### Part IIB Chemical Engineering Tripos.

# Rheology and Processing

By

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## Rheology and Processing

These lectures are intended as an introduction to rheology and processing. In particular they cover the flow behaviour of **Non-Newtonian Fluids** and **Viscoelastic Fluids**. Most of the course is quantitative and uses relatively simple mathematical modelling. By the end of the course it is hoped that you will have greater insight into the way different complex fluids can be processed.

## a) Newtonian fluids.

Most common and reference state

**Stress linearly dependant on Shear rate.**

Basis of most engineering fluid mechanics modelling (correlation, analytic, approximation and numerical) for **liquids** and **gas**.

Newtonian Liquids.

Incompressible……

Density……

Examples
Water, organic solvents; usually considered to be incompressible
These fluids are Newtonian over a wide range of,

| | | |
|---|---|---|
| Temperatures | Pressures | Shear rates |

Newtonian Gases.

Compressible ……..
Density…….
Examples

These gases are Newtonian over a wide range of,

| | | |
|---|---|---|
| Temperatures | Pressures | Shear rates |

## b) Non Newtonian liquids,

Fluids where the stress, shear rate relation is **non linear.**

Typical examples; anything to do with polymers, Complex fluids containing particles, fibres, bubbles and drops.

Examples; Molten polymers, Polyethylene, PET, Nylon
Examples; Clay suspensions, foodstuffs, cosmetics, pharmacuticals, bioprocessing, biomedical,, heavy crude oil, tar sands and lots of other stuff foodstuffs, pastes,

## c) Viscoelastic liquids and solids

Materials where both **viscosity and elasticity** play a role in the RHEOLOGY (deformation process)
Viscosity. stress depends on **shear rate**
Elasticity. stress depends on **strain**.

Viscoelastic materials have both strain and strain rate dependence.
A material, such as a polymer may be **both** Non Newtonian and viscoelastic.

# The “intellectual” content of course

## The “physical core” of the course

1. Understanding why certain fluids are Non Newtonian and viscoelastic. Understanding the “molecular, nano and microstructure” of different fluids.

## The “mathematical modelling core” of the course

1. Understanding importance of **linear and nonlinear** systems.

2. Understanding **generalised formulation** of stress, strain and strain rate.

3. Understanding how **complex engineering processing** problems can be solved.

## The “engineering core” of the course

1. Understanding where **Non Newtonian and viscoelastic** problems are important in process engineering.

# Lectures

## Section 1.   Constitutive equations

Background and definitions. Analytic Non Newtonian constitutive equations.
Power law, Bingham, Herschel Buckley, Carreau,  Cross Equation,
A slight digression.  Cross equation, Micro structure model.

## Section 2.  Analytic Engineering Flows

Application of constitutive equations to simple geometries. Pipes,Newtonian,
Pipes, Power law, Pipes,  Bingham,  Pipe complications.  Rabinowitch., Bagley.
Rotational (torsional) flow

*Supervision 1*

## Section 3.  Viscoelasticty

Viscoelasticity. Rheological measurement, Stress growth, Step strain, Oscillatory,
Viscoelasticity modelling.  Differential Maxwell, Integral Maxwell,
Non Linear, Wagner. The Cox Merz rule

*Supervision 2*

## Section 4. Generalised deformations

Generalised types of flow; Simple shear and Extensional flow
Stress, strain rate and strain as tensors
Generalised description of constitutive equations and their application to problem solving.
Application of rheology to polymer processing .

*Supervision 3*  (Maybe at end of term or beginning of  Easter term)

## Background/ References, Rheology.

**C.W.Macosko**
**Rheology, principles, measurement and applications**
**Wiley-VCH (1994)**
*A good read*

**J.M. Dealy and K.F. Wissbrum.**
**Melt rheology and its role in plastics processing. (1989)**
*A very good book, particularly for viscoelastic integral model.*

**R.B. Bird, R.C. Armstrong and O. Hassager.**
**Dynamics of polymer liquids. Vol 1 and 2. (1977)**
*Big, extensive, Vol 1 covers basic fluid mechanics and constitutive equations. Vol 2 is specialist polymer stuff.*

**R.G. Larson.**
**Constititve equations (1988).**
*Definative, a bit advanced for this course. Read this if you want to know more.*

**H.A. Barnes. J.F. Hutton and K. Walters**
**Introduction to rheology,**
*Generally non mathematical and quite readable (1989)*

**J.F.Nye**
**The Physical Properties of Crystals**
**Oxford Univ Press, (1957)**
*Old book, but definitive on tensors.*

**F. Morrison**
**Understanding Rheology**
Oxford Univ Press (2001)
*New and definative*

**Periodicals**

| | |
|---|---|
| Journal of Non Newtonian Fluid Mechanics | (SPL) |
| Journal of Rheology | (MRM's room) |
| Rheological Acta | (SPL) |
| Polymer Engineering and Science | (Chem Eng) |
| British Society of Rheology | http://innfm.swan.ac.uk/bsr/frontend/home.asp |
| American Society of Rheology | http://www.rheology.org/sor/ |

# Rheology. Past Tripos questions.

| | |
|---|---|
| 01.4.2 | Viscoelastic Maxwell |
| 01.4.3 | Casson capillary |
| 02.4.7 | Power law with slip |
| 02.4.8 | Differential Maxwell |
| 03.4.4 | Herchel Buckley |
| 03.4.5 | Integral Maxwell |
| 04.4.4 | Power Law |
| 04.4.5 | Integral Maxwell |
| 04.4.6 | Tensors |
| 05.4.1 | Misc |
| 05.4.2 | Couette |
| 05.4.3 | Integral Maxwell |
| 05.4.4 | PSD shear |
| 06.9.1 | Cross eqn |
| 06.9.2 | Power Law |
| 06.9.3 | Maxwell G’, G’’ |
| 07.9.1 | Carreau and Power Law |
| 07.9.2 | Voigt model |
| 07.9.3 | Integral Maxwell |
| 08.9.1 | Rotating shaft; Non Newtonian |
| 08.9.2 | Differential and integral Viscoelastic |
| 08.9.3 | Tensor transformations. |
| 09.9.1 | Couette flow |
| 09.9.2 | Diff and integral Maxwell |
| 09.9.3 | Normal stress differences |
| 10.9.1 | Core annular flow of waxy crude |
| 10.9.2 | Integral strain equation |
| 10.9.3 | Extension and shear of polymer solutions and drops |

There will be three rheology questions in 2011.

# **Rheology;** “The **Theology** of Complex Fluids”

# Complex Fluids; many engineering fluids

# Complex Flows; many engineering flows

# We aspire to model both complex fluids and complex flows

## 1. Background and Definitions

**Rheology** is concerned with **Deformation and Flow.**

**Usually, but not always,** associated with “high” viscosity and “low” inertia flow.

Often associated with, Non Newtonian flow, Viscoelastic flow, Plastic flow.

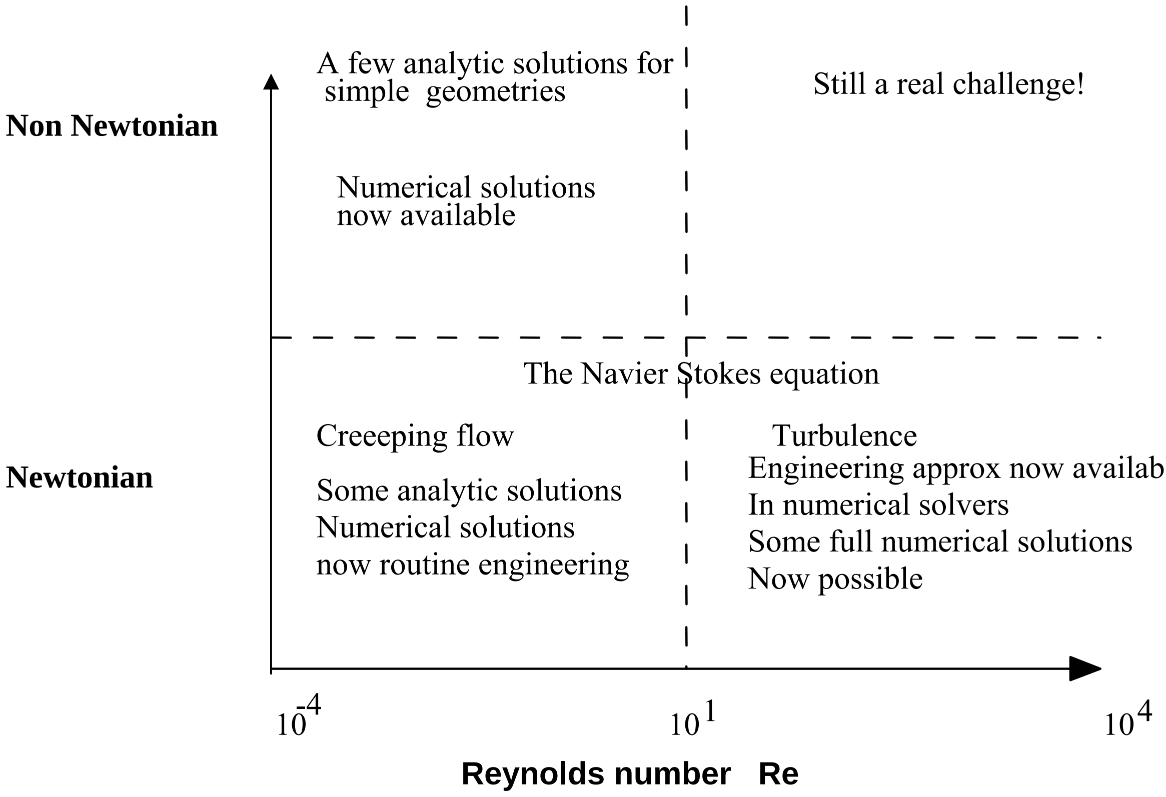
### Fluid / Rheology map

There are two very important, and difficult, **non linear** problems in fluid flow. **Inertial**, high Reynolds number flow, ( ie, turbulence), and **non linear** ( Non Newtonian) constitutive equations.

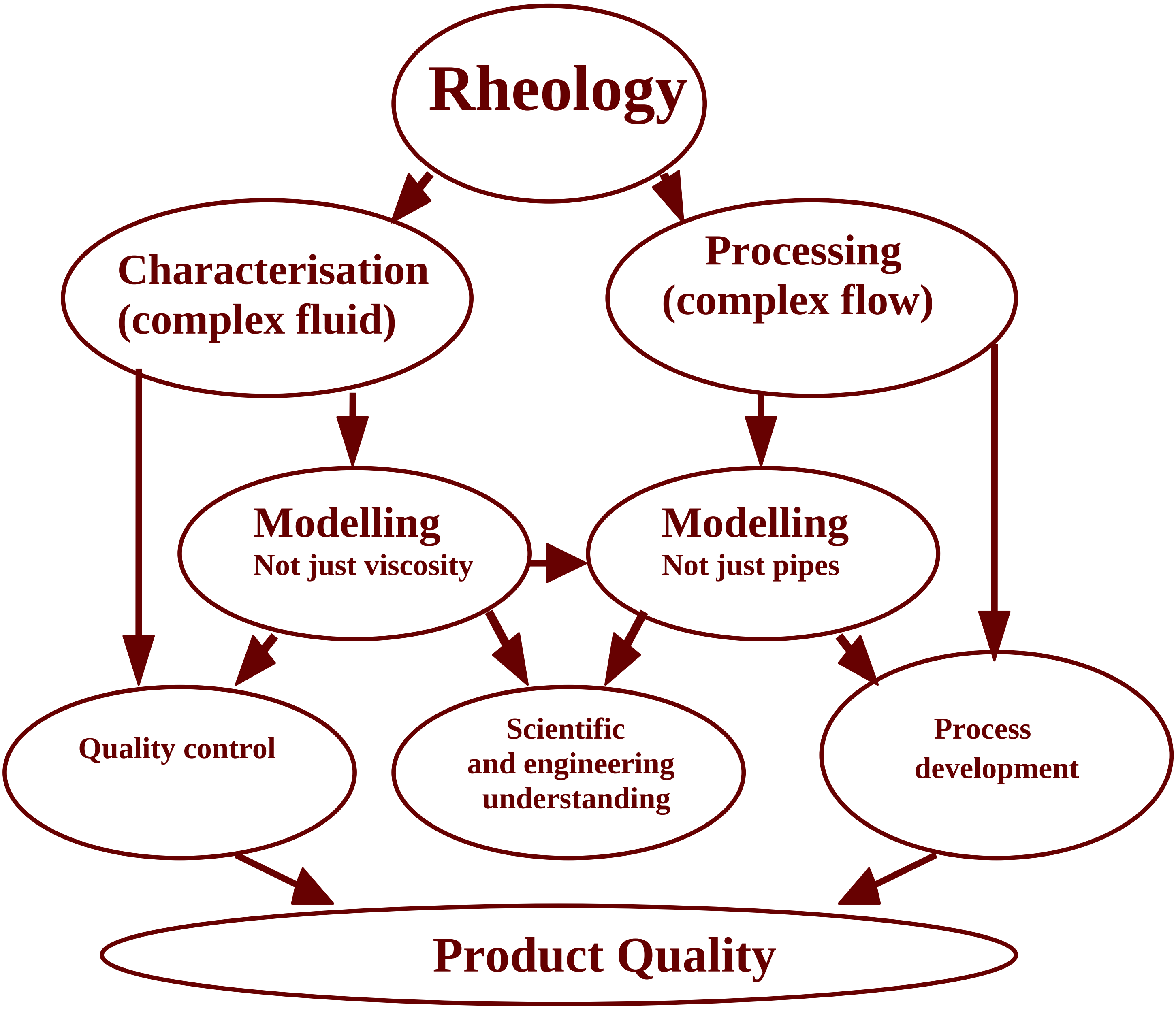
We will ignore inertia for the rest of course.

**Non Newtonian flow**. Deviation from Newtonian viscous flow

**Viscoelastic flow**; Material has both viscous and elastic response



# Why rheology is important!



Rheology

Characterisation
(complex fluid)

Processing
(complex flow)

Modelling
Not just viscosity

Modelling
Not just pipes

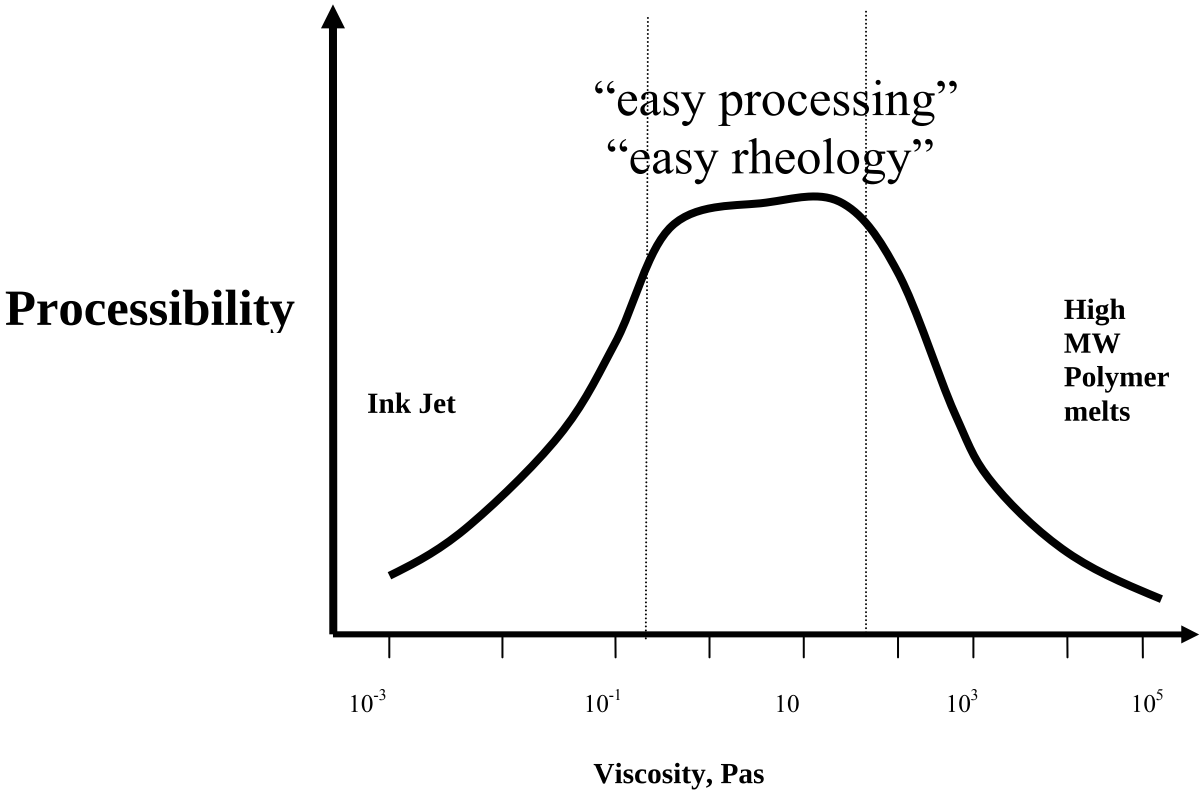
Quality control

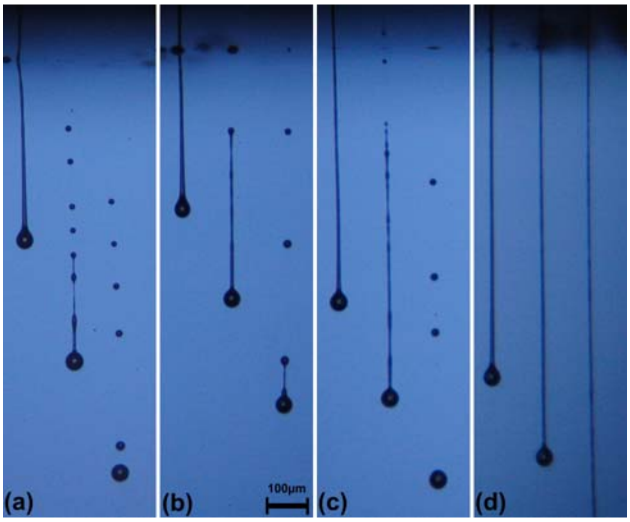
Scientific
and engineering
understanding

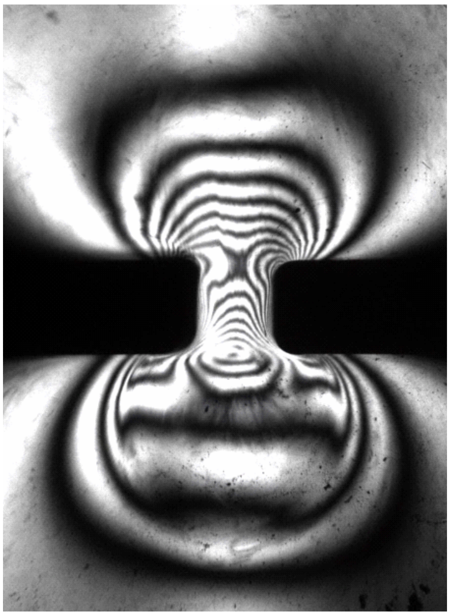
Process
development

Product Quality

# Viscosity and Processibility





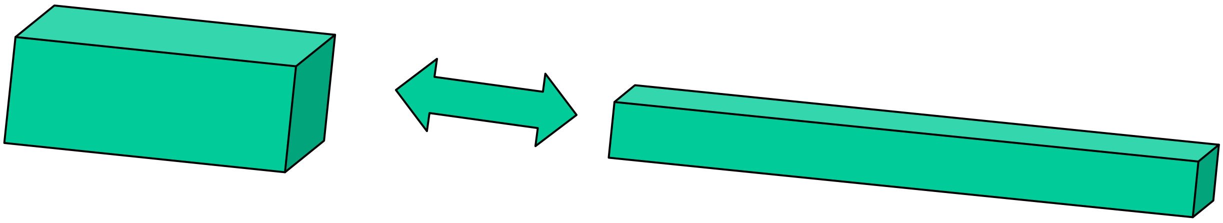


**Drop On Demand (DOD) ink jet printing**

**Polymer melt flow**

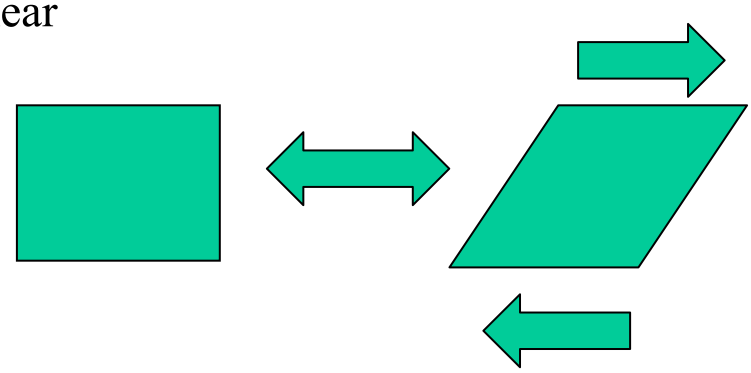
# Types of deformation

Uniaxial extension



**Tensile stresses**

Simple shear



**Shear stresses**

# "Stresses and Strain rates"

## Revision, Stress

Consider an elementary cuboid with edges parallel to the coordinate directions *x,y,z*.

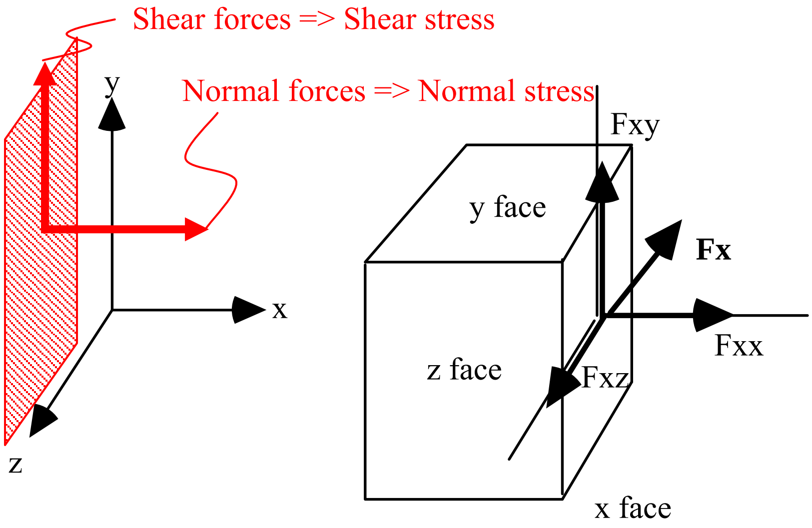


**Figure 1**

The faces on this cuboid are named according to the *directions of their normals*. There are thus two x-faces, one facing greater values of *x*, as shown in Figure 1 and one facing lesser values of *x* (not shown in the Figure).
The force $\mathbf{F_x}$ can be divided into its components parallel to the coordinate directions, $\mathbf{F_{xx}}$, $\mathbf{F_{xy}}$, $\mathbf{F_{xz}}$. Dividing by the area of the x-face gives the stresses on the x-plane, which we write as

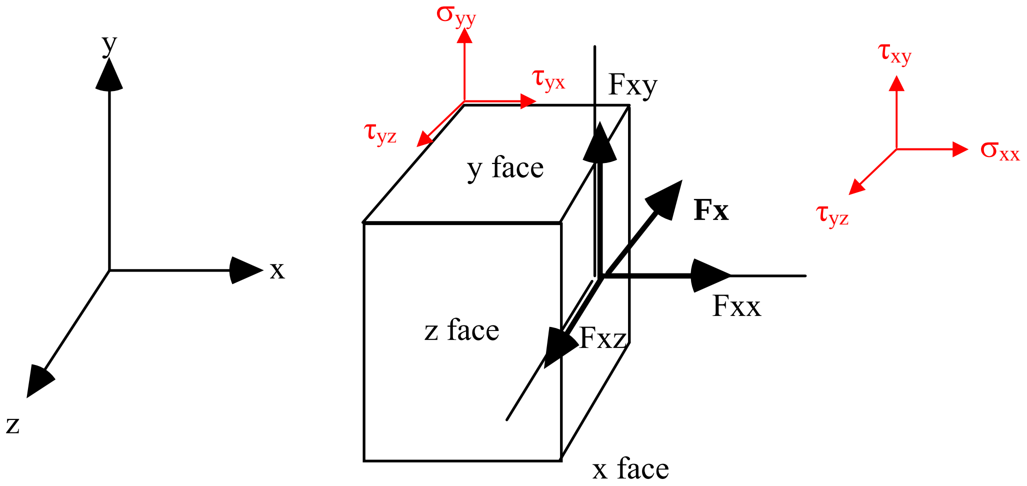
$$\sigma_{xx},\ \tau_{xy},\ \tau_{xz}$$

$$\tau_{ij} \quad \mathbf{i = \text{the face} \quad j = \text{the direction,}}$$

**Face First**

$\tau_{xy}$ – the shear stress on the x plane in the y direction
$\sigma_{xx}$ – the normal stress on the x plane in the x direction

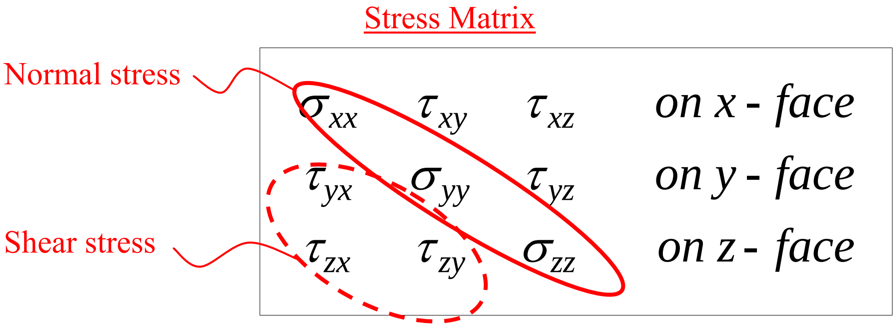
In some cases we write normal stresses as $\sigma$ and shear stresses as $\tau$.



Similarly, on the y-face we have $\tau_{yx}, \sigma_{yy}, \tau_{yz}$

and on the z-face we have $\tau_{zx}, \tau_{zy}, \sigma_{zz}$

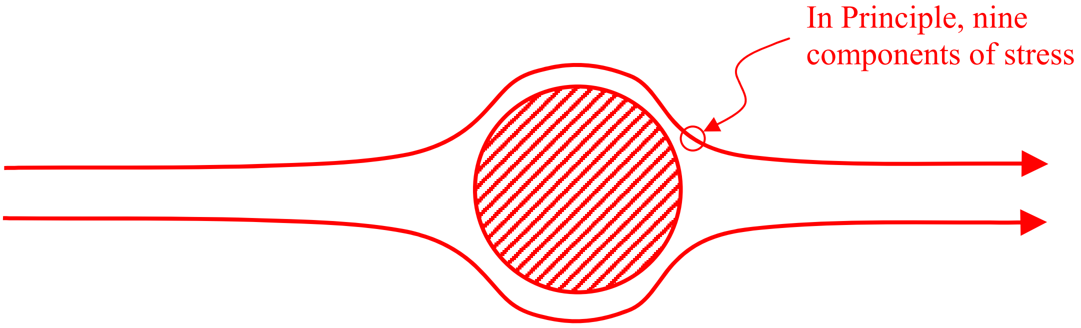
There are therefore 9 components of stress;



$$\begin{array}{cccl} \sigma_{xx} & \tau_{xy} & \tau_{xz} & \text{on } x\text{ - face} \\ \tau_{yx} & \sigma_{yy} & \tau_{yz} & \text{on } y\text{ - face} \\ \tau_{zx} & \tau_{zy} & \sigma_{zz} & \text{on } z\text{ - face} \end{array}$$

Note in this definition, the **first** subscript refers to the **face** on which the stress acts and the **second** subscript refers to the **direction** in which the associated force acts.

In a 3-D system, vectors have three components. Stresses are not vectors but are an example of a **tensor** quantity.



### Sign Conventions

The usual sign convention is

> The stress on a face, facing greater values of the coordinate, is positive if the associated force acts in the direction of the coordinate increasing.

Thus in two dimensions the stresses are positive when acting in the directions

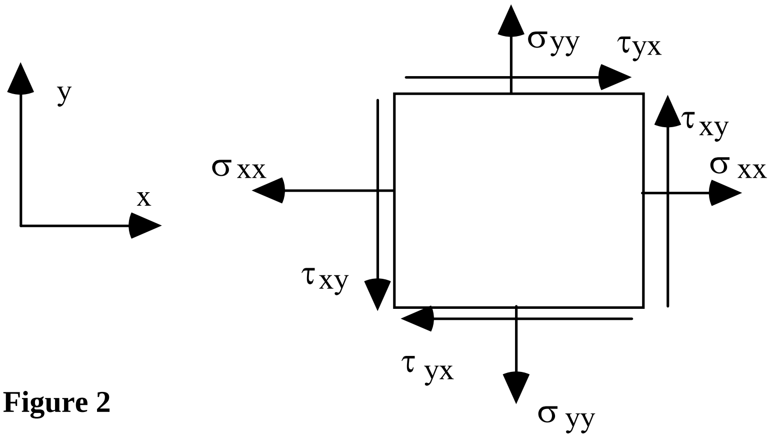


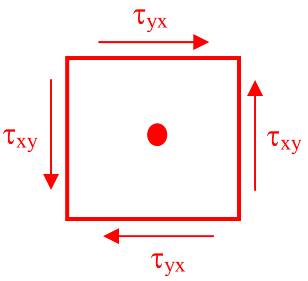
**Figure 2**

shown in Figure 2.

### Complementary Stresses

Reduce the number of stress components

### Take moments



$\tau_{yx} = \tau_{yx}$ for equilibrium

In the limit as $\delta x$ and $\delta y. \rightarrow 0$, $\tau xy \rightarrow \tau yx$ even if the material is accelerating. For a non-accelerating body, $\tau xy = \tau yx$ exactly.

The shear stresses therefore appear in complementary pairs and the stress tensor contains **6** independent components.

$$\tau_{ij} = \tau_{ji}$$

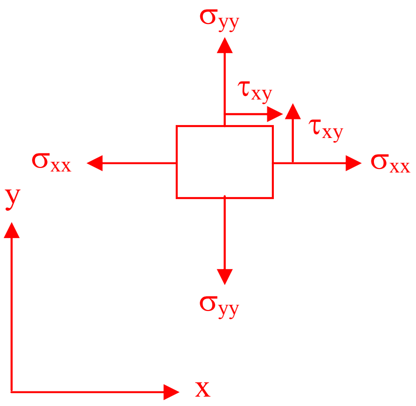
$$\begin{bmatrix} \sigma_{xx} & \tau_{xy} & \tau_{xz} \\ \tau_{xy} & \sigma_{yy} & \tau_{yz} \\ \tau_{xz} & \tau_{yz} & \sigma_{zz} \end{bmatrix}$$

Stress matrix is symmetric about the leading diagonal

Stress is a tensor and transforms by rotation from one coordinate axis to another in a particular way. In 2D this can be done using Mohrs circle or more generally using the tensor transformation equation.

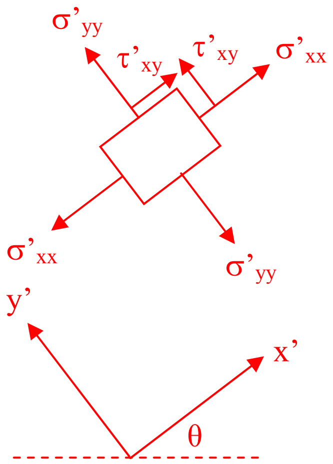
$$\sigma'_{xy} = a_{xk}\, a_{yl}\, \sigma_{kl} \longrightarrow$$

see Section 4 of course for further details



$$\begin{vmatrix} \sigma_{xx} & \tau_{xy} \\ \tau_{xy} & \sigma_{yy} \end{vmatrix}$$

What if it's in a different co-ordinate frame?



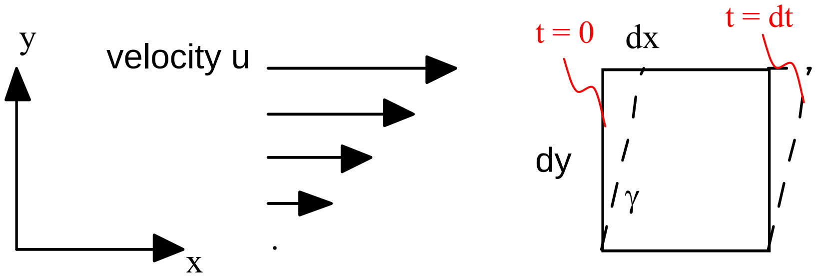
$$\begin{vmatrix} \sigma'_{xx} & \tau'_{xy} \\ \tau'_{xy} & \sigma'_{yy} \end{vmatrix}$$

(We will do this in the second part of the course)

## Strain rates

There are complications for generalised description of strain and strain rate. In the first part of the course we will limit ourselves to **simple shear flow** deformation only, where velocity change is perpendicular to streamlines.

dominates most, but not all, engineering



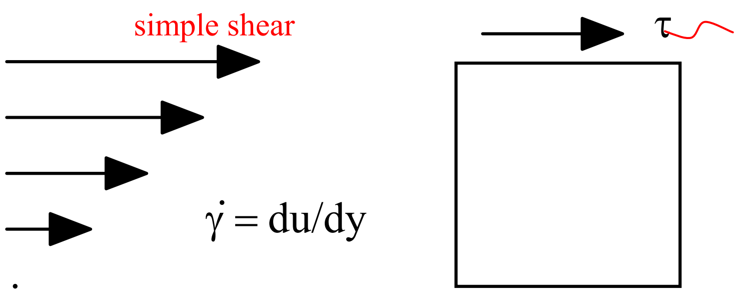
infinitesimal strain

$\gamma = dx / dy$ strain

$$\text{strain rate}\ \dot{\gamma} = \frac{\partial \gamma}{\partial t} = \frac{\partial \left( \frac{\partial x}{\partial y} \right)}{\partial t} = \frac{\partial \left( \frac{\partial x}{\partial t} \right)}{\partial y} = \frac{\partial u}{\partial y}\ s^{-1}\ \text{velocity gradient}$$

**strain rates $\dot{\gamma}$, typically $10^{-3}$ to $10^{3}$ $s^{-1}$**

**Constitutive equations.** **“The heart of rheology”.**



$\dot{\gamma} = du/dy$

simple shear flow leads to development of shear stress

**Constitutive equations link stress with strain or strain rate**

shear stress $\tau$, typically $1$ to $10^6$ N/m$^2$

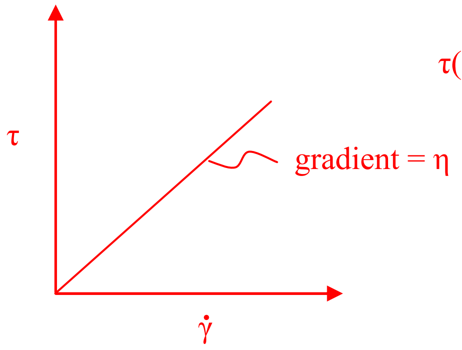
**Newtonian constitutive equation**

$$\tau = \eta \dot{\gamma} \qquad \eta,\ \text{Ns/m}^2,\quad \text{Pas}$$

**A linear** coupling constitutive equation between stress and strain rate.

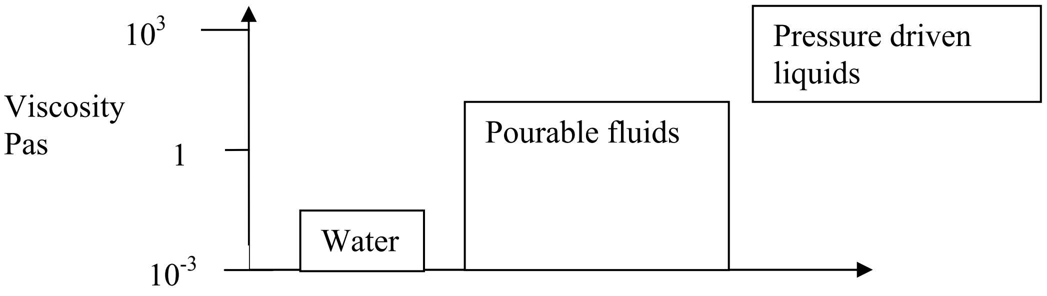
Typically. $\eta$ = of order, $10^{-3}$ Pas for many organic liquids

= 10 Pas for glycerol and honey = $10^3$ Pas for polymer melts



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

Newtonian fluids have no memory and only respond to instantaneous shear rate



For Newtonian fluids:- stress depends linearly on magnitude of instantaneous shear rate. Newtonian fluids in general do not remember the past.

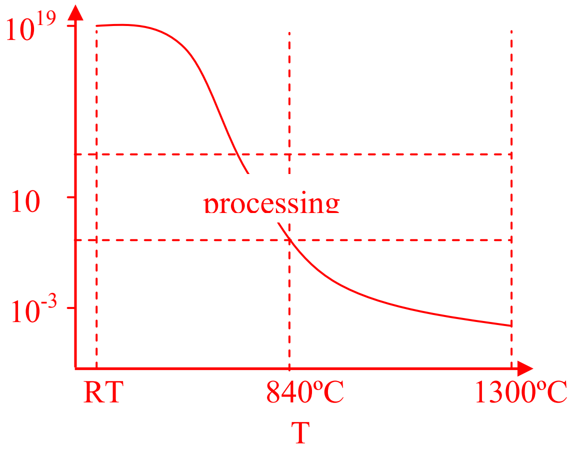
$\eta$ is independent of $\dot{\gamma}$ but is usually a strong function of temperature.

$$\eta = \eta_o e^{E/RT}$$

Remember glass

viscosity is a thermally activated process

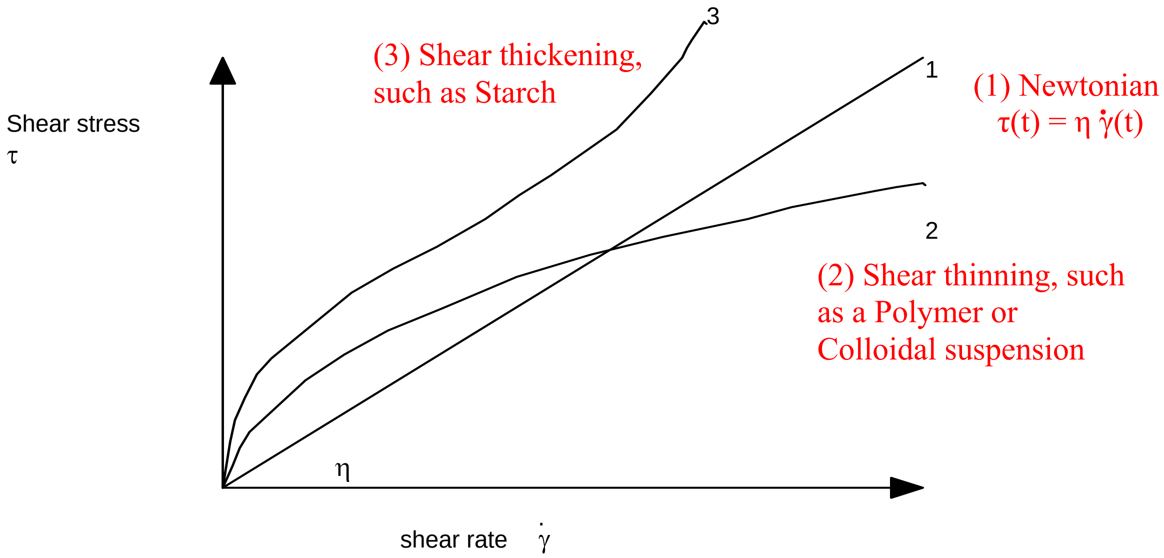
If interested see book
Gases, Liquids and Solids. D Tabor



## Non Newtonian viscous constitutive equations

There are two equivalent ways of presenting data

a) **Shear stress in terms of shear rate**

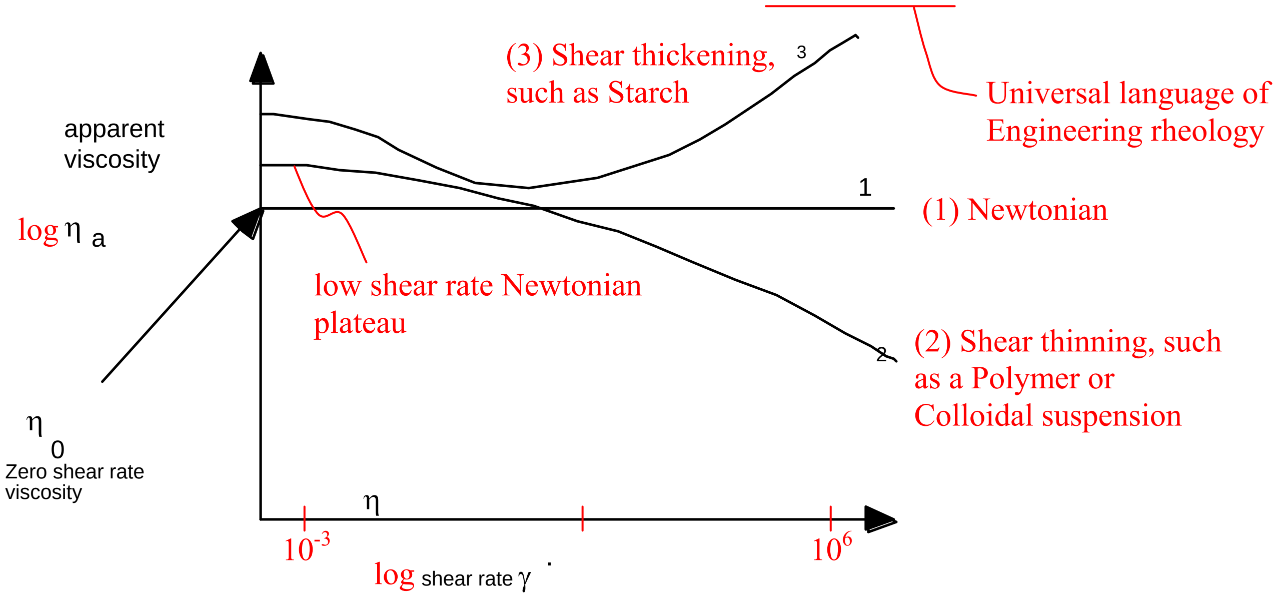


1= Newtonian, 2= Non Newtonian, shear thinning, 3= Non Newtonian, shear thinning and then thickening.

viscosity $(\dot{\gamma})$

b) **Apparent viscosity** $\eta_a$ **"Flow curve"**

$$\tau = \eta_a\left(\dot{\gamma}\right)\dot{\gamma}$$



1= Newtonian, 2= Non Newtonian, shear thinning, 3= Non Newtonian, shear thinning followed by shear thickening. $\eta_a$ may be an analytic function, or a set of data.

## Analytic Non linear viscous constitutive equations

**Power law fluids** Popular, Mathematics tractable

$$\tau = k\,\dot{\gamma}^{\,n}$$

$\tau(t) = k\,\dot{\gamma}^n$

$\tau(t) = \eta_a\,\dot{\gamma}$

$\eta_a = k\,\dot{\gamma}^{n-1}$

$\ln(\eta_a) = \ln(k) + (n-1)(\ln\dot{\gamma})$

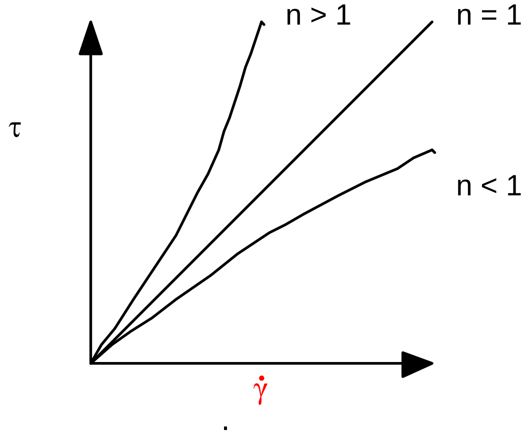
n = power law index

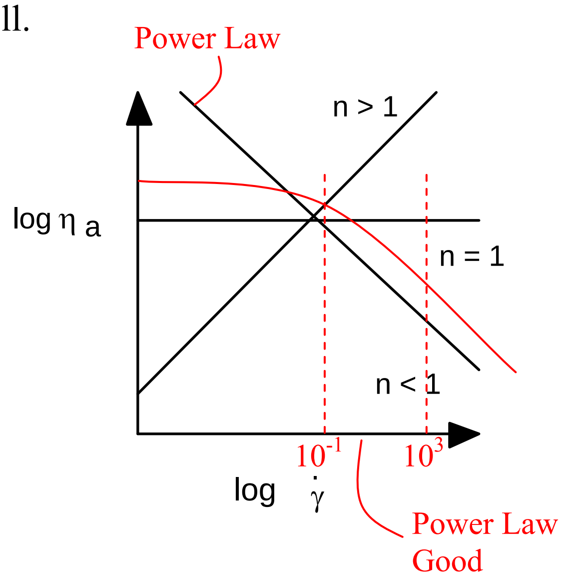
n = 1 Newtonian

n < 1 Shear thinning (usual case) ~ 0.6

n > 1 " thickening

Can Fit data for molten polymers quite well.



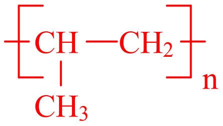
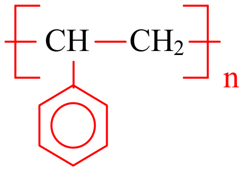


| | | |
|---|---|---|
| n | 1 | low molecular mass |
| n | 0.4 – 0.8 | most processing grade molten polymers |
| n | 0.2 | high molecular mass polymers |

units of k depend on value of n.

typical polymer k = 1.3 x $10^3$ Ns$^{-0.52}$, n = 0.52

Molten Polymers

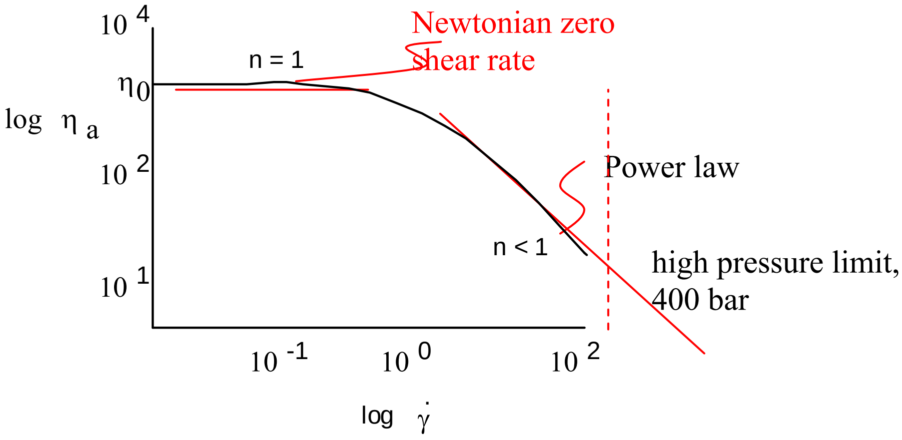
| | | | |
|---|---|---|---|
| PE (Polyethylene) | $\left[-CH_2-CH_2-\right]_n$ | $T_m$~135ºC | $T_p$~150-200ºC |
| PP (Polypropylene) |  $\left[-\underset{CH_3}{CH}-CH_2-\right]_n$ | $T_m$~170ºC | $T_p$~180-200ºC |
| PS (Polystyrene) |  | $T_g$~100ºC | $T_p$~180-200ºC |

## Apparent viscosity presentation; Flow curves

PE, PS, PP

molten polymers.
are generally power law fluids
at high shear rates, but at low
shear rates they behave as
Newtonian fluids.

$\eta_0$ is zero shear rate viscosity



$$\tau = \underline{\eta_a}\,\dot{\gamma} = k\,\dot{\gamma}^{\,n}$$

$$\therefore \eta_a = k\,\dot{\gamma}^{\,n-1}$$

Power law fluids should give straight line on log – log plot

Note 3 decade change in viscosity.

**<u>Carreau Equation</u>** ~ 1970’s

$$\eta_a = \eta_0\left[1 + (\lambda\dot{\gamma})^2\right]^{-p}$$

nice, but mathematically difficult

<u>Low shear rate</u>

$(\lambda\dot{\gamma})<1$ $\eta_a = \eta_0$

Newtonian

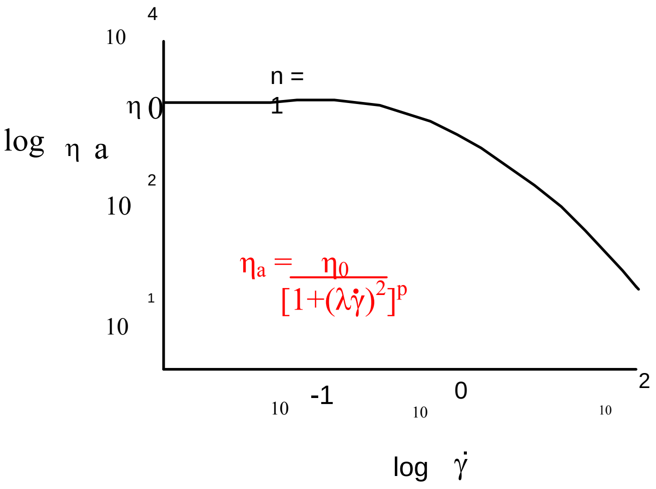
$(\lambda\dot{\gamma})>>1$ $\eta_a = \dfrac{\eta_0}{[(\lambda\dot{\gamma})^2]^p}$

$\eta_a = \dfrac{\eta_0}{\lambda^{2p}}\;\dfrac{1}{\dot{\gamma}^{2p}}$

$\eta_a = k\dot{\gamma}^{n-1}$

$n - 1 = - 2p$

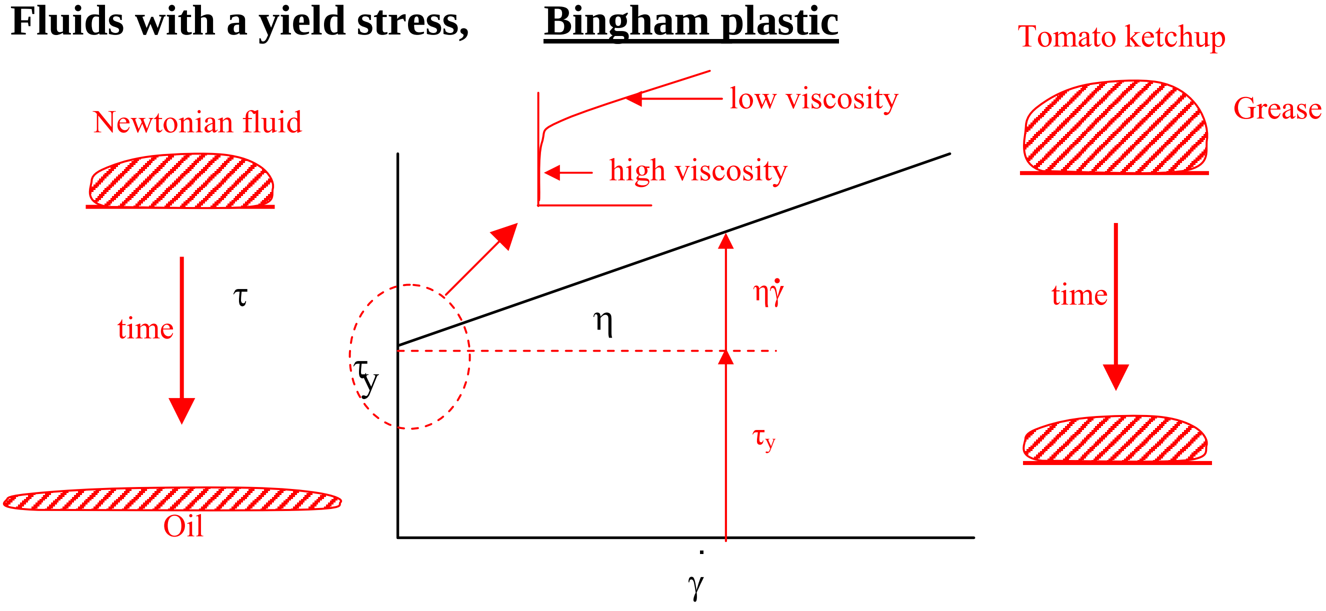
$p = \dfrac{1 - n}{2}$



Low shear – Newtonian
High shear – Power Law

**Another important class of constitutive equation.**

## Fluids with a yield stress, <u>Bingham plastic</u>



mind the sign

For $\tau > \tau_y$ $\tau = \pm\tau_y + \eta\dot{\gamma}$ good engineering model

Signs can be tricky, ensure shear stress acts against direction of flow

For $\tau < \tau_y$ $\dot{\gamma} = 0$ no flow leads to no relative shear

Ex. Tomato ketchup $\tau_y \approx 15$ Pa, $\eta \approx 1$ Pas

$\tau_y$ is often between 1 and $10^3$ Pa

**Herchel Buckley** combines Bingham and Power Law

$$\tau = \pm\tau_y + k\dot{\gamma}^n$$

3 parameters

Ex Toothpaste

**Casson**

$$\tau^{0.5} = \tau_y^{0.5} + \left(\eta\dot{\gamma}\right)^{0.5}$$

Well drilling fluids

Chocolate

Ex. Favoured for drilling muds

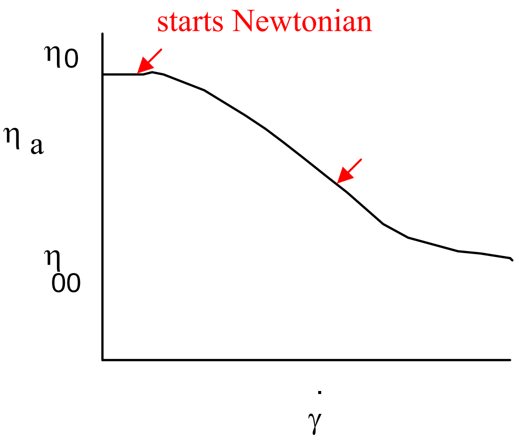
Yield stress fluids difficult to present in terms of apparent viscosity.

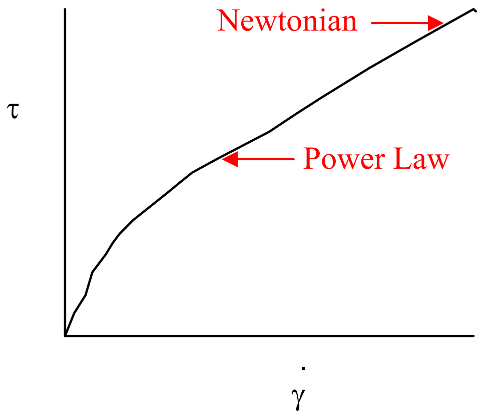
**Fluid suspensions and some structured fluids** ⟶ suspensions

## The Cross equation ⟶ empirical correlation – Malcolm Cross1956

$$\eta_a = \eta_\infty + \frac{(\eta_o - \eta_\infty)}{\left(1 + \alpha \dot{\gamma}^{n}\right)} \quad or \quad \tau = \eta_\infty \dot{\gamma} + \frac{(\eta_o - \eta_\infty)}{\left(1 + \alpha \dot{\gamma}^{n}\right)} \dot{\gamma}$$

where $\eta_\infty$ and $\eta_o$ are limiting viscosities and n and α are parameters.





Equation, initially empirical; reflects observation that fluid viscosity moves from a higher viscosity at low shear rate to a lower viscosity at high shear rate

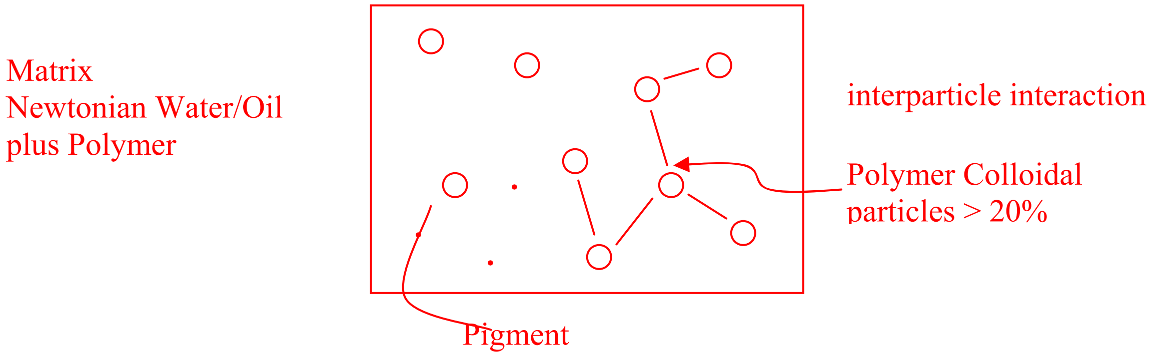
Ex, Fluids such as

Pig slurry, Colloids; stable of phase dispersion.

Colloids

## Examples of rheologically Complex fluids.

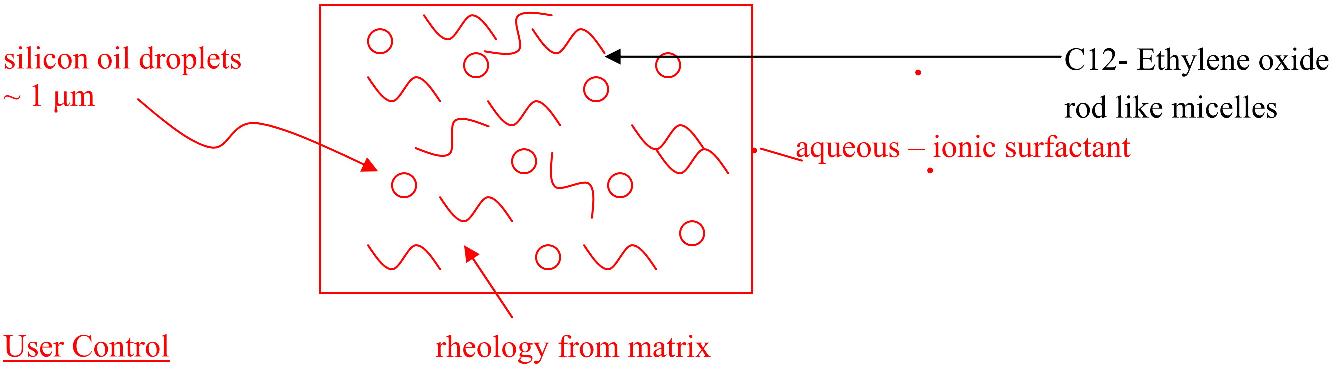
## Paint



## Timotei Shampoo

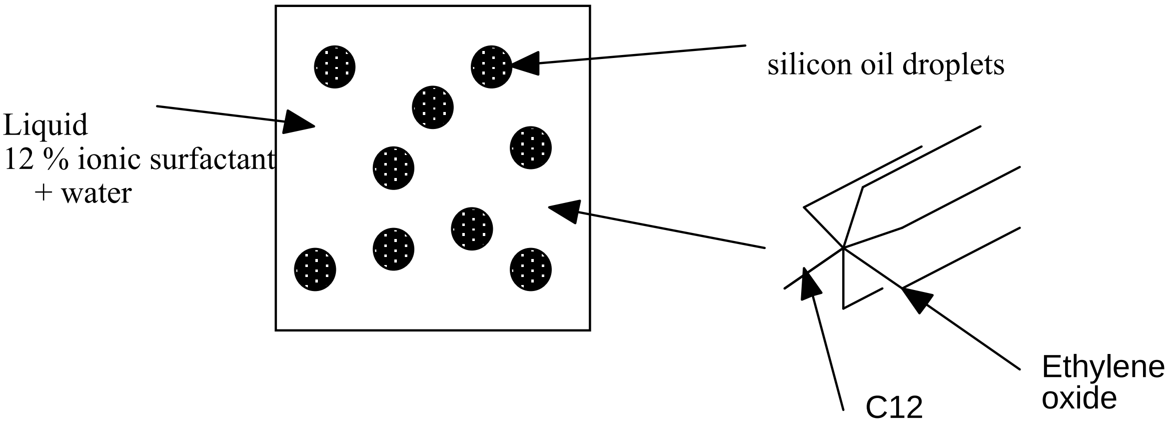
→ High Tech personal products

Entangled network



User Control

- Colloidal Stability



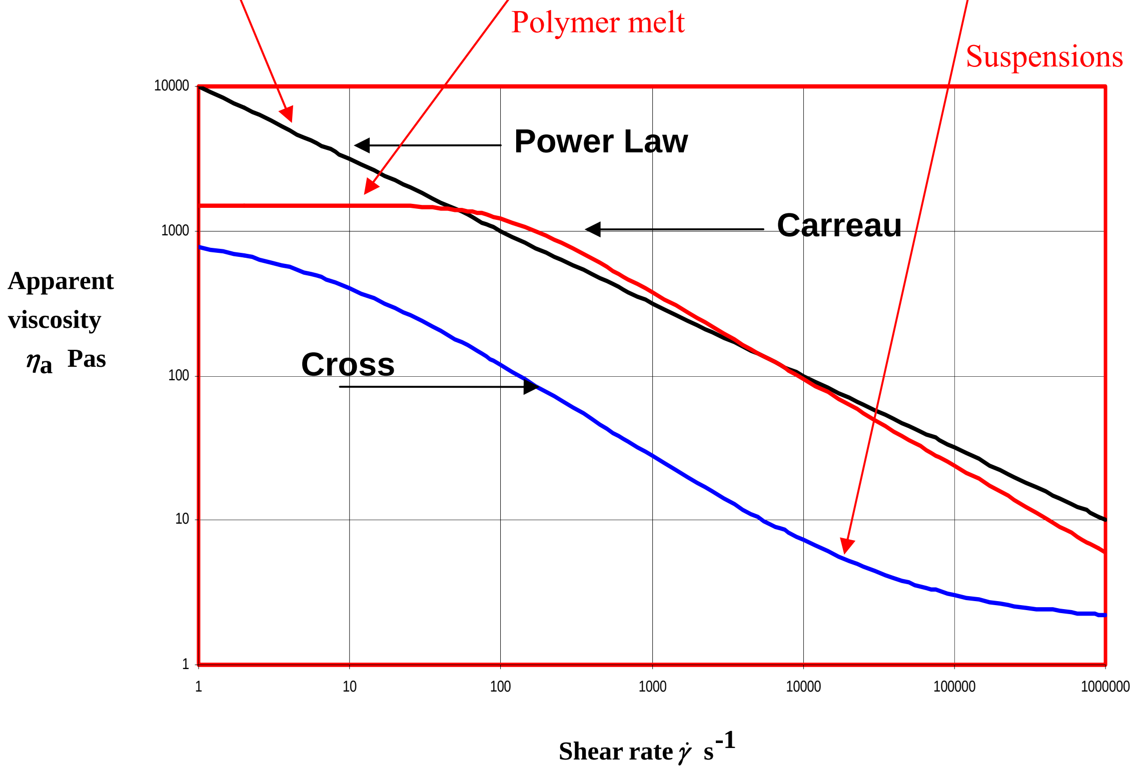
# Non Newtonian flow;  Shear thinning equations

**Power law fluid.** **Carreau Equation.** **Cross equation.**

$$\eta_a = k \dot{\gamma}^{n-1}$$

$$\eta_a = \eta_0 \left[1 + (\lambda \dot{\gamma})^2\right]^{-p}$$

$$\eta_a = \eta_\infty + \frac{(\eta_0 - \eta_\infty)}{\left(1 + \alpha \dot{\gamma}\right)^n}$$

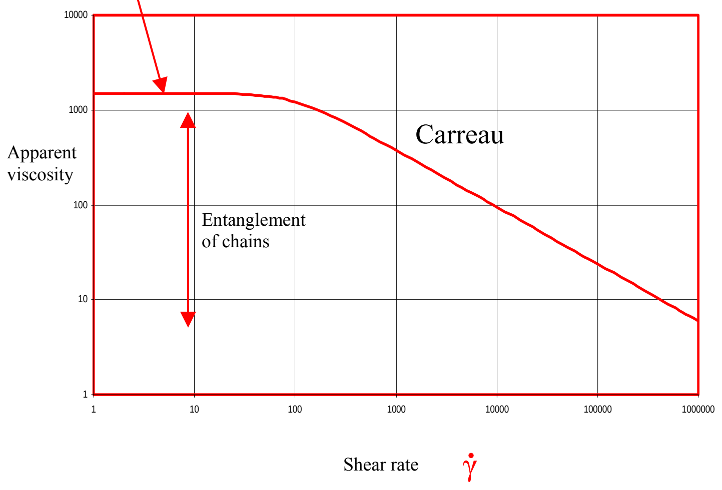


## But why do some fluids shear thin??????

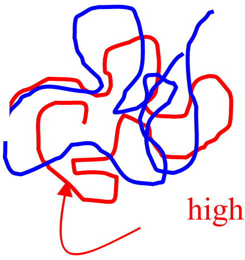
# Mechanisms for shear thinning

$\eta_0 \ \alpha \ MW^{3.4}$

**Molten Polymers.**



spaghetti



thread motion

high entanglement

**Chain orientation** Doi and Edwards 1978

**Chain stretch** Mcleish and Larson 1987

**Chain disentanglement** ?

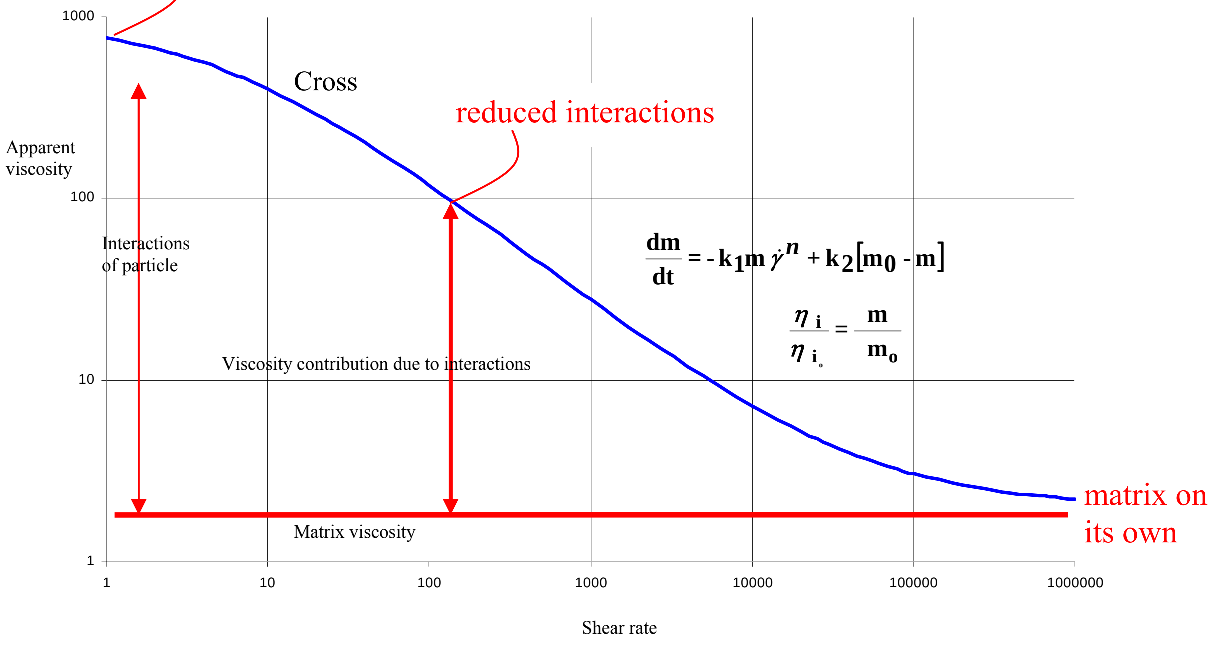
Pino Marrucci

deGennes – Nobel Prize

**Particle suspensions.**

many interactions

**Effect of shear on number of interactions**
Moore and Chen 1967



$$\frac{dm}{dt} = -k_1 m \dot{\gamma}^n + k_2 [m_0 - m]$$

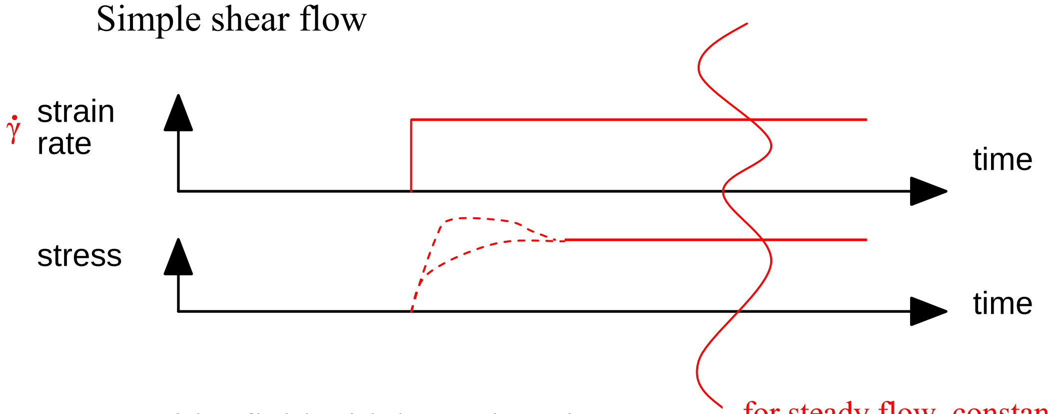
$$\frac{\eta_i}{\eta_{i_o}} = \frac{m}{m_o}$$

## A Slight digression. Complex fluid microstructure.

A number of fluids contain a microstructure. When flow is applied this microstructure can be modified and the flow properties of the fluid changes. It is possible to model this type of microstructure change using simple kinetic “rate” equations.

For example. **A simple derivation of Cross equation using kinetic rate equations.**

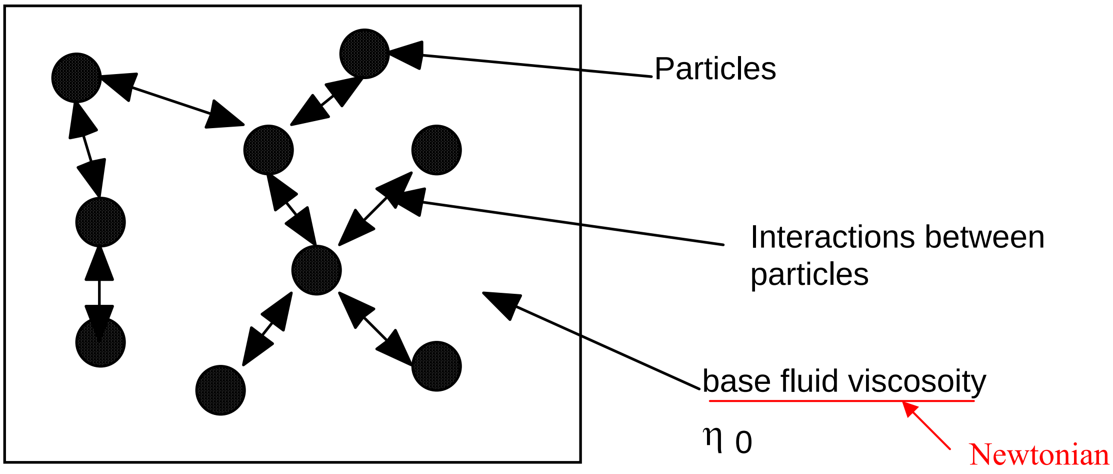
Simple shear flow



for steady flow, constant $\dot{\gamma}$ means that stress, ($\tau$), is also constant.

Consider fluid with base viscosity

Embedded structure within fluid



Let **m** = number of interactions/volume (for any state of flow)

At rest, $m_o$ = “ “ /volume ( No flow)

Assume shearing causes number of interaction points to decrease by

1st order with respect to m

Rate of loss of m

$$\frac{dm}{dt} = -k_1 m \dot{\gamma}^n$$

nth order with respect to m

rate constant

Assume on flow cessation, (and during flow) there is a driving force returning interaction points back to an equilibrium state.

difference from equilibrium

Rate of creation of m

$$\frac{dm}{dt} = k_2[m_o - m]$$

rate constant

So at any instant in time during stress

recovery

Rate of change of m

$$\frac{dm}{dt} = -k_1 m \dot{\gamma}^n + k_2[m_0 - m]$$

shear

In steady state (≡ steady flow after a long time)

Steady shear

$$\frac{dm}{d\,t} = 0$$

number of interactions at steady shear $\dot{\gamma}$

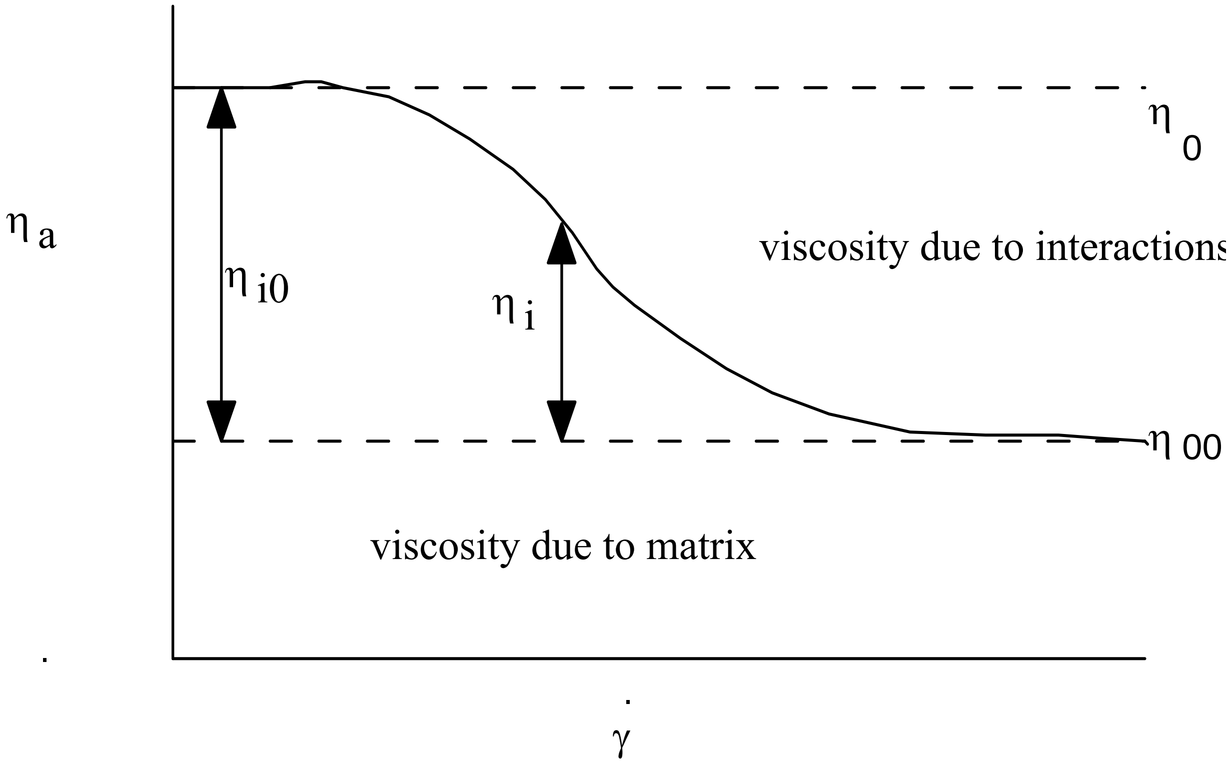
Then

$$\frac{m}{m_0} = \frac{1}{1 + \frac{k_1}{k_2}\dot{\gamma}^n}$$

ratio of interactions

number of interactions at $\dot{\gamma} = 0$

Assume viscosity is the sum of two components



m

Assume $$\frac{\eta_i}{\eta_{i_o}} = \frac{m}{m_o}$$

$m_0$

Then $$\eta_i = \eta_{i_o}\left[\frac{1}{1+\alpha\dot{\gamma}^n}\right]$$

where $$\alpha = \frac{k_1}{k_2}$$

Note $$\left.\begin{aligned}\eta_{i_o} &= \eta_o - \eta_\infty \\ \eta_a &= \eta_i + \eta_\infty\end{aligned}\right\}$$

viscosity due to
Interactions at $\dot{\gamma}$

***see diagram***

Total apparent viscosity = Σ matrix + interaction

Then $$\eta_a = \eta_\infty + \frac{(\eta_o - \eta_\infty)}{\left(1 + \alpha\dot{\gamma}^n\right)}$$

correct answer supports the base assumption

Which is the The **Cross Equation**, for steady flow.

Shearing breaks up structure during flow – dynamic equilibrium is achieved between destruction during shear and recovery and recovery to equilibrium state. model can predict time dependence

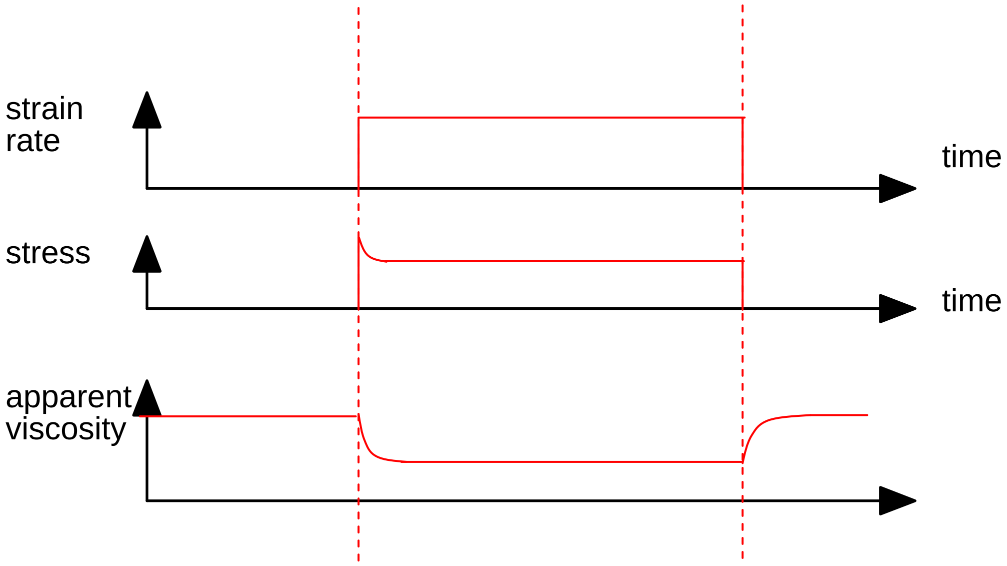
Full time dependence of model can be explored by using the full equation.

$$\frac{dm}{dt} = -k_1 m \dot{\gamma}^n + k_2[m_0 - m]$$

And using $$\frac{\eta_i}{\eta_{i_o}} = \frac{m_t}{m_o}$$

number of interactions at any time t

Go to example sheet



$\tau = \eta_a \dot{\gamma}$

viscosity changes

$$\frac{dm}{dt} = k_2[m_0 - m]$$

More complex shear rate history problems can be addressed.

( see example sheet)