Rheology and Rheometry

Paula Moldenaers
Department of Chemical Engineering
Katholieke Universiteit Leuven
W. De Croylaan 46, B-3001 Leuven

Tel. 32(0)16 322675  Fax 32(0)16 322991
What is Rheology?

Rheology = The Science of Deformation and Flow

Why do we need it?
- measure fluid properties
- understand structure-flow property relations
- modelling flow behaviour
- simulate flow behaviour

of melts under processing conditions
<table>
<thead>
<tr>
<th>Processing conditions</th>
<th>shear rate [s$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sedimentation</td>
<td>$10^{-6} - 10^{-4}$</td>
</tr>
<tr>
<td>Leveling</td>
<td>$10^{-3}$</td>
</tr>
<tr>
<td>Extrusion</td>
<td>$10^0 - 10^2$</td>
</tr>
<tr>
<td>Chewing</td>
<td>$10^1 - 10^2$</td>
</tr>
<tr>
<td>Mixing</td>
<td>$10^1 - 10^3$</td>
</tr>
<tr>
<td>Spraying, brushing</td>
<td>$10^3 - 10^4$</td>
</tr>
<tr>
<td>Rubbing</td>
<td>$10^4 - 10^5$</td>
</tr>
<tr>
<td>Injection molding</td>
<td>$10^2 - 10^5$</td>
</tr>
<tr>
<td>coating flows</td>
<td>$10^5 - 10^6$</td>
</tr>
</tbody>
</table>
How about Newtonian behaviour?

1. Constant viscosity
2. No time effects
3. No normal stresses in shear flow
4. $\eta(\text{ext})/\eta(\text{shear}) = 3$

Symbols: 
- $\varepsilon \Rightarrow D$
- $\sigma \Rightarrow T$
- $s \Rightarrow \sigma$

Newton’s law: $T = -pl + \eta \ 2D$
Contents

1. Rheological phenomena

2. Constitutive equations
   2.1. Generalized Newtonian fluids
   2.2. Linear visco-elasticity
   2.3. Non-linear viscoelasticity

3. Rheometry

4. Parameters affecting rheology
1. Rheological Phenomena:

Do real melts behave according to Newton’s law?

Deviation 1:

**Mayonnaise**: resistance (viscosity) decreases with increasing shear rate: shear thinning

**Starch solution**: resistance increases with increasing shear rate: shear thickening

This is a non-linearity:

\[ \eta(\dot{\gamma}) \]
Do real melts behave according to Newton’s law?

Deviation 2: example silly putty

The response of the material depends on the time scale:
* Short times: elastic like behaviour
* Long times: liquid-like behaviour

VISCO-ELASTIC BEHAVIOUR

\[ G(t) \text{ or } G(t, \gamma) \]

Linear            non-linear
Do real melts behave according to Newton’s law?

Deviation 3:

- Weissenberg effect
- Die Swell

Normal stresses
Do real melts behave according to Newton’s law?

Deviation 4: Ductless Syphon

\[ \eta(\text{ext}) > > \eta(\text{shear}) \]
In summary:

Newtonian behaviour

1. Constant viscosity
2. No time effects
3. No normal stresses in shear flow
4. $\eta(\text{ext})/\eta(\text{shear}) = 3$

3 dim: $T = -pI + \eta(2D)$
Simple shear: $\sigma = \eta \frac{d\gamma}{dt}$

real behaviour

1. Variable viscosity
2. Time effects
3. Normal stresses
4. Large $\eta(\text{ext})$
Contents

1. Rheological phenomena

2. Constitutive equations
   2.1. Generalized Newtonian fluids
   2.2. Linear visco-elasticity
   2.3. Non-linear viscoelasticity

3. Rheometry

4. Parameters affecting rheology
2. Constitutive equations
2.1 Generalized Newtonian fluids

Examples of non-Newtonian behaviour:

Macosko, 1992
2.1 Generalized Newtonian fluids

Non-Newtonian behaviour is typical for polymeric solutions and molten polymers

e.g. ABS polymer melt (Cox and Macosko)
2.1 Generalized Newtonian fluids

\[ T = -pI + f_1(\Pi_{2D}) \cdot 2D \]

The viscosity is now replaced by a function of the second invariant of \(2D\) for a shear flow this becomes:

\[ \sigma_{xy} = \eta_1(\dot{\gamma}^2) \cdot \dot{\gamma} \]

and different forms for this function have been proposed

With: \( \Pi_{2D} = 1/2 (\text{tr}^2_{2D} - \text{tr} (2D)^2) \)

\( \text{tr} = \text{trace} = \text{sum of the diagonal elements} \)
Model 1: Power Law

\[ T = -pI + k \cdot |\Pi_{2D}|^{(n-1)/2} \cdot 2D \]

\[ \sigma_{xy} = k\dot{\gamma}^n \quad \eta = k\dot{\gamma}^{n-1} \]

- \( n < 1 \): shear-thinning
- \( n > 1 \): shear-thickening

\( n = 0.4, k = 1 \)
\( n = 0.8, k = 1 \)
\( n = 1.4, k = 0.01 \)
Model 2: Ellis model

\[ \frac{\eta}{\eta_0} = \frac{1}{1 + k \cdot \dot{\gamma}^{(1-n)}} \]

3 parameters
Model 3: CROSS model

\[ \frac{\eta - \eta_\infty}{\eta_0 - \eta_\infty} = \frac{1}{1 + k \cdot \dot{\gamma}^{(1-n)}} \]

3D

\[ \frac{\eta - \eta_\infty}{\eta_0 - \eta_\infty} = \frac{1}{1 + \left(k^2 \cdot \|l\|_2D\right)^{(1-n)/2}} \]

4 parameters
Special case: plastic Behaviour

**Yield stress**  \( \sigma < \sigma_y \rightarrow \dot{\gamma} = 0 \),  \( \sigma = G \cdot \gamma \)  
No flow, only deformation

\( \sigma > \sigma_y \rightarrow \dot{\gamma} \neq 0 \)
What have we gained in generalized Newtonian?

**Newtonian behaviour**

1. Constant viscosity
2. No time effects
3. No normal stresses in shear flow
4. $\eta(\text{ext}) / \eta(\text{shear}) = 3$

- 3 dim: $T = -pI + \eta \ (2D)$
- Simple shear: $\sigma = \eta \ \frac{d\gamma}{dt}$

**real behaviour**

1. Variable viscosity
2. Time effects
3. Normal stresses
4. Large $\eta(\text{ext})$

- $T = -pI + \eta(\text{II}_{2D}) \ (2D)$
Contents

1. Rheological phenomena

2. Constitutive equations
   2.1. Generalized Newtonian fluids
   2.2. Linear visco-elasticity
   2.3. Non-linear viscoelasticity

3. Rheometry

4. Parameters affecting rheology
2. Constitutive equations
2.2 Linear visco-elasticity

Reference: 2 extremes

Hooke’s Law (solid mechanics)

\[ \sigma = G \gamma \]

G = modulus (Pa)
Material property

Newton’s Law (fluid mechanics)

\[ \sigma = \eta \frac{d\gamma}{dt} \]

\( \eta \) = viscosity (Pa.s)
material property
Time effects (linear visco-elastic phenomena):

Example 1: creep

Apply constant stress $\sigma$

Compliance

$$J(t) = \frac{\gamma(t)}{\sigma_0}$$
Time effects (linear visco-elastic phenomena):
Example 2: stress relaxation upon step strain

Apply constant strain

Modulus

\[ G(t) = \frac{\sigma(t)}{\gamma} \]
Example for molten LDPE

How to describe this behaviour?
Example: differential models

Phenomenological models

Hookean spring

\[ \sigma_1 = G_0 \gamma_1 \]

Newtonian dashpot

\[ \sigma_2 = \eta_0 \cdot \dot{\gamma}_2 \]
Maxwell model:

\[ \gamma = \gamma_1 + \gamma_2 \]
\[ \sigma = \sigma_1 = \sigma_2 \]
\[ \dot{\gamma} = \dot{\gamma}_1 + \dot{\gamma}_2 \]

\[ \dot{\gamma} = \frac{\dot{\sigma}_1}{G_0} + \frac{\sigma_2}{\eta_0} \]

\[ \sigma + \left( \frac{\eta_0}{G_0} \right) \dot{\sigma} = \eta_0 \dot{\gamma} \]

\[ \sigma + \tau \dot{\sigma} = \eta_0 \dot{\gamma} \]

\[ \tau = \text{relaxation time} \]
Example: Stress relaxation upon step strain for a Maxwell element

\[ \gamma = \gamma_0 \quad t \geq 0 \]

\[ \sigma + \tau \frac{d\sigma}{dt} = 0 \]

\[ t = 0; \sigma = G_0 \gamma_0 \]

\[ \frac{\sigma(t)}{\gamma} = G(t) = G_0 \cdot \exp\left(-\frac{t}{\tau}\right) \]
Generalized Maxwell model to describe molten polymers:

\[
\sigma_{TOT} = \sum_i \sigma_i \\
\sigma_i + \tau_i \dot{\sigma}_i = \eta_i \dot{\gamma} \\
G(t) = \sum_i G_{0i} \exp(-t / \tau_i)
\]
Relaxation functions:
For a simple Maxwell model: single exponential (single relaxation time $\tau$):

$$G(t) = G_0 \exp(-t / \tau)$$

For a generalized Maxwell fluid (discrete number of relaxation times $\tau_i$):

$$G(t) = \sum G_i \exp(-t / \tau_i)$$

We can replace the discrete relaxation times by a continuous spectrum:

$$G(t) = \int_0^\infty F(\tau) \exp\left(-\frac{t}{\tau}\right) d\tau$$

Or based on a logarithmic time scale: the relaxation spectrum is defined by:

$$G(t) = \int_0^\infty H(\tau) \exp\left(-\frac{t}{\tau}\right) \frac{d\tau}{\tau}$$
Time effects (linear visco-elastic phenomena): Example 3: Oscillatory experiments

**STRAIN:**
\[ \gamma = \gamma_0 \sin(\omega t) \]
\[ \gamma = \gamma_0 \exp(i\omega t) \]

**STRAIN RATE**
\[ \dot{\gamma} = \gamma_0 \omega \cos(\omega t) = \gamma_0 \sin(\omega t + 90^\circ) \]
\[ \dot{\gamma} = i\omega \gamma_0 \exp(i\omega t) \]

**HOOKEAN SOLID**
\[ \sigma = G \gamma = G \gamma_0 \sin(\omega t) \]
\[ \sigma = G \gamma_0 \exp(i\omega t) \]

**NEWTONIAN FLUID**
\[ \sigma = \eta \dot{\gamma} = \eta \gamma_0 \omega \sin(\omega t + 90^\circ) \]
\[ \sigma = \eta \dot{\gamma}_0 \omega \exp(i\omega t) = \eta \dot{\gamma}_0 \omega \]
VISCOELASTIC MATERIAL

\[ \sigma = \sigma_{el} + \sigma_{visc} \]

\[ \sigma = G\gamma + i\omega \eta \gamma \]

\[ \sigma = (G + i\omega \eta)\gamma \]

complex modulus:

\[ \sigma = G^* \gamma \]

\[ \sigma = G^* \gamma_0 \sin(\omega t + \delta) \]

\[ \sigma = G^* \gamma_0 [\sin(\omega t) \cdot \cos(\delta) + \cos(\omega t) \cdot \sin(\delta)] \]

\[ \sigma = (G^* \cos(\delta)) \cdot \gamma_0 \sin(\omega t) + (G^* \sin(\delta)) \cdot \gamma_0 \cos(\omega t) \]

\[ \sigma = [G^' \cdot \sin(\omega t) + G'' \cdot \cos(\omega t)] \gamma_0 \]

\[ \sigma = (G^' + iG'') \gamma \]

Storage and Loss modulus:

\[ \tan \delta = \frac{G''}{G'} \]
Dynamic moduli of a Maxwell fluid

\[ G'(\omega) = \frac{G_0 \omega^2 \tau^2}{1 + \omega^2 \tau^2} \]

\[ G''(\omega) = \frac{G_0 \omega \tau}{1 + \omega^2 \tau^2} \]
G' and G” for a generalized Maxwell fluid:

\[ G'' = \omega \int_0^\infty G(s) \cdot \cos(\omega s) ds = \omega \int_0^\infty \left( \sum_{i=1}^N G_i e^{-\tau_i s} \right) \cdot \cos(\omega s) ds \]

\[ = \sum_{i=1}^N G_i \frac{\omega \tau_i}{1 + (\omega \tau_i)^2} \]

\[ G' = \omega \int_0^\infty G(s) \cdot \sin(\omega s) ds \]

\[ = \sum_{i=1}^N G_i \frac{(\omega \tau_i)^2}{1 + (\omega \tau_i)^2} \]
### What have we gained in **linear visco-elasticity**?

<table>
<thead>
<tr>
<th>Newtonian behaviour</th>
<th>real behaviour</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Constant viscosity</td>
<td>1. Variable viscosity</td>
</tr>
<tr>
<td>2. No time effects</td>
<td>2. Time effects</td>
</tr>
<tr>
<td>3. No normal stresses in shear flow</td>
<td>3. Normal stresses</td>
</tr>
<tr>
<td>4. $\eta(\text{ext})/\eta(\text{shear}) = 3$</td>
<td>4. Large $\eta(\text{ext})$</td>
</tr>
</tbody>
</table>

3 dim: $T = -p I + \eta \ (2D)$  
Simple shear: $\sigma = \eta \ dy/dt$

$G(t)$, $H(\tau)$,… fully describes linear VE
Contents

1. Rheological phenomena

2. Constitutive equations
   2.1. Generalized Newtonian fluids
   2.2. Linear visco-elasticity
   2.3. Non-linear viscoelasticity

3. Rheometry

4. Parameters affecting rheology
2. Constitutive equations

2.3. Non-linear visco-elasticity

Example 1: Steady state shear flow

\[
\begin{align*}
\sigma_{xy} &= \\
N_1 &= \sigma_{xx} - \sigma_{yy} \\
N_2 &= \sigma_{yy} - \sigma_{zz}
\end{align*}
\]

PIB in decalin, Keentok et al.

\[
\eta = \frac{\sigma_{xy}}{\dot{\gamma}}
\]

\[
\Psi_1 = \frac{\sigma_{xx} - \sigma_{yy}}{\dot{\gamma}^2}
\]

\[
\Psi_2 = \frac{\sigma_{yy} - \sigma_{zz}}{\dot{\gamma}^2}
\]

LDPE, Laun et al.
Example 2: Non-linear stress relaxation upon step strain

LDPE, Laun et al.
Example 3: Stress evolution upon inception of shear or elongational flow
<table>
<thead>
<tr>
<th>Newtonian behaviour</th>
<th>real behaviour</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Constant viscosity</td>
<td>1. Variable viscosity</td>
</tr>
<tr>
<td>2. No time effects</td>
<td>2. Time effects</td>
</tr>
<tr>
<td>3. No normal stresses in shear flow</td>
<td>3. Normal stresses</td>
</tr>
<tr>
<td>4. $\eta(\text{ext})/\eta(\text{shear}) = 3$</td>
<td>4. Large $\eta(\text{ext})$</td>
</tr>
</tbody>
</table>

3 dim: $T = -pI + \eta(2D)$

Simple shear: $\sigma = \eta \frac{d\gamma}{dt}$

$\eta$ represents viscosity.
Contents

1. Rheological phenomena

2. Constitutive equations
   2.1. Generalized Newtonian fluids
   2.2. Linear visco-elasticity
   2.3. Non-linear viscoelasticity

3. Rheometry

4. Parameters affecting rheology
3. Rheometry

**Why?**
1. Input for Constitutive Equations
2. Quality control
3. Simulate industrial flows

A rheometer is an instrument that measures both stress and deformation.

↔ indexer
↔ viscometer

**What do we want to measure?**
- steady state data
- small strain (LVE) functions
- large strain deformations
Introduction: classifications

- Kinematics: shear vs elongation

- Homogeneous vs non-homogeneous vs complex flow fields

- Type of straining:
  - Small: $G'(\omega)$, $G''(\omega)$, $\eta^+(t)$, $\eta^-(t)$, $G(t)$, $\sigma_y$
  - Large: $G'(\omega,\gamma)$, $G''(\omega,\gamma)$, $\eta^+(t,\gamma)$, $\eta^-(t,\gamma)$, $G(t,\gamma)$, $\eta(t,\epsilon)$
  - Steady: $\bar{\eta}(\ )$, $\Psi_1(\ )$

- Shear rheometry: Drag or pressure driven flows.
Shear flow geometries

Drag flows

- Sliding plates
- Couette
- Cone and Plate
- Parallel plates

Pressure driven flows

- Capillary
- Slit
- Annulus

Macosko, 1992
Drag flows: Cone and plate

Probably most popular geometry Mooney (1934)

1. Steady, laminar, isothermal flow
2. Negligible gravity and end effects
3. Spherical boundary liquid
4. \( v_r = v_z = 0 \) and \( v_\phi (r, \theta) \)
5. Angle \( \alpha < 0.1 \) radians

Equations of motion:

\[
\begin{align*}
    r: \quad & \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \sigma_{rr} \right) - \frac{\sigma_{\theta\theta} + \sigma_{\phi\phi}}{r} = -\rho \frac{v^2_\theta}{r} \\
    \theta: \quad & \frac{1}{r \sin \theta} \frac{\partial}{\partial r} \left( \sigma_{r\theta} \sin \theta \right) - \cot \theta \cdot \frac{\partial \sigma_{\theta\theta}}{\partial r} = 0 \\
    \phi: \quad & \frac{1}{r} \frac{\partial \sigma_{\theta\phi}}{\partial \theta} + \frac{2}{r} \cot \theta \cdot \sigma_{\theta\phi} = 0
\end{align*}
\]
**Drag flows: Cone and plate geometry**

Boundary conditions
1. \( v_\phi(\pi/2) = 0 \)
2. \( v_\phi(\pi/2-\alpha) = \omega r \sin(\pi/2-\alpha) \approx \omega r \)

Shear stress

\[
\phi: \quad \frac{1}{r} d\left(\frac{\sigma_\theta}{d\theta}\right) + \frac{2}{r} \cot \phi \cdot \sigma_\theta = 0 \quad \rightarrow \quad \sigma_\theta = \frac{C}{\sin^2 \theta} \approx Cte
\]

\[
M = \int_0^{2\pi} \int_0^R r^2 \sigma_\theta d\phi dr
\]

Independent of fluid characteristics because of small angle!
Drag flows: Cone and plate geometry

**Shear rate**: is also constant throughout the sample: homogeneous!

\[
\dot{\gamma} = \frac{V_r}{h(r)} = \frac{\omega \cdot r}{r \cdot \text{tg}(\alpha)} = \frac{\omega}{\text{tg}(\alpha)} \approx \frac{\omega}{\alpha}
\]

Normal stress differences: total force on the plate is measured \( F_z \)

\[
F_z = \frac{\pi R^2}{2} \left( \sigma_{\theta\theta} - \sigma_{\phi\phi} \right)
\]

\[
N_1 = \frac{2F_z}{\pi R^2}
\]
Drag flows: Cone and plate geometry

+ 
- constant shear rate, constant shear stress - homogeneous!
- most useful properties can be measured
- both for high and low viscosity fluids
- small sample
- easy to fill and clean

- 
- high visc: shear fracture - limits max. shear rate
-(low visc : centrifugal effects/inertia - limits max. shear rate)
- (settling can be a problem)
- (solvent evaporation)
- stiff transducer for normal stress measurements
- viscous heating
Drag flows : Parallel plates

Again proposed by Mooney (1934)

1. Steady, laminar, isothermal flow
2. Negligible gravity and end effects
3. Cylindrical edge
4. \( v_r = v_z = 0 \) and \( v_\phi (r, z) \)

Equations of motion:

\[
\begin{align*}
    r: & \quad \frac{1}{r} \frac{\partial (r \sigma_{rr})}{\partial r} - \frac{\sigma_{\theta\theta}}{r} = -\rho \frac{v_\theta^2}{r} \\
    \theta: & \quad \frac{\partial (\sigma_{\theta z})}{\partial z} = 0 \\
    z: & \quad \frac{\partial (\sigma_{zz})}{\partial z} = 0
\end{align*}
\]
Drag flows: Parallel plates

Shear rate: is not constant throughout the sample

\[ \dot{\gamma} = \frac{V_r}{h} = \frac{\omega \cdot r}{h} \]

Shear stress

\[ \sigma = \frac{M}{2\pi R^3} \left[ 1 + \frac{d\ln M}{d\ln \dot{\gamma}_R} \right] \]

Normal stresses

\[ N_1 - N_2 = \frac{F_z}{\pi R^2} \left[ 2 + \frac{d\ln F_z}{d\ln \dot{\gamma}_R} \right] \]
Drag flows: Parallel plate geometry

- preferred geometry for viscous melts - small strain functions
- sample preparation is much simpler
- shear rate and strain can be changed also by changing h
- determination of wall slip easy
- $N_2$ when $N_1$ is known
- edge fracture can be delayed

- non-homogeneous flow field (correctable)
- inertia/secondary flow - limits max. shear rate
- edge fracture still limits use
- (settling can be a problem)
- (solvent evaporation)
- viscous heating
Pressure driven flows: capillary rheometry

1. Steady, laminar, isothermal flow
2. No slip at the wall, \( v_x = 0 \) at \( R = 0 \)
3. \( v_r = v_\theta = 0 \)
4. Fluid is incompressible, \( \eta \neq f(p) \)

Equation of motion:

\[
\begin{align*}
\sigma_z & = \frac{1}{r} \frac{d}{dr} \left( r \sigma_{rz} \right) - \frac{\partial p}{\partial z} = 0 \\
\frac{1}{r} \frac{d}{dr} \left( r \sigma_{rz} \right) & = \frac{dp}{dz}
\end{align*}
\]

Only a function of \( r \)

Only a function of \( z \)
\[ \frac{1}{r} \frac{d(r\sigma_{rz})}{dr} = \frac{P_o - P_L}{L} \]

\[ \sigma_{rz} = \frac{P_o - P_L}{L} \cdot \frac{r}{2} + \frac{C_2}{r} \]

\[ C_2 = 0 \quad because \quad \sigma_{rz} \not= \infty \quad @ \quad r = 0 \]

\[ \sigma_{rz}(R) = \sigma_w = \frac{P_o - P_L}{L} \cdot \frac{R}{2} \]

\[ \sigma_{rz}(r) = \sigma_w \frac{r}{R} \]

Note: independent of fluid properties
Shear rate calculation from $Q$

Integration by parts + assume :no slip

substitute $r$ and $dr$

Typical “trick” to deal with inhomogeneous flows:
changing of variables

Differentiate with respect to $\sigma_w$
using Leibnitz’s rule

$\dot{\gamma}_w = \left. \frac{d\nu_z}{dr} \right|_{\sigma_w} = \frac{3Q}{4\pi R^3} + \frac{3Q}{4\pi R^3} \cdot \frac{d\ln Q}{d\ln \sigma_w}$

$\dot{\gamma}_w = \frac{\dot{\gamma}_a}{4} \left( 3 + \frac{d\ln Q}{d\ln \sigma_w} \right)$
Weissenberg-Rabinowitsch “Correction”

\[ \gamma_w = \frac{\dot{\gamma} a}{4} \left( 3 + \frac{d \ln Q}{d \ln \sigma_w} \right) \]

“Correction” factor accounts for material behaviour

Physical meaning:

e.g. power law fluid

\[ \gamma_w = \frac{\dot{\gamma} a}{4} \left( 3 + \frac{1}{n} \right) \]

Steepness of the velocity profile changes
Shear rate is increased with respect to the Newtonian case:

\[ \dot{\gamma} a = \frac{4Q}{\pi R^3} \]
What pressure drop do we really measure?

$$\sigma_w = \frac{P_0 - P_L}{L} \cdot \frac{R}{2}$$

Cannot be measured!
BAGLEY plots

\[ \sigma_w = \frac{\Delta P \cdot R}{2(L + eR)} \]

\( \Delta p_e \) can be used to estimate the elongational viscosity (contraction flow)
Are these conditions met?

1. Steady, laminar, isothermal flow
2. No slip at the wall, $v_x = 0$ at $R=0$
3. $v_r = v_\theta = 0$
4. Fluid is incompressible, $\eta \neq f(p)$

Problem 1: Melt distortion

Melt fracture typically occurs at $\sigma_w 10^5$ Pa
Are these conditions met?

1. Steady, laminar, isothermal flow
2. No slip at the wall, \( v_x = 0 \) at \( R = 0 \)
3. \( v_r = v_\theta = 0 \)
4. Fluid is incompressible, \( \eta \neq f(p) \)

**Problem 2: Viscous heating**

\[
N_a = \frac{\alpha R^2 \dot{\gamma}}{4k}
\]
Are these conditions met?

1. Steady, laminar, isothermal flow
2. No slip at the wall, \( v_x = 0 \) at \( R=0 \)
3. \( v_r = v_0 = 0 \)
4. Fluid is incompressible, \( \eta \neq f(p) \)

**Problem 3: Wall slip**

\[
\dot{\gamma}_a = \dot{\gamma} + \frac{4v_s}{R} \quad \sigma = \text{cst}
\]
Are these conditions met?

1. Steady, laminar, isothermal flow
2. No slip at the wall, $v_x = 0$ at $R=0$
3. $v_r = v_\theta = 0$
4. Fluid is incompressible, $\eta \neq f(p)$

**Problem 4:** Melt compressibility, $\eta = f(p)$

![Graph showing pressure drop vs. L/D with different symbols for various strain rates](image-url)
Capillary rheometry: conclusions

- Simple yet accurate!
- High shear rates possible
- Sealed system, can be pressurized
- Process simulator
- Entrance flows and exit flows can be used
- MFI

- Non-homogeneous flow field (correctable)
- Only viscosity data, some indications for $N_1$, $\eta_e$
- Lot of data required (Bagley plots)
- Melt fracture limits shear rate
- Wall slip can be a problem
- Viscous heating
- Shear history / degradation
Melt Flow index

![Diagram of Melt Flow Index](image)
# Shear rheometers: the verdict

<table>
<thead>
<tr>
<th>Type</th>
<th>Pros</th>
<th>Cons</th>
</tr>
</thead>
<tbody>
<tr>
<td>Couette</td>
<td>+ low $\eta$, high rates</td>
<td>- end corrections</td>
</tr>
<tr>
<td></td>
<td>+ can be homogeneous</td>
<td>- high visc. : too difficult</td>
</tr>
<tr>
<td></td>
<td>+ settling</td>
<td>- no $N_1$</td>
</tr>
<tr>
<td>Cone and Plate</td>
<td>+ best for $N_1$</td>
<td>- edges, low shear rate</td>
</tr>
<tr>
<td></td>
<td>+ homogeneous</td>
<td>- free surface</td>
</tr>
<tr>
<td></td>
<td>+ transient meas.</td>
<td>- alignment</td>
</tr>
<tr>
<td>Parallel Plate</td>
<td>+ easy to load</td>
<td>- edges</td>
</tr>
<tr>
<td></td>
<td>+ $G', G''$ for melts</td>
<td>- non-homogenous</td>
</tr>
<tr>
<td></td>
<td>+ vary $h$!</td>
<td>- free surface</td>
</tr>
<tr>
<td>Capillary</td>
<td>+ high rates</td>
<td>- corrections:</td>
</tr>
<tr>
<td></td>
<td>+ accurate</td>
<td>- non-homogenous</td>
</tr>
<tr>
<td></td>
<td>+ sealed</td>
<td>- no $N_1$</td>
</tr>
</tbody>
</table>
Contents

1. Rheological phenomena

2. Constitutive equations
   2.1. Generalized Newtonian fluids
   2.2. Linear visco-elasticity
   2.3. Non-linear viscoelasticity

3. Rheometry

4. Parameters affecting rheology
4. Parameters affecting rheology

• Chemistry
• Molecular weight
• Molecular weight distribution
• Molecular architecture (branching)
• Fillers/additives
• Temperature
• Pressure
• …
Effect of molecular weight on the viscosity curve

Example: narrow MW polystyrenes

\[ \eta/\eta_0 \text{ vs } \dot{\gamma}\tau_0 : \text{single curve} \]

From Stratton
Effect of the MW on the zero shear viscosity for linear molten polymers

\[
\log \eta + ct = \log M_w + ct
\]

Berry and Fox

\[
\eta \propto M_w^{3.4}
\]

PS, 217°C

\[
2M_w = 39000
\]
Effect of molecular weight on moduli

Onogi et al., 1970

PS 160°C

$\overline{M}_w = 581000$

$\overline{M}_w = 8900$
Effects of molecular weight distribution

Viscosity:

Shear thinning sets in earlier with increasing molecular weight distribution

A - $M_w/M_n = 1.09$
B - $M_w/M_n = 2.0$
C - branched

From Uy and Greassley
Effect of chain architecture (branching)

Low shear rates

Higher shear rates

\( O = \text{linear} \)

\( \square \) and \( \Delta = \text{branched} \)

Kraus and Gruver
Effect of fillers

Chapman and Lee
Effect of temperature: time-temperature superposition

WLF-relation:

\[
\log a_T = \frac{-C_1 (T - T_r)}{C_2 + T - T_r}
\]
Effect of pressure on viscosity

- Relevant for injection moulding
- Add-on ‘pressure chamber’ on Gottfert capillary rheometer
“Corrected” viscosity for PMMA (210° C)

Shear rate (s⁻¹)

Viscosity (Pas)

Mean pressures:
- 80 MPa
- 70 MPa
- 55 MPa
- 40 MPa
- 30 MPa
- 0.1 MPa
Viscosity curves for PαMSAN and LDPE
Determination of $\beta$ at several shear rates

$$\beta = \left( \frac{d \ln \eta}{dP} \right)_T$$

Shear rates:
- 6 s\(^{-1}\)
- 13 s\(^{-1}\)
- 33 s\(^{-1}\)
- 70 s\(^{-1}\)
- 108 s\(^{-1}\)
- 146 s\(^{-1}\)
- 223 s\(^{-1}\)
- 260 s\(^{-1}\)
- 290 s\(^{-1}\)
$\beta$ at several shear rates

![Graph showing shear rate (s$^{-1}$) vs. $\beta$ (GPa$^{-1}$) for different polymers: PMMA, P$_{\alpha}$MSAN, and LDPE.](image)
Determination of $\beta$ at several shear stresses (PMMA)

$$\beta = \left( \frac{d \ln \eta}{dP} \right)_T$$

![Graph showing the relationship between $\ln \eta$ and $P_{\text{mean}}$ at different stresses.](image-url)
β at several shear stresses (PMMA)
Useful references concerning rheology

Rheology: Principles, Measurements and Applications
C. Macosko Ed, VCH (1994)

Understanding Rheology
F. Morrison, Oxford University Press (2001)

Structure and Rheology of Molten Polymers