Section 3
Viscoelasticity; (still in scalar form; no tensors yet!)

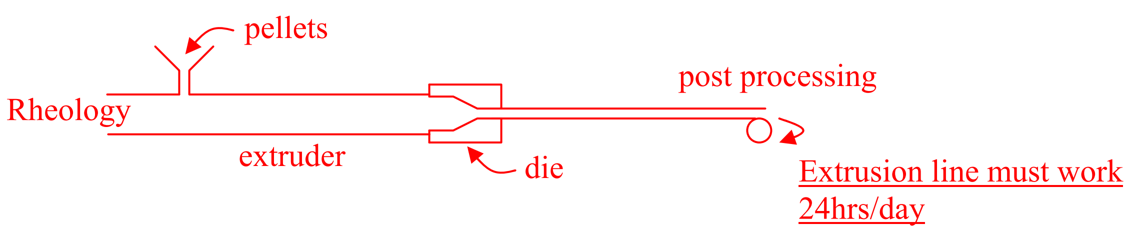
In this section we consider the issue that our material may be viscoelastic. That is the material can exhibit both viscous and elastic properties at the same time. Viscoelasticity is important, particularly for polymers both in the solid and liquid state. The approach is mostly directed at the liquid (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!

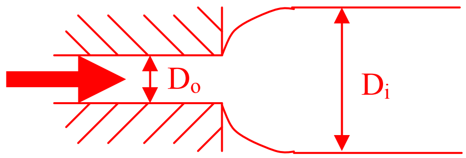
Processing issues where viscoelasticity is important.

1 **Processibility.**



2 Die swell

$\chi = D_i/D_o$

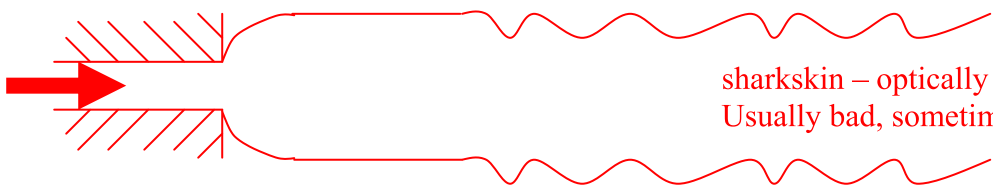


Newtonian $\chi = 1.14$

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

3 Extrusion Instabilities

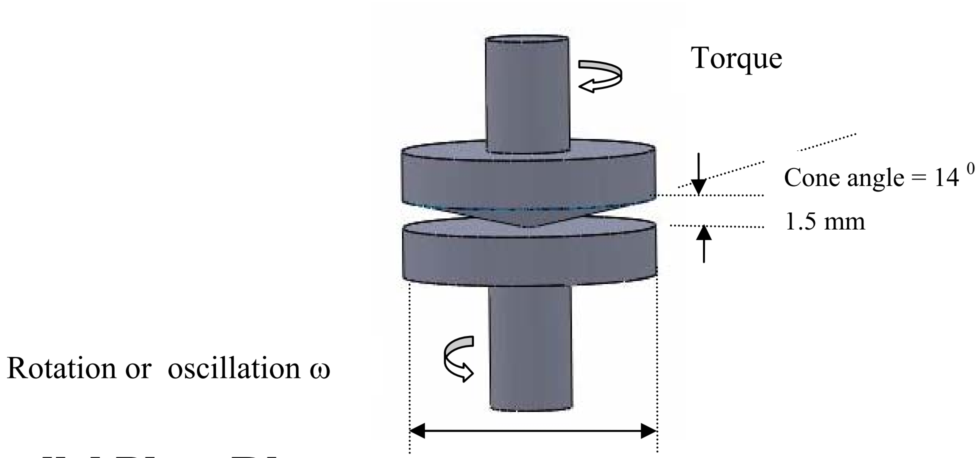
production rate



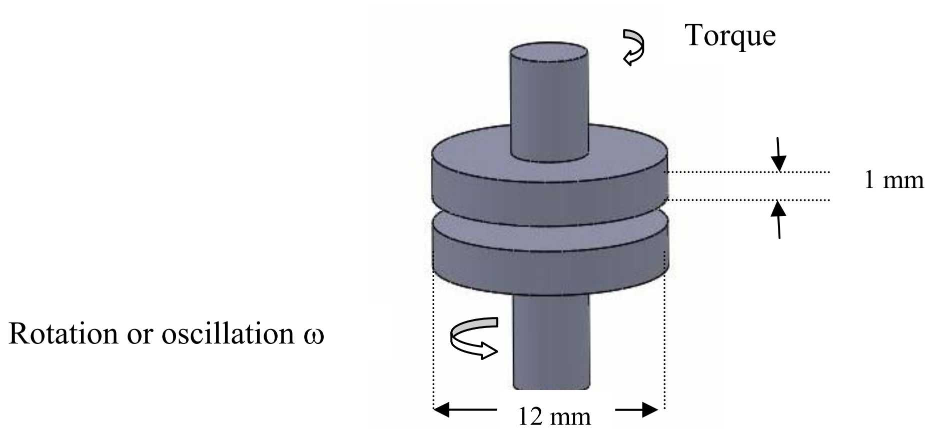
sharkskin – optically observed
Usually bad, sometimes good

Rheometers.

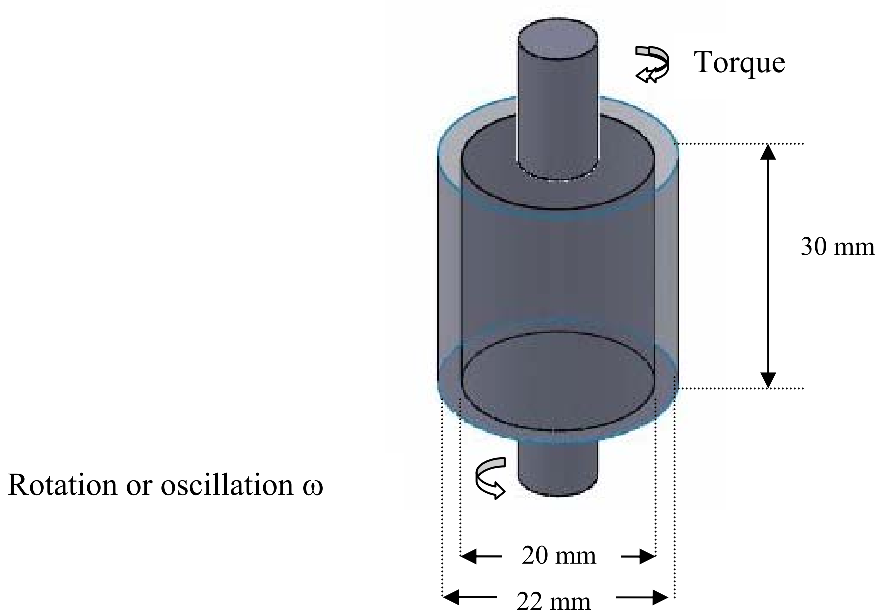
Cone and Plate Rheometer



Parallel Plate Rheometer



Couette Rheometer



Viscoelasticity measurement

Parallel plate or cone and plate rheometers.

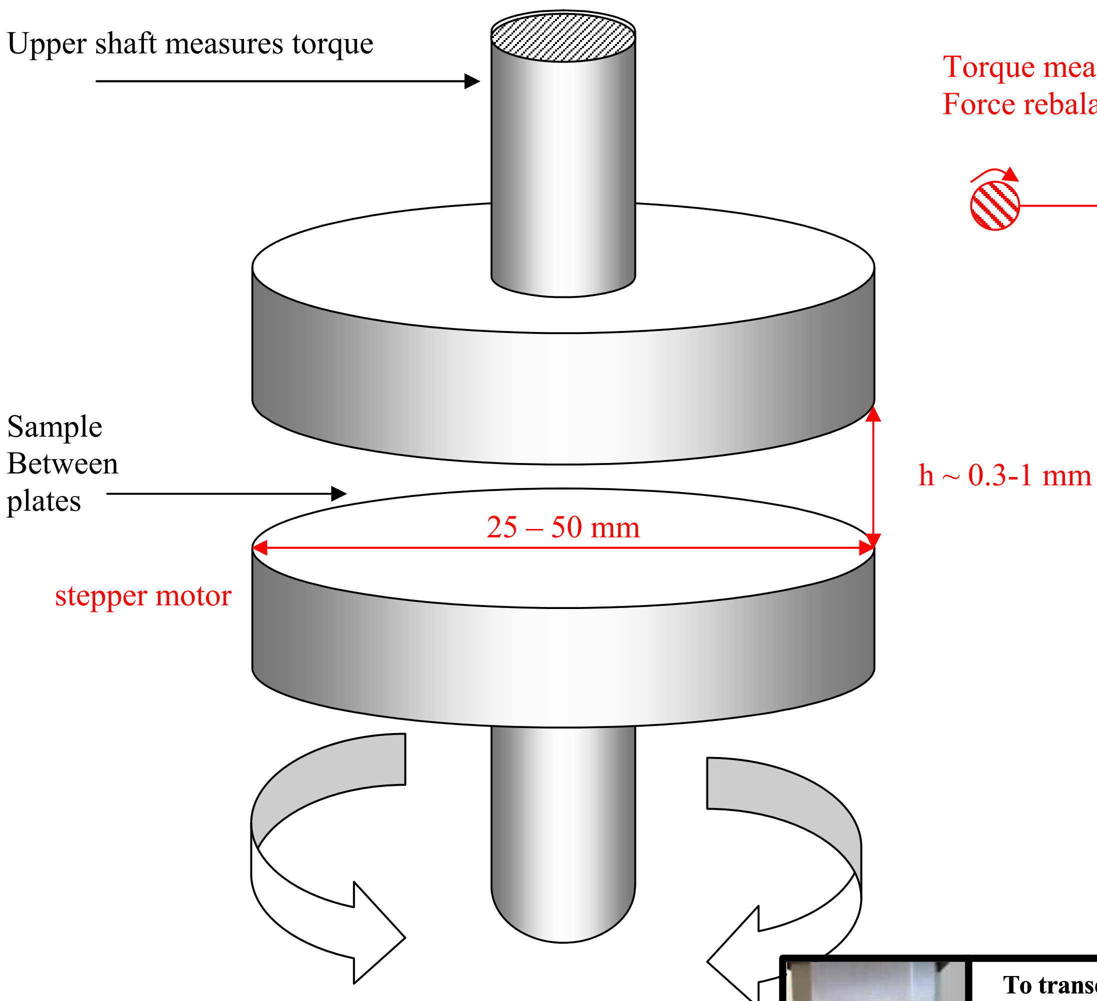
A device where ideally the strain or stress is uniform.

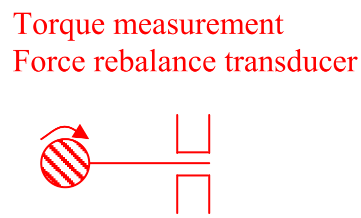
A) **Apply strain , measure stress.** **Controlled strain rheometer**

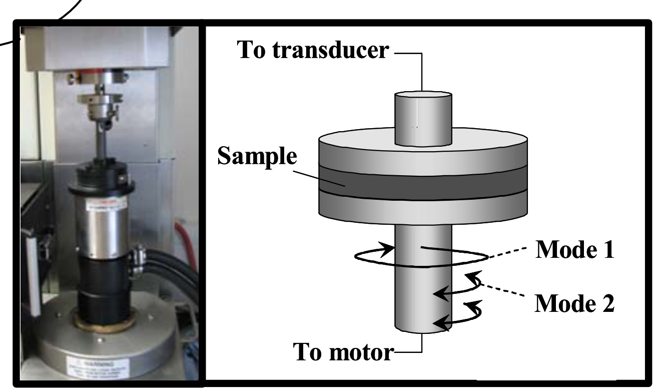
Or B) **Apply stress , measure strain.** **Controlled stress rheometer**

yield stress – £20,000-50,000/machine

TA Ares, Controlled strain rheometer.







(1)Steady

ω (angular velocity)

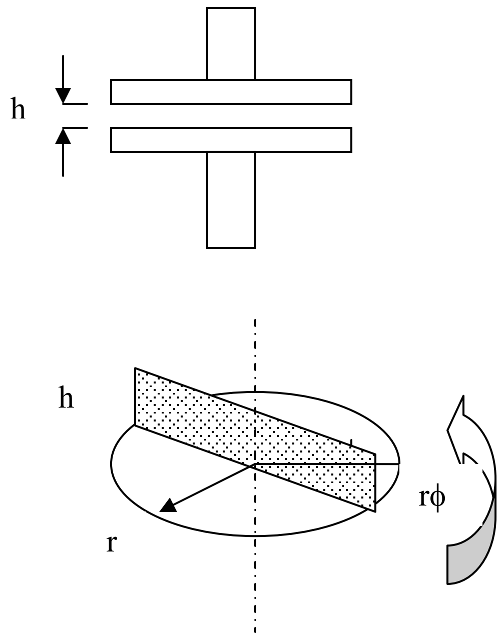
(2)Oscillate

ω (angular frequency)
γ (strain)

(3)Step strain

Different test geometries.

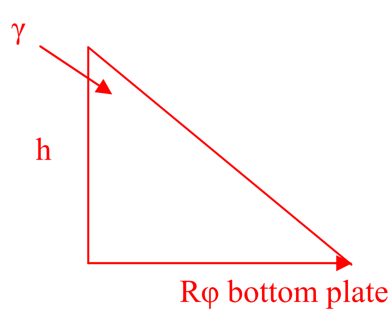
Parallel plate geometry



strain $\gamma = \dfrac{r\,\varphi}{h}$

strain rate $\dot{\gamma} = \dfrac{r\,\omega}{h}$

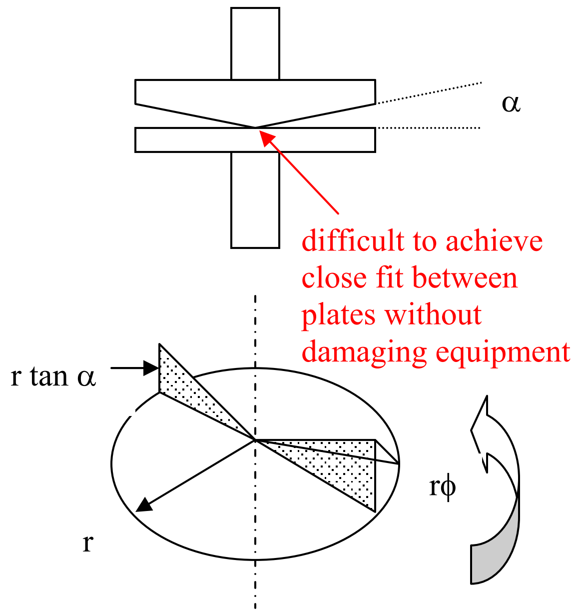
both depend on radius



$\gamma = \dfrac{r\varphi}{h}$

Stain rate depends on r

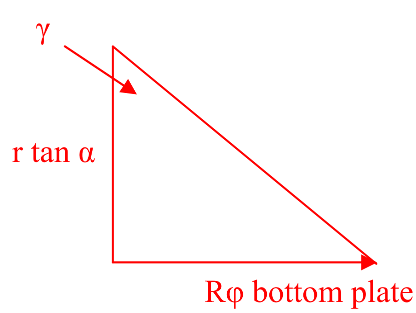
Cone and plate geometry



strain $\gamma = \dfrac{r\,\varphi}{r\,\tan\alpha} = \dfrac{\varphi}{\tan\alpha}$

strain rate $\dot{\gamma} = \dfrac{r\,\omega}{r\;\tan\alpha} = \dfrac{\omega}{\tan\,\alpha}$

both independant on radius



$\gamma = \dfrac{r\varphi}{r\,\tan\,\alpha} = \dfrac{\varphi}{\tan\,\alpha}$

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.

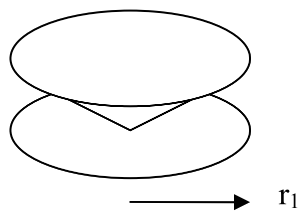
Cone and plate

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

Force

$$\Gamma = \int_0^{r_1} 2\Pi\ \tau\ r^2\,dr$$

$$\Gamma = \frac{2}{3}\pi\,\tau\,r_1^3 \qquad \Gamma\ \alpha\ \tau$$

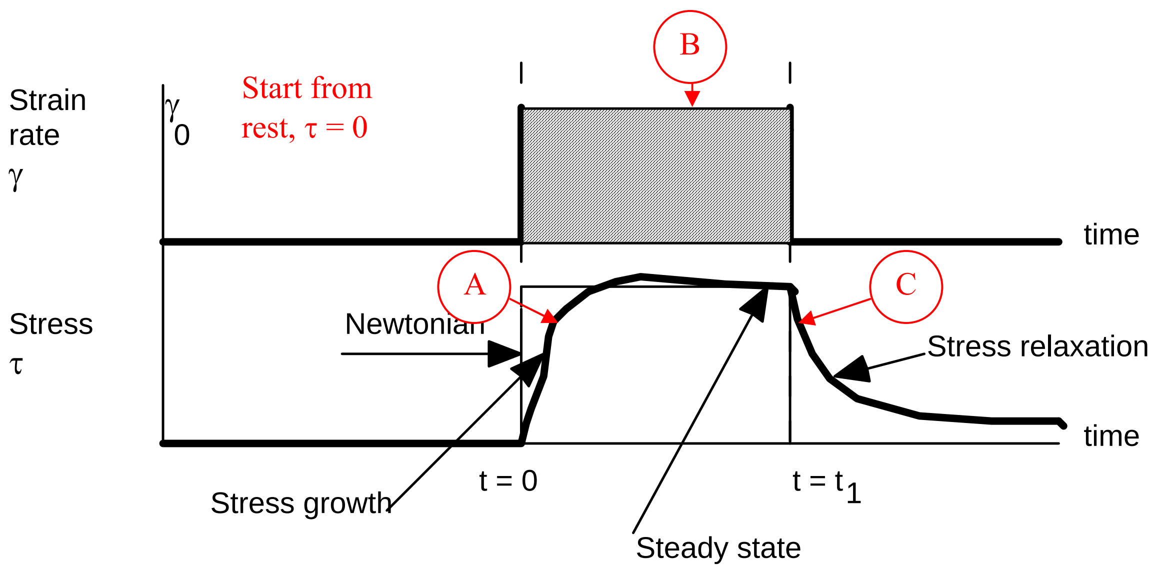


Parallel plate more tricky because τ is a function of r.

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



$t < 0 \qquad \dot{\gamma} = 0$

$t > 0 \qquad \dot{\gamma} = \dot{\gamma}_o$

$t > t_1 \qquad \dot{\gamma} = 0$

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

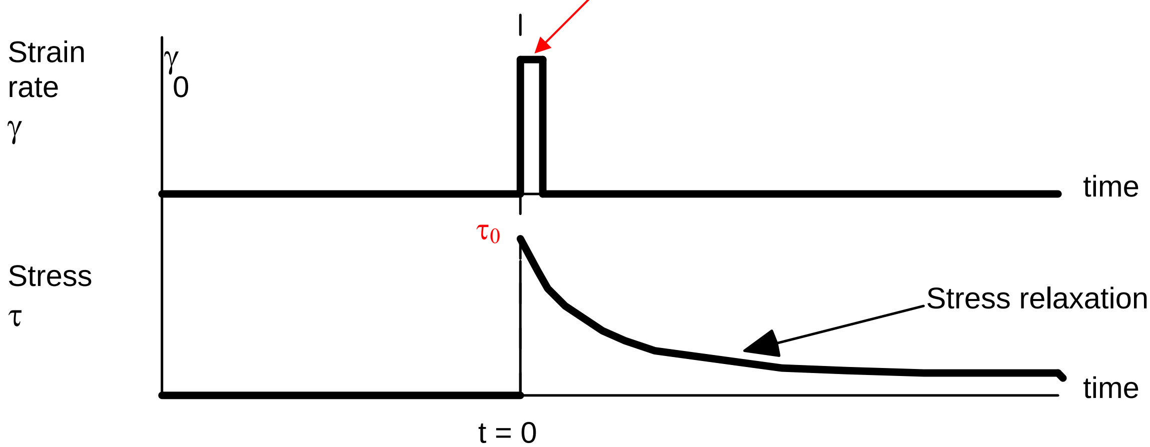
(A) Stress growth	(Viscoelastic response)
(B) Steady shear	(Non Newtonian behaviour)?
(C) Stress relaxation	(Viscoelastic response)

Time dependence can be explored

Steady shear is the most used deformation, obtain "flow curve"

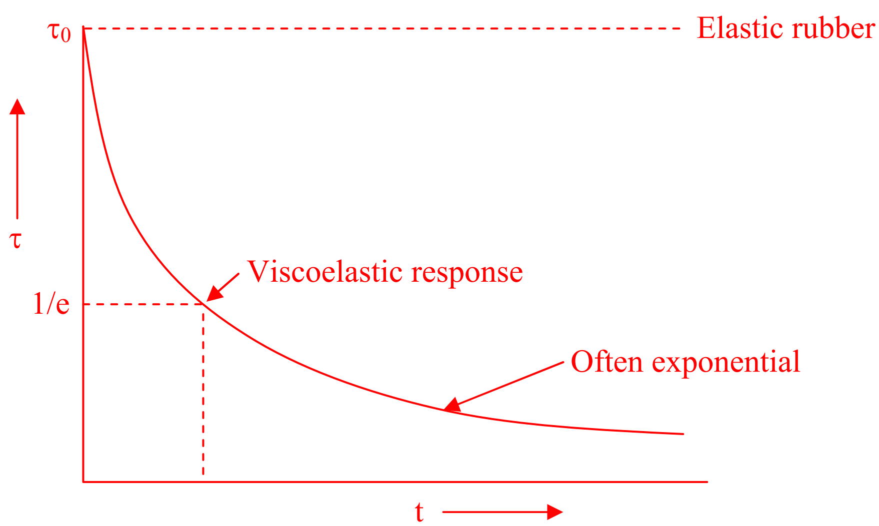
b) Step strain

At t= o, instantaneously strain material by $\gamma_0 = \dot{\gamma}_0 \delta t$, subsequently measure stress relaxation as a function of t



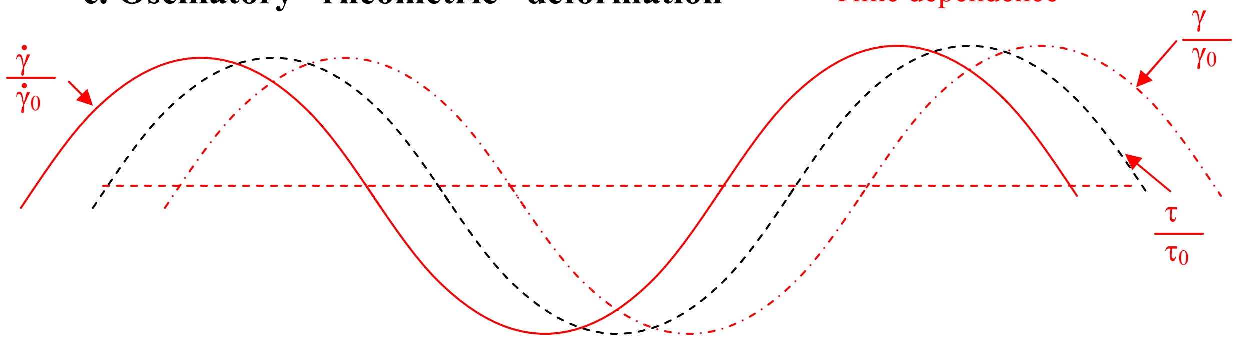
Relaxation modulus G(t)

$$G(t) = \frac{\tau(t)}{\gamma_0}$$



Characteristic relaxation time
$10^{-3} - 10^{3}$ s

c. Oscillatory "rheometric" deformation → Time dependence



strain ↘ ↙ angular frequency

Apply $\gamma = \gamma_o \sin \omega t$ Strain $\gamma = \gamma_o e^{i\omega t}$

then $\dot{\gamma} = \gamma_o \omega \cos \omega t$ Strain rate $\dot{\gamma} = i\omega\gamma_o e^{i\omega t}$

measure $\tau = \tau_o \sin(\omega t + \delta)$

variable γ_o = max strain amplitude, typically 0.1 (10%)

ω = angular frequency, typically $10^{-2} - 10^{3}$ rad/s

~ 1 hour to complete the experiment ↗ ↖ ω limit of oscillator

$\dot{\gamma} = \gamma_o \; \omega \cos \omega t$ or $\dot{\gamma} = i\omega\gamma_o e^{i\omega t}$

$\tau = \tau_o \sin(\omega t + \delta)$ or $\tau = \tau_o e^{i(\omega t + \delta)}$

$= \tau_o \sin \omega t \cos \delta \quad + \tau_o \cos \omega t \sin \delta$

⇓

component of stress in phase with γ — Elastic bit!

component of stress in phase with $\dot{\gamma}$ — Viscous bit!

Defn $\tau = G' \gamma_o \sin \omega t \quad + \quad G'' \gamma_o \cos \omega t$ τ α strain

So $G' = \dfrac{\tau_o}{\gamma_o} \cos\delta$, $G'' = \dfrac{\tau_o}{\gamma_o} \sin\delta$ Pa

Storage Modulus → Elastic

Loss Modulus → Viscous

$\tau = G^* \gamma$

Complex modulus G* (another way of saying the same thing).

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

⇓ Elastic Modulus ⇓ Loss Modulus

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

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

So $G' = \frac{\tau_o \cos\delta}{\gamma_o}$ $G'' = \frac{\tau_o}{\gamma_o}\sin\delta$ 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, γ_0 if we know τ_0 and δ from the rheometer

dimensions of viscosity

Complex viscosity $\eta^* = \frac{\left[G'^2 + G''^2\right]^{1/2}}{\omega}$ Pas

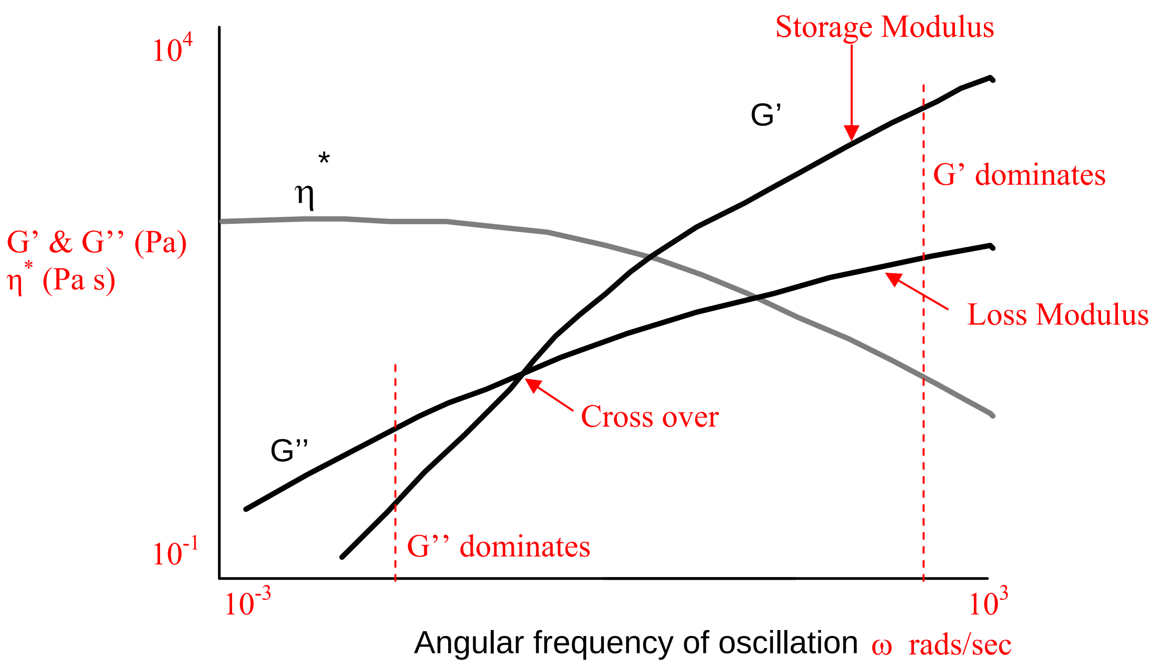
For given ω, and known γ_o.

G' :- Storage modulus
G'' :- Loss modulus
η^* :- Complex viscosity

These properties capture the viscoelastic properties of a material, but the values will depend on the test frequency (time scale applied).

Measure τ_o and δ using TA instruments rheometer or other instrument, then we know the following, for a given ω

1. G' storage modulus. 2. G" Loss modulus. 3. η*Complex viscosity

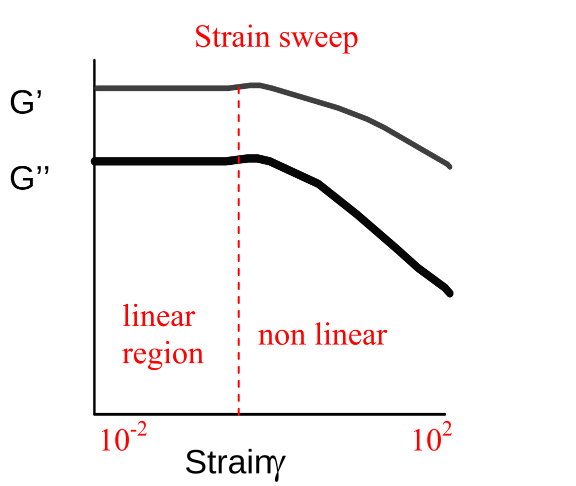


Rheometer measures Torque and from this we need shear stress

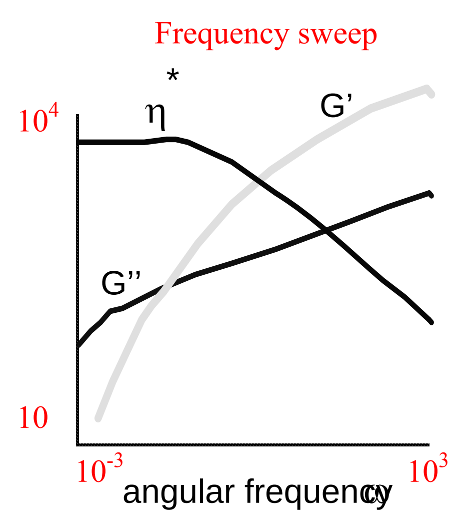
Typical viscoelastic data that we wish to model. (See appendix)

1. Oscillatory Viscoelastic response.

linear viscoelastic response ω,γ

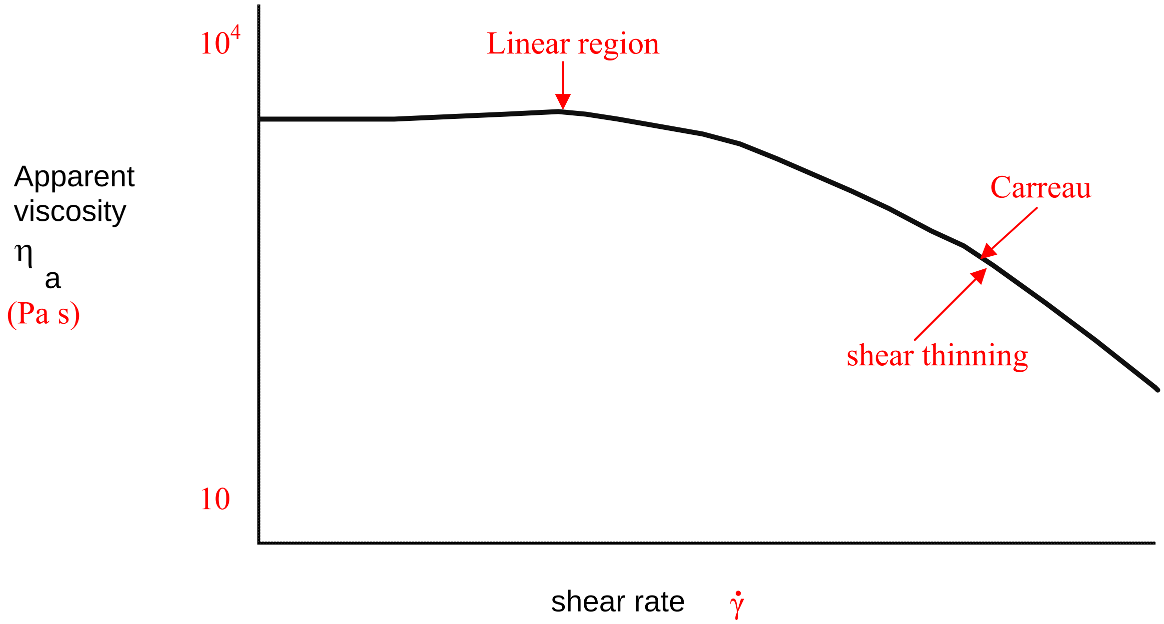


at fixed frequency $\omega_0 \sim 1$ rads/sec

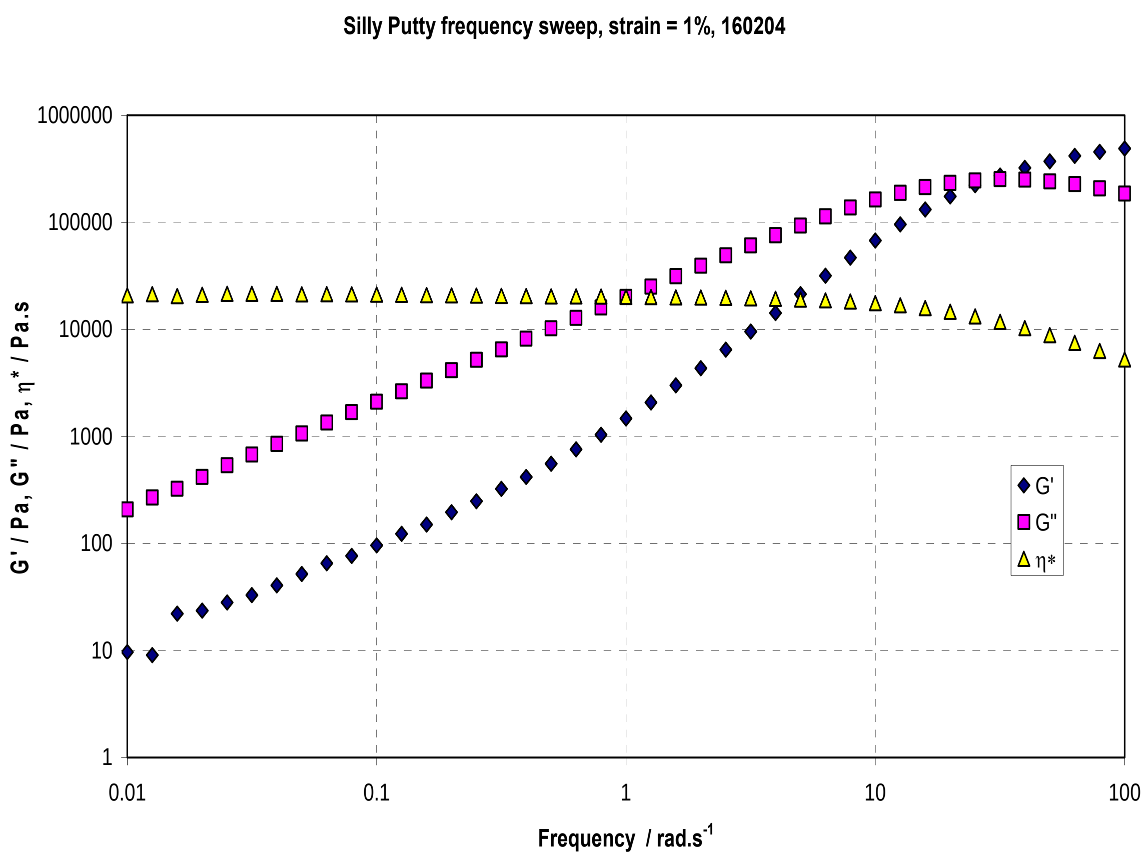


at fixed strain γ_0

2. Steady Shear



Silly Putty; real data.



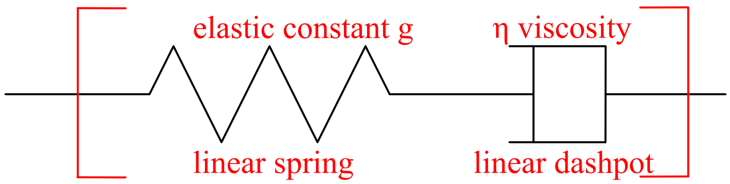
Modelling of viscoelasticity

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

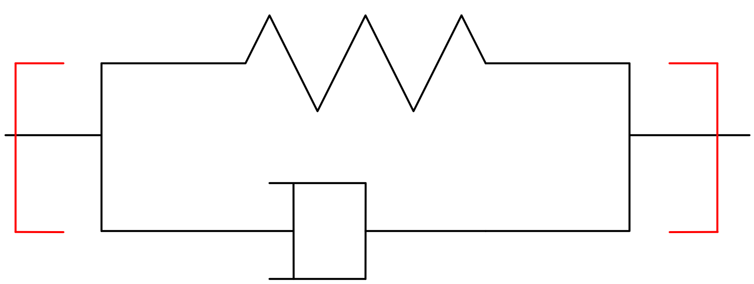


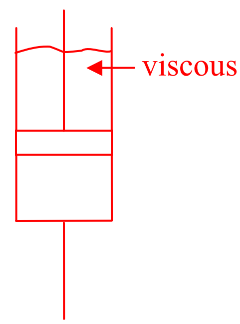
Maxwell often favoured for stress relaxation

The Voigt element. parallel coupling

$\gamma = \gamma_1 = \gamma_2$

$\tau = \tau_1 + \tau_2$



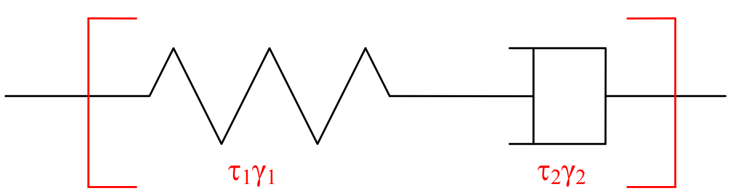


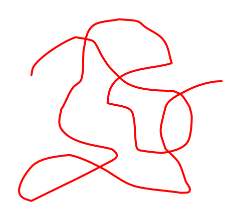
Voigt often favoured for creep (constant stress experiments)

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

The Maxwell Model (Differential form)

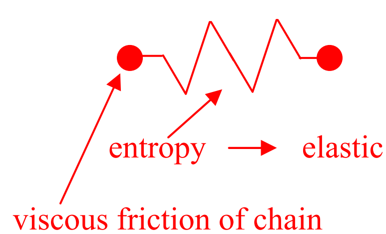
(τ, γ)





Local (τ_1, γ_1) $(\tau_2 \gamma_2)$

$\tau_1 = g\,\gamma_1$ $\tau_2 = \eta\,\dot{\gamma}_2$



Coupling $\tau =$ $\tau_1 = \tau_2$ Stress continuity

$\gamma = \gamma_1 + \gamma_2$ Strain additivity

Then $\dot{\gamma} = \dot{\gamma}_1 + \dot{\gamma}_2$

$\tau_1 = \tau_2 = \tau$

Governing ordinary differential equation

relaxation times (s)

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

$\lambda = \dfrac{\eta}{g}$ (Pa s) / (Pa)

1st order ODE

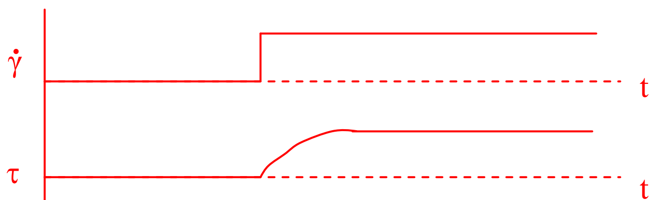
$$g\frac{d\gamma}{dt} = \frac{d\tau}{dt} + \frac{\tau}{\lambda}$$

→ Maxwell equation

where the relaxation time of the element λ is given by η/g, (s)

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

a..Steady shear



$\frac{d\tau}{dt} = 0$

$\tau = \lambda g\dot{\gamma}$
$\tau = \eta\dot{\gamma}$

$$\frac{d\tau}{dt} = 0 \quad \text{Then} \quad \tau = \eta\dot{\gamma}_0$$

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

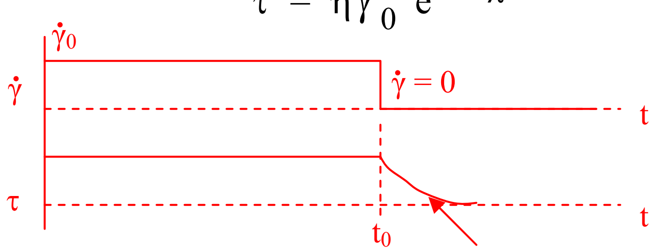
Maxwell model predicts Newtonian behaviour in simple shear.Most complex VE Fluids are shear thinning and so we will have to fix this later.

b. Stress relaxation after steady shear

$$\frac{d\tau}{dt} = -\frac{\tau}{\lambda}$$

$$\tau = \eta\dot{\gamma}_0 \, e^{-\frac{[t - t_0]}{\lambda}}$$

$$\int_{\tau_0}^{\tau}\frac{d\tau}{\tau} = -\int_{t_0}^{t}\frac{dt}{\lambda}$$



$\tau = \tau_0 e^{-[t-t_0]/\lambda}$
$\tau = \eta\dot{\gamma}_0 e^{-[t-t_0]/\lambda}$

All elastic $\lambda \to \infty$
All viscous $\lambda \to 0$

exponential decay
time constant λ, 10^{-3} - 10^{3}

c. Oscillatory motion. (Important and frequently used)

Use complex notation
Variables (γ_0, ω)

Apply $$\gamma(t) = \gamma_o e^{i\omega t}$$

Measure $$\tau(t) = \tau_o e^{i(\omega t + \delta)}$$

Strain rate $$\dot{\gamma}(t) = i\omega\gamma_o e^{i\omega t}$$

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

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

Remember, $$g\frac{d\gamma}{dt} = \frac{d\tau}{dt} + \frac{\tau}{\lambda},$$ so, Maxwell equation

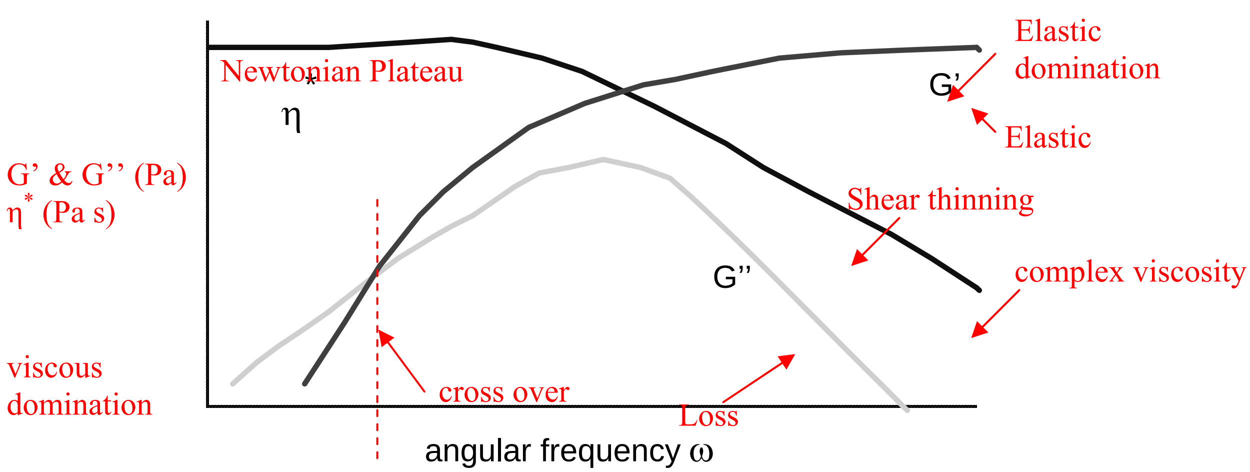
Substitute for γ, τ

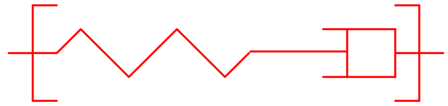
$$gi\omega\gamma_o e^{i\omega t} = i[G' + iG'']\gamma_o \omega e^{i\omega t} + \frac{1}{\lambda}\left[(G' + iG'')\gamma_o e^{i\omega t}\right]$$

Yields

$$G' = \frac{g\lambda^2\omega^2}{\left(1 + \lambda^2\omega^2\right)}, \quad G'' = \frac{g\lambda\omega}{\left(1 + \lambda^2\omega^2\right)}, \quad \eta^* = \frac{g\lambda}{\left(1 + \lambda^2\omega^2\right)^{1/2}}$$

$\omega \to 0$	$G' \to 0$	$\omega \to 0$	$G'' \to 0$	$\omega \to 0$	$\eta^* = g\lambda = \eta$
$\omega \to \infty$	$G' \to g$	$\omega \to \infty$	$G'' \to 0$	$\omega \to \infty$	$\eta^* \to 0$





A bit of maths. Differential equations versus integral equations.

The Maxwell Model (Integral form wrt strain rate)

Differential equation

$$\frac{\tau}{\lambda} + \frac{d\tau}{dt} = g\frac{d\gamma}{dt} \qquad \lambda = \frac{\eta}{g}$$

1st order ODE

Multiply by integrating factor

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

$$\frac{d}{dt}\left(\tau e^{t/\lambda}\right) = \frac{\tau e^{t/\lambda}}{\lambda} + e^{t/\lambda}\frac{d\tau}{dt}$$

assume $\tau = 0$ at $t' = -\infty$

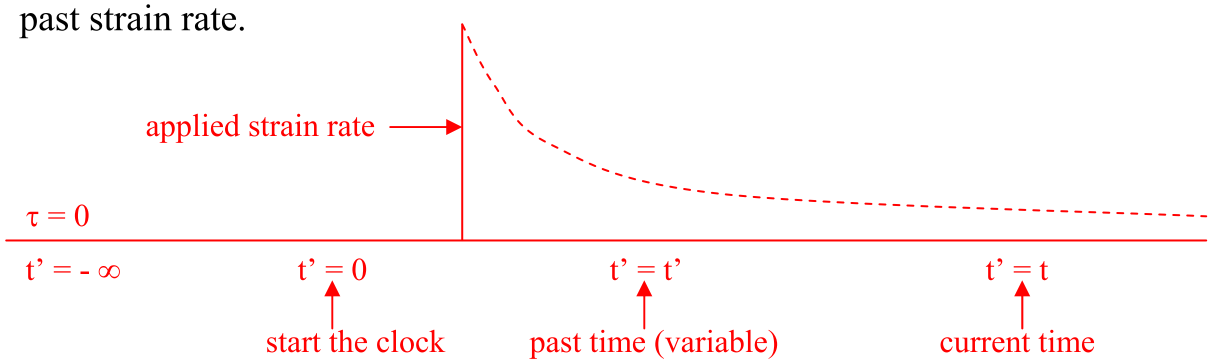
current time

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

Past time

Stress at current time → $$\tau(t) = \int_{-\infty}^{t} g\, e^{-(t-t')/\lambda}\, \dot{\gamma}(t')dt'$$ ← strain rate at past time t'

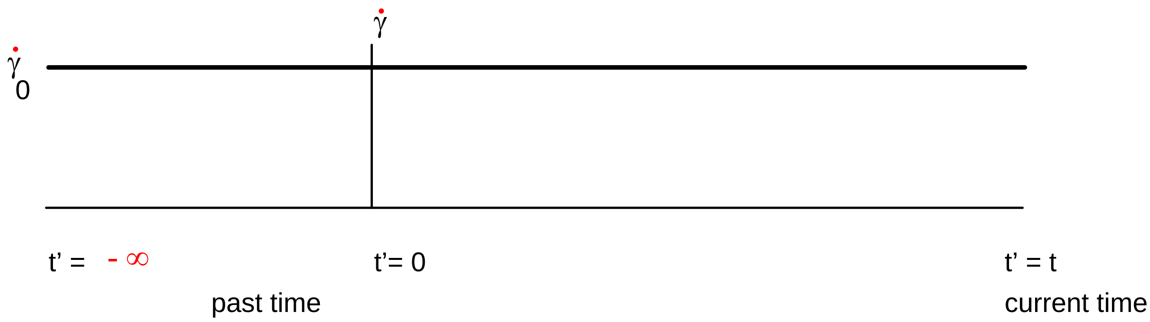
Maxwell equation in terms of past strain rate – current stress depends on past strain rate.



$\tau(t) = g\, e^{-(t-t')/\lambda}\, \dot{\gamma}(t')dt'$

Fading memory

Test strain rate equation **Steady shear**



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

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

$$= g\dot{\gamma}_o \left[\lambda\, e^{-(t - t')/\lambda}\right]_{-\infty}^{t} = g\,\lambda\,\dot{\gamma}_o$$

$$\underline{\tau_{ss} = \eta\dot{\gamma}_o}$$ as before

current time t is a constant

$$\tau\,(t) = \int_{-\infty}^{t} g e^{-(t-t')/\lambda}\dot{\gamma}_0 dt'$$

$$= g\dot{\gamma}_0 e^{-t/\lambda}\int_{-\infty}^{t} e^{t'/\lambda} dt'$$

$$= g\dot{\gamma}_0 e^{-t/\lambda}\left[\lambda e^{t'/\lambda}\right]_{-\infty}^{t}$$

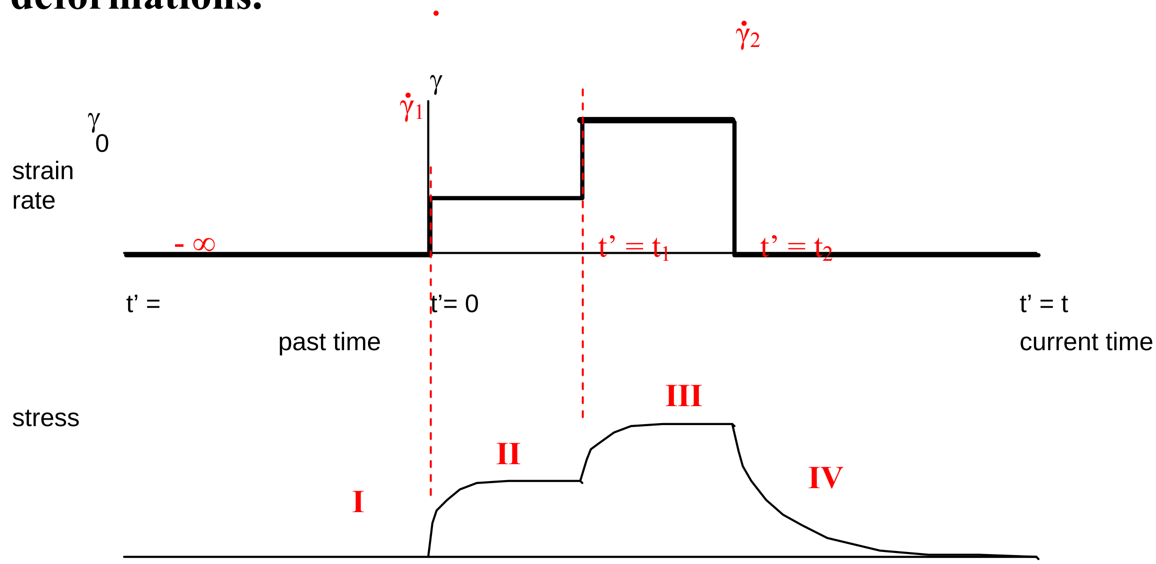
$$= g\dot{\gamma}_0\lambda$$

$$\lambda = \frac{\eta}{g}$$

$$\tau = \eta\dot{\gamma}_0$$ 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.



I $\quad \tau(t) = \int_{-\infty}^{t} g e^{-(t-t')/\lambda}\, \dot{\gamma}(t')dt' \qquad \tau = 0$

II $\quad \tau(t) = \int_{0}^{t} g e^{-(t-t')/\lambda}\, \dot{\gamma}_1\, dt' = \gamma_1\, g e^{-t/\lambda} \int_{0}^{t} e^{t'/\lambda} dt'$

If $t = t_1$ then $\tau = \tau_1$

III $\quad \tau(t) = \cancel{\int_{-\infty}^{0}} + \int_{0}^{t_1} g e^{-(t-t')/\lambda}\, \dot{\gamma}_1\, dt' + \int_{t_1}^{t} g e^{-(t-t')/\lambda}\, \dot{\gamma}_2\, dt'$

If $t = t_2$ then $\tau = \tau_2$

IV $\quad \tau(t) = \cancel{\int_{-\infty}^{0}} + \int_{0}^{t_1} g e^{-(t-t')/\lambda}\, \dot{\gamma}_1\, dt' + \int_{t_1}^{t_2} g e^{-(t-t')/\lambda}\, \dot{\gamma}_2\, dt' + \int_{t_2}^{t} \cancel{g e^{-(t-t')/\lambda}}\, dt'$

Exponential decay

Lets integrate again in order to obtain the Maxwell integral strain equation.

The Maxwell Model (Integral form wrt strain)

We know,

Stress at time t

$$\tau(t) = \int_{-\infty}^{t} g\, e^{-(t-t')/\lambda} \frac{d\gamma}{dt'} dt'$$

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

let $u = ge^{-(t-t')/\lambda}, \quad dv = d\gamma$

integrate above by parts,

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

strain — strain

where strain is given by

Define strain

Two strain terms
Strain = 0 at current time t

$$\gamma(t,t') = \int_{t}^{t'} \dot{\gamma}(t'') dt''$$

where t =current time and t' = past time

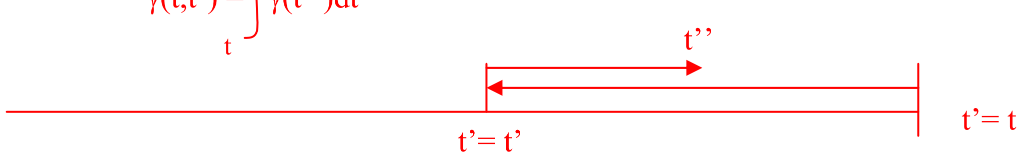
Note when $t' = t$ $\gamma = 0$
We are measuring strain from current time
So

Integral Maxwell equation – past strain

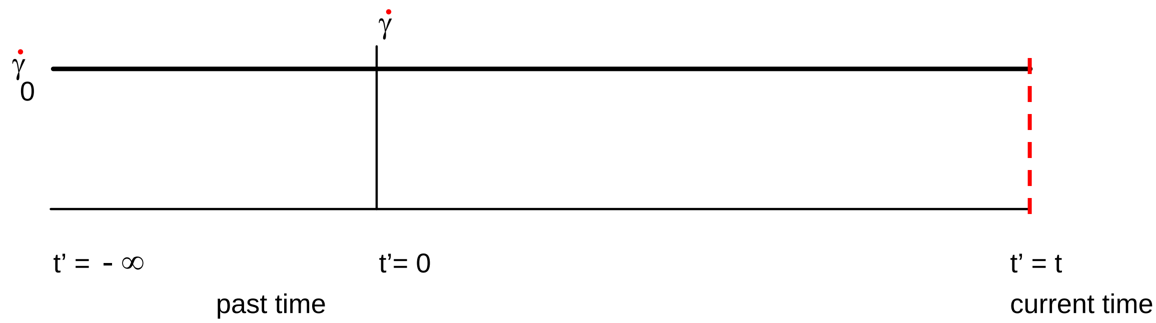
$$\tau(t) = - \int_{-\infty}^{t} \frac{g}{\lambda} e^{-(t-t')/\lambda} \gamma(t,t') dt'$$

Stress at time t — Past strain history

$$\dot{\gamma}(t,t') = \int_{t}^{t'} \dot{\gamma}(t'')dt$$



Test Maxwell strain integral equation. **steady shear** $\dot{\gamma}$ = const

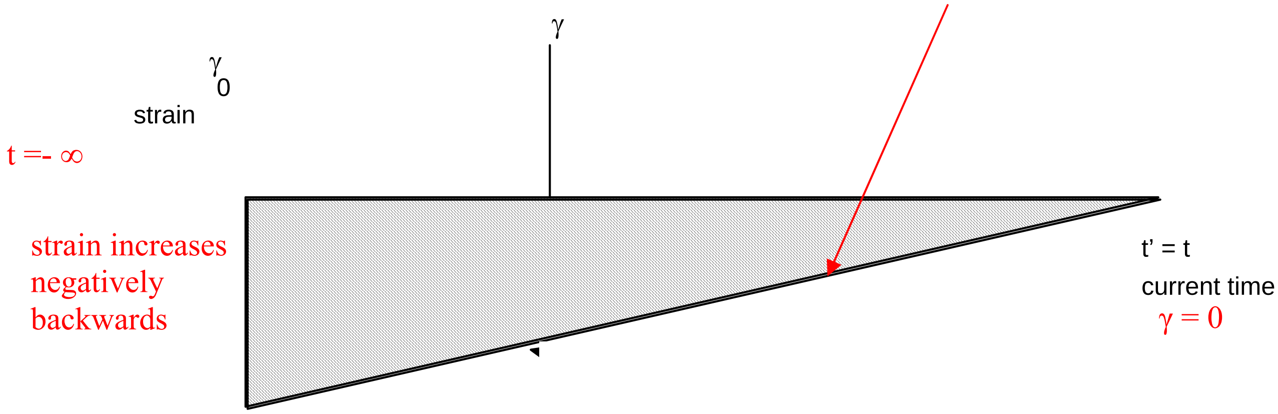


Determine past strain history

By definition $\gamma(t,t') = \int_t^{t'} \dot{\gamma}(t'')\,dt''$

For steady shear $\gamma(t,t') = \dot{\gamma}_o \int_t^{t'} dt'' = \dot{\gamma}_o (t' - t)$

$= - \dot{\gamma}_o (t - t')$



Introduce new variable s, (you don't have to do this, but it generally makes calculation simpler).

Let $s = t - t^1$
$ds = - dt^1$

$s = \infty$	$s = t$	$s = t - t^1$	$s = 0$
$t' = -\infty$	$t' = 0$	$t' = t^1$	$t' = t$

Integral strain equation $\tau(t) = +\int_{\infty}^{o} \frac{g}{\lambda} e^{-s/\lambda} \gamma(o, s)\, ds$

Also, strain $\gamma = -\dot{\gamma}_o (t - t') = -\dot{\gamma}_o s$

$$\tau(t) = -\int_{\infty}^{o} \frac{g}{\lambda} \dot{\gamma}_o s\, e^{-s/\lambda} ds$$

$$\tau(t) = -\frac{g}{\lambda}\dot{\gamma}_o \left[\left(-\lambda s\, e^{-s/\lambda}\right)_{\infty}^{o} + \int_{\infty}^{o} \lambda e^{-s/\lambda} ds \right]$$

$$= + g\lambda \dot{\gamma}_o \left[e^{-s/\lambda} \right]_{\infty}^{o}$$

$$\underline{\tau = g\lambda\dot{\gamma}_o = \eta\dot{\gamma}_o}$$ Newtonian, as before.

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

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

$$\tau(t) = +\frac{g}{\lambda} \dot{\gamma}_0 e^{-t/\lambda} \int_{-\infty}^{t} (t - \underline{t')e^{t'/\lambda}} dt'$$

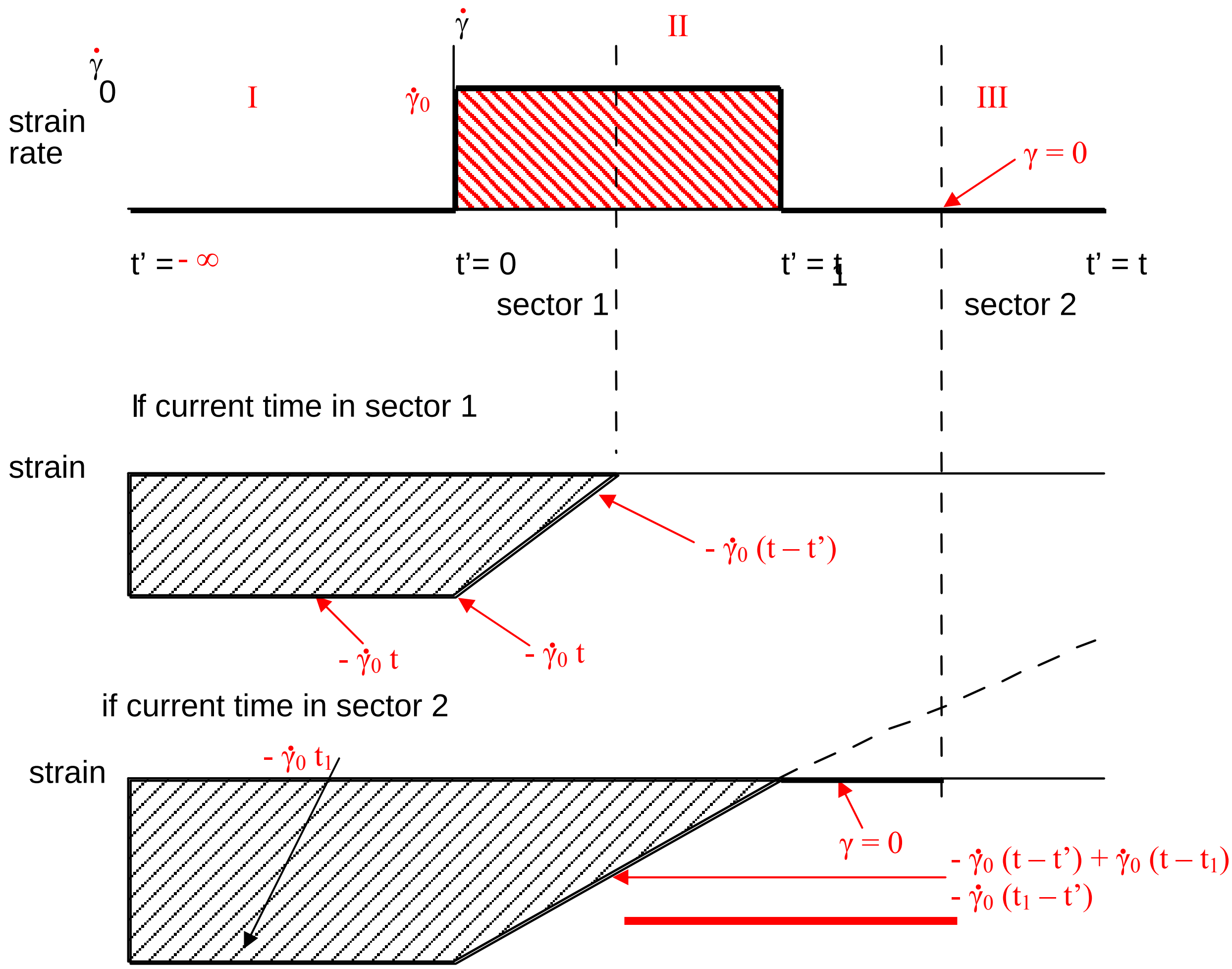
integrate by parts

$$\tau = \dot{\eta}\, \gamma_0 \quad = \quad \dot{} \lambda\, g\, \gamma_0$$

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!)



II $$\tau(t) = -\int_{-\infty}^{0} \frac{g}{\lambda} e^{-(t-t')/\lambda} (-\dot{\gamma}_0 t) dt' - \int_{0}^{t} \frac{g}{\lambda} e^{-(t-t')/\lambda} (-\dot{\gamma}_0 (t-t')) dt'$$

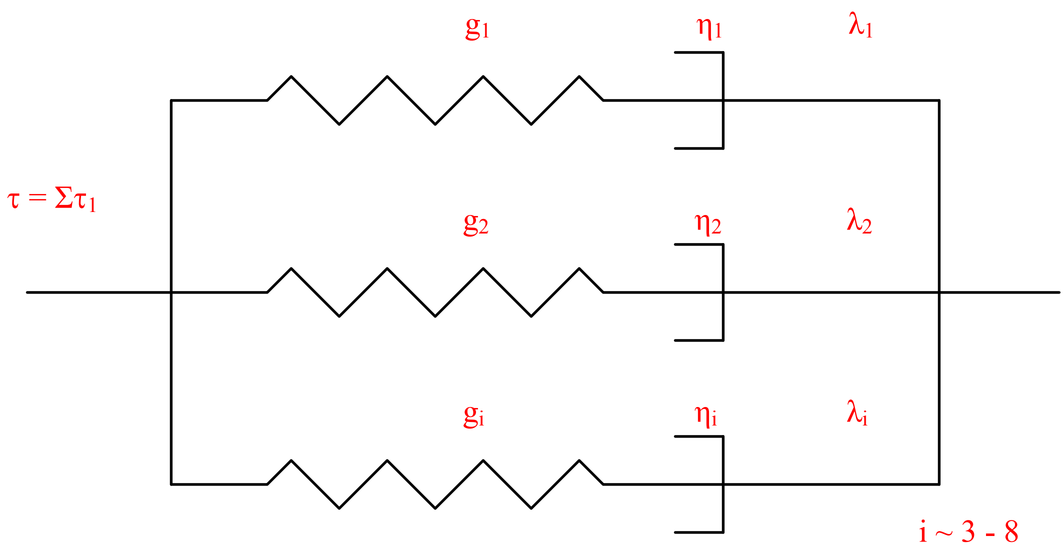
III $$\tau(t) = -\int_{-\infty}^{0} \frac{g}{\lambda} e^{-(t-t')/\lambda} (-\dot{\gamma}_0 t_1) dt' - \int_{0}^{t_1} \frac{g}{\lambda} e^{-(t-t')/\lambda} (-\dot{\gamma}_0 (t_1-t')) dt' + \int_{t_1}^{t} (0)$$

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



$$\lambda_i = \frac{\eta_i}{g_i}$$

The integral constitutive equation then becomes,

$$\tau(t) = -\int_{-\infty}^{t} \sum_i \frac{g_i}{\lambda_i} e^{-(t-t')/\lambda_i} \gamma(t,t')\,dt'$$

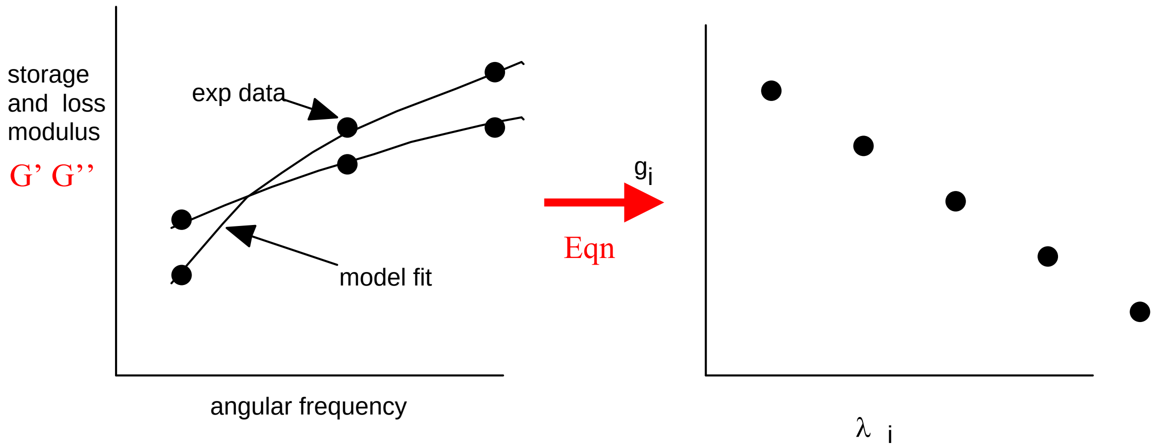
multi-mode Maxwell integral equation in terms of past strain

For oscillatory data the equations become.

$$G'(\omega) = \sum_i \frac{g_i \lambda_i^2 \omega^2}{\left(1 + \lambda_i^2 \omega^2\right)}, \qquad G''(\omega) = \sum_i \frac{g_i \lambda_i \omega}{\left(1 + \lambda_i^2 \omega^2\right)}$$

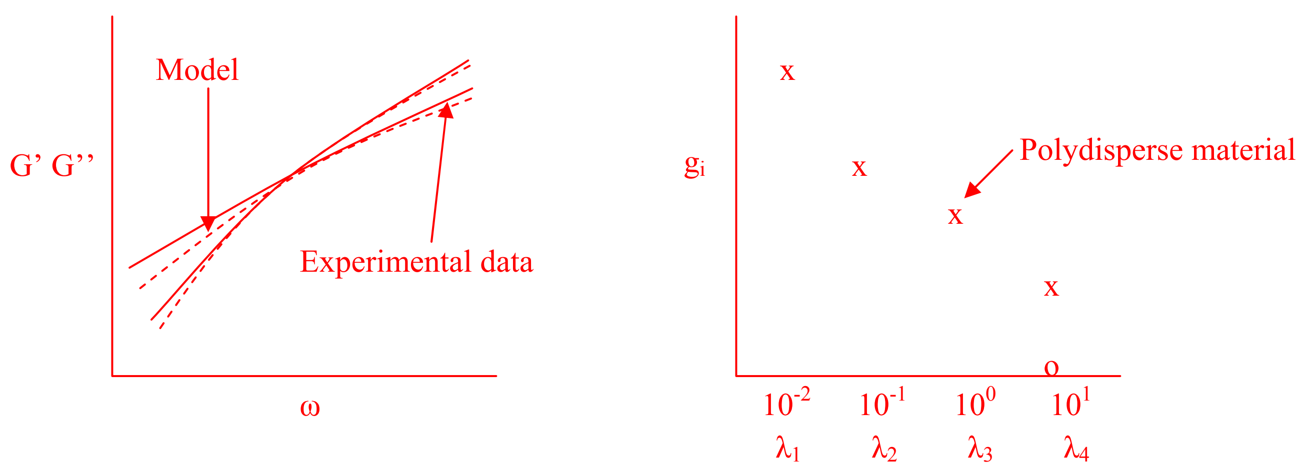
$$\eta^*(\omega) = \sum_i \frac{g_i \lambda_i}{\left(1 + \lambda_i^2 \omega^2\right)^{1/2}}$$

We now need to find the "best fit" g_I, λ_ι. This is potentially a tricky problem. Use software on Rheometrics to get best fit.



ill posed problem, there are multiple answers

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



Choose a range of λ_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

Mainly due to M H Wagner Rheol Acta 15, 136, (1976)

one only

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

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

strain dependant equation

This is the new bit!

damping factor

$e^{-k\left|\gamma(t,t')\right|}$ ← Modulus

Modulus (always pos)
damping parameter
k = 0 Maxwell
k ranges from 0 → 1
⇑
Non linear

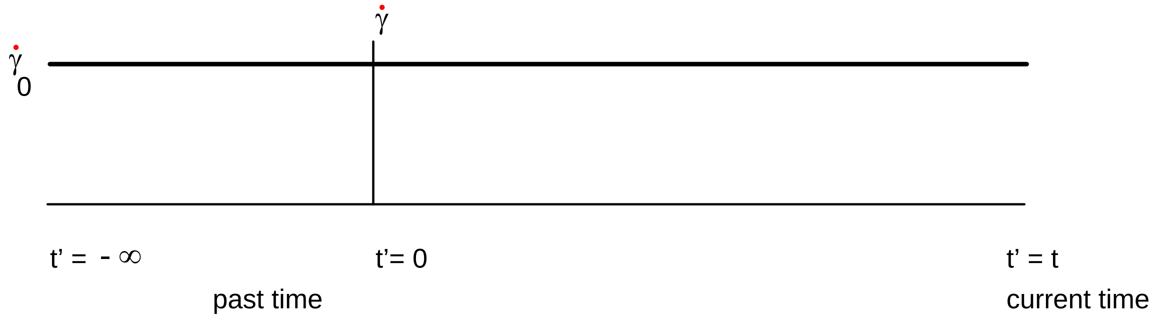
$$\tau[t] = -\int \underbrace{\left[\sum \frac{g_i e^{(t-t)/\lambda_i}}{\lambda_i}\right]}_{\text{Time dep of material}} \underbrace{e^{-k\left|\gamma(t,t')\right|}}_{\text{strain dep of material}} \gamma(t,t')\,dt'$$

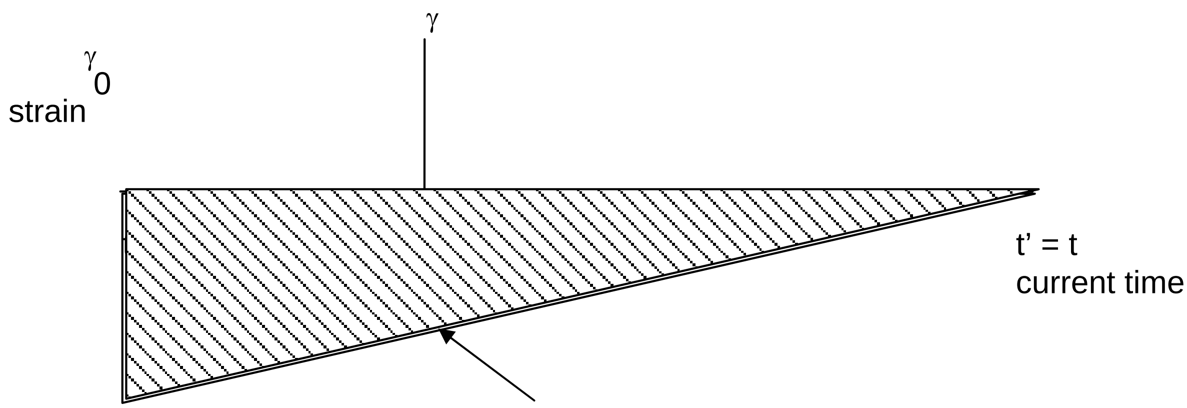
The equation has been "factored" in terms of a separated time and strain dependance.

Multi - mode integral strain dependant Maxwell equation with Wagner damping factor

The effect of the damping parameter on different deformations

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





γ = - γ0 (t – t')

$$\gamma(t,t') = -\dot{\gamma}_o(t - t')$$

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

use s =(t-t')
(Optional)

$$\gamma(o, s) = -\dot{\gamma}_o s$$

$$ds = -dt'$$

$$\tau(t) = -\int_{\infty}^{o}\sum \frac{g_i}{\lambda_i} e^{-s/\lambda_i} e^{-k\dot{\gamma}_o s}\dot{\gamma}_o s ds$$

$$\tau(t) = -\int_{\infty}^{o}\sum^{i} \frac{g_i}{\lambda_i}\dot{\gamma}_o e^{-\alpha_i s} s ds$$

$$\text{where } \alpha_i = \frac{1}{\lambda_i} + k\dot{\gamma}_o$$

integrate by parts

$$\tau\left(\dot{\gamma}_o\right) = \sum^{i} \frac{g_i \lambda_i \dot{\gamma}_o}{\left(1 + k\lambda_i \dot{\gamma}_o\right)^2}$$

steady shear ←

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

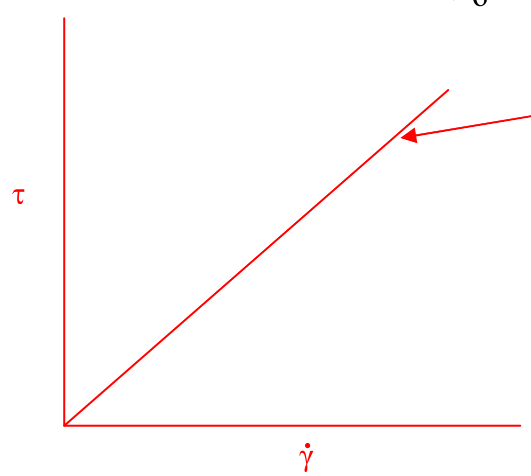
$k = 0 \rightarrow$ Newtonian

Check the form of steady shear equation

Relaxation modes	single mode	or multi-mode
Non linear k	$k = 0$	$k \neq 0$
		$k \sim 0 \rightarrow 1$

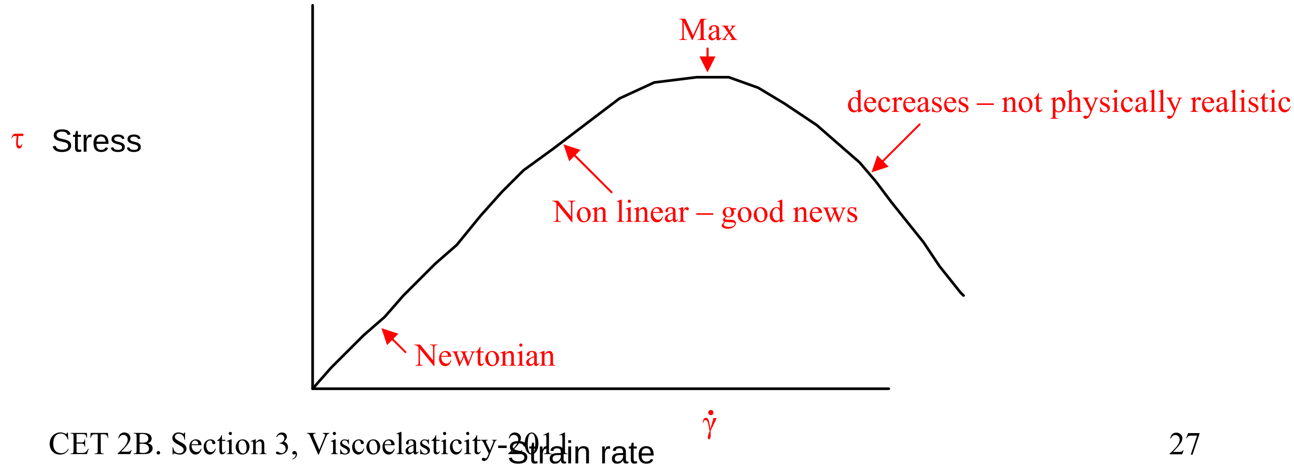
a) **single λ , $k = 0$**

$$\tau = \eta \dot{\gamma}_o$$ Newtonian as before

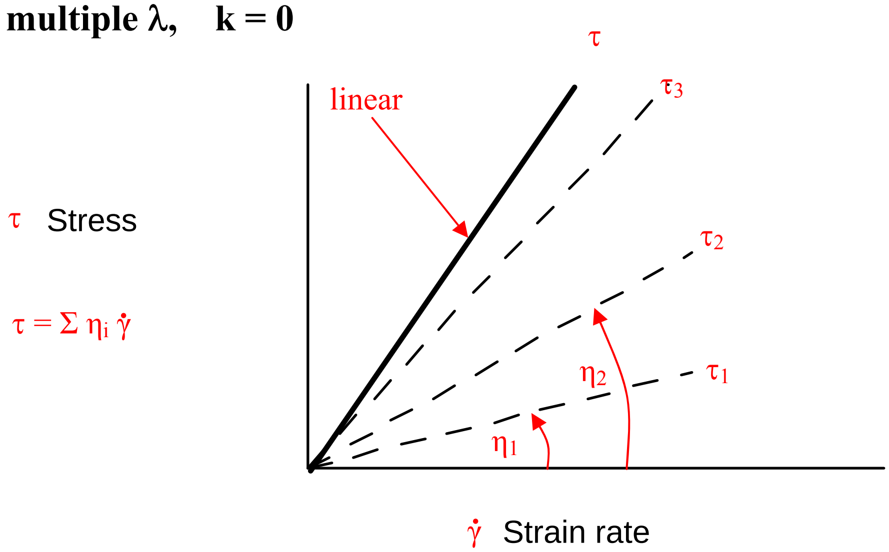


b) **single λ, $k \neq 0$**

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



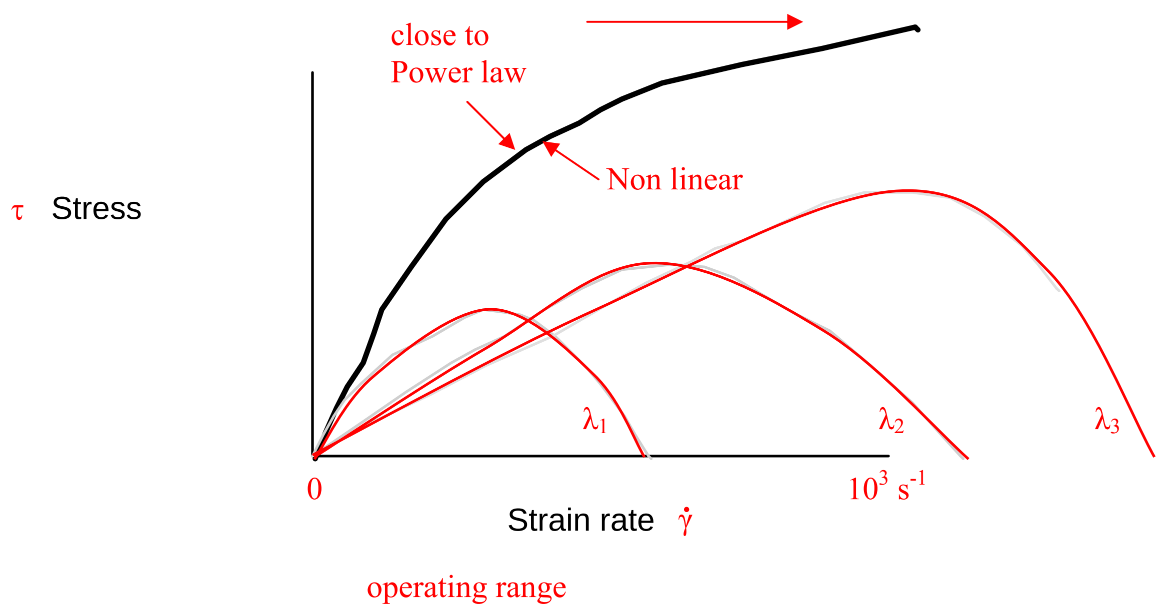
c) multiple λ, k = 0



response is still linear

d) multiple λ, k ≠ 0

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



This non linear response may match "Power law" Bingham …. Or other steady shear constitutive equation.

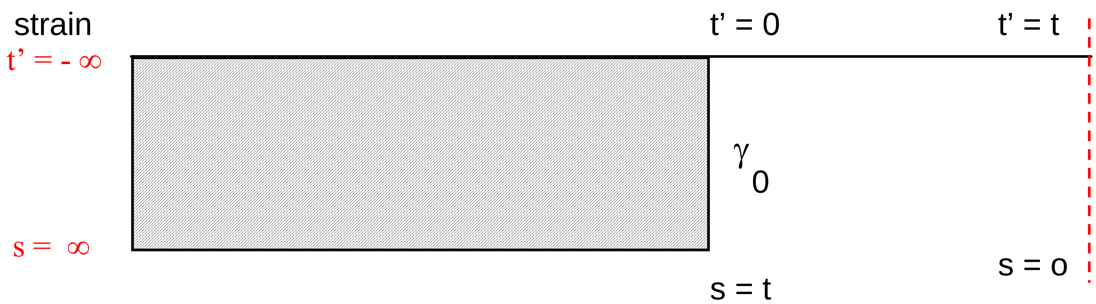
We now have a model that describes LVE response and the non linear steady shear response. **This is what we want!**

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



s < t $\gamma = 0$
s > t $\gamma = -\gamma_o$
recall

$e^{-k|\gamma(t,t')|}$ ↑ γ_0

$$\tau(t) = -\int_{-\infty}^{t} \sum^{i} \frac{g_i}{\lambda_i} e^{-(s)/\lambda_i} \gamma_0 e^{-k\gamma_0} \, ds$$

stress at time t

$$\boldsymbol{\tau(t) = \gamma_0 \, e^{-k\gamma_0} \sum^{i} g_i \, e^{-t/\lambda_i}}$$

Relaxation modulus at finite strain

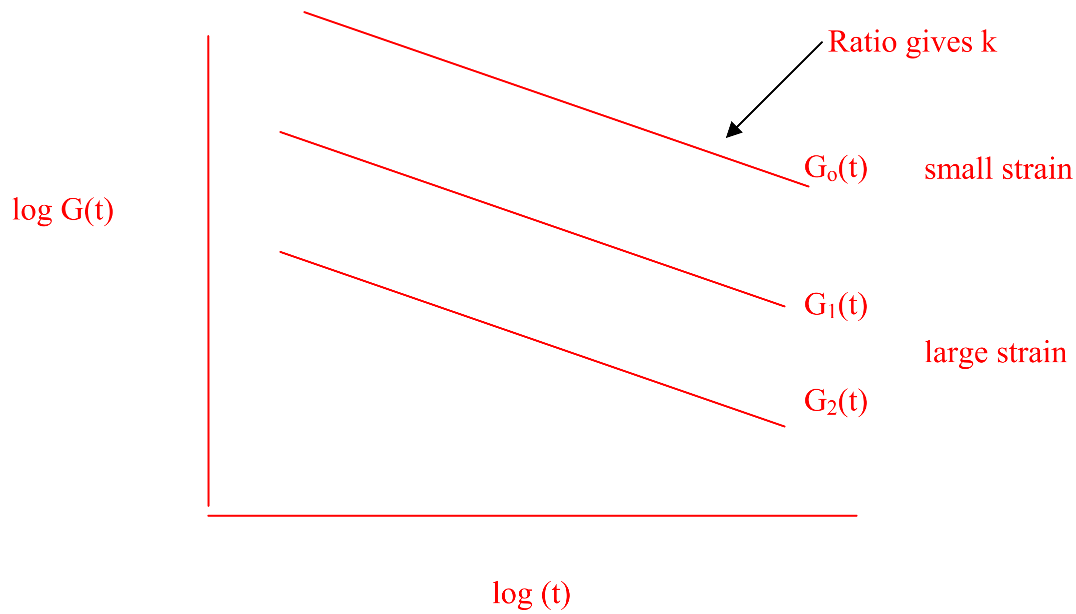
$$G\gamma_j(t) = \frac{\tau(t)}{\gamma_j} = e^{-k\gamma j} \sum^{i} g_i e^{-t/\lambda_i}$$

but small strain modulus given by

$$G_0(t) = \frac{\tau(t)}{\gamma_0} = \sum^{i} g_i e^{-t/\lambda_i}$$

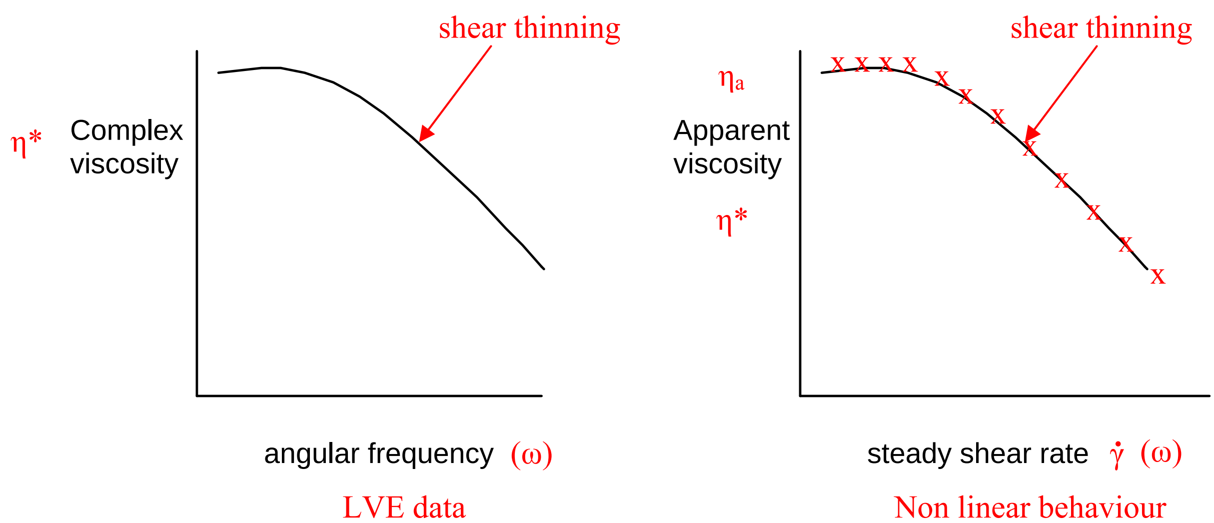
so $$e^{-k\gamma} = \frac{G_{\gamma j}(t)}{G_0(t)}$$

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



Cox Merz rule $\eta^*(\omega) = \eta_a\left(\dot{\gamma}\right)$

where $\omega = \dot{\gamma}$

Maxwell model with damping function predicts,

Complex viscosity. $$\eta^*(\omega) = \sum^{i} \frac{\eta_i}{\left(1 + \lambda_i^2\omega^2\right)}$$ no k in equation

Apparent viscosity

$$\eta_a\left(\dot{\gamma}_s\right) = \sum \frac{\eta_i}{\left(1 + k\lambda_i\dot{\gamma}_o\right)^2}$$

non linear term

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.

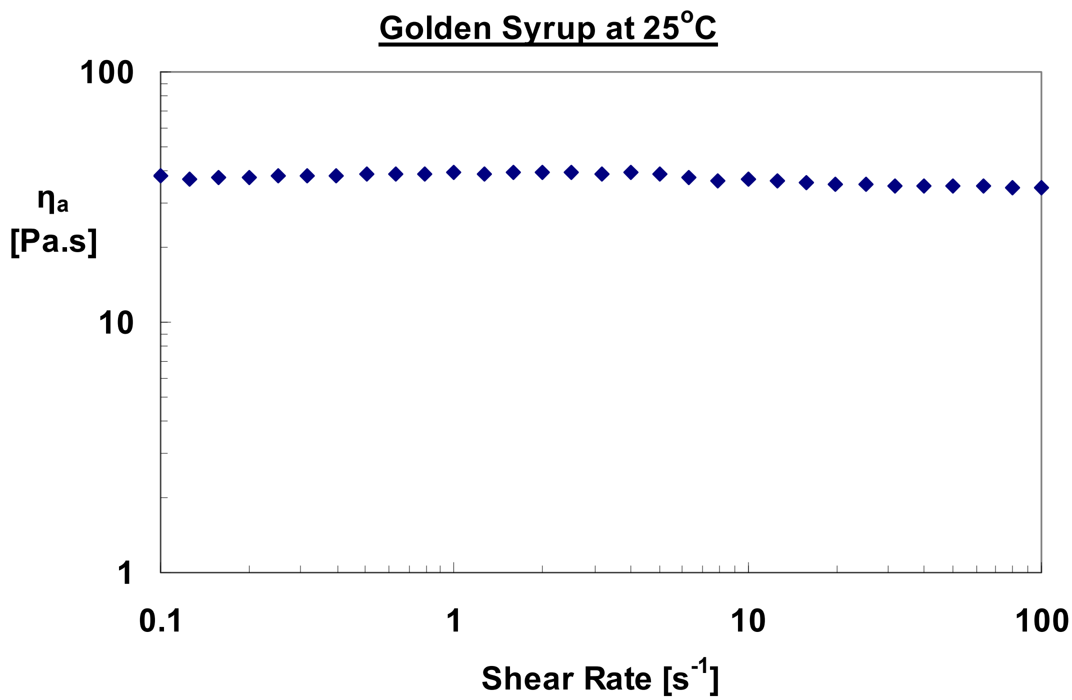
Cox Merz Rule → is an accidental coincidence !

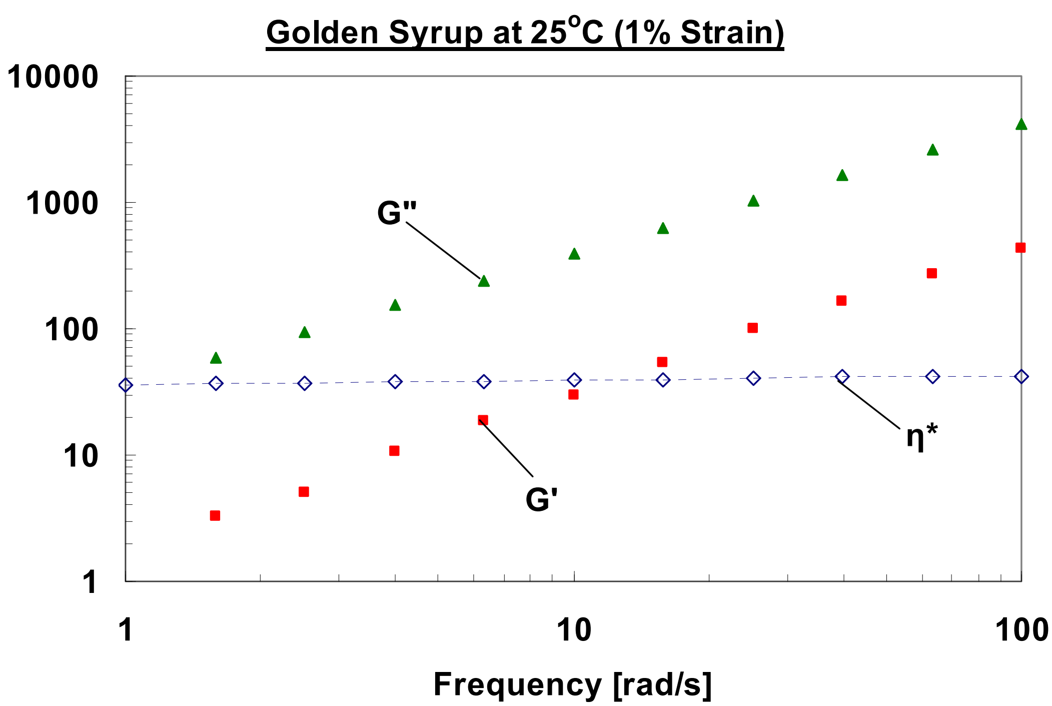
Summary of this important section.

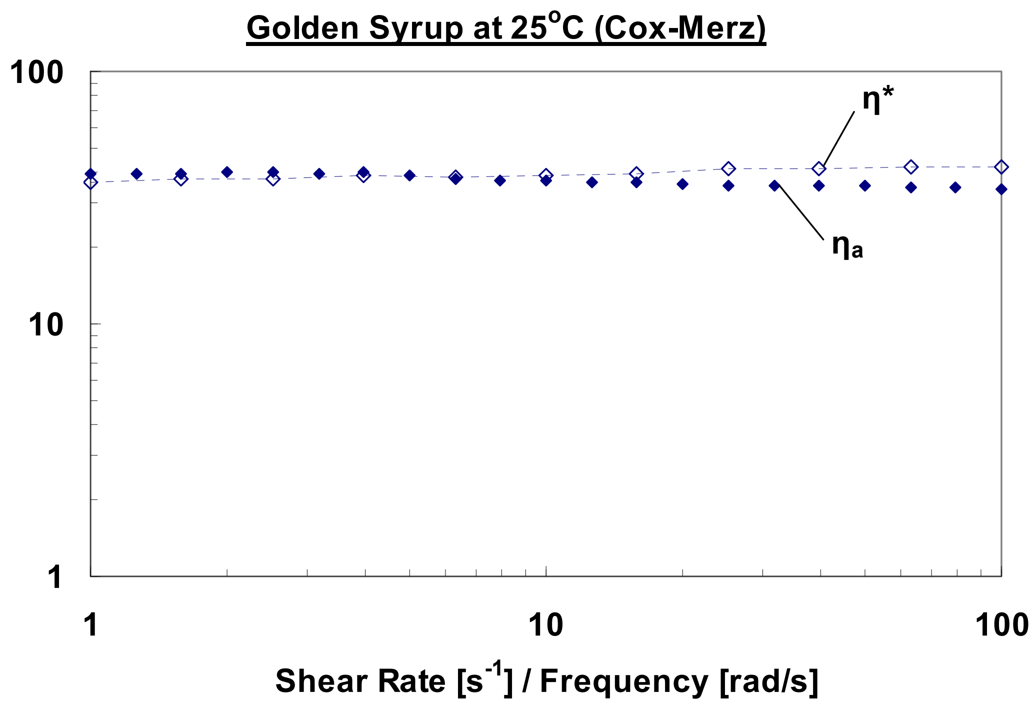
Appendix 1
Rheological data. Golden Syrup

A high viscosity Newtonian Fluid.
Note. No Shear thinning, very little elasticity, G' low, and Cox Merz obeyed.

Apparent visocosity



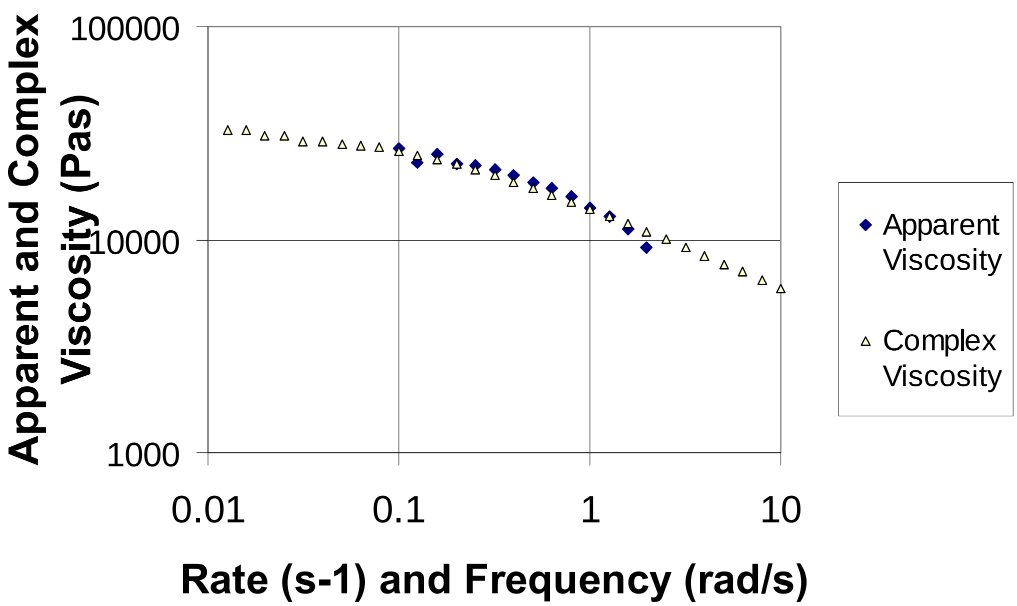



Golden Syrup at 25°C (Cox-Merz)
100
10
1
1
10
100
Shear Rate [s-1] / Frequency [rad/s]
η*
ηa

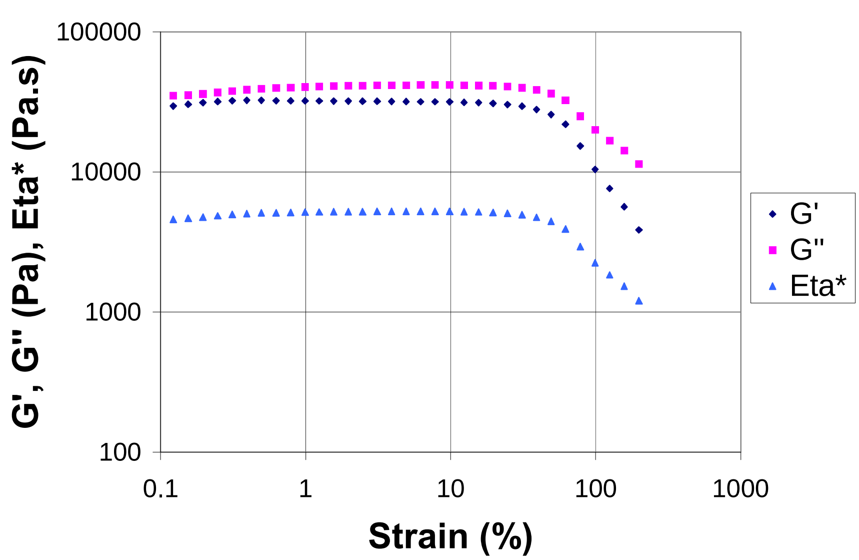
Appendix 2
Rheological data. A molten Polyethylene
(typical data for a commercial PE)

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 scross over for G', G'' curves.