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.

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, pharmaceuticals, bioprocesing, 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


Section 2. Analytic Engineering Flows


Supervision 1

Section 3. Viscoelasticity


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.

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.
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.

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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) ➔ Modelling Not just viscosity ➔ Quality control

Processing (complex flow) ➔ Modelling Not just pipes ➔ Process development

Scientific and engineering understanding

Product Quality
Viscosity and Processibility

Processibility

Ink Jet

Viscosity, Pas

"easy processing"
"easy rheology"

High MW Polymer melts

Drop On Demand (DOD)
ink jet printing

Polymer melt flow

CET 2B. Section 1, Intro- constitutive eqns-2011
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 
\( x, y, z \).

Shear forces => Shear stress
Normal forces => Normal stress

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 \( F_x \) can be divided into its components parallel to the coordinate directions, \( F_{xx}, F_{xy}, F_{xz} \). Dividing by the area of the x-face gives the stresses on the x-plane, which we write as

\[
\sigma_{xx}, \tau_{xy}, \tau_{xz}
\]

\( \tau_{ij} \quad i = \text{the face} \quad j = \text{the direction}, \quad \text{Face First} \)

\( \tau_{xy} \quad \text{– the shear stress on the x plane in the y direction} \)
\( \sigma_{xx} \quad \text{– the normal stress on the x plane in the x direction} \)
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:

\[
\begin{array}{ccc}
\sigma_{xx} & \tau_{xy} & \tau_{xz} \\
\tau_{yx} & \sigma_{yy} & \tau_{yz} \\
\tau_{zx} & \tau_{zy} & \sigma_{zz}
\end{array}
\]

on x-face, on y-face, on z-face

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 shown in Figure 2.

Complementary Stresses

Reduce the number of stress components

Take moments

In the limit as $\delta_x$ and $\delta_y \to 0$, $\tau_{xy} \to \tau_{yx}$ 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.

\[ \tau_{ij} = \tau_{ji} \]

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.

\[ \sigma_{xy}' = a_{xk} a_{yl} \sigma_{kl} \]

(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.

\[ \gamma = \frac{dx}{dy} \]

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

\[ \text{strain rates } \dot{\gamma}, \text{ typically } 10^{-3} \text{ to } 10^3 \text{ s}^{-1} \]

Constitutive equations. “The heart of rheology”.

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

A linear coupling constitutive equation between stress and strain rate.

Typically. \( \eta = \text{of order, } 10^{-3} \text{ Pas for many organic liquids} = 10 \text{ Pas for glycerol and honey} = 10^3 \text{ Pas for polymer melts} \)
For Newtonian fluids: stress depends linearly on magnitude of instantaneous shear rate. Newtonian fluids in general do not remember the past.

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

\[ \eta = \eta_0 e^{E/RT} \]

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

\[ \tau(t) = \eta \dot{\gamma}(t) \]

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

b) Apparent viscosity \( \eta_a \) “Flow curve”

\[ \tau = \eta_a \left( \frac{\dot{\gamma}}{\dot{\gamma}} \right) \dot{\gamma} \]

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

\[ \tau = k \dot{\gamma}^n \]

\( n = \) power law index

\( n = 1 \) Newtonian

\( n < 1 \) Shear thinning (usual case) \( \sim 0.6 \)

\( n > 1 \) thickening

Can Fit data for molten polymers quite well.

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

\( n = 1 \) 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 \( n \).

**Molten Polymers**

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Chain Structure</th>
<th>( T_m ) (°C)</th>
<th>( T_p ) (°C)</th>
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<tr>
<td>PE (Polyethylene)</td>
<td>[( \text{CH}_2 - \text{CH}_2 )]_n</td>
<td>( T_m \sim 135^\circ )C</td>
<td>( T_p \sim 150-200^\circ )C</td>
</tr>
<tr>
<td>PP (Polypropylene)</td>
<td>[( \text{CH} - \text{CH}_2 )]_n</td>
<td>( T_m \sim 170^\circ )C</td>
<td>( T_p \sim 180-200^\circ )C</td>
</tr>
<tr>
<td>PS (Polystyrene)</td>
<td>[( \text{CH} - \text{CH}_2 )]_n</td>
<td>( T_g \sim 100^\circ )C</td>
<td>( T_p \sim 180-200^\circ )C</td>
</tr>
</tbody>
</table>
Apparent viscosity presentation; Flow curves

\[ \tau = \eta a \dot{\gamma} = k \dot{\gamma}^n \]

\[ \therefore \eta a = k \dot{\gamma}^{n-1} \]

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

Note 3 decade change in viscosity.

**Carreau Equation** ~ 1970’s

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

nice, but mathematically difficult

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

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

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

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

\[ n - 1 = -2p \]

\[ p = \frac{1 - n}{2} \]

Low shear rate

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

Newtonian

\((\lambda \dot{\gamma}) \gg 1\)

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

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

\[ n - 1 = -2p \]

\[ p = \frac{1 - n}{2} \]

Low shear – Newtonian

High shear – Power Law

melted 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
Another important class of constitutive equation.

**Fluids with a yield stress, Bingham plastic**

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 \( \tau_y \approx 15 \text{ Pa}, \eta \approx 1 \text{ Pas} \)

\( \tau_y \) is often between 1 and \( 10^3 \) Pa

**Hercel Buckley** combines Bingham and Power Law

\[ \tau = \pm \tau_y + k \gamma^n \]

3 parameters

**Ex.** Toothpaste

**Casson**

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

Ex. Favoured for drilling muds

Yield stress fluids difficult to present in terms of apparent viscosity.
Fluid suspensions and some structured fluids

The Cross equation

\[ \eta = \eta_\infty + \left( \eta_0 - \eta_\infty \right) \left( 1 + \alpha \gamma \right)^n \quad \text{or} \quad \tau = \eta_\infty \gamma + \left( \eta_0 - \eta_\infty \right) \left( 1 + \alpha \gamma \right)^n \]

where \( \eta_\infty \) and \( \eta_0 \) are limiting viscosities and \( n \) and \( \alpha \) 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

Matrix
Newtonian Water/Oil
plus Polymer

interparticle interaction

Polymer Colloidal
particles > 20%

Pigment

Timotei Shampoo

Entangled network

silicon oil droplets
~ 1 μm

user Control
• Colloidal Stability

rheology from matrix

c12- Ethylene oxide
rod like micelles

aqueous – ionic surfactant

Liquid
12 % ionic surfactant
+ water

silicon oil droplets

c12

Ethylene oxide
Non Newtonian flow; Shear thinning equations

Power law fluid.

\[ \eta_a = k \gamma^{n-1} \]

Carreau Equation.

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

Cross equation.

\[ \eta_a = \eta_\infty + \frac{(\eta_a - \eta_\infty)}{1 + \alpha \dot{\gamma}^n} \]

But why do some fluids shear thin???????
Mechanisms for shear thinning

- Molten Polymers.
- Particle suspensions.

- Chain orientation: Doi and Edwards 1978
- Chain stretch: Mcleish and Larson 1987
- Chain disentanglement: Pino Marrucci

Effect of shear on number of interactions
Moore and Chen 1967

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

\[
\frac{\eta_i}{\eta} = \frac{m}{m_0}
\]

- Matrix viscosity
- Viscosity contribution due to interactions
- Many interactions
- Reduced interactions
- Matrix on its own

\[\eta_0 \propto MW^{3.4}\]
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

Consider fluid with base viscosity

Embedded structure within fluid

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

At rest, \( m_0 = \) “ \( \ell \) /volume (No flow)
Assume shearing causes number of interaction points to decrease by

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

1\(^{\text{st}}\) order with respect to m

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

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

Rate of creation of m

Rate of loss of m

Rate constant

Rate constant

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

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

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

\[
\frac{dm}{dt} = 0
\]

Steady shear

Then

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

number of interactions at steady shear \(\dot{\gamma}\)

number of interactions at \(\dot{\gamma} = 0\)

ratio of interactions
Assume viscosity is the sum of two components

\[ \eta_a = \eta_{i0} + \eta_i \]

\[ \eta_{i0} = \eta_o - \eta_\infty \]

\[ \eta_i = \eta_i o \left[ \frac{1}{1 + \alpha \dot{\gamma}^n} \right] \]

where \( \alpha = \frac{k_1}{k_2} \)

Note

\[ \eta_i = \eta_i o + \eta_\infty \]

Total apparent viscosity = \( \Sigma \) matrix + interaction
Then \[ \eta_a = \eta_\infty + \frac{(\eta_0 - \eta_\infty)}{1 + \alpha \gamma^n} \]

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.

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

And using \[ \frac{\eta_i}{\eta_{i_0}} = \frac{m_t}{m_0} \]

number of interactions at any time t
\[ \tau = \eta_a \dot{\gamma} \]

\[ \frac{dm}{dt} = k_2 [m_0 - m] \]
More complex shear rate history problems can be addressed. (see example sheet)

\[ \gamma \]

\[ \eta_a \]