In this section we consider the issue that our material may be viscoelastic. That is the material can exhibit both viscous and elastic properties at the same time. Viscoelasticity is important, particularly for polymers both in the solid and liquid state. The approach is mostly directed at the liquid (melt) state, however the mathematical analysis is also relevant to viscoelastic solids. Viscoelasticity is relevant to polymer melts, concentrated biotech solutions such as xantham gum. It is also relevant to certain foodstuffs (custard, sauces), personal products (shaving cream, lotions, shampoo), and a range of other materials, such as explosives, rocket fuel & certain natural materials.

An understanding of viscoelasticity is useful in relation to help understand certain processing issues, in addition it is useful in characterising rheologically complex materials. This is important in terms of quality control.

The mathematics involved in the modelling is relatively simple but needs a bit of thought. The modelling is highly suitable for setting Tripos questions!

Processing issues where viscoelasticity is important.

1 Processibility.

![Diagram: Rheology process with extruder, die, post processing, pellets, and Extrusion line must work 24hrs/day]
2 Die swell

\[ \chi = \frac{D_i}{D_o} \]

Newtonian \( \chi = 1.14 \)

Viscoelastic fluid \( \chi = 1 - 5 \) big factor when making tubes

3 Extrusion Instabilities

sharkskin – optically observed
Usually bad, sometimes good
Rheometers.

**Cone and Plate Rheometer**

- Torque
- Cone angle = 14°
- 1.5 mm

**Parallel Plate Rheometer**

- Torque
- 1 mm
- 12 mm

**Couette Rheometer**

- Torque
- 30 mm
- 20 mm
- 22 mm
Viscoelasticity measurement

Parallel plate or cone and plate rheometers.
A device where ideally the strain or stress is uniform.

A) Apply strain, measure stress. Controlled strain rheometer

Or B) Apply stress, measure strain. Controlled stress rheometer

TA Ares, Controlled strain rheometer.

Upper shaft measures torque

Sample Between plates

stepper motor

h ~ 0.3-1 mm

25 – 50 mm

(1) Steady
   \( \omega \) (angular velocity)

(2) Oscillate
   \( \omega \) (angular frequency)
   \( \gamma \) (strain)

(3) Step strain

CET 2B. Section 3, Viscoelasticity-2011
Different test geometries.

Parallel plate geometry

\[ \text{strain } \dot{\gamma} = \frac{r \omega}{h} \]

\[ \text{strain rate } \dot{\gamma} = \frac{r \omega}{h} \]

both depend on radius

Cone and plate geometry

\[ \text{strain } \dot{\gamma} = \frac{r \varphi}{r \tan \alpha} = \frac{\varphi}{\tan \alpha} \]

\[ \text{strain rate } \dot{\gamma} = \frac{r \omega}{r \tan \alpha} = \frac{\omega}{\tan \alpha} \]

both independant on radius

\[ \dot{\gamma} = \frac{r \varphi}{h} \]

Stain rate depends on r

\[ \dot{\gamma} = \frac{r \varphi}{r \tan \alpha} = \frac{\varphi}{\tan \alpha} \]

Strain rate independent of r

This is the best option, but often parallel plates are used.
Rheometers measure Torques; so we need to express Torque in terms of fluid shear stress.

Cone and plate

\[ \Gamma = \int_0^{r_1} 2\pi r \tau r \, dr \]

\[ \Gamma = 2\pi \tau r_1^2 \, dr \]

Force

\[ \Gamma = \frac{2}{3} \pi \tau r_1^3 \]

\[ \Gamma \propto \tau \]

Parallel plate more tricky because \( \tau \) is a function of \( r \).
Rheological “Rheometric” measurements.

We now examine the types of deformation that can be applied using, for example, a Rheometrics controlled strain rheometer.

a) Stress growth, steady shear, stress relaxation

\[ \begin{align*}
 &t < 0 & \gamma = 0 \\
 &t > 0 & \gamma = \gamma_0 \\
 &t > t_1 & \gamma = 0
\end{align*} \]

measure stress as a function of time for above strain rate history.

(A) Stress growth (Viscoelastic response)
(B) Steady shear (Non Newtonian behaviour)?
(C) Stress relaxation (Viscoelastic response)

Time dependence can be explored

Steady shear is the most used deformation, obtain “flow curve”
b) Step strain
At $t=0$, instantaneously strain material by $\gamma_0 = \gamma_0 \delta t$, subsequently measure stress relaxation as a function of $t$.

\begin{align*}
\gamma(t) &= \gamma_0 \\
\tau(t) &= \tau_0 \\
G(t) &= \frac{\tau(t)}{\gamma_0}
\end{align*}

Characteristic relaxation time
$10^{-3} - 10^3$ s
c. Oscillatory “rheometric” deformation

Apply: \[ \dot{\gamma} = \gamma_0 \sin \omega t \]

Then: \[ \gamma = \gamma_0 \cos \omega t \]

Strain: \[ \gamma = \gamma_0 e^{i\omega t} \]

Strain rate: \[ \dot{\gamma} = i \omega \gamma_0 e^{i\omega t} \]

Measure: \[ \tau = \tau_0 \sin(\omega t + \delta) \]

Variable \( \gamma_0 \) = max strain amplitude, typically 0.1 (10%) 
\( \omega \) = angular frequency, typically \( 10^2 - 10^3 \) rad/s

\[ \tau = \tau_0 \sin(\omega t + \delta) \]

or

\[ \tau = \tau_0 e^{i(\omega t + \delta)} \]

\[ = \tau_0 \sin \omega t \cos \delta + \tau_0 \cos \omega t \sin \delta \]

\[ \downarrow \]

Component of stress in phase with \( \gamma \) \( \Downarrow \)

Elastic bit!

Defn: \[ \tau = G' \gamma_0 \sin \omega t + G'' \gamma_0 \cos \omega t \]

So: \[ G' = \frac{\tau_0}{\gamma_0} \cos \delta \text{ Pa} \]

\[ G'' = \frac{\tau_0}{\gamma_0} \sin \delta \text{ Pa} \]

Storage Modulus Elastic

Loss Modulus Viscous
Complex modulus $G^*$  (another way of saying the same thing).

$$\frac{\tau(t)}{\gamma(t)} = G^* = G' + iG'' = \frac{\tau_o e^{i(\omega t + \delta)}}{\gamma_o e^{i\omega t}}$$

$$\Downarrow \Downarrow$$

Elastic  Loss
Modulus  Modulus

So  $G' + iG'' = \frac{\tau_o}{\gamma_o} e^{i\delta}$

now  $(e^{i\delta} = \cos\delta + i\sin\delta)$

So  $G' = \frac{\tau_o \cos\delta}{\gamma_o}$  $G'' = \frac{\tau_o \sin\delta}{\gamma_o}$  N/m$^2$

As before

So

$$\tau = \gamma_0 G' \sin \omega t + \gamma_0 G'' \cos \omega t \quad \text{or} \quad \tau = \gamma_0 G^* e^{i\omega t}$$

Another definition

For a given strain, $\gamma_0$ if we know $\tau_0$ and $\delta$ from the rheometer

Complex viscosity

$$\eta^* = \frac{\sqrt{G'^2 + G''^2}}{\omega} \quad \text{Pas}$$

For given $\omega$, and known $\gamma_o$.

$G'$  :- Storage modulus
$G''$  :- Loss modulus
$\eta^*$  :- Complex viscosity

These properties capture the viscoelastic properties of a material, but the values will depend on the test frequency (time scale applied).
Measure \( \tau_o \) and \( \delta \) using TA instruments rheometer or other instrument, then we know the following, for a given \( \omega \)
1. \( G' \) storage modulus.  
2. \( G'' \) Loss modulus.  
3. \( \eta^* \) Complex viscosity

Rheometer measures Torque and from this we need shear stress

Typical viscoelastic data that we wish to model. (See appendix)

1. Oscillatory Viscoelastic response.
   linear viscoelastic response \( \omega, \gamma \)

CET 2B. Section 3, Viscoelasticity-2011
2. Steady Shear

Apparent viscosity \( \eta_a \) (Pa s)

shear rate \( \dot{\gamma} \)

Linear region

Carreau

shear thinning

Silly Putty; real data.

Silly Putty frequency sweep, strain = 1%, 160204
Modelling of viscoelasticity

We are going to build a model that, eventually is going to be able to predict both the linear viscoelastic and non linear shear thinning behaviour of a viscoelastic material such as a polymer melt.

Stage 1 The linear viscoelastic part

Coupling of linear viscous and elastic elements

The Maxwell element series coupling of elastic and viscous component

\[
\tau_1 = g \gamma_1 \\
\tau_2 = \eta \gamma_2
\]

Maxwell often favoured for stress relaxation

The Voigt element parallel coupling

\[
\gamma = \gamma_1 = \gamma_2 \\
\tau = \tau_1 + \tau_2
\]

Voigt often favoured for creep (constant stress experiments)

We will follow Maxwell, but you should “play with” Voigt model.

The Maxwell Model (Differential form)

\[
\tau_1 = g \gamma_1 \\
\tau_2 = \eta \gamma_2
\]

Local \((\tau_1, \gamma_1)\) \((\tau_2, \gamma_2)\)

Coupling \(\tau = \tau_1 = \tau_2\) Stress continuity
\[ \gamma = \gamma_1 + \gamma_2 \quad \text{Strain additivity} \]

Then \[ \dot{\gamma} = \dot{\gamma}_1 + \dot{\gamma}_2 \]

Governing ordinary differential equation

\[ \frac{d\gamma}{dt} = \frac{d\tau}{dt} \frac{1}{g} + \frac{\tau}{\eta} \quad \text{or} \]

\[ \frac{d\tau}{dt} = \frac{\lambda}{g} \left( \frac{d\gamma}{dt} - \frac{\tau}{\eta} \right) \]

1st order ODE

where the relaxation time of the element \( \lambda \) is given by \( \eta/g \), (s)

Example. Response of Maxwell element → Spring and dashpot in series

a. Steady shear

\[ \tau = \lambda g \dot{\gamma} \]

\[ \frac{d\tau}{dt} = \eta \dot{\gamma} \]

\[ \frac{d\tau}{dt} = 0 \quad \text{Then} \quad \tau = \eta \gamma_0 \]

Linear response, Newtonian. We will have to make the model Non Newtonian later.

Maxwell model predicts Newtonian behaviour in simple shear. Most complex VE Fluids are shear thinning and so we will have to fix this later.

b. Stress relaxation after steady shear

\[ \int_t^{t_0} \frac{dt}{\tau} = \int_0^{t_0} \frac{dt}{\lambda} \]

\( \tau = \tau_0 e^{-t/t_0} \]

\[ \tau = \eta \dot{\gamma}_0 e^{-t/t_0} \]

All elastic \( \lambda \rightarrow \infty \)

All viscous \( \lambda \rightarrow 0 \)

Exponential decay time constant \( \lambda, 10^{-3} - 10^{3} \)
c. Oscillatory motion. (Important and frequently used)

Apply
\[ \gamma(t) = \gamma_0 e^{i\omega t} \]

Use complex notation
Variables (\(\gamma_0, \omega\))

Measure
\[ \tau(t) = \tau_0 e^{i(\omega t + \delta)} \]

Strain rate
\[ \dot{\gamma}(t) = i\omega \gamma_0 e^{i\omega t} \]

\[ \tau(t) = G^* \gamma_0 e^{i\omega t} = (G' + iG'')\gamma_0 e^{i\omega t} \]

\[ \frac{d\tau(t)}{dt} = i\left[G' + iG''\right]\gamma_0 \omega e^{i\omega t} \]

Remember,
\[ g \frac{d\gamma}{dt} = \frac{d\tau}{dt} + \frac{\tau}{\lambda}, \quad \text{so, Maxwell equation} \]

Substitute for \(\gamma, \tau\)
\[ g i\omega \gamma_0 e^{i\omega t} = i[G' + iG'']\gamma_0 \omega e^{i\omega t} + \frac{1}{\lambda} \left[(G' + iG'')\gamma_0 e^{i\omega t}\right] \]

Yields
\[ G' = \frac{g\lambda^2 \omega^2}{(1 + \lambda^2 \omega^2)}, \quad G'' = \frac{g\lambda\omega}{(1 + \lambda^2 \omega^2)}, \quad \eta^* = \frac{g\lambda}{(1 + \lambda^2 \omega^2)^{1/2}} \]

\[ \omega \rightarrow 0 \quad G' \rightarrow 0 \quad \omega \rightarrow 0 \quad G'' \rightarrow 0 \quad \omega \rightarrow 0 \quad \eta^* = g\lambda = \eta \]

\[ \omega \rightarrow \infty \quad G' \rightarrow g \quad \omega \rightarrow \infty \quad G'' \rightarrow 0 \quad \omega \rightarrow \infty \quad \eta^* \rightarrow 0 \]

Newtonian Plateau
\(\eta\)

\(G'\) & \(G''\) (Pa)
\(\eta^*\) (Pa s)

Elastic domination
Elastic

viscous domination

cross over

Loss

complex viscosity

angular frequency \(\omega\)

G' & G'' (Pa)
\(\eta^*\) (Pa s)

The Maxwell Model (Integral form wrt strain rate)

Differential equation

\[ \frac{\tau}{\lambda} + \frac{d\tau}{dt} = g \frac{d\gamma}{dt} \]

\[ \lambda = \frac{\eta}{g} \]  

1st order ODE

Multiply by integrating factor

\[ \frac{\tau}{\lambda} e^{t/\lambda} + e^{t/\lambda} \frac{d\tau}{dt} = g \frac{d\gamma}{dt} e^{t/\lambda} \]

\[ \frac{d}{dt} (\tau e^{t/\lambda}) = \frac{\tau e^{t/\lambda}}{\lambda} + e^{t/\lambda} \frac{d\tau}{dt} \]

assume \( \tau = 0 \) at \( t' = -\infty \)

current time

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

Past time

Stress at current time

Maxwell equation in terms of past strain rate – current stress depends on past strain rate.

\[ \tau(t) = g e^{-\left(t-t'\right)/\lambda} \cdot \dot{\gamma}(t') dt' \]

Fading memory

\[ \tau(t) = \int_{-\infty}^{t} g e^{-\left(t-t'\right)/\lambda} \cdot \dot{\gamma}(t') dt' \]
Test strain rate equation

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

\[ \tau(t) = g \gamma_0 \int_{-\infty}^{t} e^{-\left(t-t'\right)/\lambda} dt' \]

\[ = g \gamma_0 \left[ -\lambda e^{-\left(t-t'\right)/\lambda} \right]_{-\infty}^{t} = g \gamma_0 \frac{\lambda}{\lambda} \]

\[ \tau_{ss} = \eta \gamma_0 \quad \text{as before} \]

\[ \tau(t) = \int_{-\infty}^{t} ge^{\left(t-t'\right)/\lambda} \gamma_0 dt' \]

\[ = g \gamma_0 e^{\gamma_0 t} \int_{-\infty}^{t} e^{\lambda t'} dt' \]

\[ = g \gamma_0 e^{\gamma_0} \left[ \frac{\lambda e^{\lambda t'}}{\lambda} \right]_{-\infty}^{t} = g \gamma_0 \frac{\lambda}{\lambda} \]

\[ \lambda = \eta \]

\[ \tau = \dot{\eta} \gamma_0 \quad \text{Newtonian as before} \]

The integral Maxwell strain rate equation gives the same result in steady and other shear deformations as the differential Maxwell equation.
Integral Maxwell in terms of past strain rate. General deformations.

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

\( \tau = 0 \)

\[ \tau(t) = \int_{0}^{t} g e^{-\frac{(t-t')}{\lambda}} \dot{\gamma}_1 dt' + \int_{t'}^{t} g e^{-\frac{(t-t')}{\lambda}} \dot{\gamma}_2 dt' \]

If \( t = t_1 \) then \( \tau = \tau_1 \)

\[ \tau(t) = \int_{0}^{t_1} g e^{-\frac{(t-t')}{\lambda}} \dot{\gamma}_1 dt' + \int_{t_1}^{t} g e^{-\frac{(t-t')}{\lambda}} \dot{\gamma}_2 dt' \]

\( \tau = 0 \)

If \( t = t_2 \) then \( \tau = \tau_2 \)

Exponential decay


**Let's integrate again** in order to obtain the Maxwell integral strain equation.

**The Maxwell Model (Integral form wrt strain)**

We know,

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

Now \[ \int udv = [uv] - \int vdu \]

let \[ u = g e^{-\left(t-t'\right)/\lambda}, \quad dv = d\gamma \]

integrate above by parts,

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

where strain is given by

**Define strain**

\[ \gamma(t, t') = \int_{t}^{t'} \gamma(t'')dt'' \]

where \( t \) = current time and \( t' \) = past time

Note when \( t' = t \) \( \gamma = 0 \)

We are measuring strain from current time

So

**Integral Maxwell equation – past strain**

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

Stress at time \( t \) \n
Past strain history

\[ \gamma(t, t') = \int_{t}^{t'} \gamma(t'')dt \]

\[ t' = t' \]

\[ t = t \]
Test Maxwell strain integral equation. \textbf{steady shear} $\gamma = \text{const}$

\[ \gamma(t, t') = \int_{t'}^{t} \gamma''(t') \, dt' \]

For steady shear

\[ \gamma(t, t') = \gamma_0 \int_{t'}^{t} \gamma''(t') \, dt' = \gamma_0 (t - t') \]

\[ = - \gamma_0 (t - t') \]

Introduce new variable $s$, \textbf{(you don’t have to do this, but it generally makes calculation simpler)}.

Let

\[ s = t - t^1 \]

\[ ds = -dt^1 \]

\[ s = \infty \quad s = t \quad s = t - t^1 \quad s = 0 \]

\[ t' = -\infty \quad t' = 0 \quad t' = t^1 \quad t' = t \]
Integral strain equation

\[ \tau(t) = + \int_{\infty}^{0} \frac{g}{\lambda} e^{-s/\lambda} \gamma(o, s) ds \]

Also, strain

\[ \gamma = - \gamma_o (t - t') = - \gamma_o s \]

\[ \tau(t) = - \int_{\infty}^{0} \gamma_o s e^{-s/\lambda} ds \]

\[ \tau(t) = - \frac{g}{\lambda} \gamma_o \left[ \left(-\lambda s e^{-s/\lambda} \right) \bigg|_0^\infty + \int_{\infty}^{0} \lambda e^{-s/\lambda} ds \right] \]

\[ \tau = g\lambda \gamma_o = \eta \gamma_o \quad \text{Newtonian, as before.} \]

\[ \tau(t) = - \frac{g}{\lambda} \int_{-\infty}^{t} e^{(t-t')/\lambda} \gamma(t, t')dT' \]

\[ \tau(t) = \int_{-\infty}^{t} \frac{g}{\lambda} e^{(t-t')/\lambda} - \dot{\gamma}_0 (t - t')dT' \]

\[ \tau(t) = + \frac{g}{\lambda} \dot{\gamma}_0 e^{t/\lambda} \int_{-\infty}^{t} (t - t')e^{t'/\lambda}dT' \]

\[ \tau = \dot{\eta} \gamma_0 = \dot{\lambda} g \gamma_0 \]

Newtonian

The Integral strain Maxwell equation will predict the same results as the integral Maxwell strain rate equation and the differential Maxwell equation.
Another example. Stress growth and stress relaxation. This one is a bit more challenging!
The key to solving these problems is to be clear in your mind what the strain rate history is and then determine the correct strain history for the appropriate time domain that is of interest to you (or the examiner!)

\[
\tau (t) = - \int_{-\infty}^{0} \frac{G}{\lambda} e^{(t-t')/\lambda} (-\dot{\gamma}_0 t) dt' - \int_{0}^{t} \frac{G}{\lambda} e^{(t-t')/\lambda} (-\dot{\gamma}_0 (t-t')) dt'
\]

II

\[
\tau (t) = - \int_{-\infty}^{0} \frac{G}{\lambda} e^{(t-t')/\lambda} (-\dot{\gamma}_0 t_1) dt' - \int_{0}^{t_1} \frac{G}{\lambda} e^{(t-t')/\lambda} (-\dot{\gamma}_0 (t_1-t')) dt' + \int_{t_1}^{t} (0)
\]

III

\[
\gamma = 0
\]

If current time in sector 1

If current time in sector 2

strain concentration
Tackle our two further problems

1. Multiple relaxation times. One Maxwell element doesn’t usually fit the data well.
2. Non linear response. Maxwell elements are linear in steady shear and we know interesting fluids can, for example, shear thin.

1. Introduce spectrum of relaxation times
The parallel coupling of Maxwell elements

\[ \tau = \sum \tau_i \]

\[ \lambda_i = \frac{\eta_i}{g_i} \]

The integral constitutive equation then becomes,

\[ \tau(t) = \int_{-\infty}^{t} \sum_i \frac{g_i \lambda_i}{(1 + \lambda_i \omega^2)} e^{-t-t'} \gamma(t,t') dt' \]

For oscillatory data the equations become.

\[ G'(\omega) = \sum_i \frac{g_i \lambda_i^2 \omega^2}{(1 + \lambda_i^2 \omega^2)} \]

\[ G''(\omega) = \sum_i \frac{g_i \lambda_i \omega}{(1 + \lambda_i^2 \omega^2)} \]

\[ \eta^*(\omega) = \sum_i \frac{g_i \lambda_i}{(1 + \lambda_i^2 \omega^2)^{1/2}} \]
We now need to find the “best fit” $g_1, \lambda_1$. This is potentially a tricky problem. Use software on Rheometrics to get best fit.

With a spectrum of relaxation times we can get a good fit to linear viscoelastic data.

Choose a range of $\lambda_1$
Perform least square fit for best fit, $g_i$ to fit $G', G''$
This requires software algorithms.

Multi-mode modelling is essential for realistic engineering predictions
Obtained $g_i\lambda_i$ parameters
2. Introduce non-linear steady shear response


Add a non-linear “damping parameter” to constitutive equation. This is best done using the strain integral equation.

\[ \tau(t) = - \sum_{i} g_i \int_{-\infty}^{t} e^{-\frac{t-t'}{\lambda_i}} \left( -k \gamma(t', t') \right) dt' \]

This is the new bit!

Modulus (always pos)
damping parameter
\[ k = 0 \] Maxwell
\[ k \text{ ranges from } 0 \to 1 \]

The equation has been “factored” in terms of a separated time and strain dependence.

Multi-mode integral strain dependant Maxwell equation with Wagner damping factor
The effect of the damping parameter on different deformations

Steady shear $\dot{\gamma}(t') = \gamma_0$, always

Let $s = (t - t')$, substitution makes calc easier

$\gamma(o, s) = -\gamma_0 s$
$ds = -dt$

$\tau(t) = -\int_0^{\infty} \sum_{i=1}^{\infty} \frac{g_i}{\lambda_i} e^{-s/\lambda_i} e^{-k\gamma_0 s} \cdot \gamma_o sds$

$\tau(t) = -\int_0^{\infty} \sum_{i=1}^{\infty} \frac{g_i}{\lambda_i} \gamma_o e^{-\alpha_i s} sds$

where $\alpha_i = \frac{1}{\lambda_i} + k\gamma_o$

integrate by parts
Check the form of steady shear equation

Relaxation modes
Non linear $k$

a) single $\lambda$, $k = 0$

$$\tau = \eta \dot{\gamma}_o$$

Newtonian as before

b) single $\lambda$, $k \neq 0$

$$\tau = \frac{\eta \dot{\gamma}_o}{\left(1 + k \lambda \dot{\gamma}_o\right)^2}$$

Non linear – good news

Max decreases – not physically realistic

Newtonian
c) multiple \( \lambda, \ k = 0 \)

Response is still linear

\[ \tau = \sum \eta_i \dot{\gamma} \]

\( \tau \) Stress

\( \dot{\gamma} \) Strain rate

\[ \tau = \sum \eta_i \dot{\gamma}_o \left( 1 + k\lambda_i \dot{\gamma}_o \right)^2 \]

good

\[ \tau \] Stress

\( \dot{\gamma} \) Strain rate

This non-linear response may match “Power law” Bingham …. Or other steady shear constitutive equation.
We now have a model that describes LVE response and the non linear steady shear response. This is what we want!

Multi-mode Wagner
Good for predicting LVE response
Good for predicting steady shear shear thinning response

But how do we get the value that non linear parameter k?

Use step strain experiments

Step Strain

\[
\begin{align*}
\text{strain} & \quad t' = -\infty & \quad t' = 0 & \quad t' = t \\
\gamma & \quad s = \infty & \quad \gamma_0 & \\
\text{s < t} & \quad \gamma = 0 & \quad e^{-k\gamma(t,t')} & \\
\text{s > t} & \quad \gamma = -\gamma_0 & \\
\text{recall} & \\
\tau(t) & = -\int_0^t \sum_i \frac{g_i}{\lambda_i} e^{-(s)/\lambda_i} \gamma_0 e^{-k\gamma_0} ds \\
\tau(t) & = \gamma_0 e^{-k\gamma_0} \sum_i g_i e^{-t/\lambda_i} \\
\end{align*}
\]

Relaxation modulus at finite strain

\[
G_{\gamma_j}(t) = \frac{\tau(t)}{\gamma_j} = e^{-k\gamma_j} \sum_i g_i e^{-t/\lambda_i}
\]

but small strain modulus given by
\[ G_0(t) = \frac{\tau(t)}{\gamma_0} = \sum_i g_i e^{-t/\lambda_i} \]

so

\[ e^{-k\gamma} = \frac{G_{\gamma j}(t)}{G_0(t)} \]

So, measure relaxation modulus at small and large strain and use above equation to get \( k \).
And finally (in this section),
Integral constitutive equation also solves another mystery in polymer science

The Cox Merz Rule

\[ \eta^*(\omega) = \eta_a(\dot{\gamma}) \]

where \( \omega = \dot{\gamma} \)

Maxwell model with damping function predicts,

Complex viscosity,

\[ \eta^*(\omega) = \sum_i \frac{\eta_i}{\left(1 + \lambda_i^2 \omega^2\right)} \]

Apparent viscosity

\[ \eta_a(\dot{\gamma}) = \sum_i \frac{\eta_i}{\left(1 + k\lambda_i \dot{\gamma}_0\right)^2} \]

equations are not identical but provided \( k > 0 \) and you have a spectrum of relaxation times, they are of similar form and give a close match.

Cox Merz Rule \( \rightarrow \) is an accidental coincidence!
Summary of this important section.
Appendix 1
Rheological data. Golden Syrup
A high viscosity Newtonian Fluid.
Note. No Shear thinning, very little elasticity, G’ low, and Cox Merz obeyed.

Apparent viscosity

Golden Syrup at 25°C

Golden Syrup at 25°C (1% Strain)
Golden Syrup at 25°C (Cox-Merz)

Shear Rate [s⁻¹] / Frequency [rad/s]

η^*

η_a
Appendix 2
Rheological data. A molten Polyethylene
( typical data for a commercial PE)

A high viscosity viscoelastic Fluid.
Note. Shear thinning, viscoelasticity, G’ and G’’ similar magnitude.
Cox Merz obeyed.

Apparent and Complex viscosity; showing shear thinning and Cox Merz rule behaviour.

Strain sweep showing linear regime
Frequency sweep showing viscoelastic response.

Data shows classic shear thinning of complex viscosity. Also across over for $G'$, $G''$ curves.