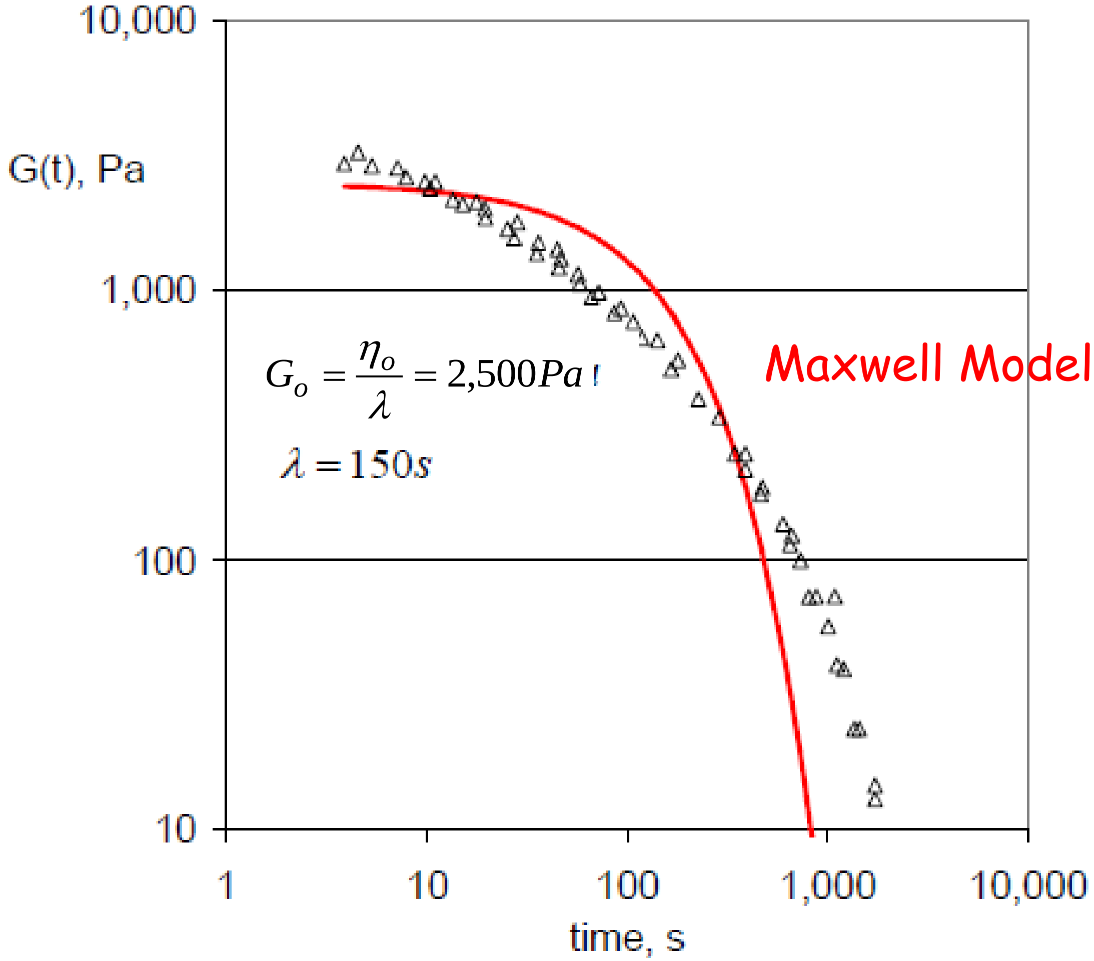


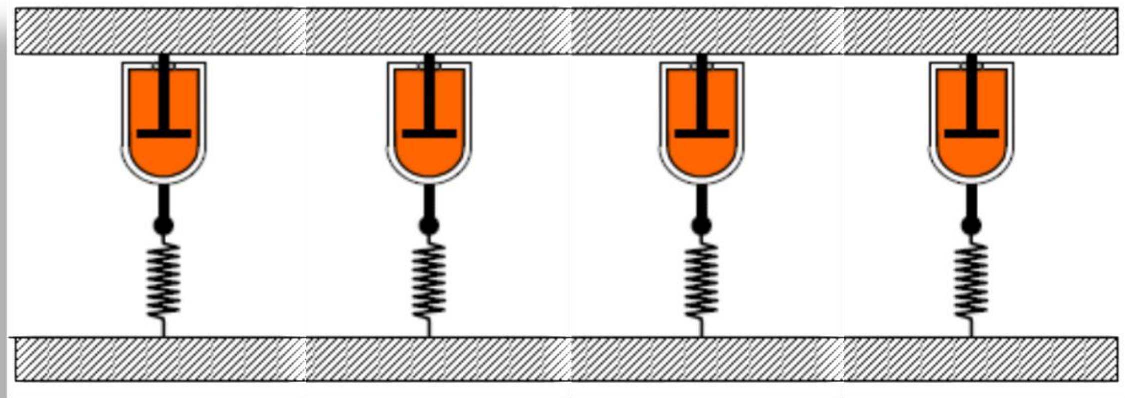
Log- Scale



Relaxation Modulus

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





Generalized Maxwell model for multiple relaxation times

UNIVERSITY OF PATRAS
Department Of Chemical Engineering
ChemEngUP

Superposition of Maxwell Models with different relaxation times $\lambda_1 > \lambda_2 > \ldots \lambda_N$

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

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

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

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

2N unknowns $\{\eta_k, \lambda_k\}$

Steady Simple & Step Shear

Steady Simple Shear

$$\eta \equiv \frac{\tau_{yx}}{\dot{\gamma}_o} = \sum_{k=1}^{N} \eta_k \qquad \Psi_1 \equiv \frac{\tau_{xx} - \tau_{yy}}{\dot{\gamma}_o^2} = 0 \qquad \Psi_2 \equiv \frac{\tau_{yy} - \tau_{zz}}{\dot{\gamma}_o^2} = 0$$

Cannot Predict shear thinning

Cannot predict normal stresses

Step Shear

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

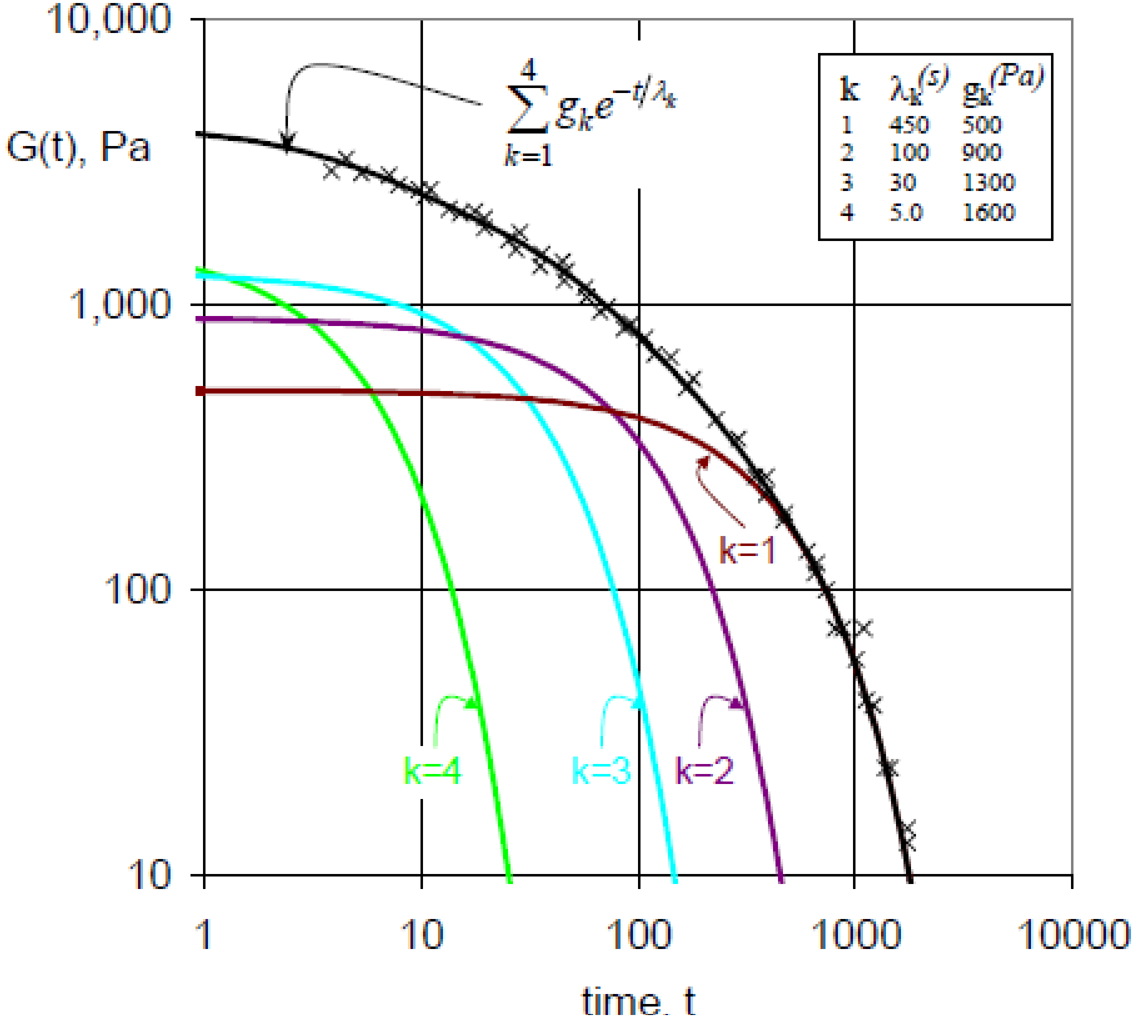
Can describe relaxation for more extended periods of time

$$G_{\Psi_1} \equiv \frac{\tau_{xx} - \tau_{yy}}{\dot{\gamma}_o^2} = 0 \qquad G_{\Psi_2} \equiv \frac{\tau_{yy} - \tau_{zz}}{\dot{\gamma}_o^2} = 0$$

UNIVERSITY OF PATRAS Department Of Chemical Engineering ChemEngUP

Comparison with Experiments

Adding four Maxwell modes improves linear data



k	λ_k (s)	g_k (Pa)
1	450	500
2	100	900
3	30	1300
4	5.0	1600

SAOS

Kinematics

$$\underline{v}(y,t) = \dot{\varsigma}(t)\, y\, \underline{e}_x$$

$$\dot{\varsigma}(t) = \dot{\gamma}_o \cos(\omega t) \quad ; \quad \gamma_o = \dot{\gamma}_o / \omega$$

Unidirectional Flow

$$\underline{\underline{\dot{\gamma}}} = \begin{pmatrix} 0 & \dot{\varsigma}(t) & 0 \\ \dot{\varsigma}(t) & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

Material Properties

$$\frac{\tau_{yx}(\gamma_o, t)}{\gamma_o} = G' \sin(\omega t) + G'' \cos(\omega t)$$

$$G'(\omega) = \frac{\tau_o}{\dot{\gamma}_o} cos(\delta)$$

Storage Modulus

$$G''(\omega) = \frac{\tau_o}{\dot{\gamma}_o} sin(\delta)$$

Loss Modulus

SAOS

Predictions of GMM

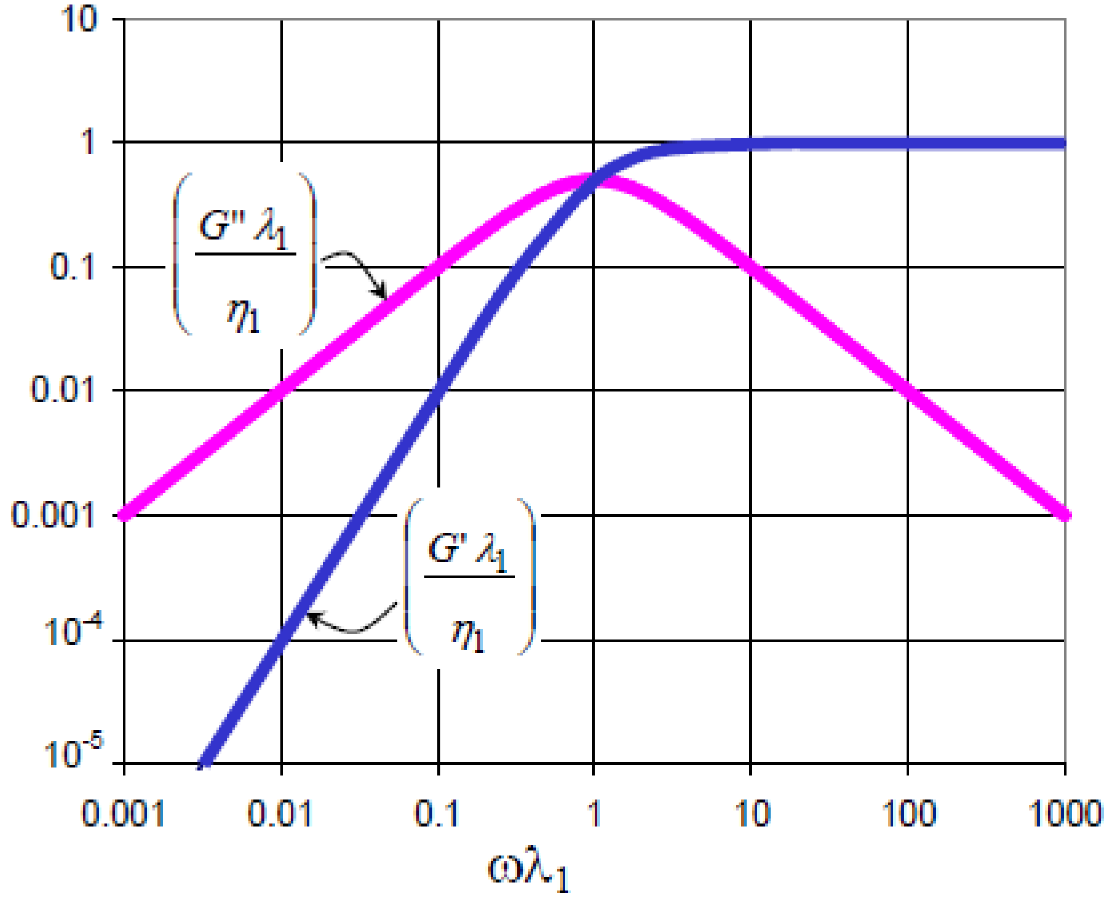
GMM

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

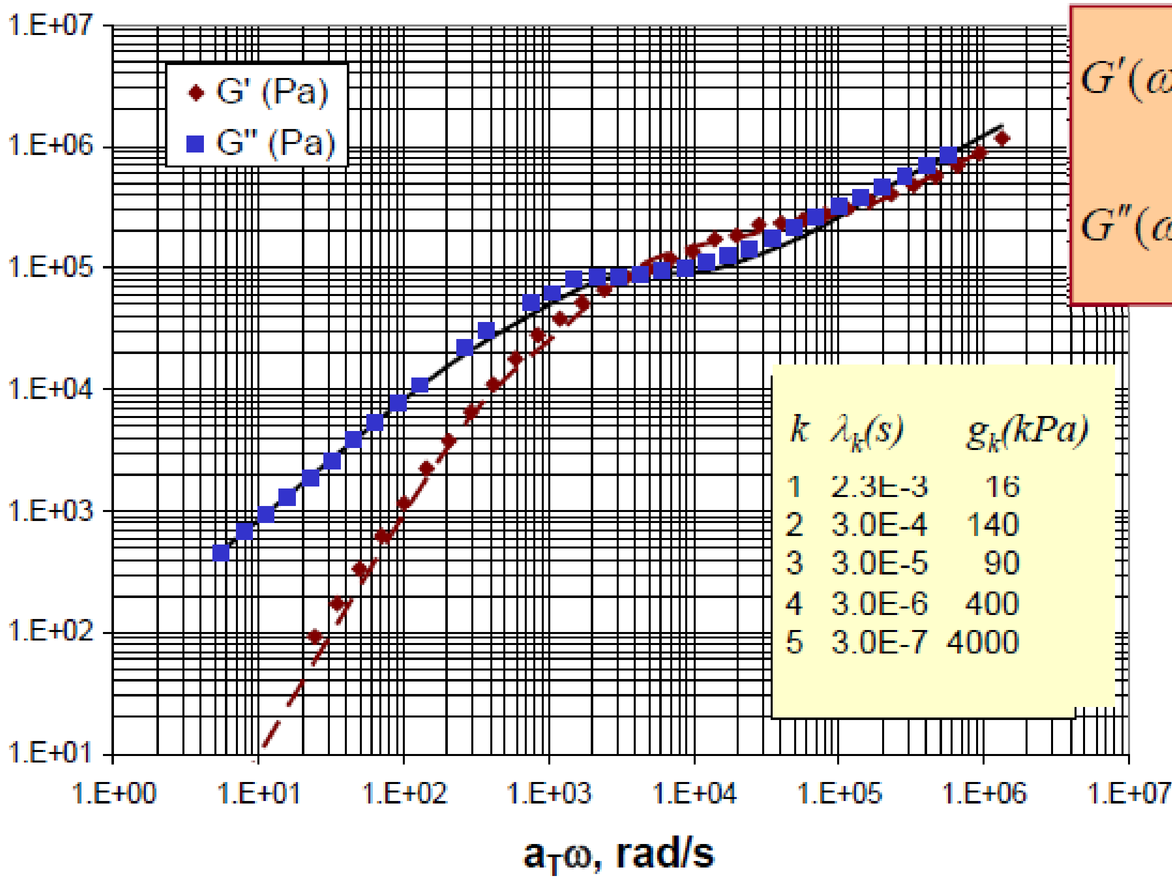
$$G'(\omega) = \sum_{k=1}^{N} \frac{\eta_k \lambda_k \omega^2}{1 + (\lambda_k \omega)^2}$$

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

SAOS prediction of the Maxwell model for a single relaxation time



Comparison with experiments of GMM for multiple relaxation times (5 modes)

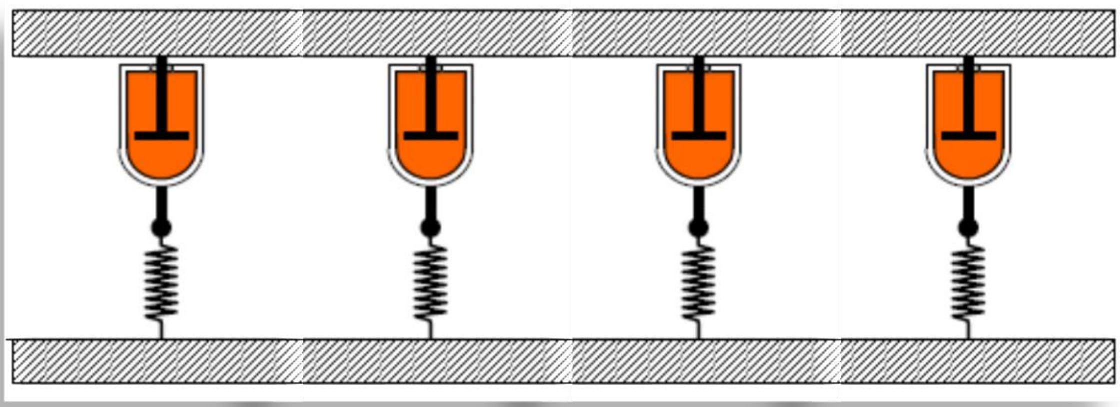


$$G'(\omega) = \sum_{k=1}^{N} \frac{\eta_k \lambda_k \omega^2}{1 + (\lambda_k \omega)^2}$$

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

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

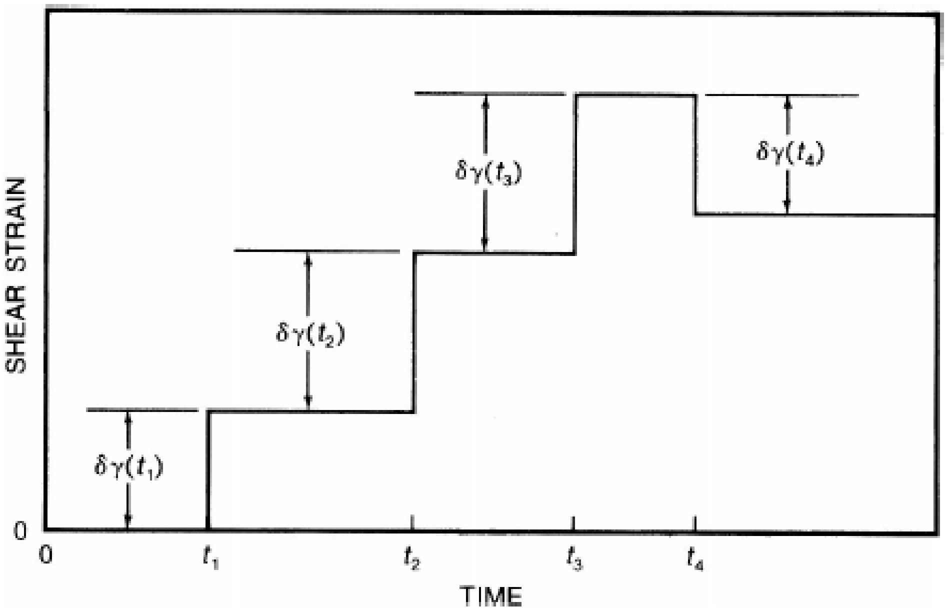
UNIVERSITY OF PATRAS
Department Of Chemical Engineering
ChemEngUP



General linear viscoelastic model

Boltzmann Superposition

The experiment of multiple step changes in shear



Consider a sequence of small deformations where their response is linear.

For the 1st deformation the stress is:

$$\tau_{yx}(t) = G(t-t_1)\,\delta\gamma_{yx}(t_1) \quad t_1 < t < t_2$$

For the 2nd deformation the stress is:

$$\tau_{yx}(t) = G(t-t_1)\,\delta\gamma_{yx}(t_1) + G(t-t_2)\,\delta\gamma_{yx}(t_2) \quad t_2 < t < t_3$$

After N deformations:

$$\tau_{yx}(t) = \sum_{i=1}^{N} G(t-t_i)\,\delta\gamma_{yx}(t_i) \quad t_N < t$$

University of Patras
Department Of Chemical Engineering
ChemEngUP

General linear viscoelastic model

Continuum Consideration:

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

Change of Variables

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

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

It reminds us that we have to take into account the history of the material.

In practise

$$\tau_{yx}(t) = \int_0^{t} G(t-t')\, \dot{\gamma}_{yx}(t') dt'$$

General linear viscoelastic model

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

For all stress components:

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

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

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

Nature of fluid

In practice:

$$\underline{\underline{\tau}}(t) = \int_{0}^{t} G(t-t')\,\underline{\underline{\dot{\gamma}}}(t')dt'$$

Steady Shear Flow

Kinematics

$$\underline{v}(y,t) = \dot{\varsigma}(t)\, y\, \underline{e}_x$$

Unidirectional Flow

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

$$\underline{\underline{\dot{\gamma}}} = \begin{pmatrix} 0 & \dot{\varsigma}(t) & 0 \\ \dot{\varsigma}(t) & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

Material Properties

$$\eta \equiv \frac{\tau_{yx}}{\dot{\gamma}_o} \qquad \Psi_1 \equiv \frac{\tau_{xx} - \tau_{yy}}{\dot{\gamma}_o^2} \qquad \Psi_2 \equiv \frac{\tau_{yy} - \tau_{zz}}{\dot{\gamma}_o^2}$$

UNIVERSITY OF PATRAS Department Of Chemical Engineering ChemEngUP

Steady Shear Flow

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

Constitutive Relation

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

$$\tau_{ii}(t) = 0$$

$$\Psi_1 \equiv \frac{\tau_{xx}-\tau_{yy}}{\dot{\gamma}_o^2} = 0 \qquad \Psi_2 \equiv \frac{\tau_{yy}-\tau_{zz}}{\dot{\gamma}_o^2} = 0$$

Cannot predict
normal stresses

UNIVERSITY OF PATRAS
Department
Of Chemical
Engineering
ChemEngUP

Steady Shear Flow

Constitutive Relation

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

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

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

With change of variables

$$s=t-t' \qquad ds=d\left(t-t'\right)=-dt'$$

$$t'=-\infty\Rightarrow s=\infty \qquad t'=t\Rightarrow s=0$$

Thus:

$$\tau_{yx}(t)=\dot{\gamma}_{o}\int_{0}^{\infty}G(s)\,ds$$

In the LVE

The viscosity is:

$$\eta\equiv\frac{\tau_{yx}}{\dot{\gamma}_{o}}=\int_{0}^{\infty}G(s)ds\rightarrow\eta_{o}$$

UNIVERSITY OF PATRAS Department Of Chemical Engineering ChemEngUP

Uniaxial Elongation

Kinematics

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

Constitutive Model

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

With change of variables

$$s = t - t' \qquad ds = d(t-t') = -dt'$$

$$t' = -\infty \Rightarrow s = \infty \qquad t' = t \Rightarrow s = 0$$

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

Extensional Stress

$$\tau_E = \tau_{zz} - \tau_{xx}$$

UNIVERSITY OF PATRAS
Department Of Chemical Engineering
ChemEngUP

Start-up of Steady Shear

Kinematics

$$\underline{v}(y,t) = \dot{\varsigma}(t)\, y\, \underline{e}_x$$

Unidirectional Flow

$$\dot{\varsigma}(t) = \dot{\gamma}_o H(t)$$

$$\underline{\underline{\dot{\gamma}}} = \begin{pmatrix} 0 & \dot{\varsigma}(t) & 0 \\ \dot{\varsigma}(t) & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

Material Properties

$$\eta^+ \equiv \frac{\tau_{yx}}{\dot{\gamma}_o} \qquad \Psi_1^+ \equiv \frac{\tau_{xx} - \tau_{yy}}{\dot{\gamma}_o^2} \qquad \Psi_2^+ \equiv \frac{\tau_{yy} - \tau_{zz}}{\dot{\gamma}_o^2}$$

Stress Growth Coefficient

UNIVERSITY OF PATRAS
Department Of Chemical Engineering
ChemEngUP

Start-up of Steady Shear

Constitutive Model

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

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

$$\tau_{ii}(t) = 0$$

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

Cannot predict
normal stresses

UNIVERSITY OF PATRAS
Department Of Chemical Engineering
ChemEngUP

Start-up of Steady Shear

Constitutive Model

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

$$\tau_{yx}(t) = \int_{-\infty}^{t} G(t-t')\,\dot{\gamma}_o H(t')dt'$$

$$= \dot{\gamma}_o \int_0^t G(t-t')\,dt'$$

With change of variables

$$s = t - t' \qquad ds = d\left(t-t'\right) = -dt'$$

$$t' = 0 \Rightarrow s = t \qquad t' = t \Rightarrow s = 0$$

Thus:

$$\tau_{yx}(t) = \dot{\gamma}_o \int_0^t G(s)\,ds$$

The viscosity is:

$$\eta^+ \equiv \frac{\tau_{yx}}{\dot{\gamma}_o} = \int_0^t G(s)ds$$

Cessation of Steady Shear

Kinematics

$$\underline{v}(y,t) = \dot{\varsigma}(t) y \underline{e}_x$$

Unidirectional Flow

$$\dot{\varsigma}(t) = \dot{\gamma}_o H(-t)$$

$$\underline{\underline{\dot{\gamma}}} = \begin{pmatrix} 0 & \dot{\varsigma}(t) & 0 \\ \dot{\varsigma}(t) & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

Material Properties

$$\eta^- \equiv \frac{\tau_{yx}}{\dot{\gamma}_o} \qquad \Psi_1^- \equiv \frac{\tau_{xx} - \tau_{yy}}{\dot{\gamma}_o^2} \qquad \Psi_2^- \equiv \frac{\tau_{yy} - \tau_{zz}}{\dot{\gamma}_o^2}$$

Stress cessation Coefficient

Cessation of Steady Shear

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

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

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

$$\tau_{yx}(t) = \int_{-\infty}^{t} G(t-t')\,\dot{\gamma}_o H(-t')dt'$$

$$= \dot{\gamma}_o \int_{-\infty}^{0} G(t-t')\,dt'$$

With Change of Variables

$$s = t - t' \qquad ds = d(t-t') = -dt'$$

$$t' = -\infty \Rightarrow s = \infty \qquad t' = t \Rightarrow s = 0$$

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

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

Integral form of the Maxwell model

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

Generalized Maxwell model (N-Modes)

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

General Viscoelastic Model

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

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

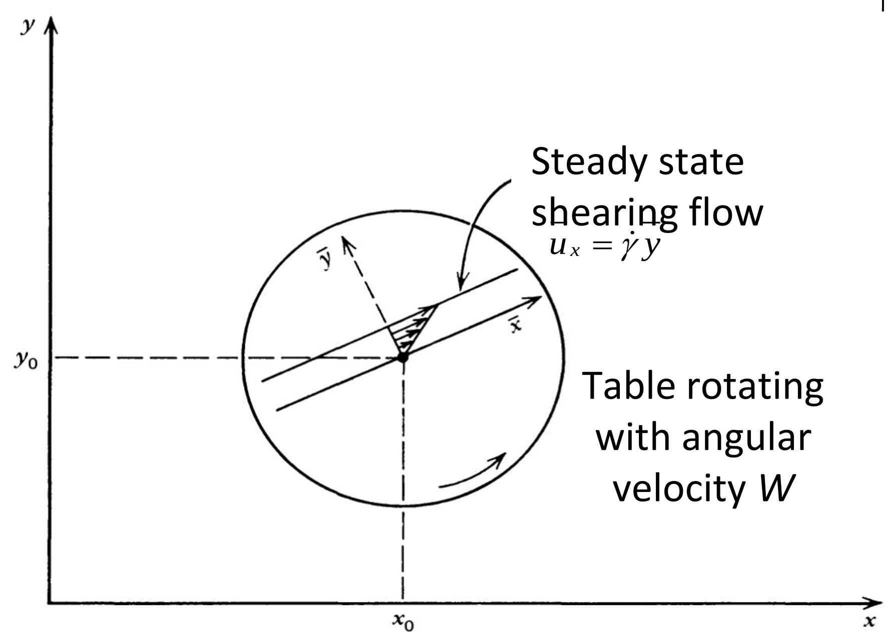
Cons

- 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:

$$\begin{cases} \bar{x} = (x - x_o)\cos(Wt) + (y - y_o)\sin(Wt) \\ \bar{y} = -(x - x_o)\sin(Wt) + (y - y_o)\cos(Wt) \end{cases}$$



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

$\bar{u}_x = \dot{\gamma}\bar{y}$ where $\dot{\gamma} \ll 1$

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

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

The integral form of the GLVM stress tensor is

$$\underline{\underline{\tau}} = -\int_0^\infty G(s)\underline{\underline{\dot{\gamma}}} ds = -\dot{\gamma}\int_0^\infty G(s) \begin{pmatrix} -\sin(2W(t-s)) & \cos(2W(t-s)) & 0 \\ \cos(2W(t-s)) & \sin(2W(t-s)) & 0 \\ 0 & 0 & 0 \end{pmatrix} ds$$

Remarks and conclusions

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

- The zero-shear viscosity for t=0 is:

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

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

University of Patras Department Of Chemical Engineering ChemEngUP

SAOS

Kinematics

$$\underline{v}(y,t) = \dot{\varsigma}(t)\, y\, \underline{e}_x$$

$$\dot{\varsigma}(t) = \dot{\gamma}_o \cos(\omega t) \quad ; \quad \gamma_o = \dot{\gamma}_o / \omega$$

Unidirectional Flow

$$\underset{=}{\dot{\gamma}} = \begin{pmatrix} 0 & \dot{\varsigma}(t) & 0 \\ \dot{\varsigma}(t) & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

Material Properties

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

$$G'(\omega) = \frac{\tau_o}{\dot{\gamma}_o} \cos(\delta)$$

Storage Modulus

$$G''(\omega) = \frac{\tau_o}{\dot{\gamma}_o} \sin(\delta)$$

Loss Modulus

UNIVERSITY OF PATRAS Department Of Chemical Engineering ChemEngUP

SAOS

GVLE Predictions

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

$$G'(\omega) = \omega \int_0^{\omega} G(s)\sin(\omega s)ds$$

$$G''(\omega) = \omega \int_0^{\omega} G(s)\cos(\omega s)ds$$

Compliance in Steady Flow

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

SAOS

RC-3 polybutadiene $M_w = 940,000$, $M_w/M_n < 1.1$, $T_g = -99°C$

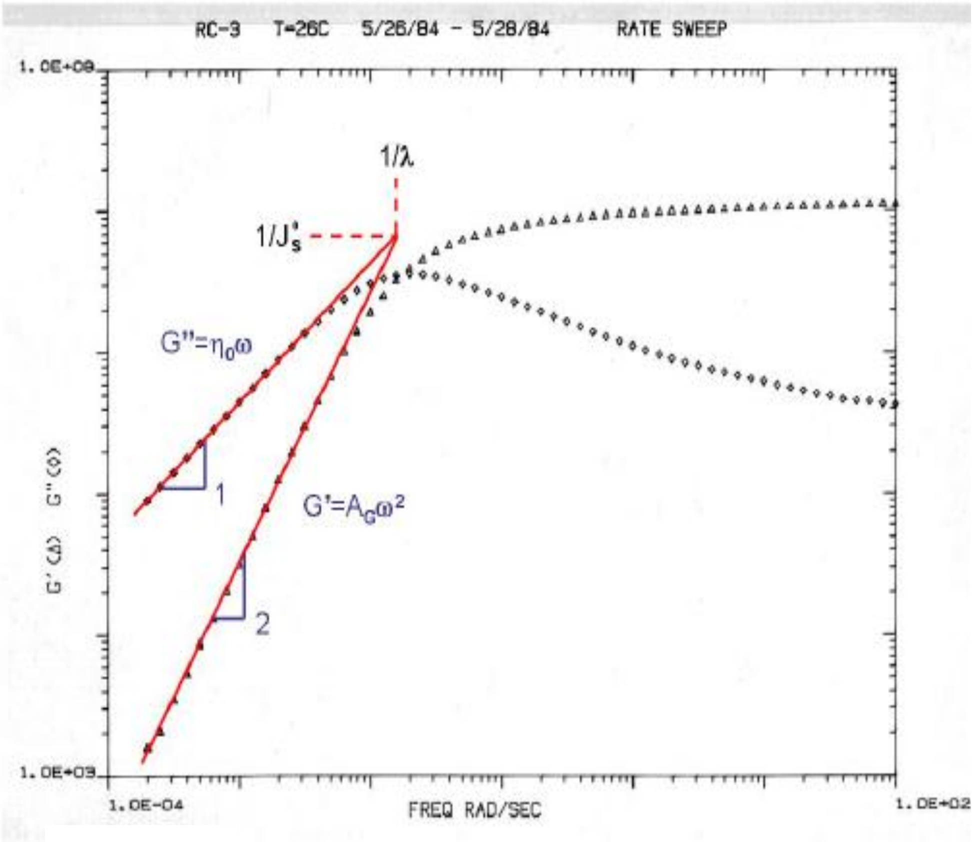
$$\eta_0 = \lim_{\omega\to 0}\left(\frac{G''(\omega)}{\omega}\right) = \lim_{\omega\to 0}\left(\eta'(\omega)\right)$$

$$\eta_0 = \frac{2}{\pi}\int_{-\infty}^{\infty}\frac{G'(\omega)}{\omega}d\left(\ln(\omega)\right)$$

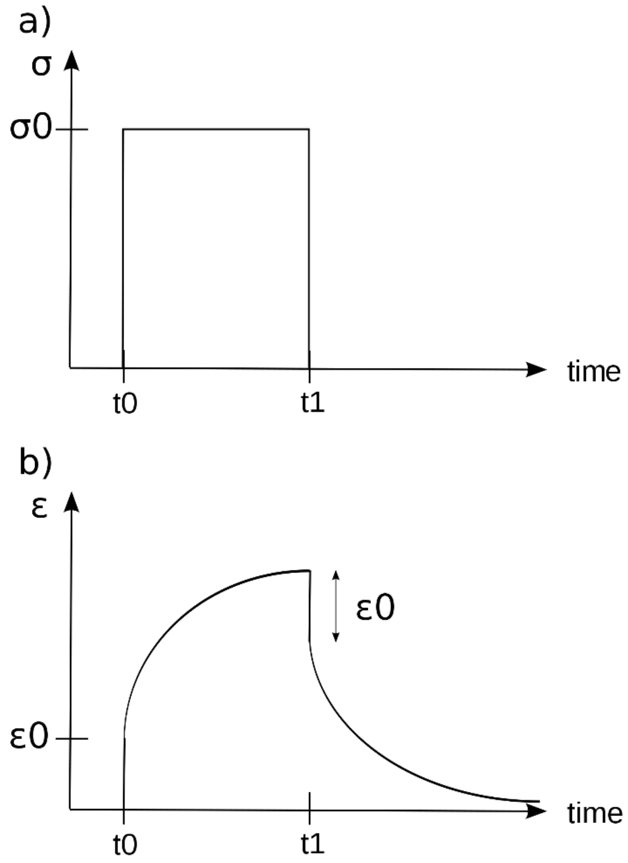
$$G_N^o = \frac{2}{\pi}\int_{-\infty}^{\infty}G''(\omega)d\left(\ln(\omega)\right)$$

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

$$A_G \equiv J_s^o\eta_o^2$$



UNIVERSITY OF PATRAS Department Of Chemical Engineering ChemEngUP



End of lecture

SAOS

Proof that: $A_G \equiv J_s^o \eta_o^2$

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

$$\lim_{\omega\to 0}\left(\sin(\omega s)\right) = \omega s$$

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

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

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

$$A_G \equiv J_s^o \eta_o^2$$

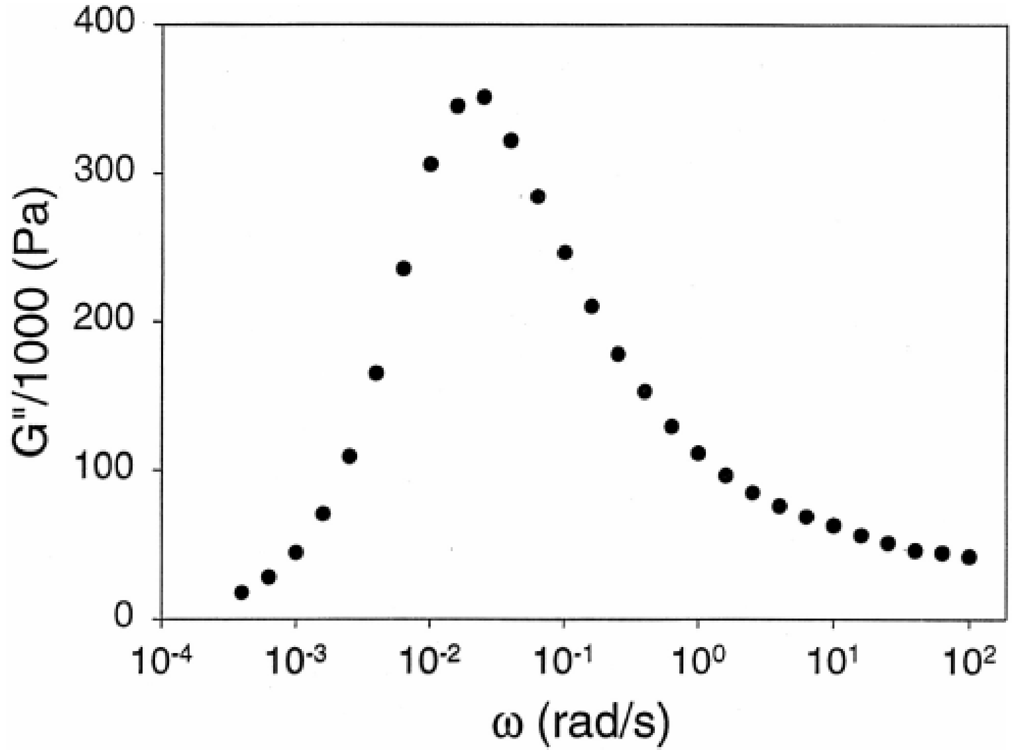
UNIVERSITY OF PATRAS
Department Of Chemical Engineering
ChemEngUP

SAOS

Plateau Modulus
Integration of
the loss modulus

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

RC-3 polybutadiene $M_w = 940,000,\ M_w/M_n < 1.1,\ T_g = -99°C$



UNIVERSITY OF PATRAS
Department Of Chemical Engineering
ChemEngUP

Creep Test

Kinematics

$$\underline{v} \equiv \dot{\gamma}_{yx}(t) y \underline{e}_x$$

$$\tau_{yx}(t) = \begin{cases} 0, & t < 0 \\ \tau_o, & t \geq 0 \end{cases} = \tau_o H(t)$$

Material Properties

$$J(t, \tau_o) \equiv \frac{\gamma_{yx}(0,t)}{\tau_o}$$

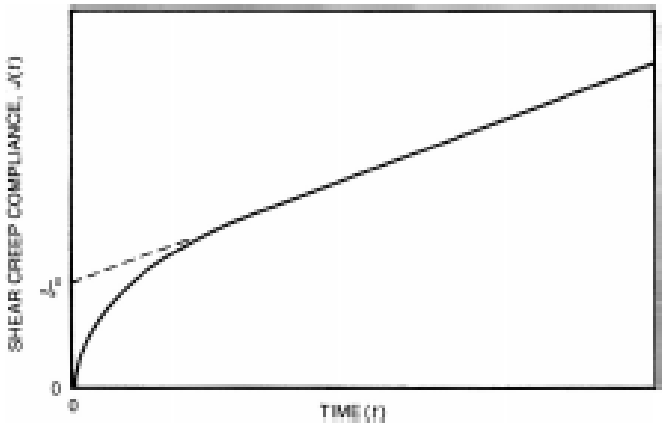
Shear Compliance

$$J_r(t', \tau_o) \equiv \frac{\gamma_r(t')}{\tau_o}$$

Recoverable Compliance

In linear viscoelasticity J is independent of τ_o ($cm^2/dyne$)

Creep Test



$$J(t,\tau_o) = J_s^o + \frac{t}{\eta_o}$$

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

Boltzmann superposition results

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

$$\eta_o = \int_0^\infty G(s)ds$$

$$J_s^o = \frac{1}{\eta_o^2}\int_{-\infty}^\infty G(s)s^2 d(\ln(s))$$

Relaxation Modulus

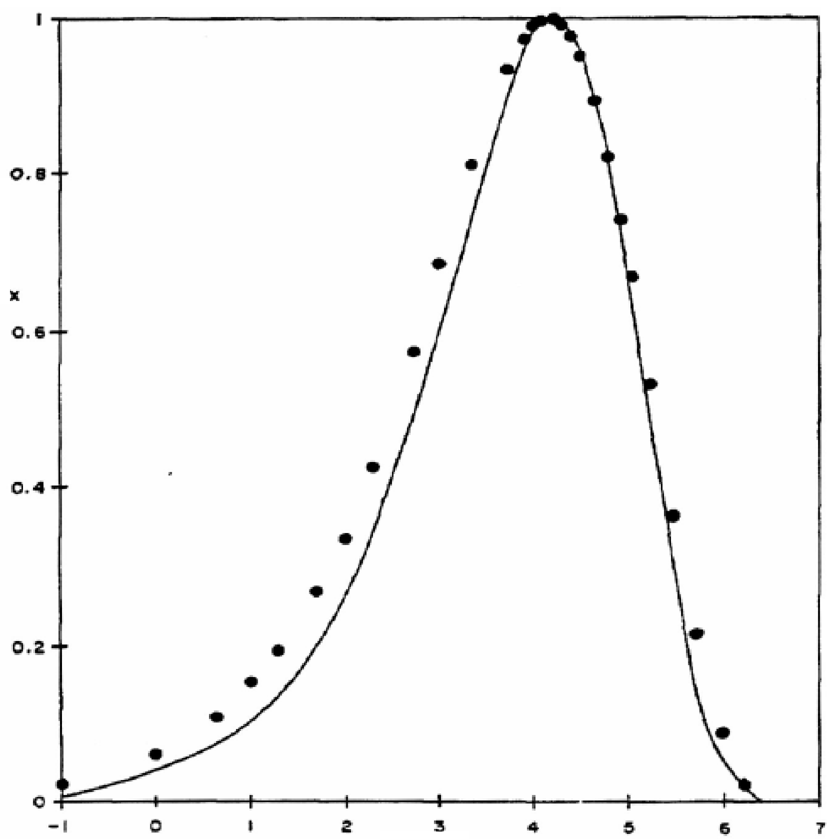
Comparison with Experiments
for the determination of the relaxation time

Maxwell Model

$$G(t) = G_o \exp(-t/\lambda)$$

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

$$\frac{tG(t)}{[tG(t)]_{max}}$$



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

UNIVERSITY OF PATRAS
Department Of Chemical Engineering
ChemEngUP