# Polymeric Fluids

GM05 Part 1

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# 1 Introduction

Polymers are long molecules made from joining together lots of small molecules (or monomers). They are the basis of all plastic materials and products.

During the manufacturing process, liquids containing polymers are subjected to flow. The way these liquids react is determined by the shapes, or configurations that the molecules adopt. Because of their size, the polymer molecules can become stretched by the flow, giving rise to some surprising behaviour.

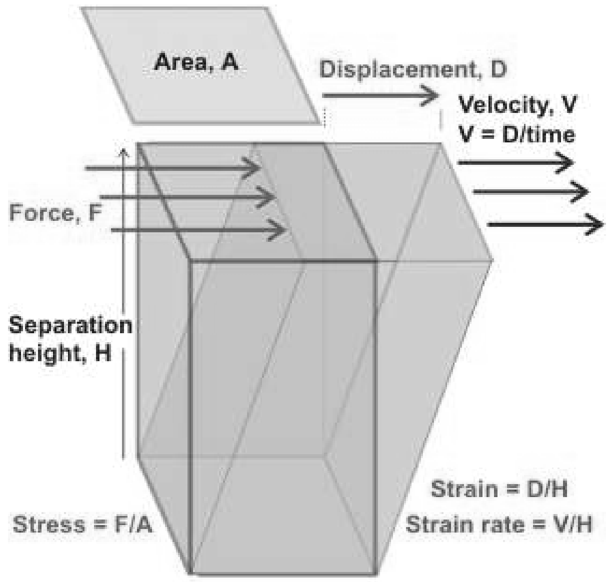
We will start by looking informally at a few samples of these fluids and how they behave. The structure of the more formal part of the course is:

**Lectures 1–3:** Modelling "top-down": experiments used to characterise a fluid, and models used to fit them; behaviour of these models in shearing flows.

**Lectures 4–6:** Modelling "bottom-up": understanding how individual molecules behave and react to flow; methods for deriving macroscopic average behaviour.

# 2 Shear flows

The simplest steady flow which is experimentally realisable is a **shear flow**:




There are two types of instrument used for shearing flows:

**Controlled strain** rheometers in which the strain (shear) and strain rate (shear rate) are prescribed, and the device measures the required force;

**Controlled stress** rheometers, in which a controlled force is applied and the mechanical response measured.

The variables which can be imposed and/or measured are:

- the stress $\sigma$ = force applied per unit area, and
- the shear rate $\dot{\gamma}$ = speed of the top plate divided by the gap between the plates.

A common first step in analysing a new material is to assume that there is a unique relationship between these, regardless of flow history. We will come back to the validity of this assumption later.

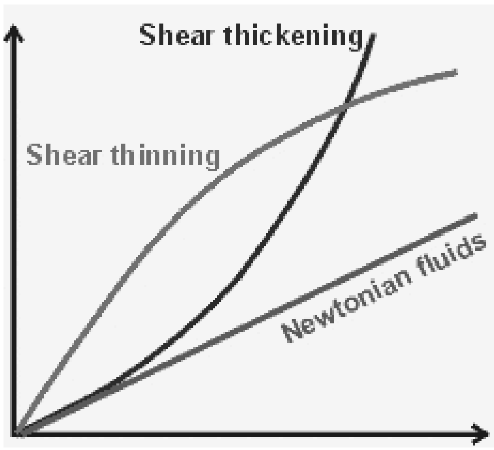
The relationship between stress and strain (or strain history) is called the **constitutive relation**.

The simplest is the law for a **Newtonian** or **viscous** fluid, in which the stress is simply proportional to the shear rate:

$$\sigma = \eta\dot{\gamma}$$

If we plot stress against shear rate, of course this is just a straight line of slope $\eta$ through the origin.

If the stress increases more slowly than linearly, the fluid is called **shear-thinning**. If it increases faster than linearly, the fluid is called **shear-thickening**. These are shown schematically below: we are plotting shear stress against shear rate.




The cornflour we passed round was an example of a shear-thickening fluid: as you stirred is faster, it resisted much harder. Toothpaste and emulsion paint are two shear-thinning fluids: for toothpaste, low stresses like gravity don't make it run off the brush, but higher stresses like brushing do make it flow. Similarly, paint flows happily as you put it on the wall, but then doesn't flow much under gravity once you leave it there.

## 2.1 Generalised Newtonian fluid

Any graph of shear stress against shear rate can be represented as a single function $\eta(\dot{\gamma})$. Probably the first, and certainly the simplest, model of non-Newtonian behaviour is to measure this "viscosity function" and then use it as the viscosity in the usual Newtonian fluid equations.

[Note for those who have either fluids or tensors experience: in a flow which is not pure shear, we need to define a shear rate. Since, in a 2D shear flow, the rate of strain tensor

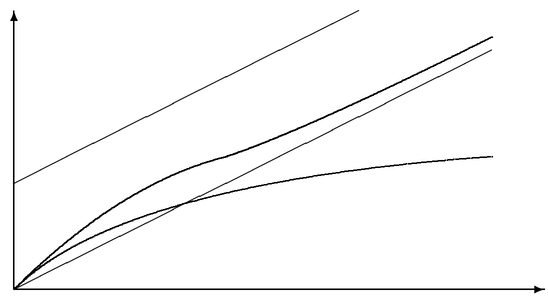
$$\underline{\underline{E}} = \frac{1}{2}\left(\underline{\nabla u} + (\underline{\nabla u})^{\top}\right) = \frac{1}{2}\begin{pmatrix} 0 & \dot{\gamma} \\ \dot{\gamma} & 0 \end{pmatrix}$$

we define the shear rate in general to be $\dot{\gamma} = \sqrt{2\underline{\underline{E}} : \underline{\underline{E}}}$.]

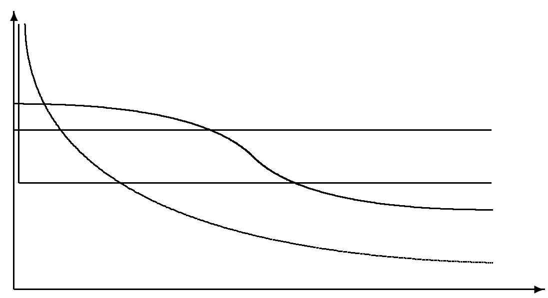
Different fluid models:

| | | |
|---|---|---|
| Newtonian | $\eta(\dot{\gamma}) = \mu \qquad \sigma = \mu\dot{\gamma}$ | |
| Power-law | $\eta(\dot{\gamma}) = \mu\lvert\dot{\gamma}\rvert^{n-1}$ | Note $n = 1$ is Newtonian, $n > 1$ shear thickening and $0 < n < 1$ shear-thinning. |
| Carreau | $\eta(\dot{\gamma}) = \eta_\infty + (\eta_0 - \eta_\infty)[1 + (\dot{\gamma}\tau)^2]^{(n-1)/2}$ | Again, $n = 1$ is Newtonian. For $n < 1$, as $\dot{\gamma} \to \infty$, $\eta \to \eta_\infty$; and as $\dot{\gamma} \to 0$, $\eta \to \eta_0$. |
| Bingham (plastic) | If $\lvert\sigma\rvert < \sigma_c$ then $\dot{\gamma} = 0$<br>For $\sigma > \sigma_c$, $\sigma = \sigma_c + \mu\dot{\gamma}$<br>For $\sigma < -\sigma_c$, $\sigma = -\sigma_c + \mu\dot{\gamma}$ | Also known as the yield fluid. |

What do these stresses look like? First, plotting stress against shear rate:

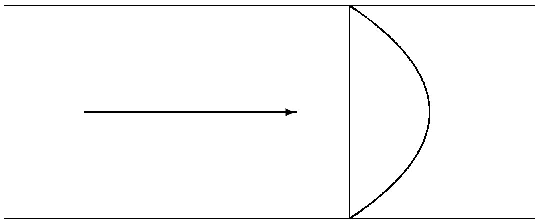


and then, plotting the effective viscosity $\eta$ against shear rate:



## 2.2 Poiseuille flow

Poiseuille flow is flow through a circular pipe or a two-dimensional slit. Here we will look at the 2D version. How does a generalised Newtonian fluid behave in a flow like this?



Let's start with the full generalised Newtonian fluid, and keep it as general as possible for a while.

The equations governing the motion (we'll assume the fluid is incompressible) are mass conservation:

$$\frac{\partial u_x}{\partial x} + \frac{\partial u_y}{\partial y} = 0$$

three stress definitions:

$$\sigma_{11} = -p + 2\eta(\dot{\gamma})\frac{\partial u_x}{\partial x}$$

$$\sigma_{12} = \eta(\dot{\gamma})\left(\frac{\partial u_x}{\partial y} + \frac{\partial u_y}{\partial x}\right)$$

$$\sigma_{22} = -p + 2\eta(\dot{\gamma})\frac{\partial u_y}{\partial y}$$

and two momentum equations:

$$\rho\left(\frac{\partial u_x}{\partial t} + u_x\frac{\partial u_x}{\partial x} + u_y\frac{\partial u_x}{\partial y}\right) = \frac{\partial \sigma_{11}}{\partial x} + \frac{\partial \sigma_{12}}{\partial y}$$

$$\rho\left(\frac{\partial u_y}{\partial t} + u_x\frac{\partial u_y}{\partial x} + u_y\frac{\partial u_y}{\partial y}\right) = \frac{\partial \sigma_{12}}{\partial x} + \frac{\partial \sigma_{22}}{\partial y}$$

The fluid density is $\rho$, $p$ is the pressure, and $u_x$ and $u_y$ are the components of the velocity. We will also have boundary conditions that both components of the fluid velocity are zero at a solid wall:

$$u_x = u_y = 0 \qquad \text{at} \qquad y = \pm H.$$

(We have put $y = 0$ on the centreline of the channel.)

The quicker way to write down these equations if you're happy with tensor notation is

$$\underline{\nabla} \cdot \underline{u} = 0 \qquad \rho\frac{D}{Dt}\underline{u} = \underline{\nabla} \cdot \underline{\underline{\sigma}}$$

$$\underline{\underline{\sigma}} = -p\underline{\underline{I}} + \eta(\dot{\gamma})\left(\underline{\nabla u} + (\underline{\nabla u})^\top\right)$$

We are looking at a flow which is all in the $x$-direction, and only varies in the $y$-direction:

$$u_x = U(y) \qquad u_y = 0 \qquad \dot{\gamma} = \mathrm{d}U/\mathrm{d}y.$$

Note that in this flow, the *shear stress* we have been talking about and calling $\sigma$ is actually $\sigma_{12}$.

This flow automatically satisfies mass conservation, and the stresses are:

$$\sigma_{11} = \sigma_{22} = -p \qquad \sigma_{12} = \eta(\dot{\gamma})\frac{\partial u_x}{\partial y} = \eta(\dot{\gamma})\dot{\gamma}$$

which is the shear stress as we expected. The two momentum equations become:

$$\frac{\partial p}{\partial x} = \frac{\partial \sigma_{12}}{\partial y} \qquad \text{and} \qquad \frac{\partial p}{\partial y} = \frac{\partial \sigma_{12}}{\partial x}$$

Looking at $\sigma_{12}$, we can see that it only depends on $y$: and so (from the second momentum equation) $p$ can only depend on $x$. Yet from the first equation, $\partial p/\partial x$ can only depend on $y$: so it must be a constant. It follows that

$$p = p_0 - Kx$$

where $p_0$ is an arbitrary base-line pressure, and $K$ is the pressure gradient which drives the flow. Now the second momentum equation is satisfied and the first becomes

$$\frac{\partial \sigma_{12}}{\partial y} = -K \qquad \frac{\partial}{\partial y}\left(\eta(\dot{\gamma})\dot{\gamma}\right) = -K \qquad \dot{\gamma} = \frac{\mathrm{d}U}{\mathrm{d}y}.$$

This is as far as we can go without specifying which constitutive law we are using. It is a differential equation for $\dot{\gamma}$ and hence for $U(y)$, with boundary conditions $U(H) = U(-H) = 0$.

### Newtonian fluid

Using a Newtonian fluid, $\eta$ is constant and our equation is

$$\eta\frac{\partial \dot{\gamma}}{\partial y} = -K = \eta\frac{\mathrm{d}^2 U}{\mathrm{d}y^2}.$$

The solution to this, satisfying $U(H) = U(-H) = 0$, is

$$U(y) = \frac{K}{2\eta}(H^2 - y^2).$$

This is a *parabolic* velocity profile; the maximum speed is at the centreline $y = 0$, where $U = KH^2/2\eta$.

### Bingham yield fluid

Here the situation is a little more complex. Recall that the Bingham fluid has three different possible actions: If $|\sigma| < \sigma_c$ then $\dot{\gamma} = 0$; for $\sigma > \sigma_c$, $\sigma = \sigma_c + \mu\dot{\gamma}$; and for $\sigma < -\sigma_c$, $\sigma = -\sigma_c + \mu\dot{\gamma}$. We can write an expression for $\dot{\gamma}$ in terms of $\sigma$ (or $\sigma_{12}$):

$$\dot{\gamma} = \begin{cases} (\sigma_{12} - \sigma_c)/\mu & \sigma_{12} > \sigma_c \\ 0 & |\sigma_{12}| < \sigma_c \\ (\sigma_{12} + \sigma_c)/\mu & \sigma_{12} < -\sigma_c \end{cases}$$

The shear rate is positive for $\sigma_{12} > \sigma_c$ and negative for $\sigma_{12} < -\sigma_c$.

We start by solving for the stress:

$$\frac{\partial \sigma_{12}}{\partial y} = -K \qquad \Longrightarrow \qquad \sigma_{12} = A - Ky$$

for some unknown constant $A$. How will we find $A$?

There is a symmetry in the problem: if we swap the top and bottom walls, we wouldn't expect the flow to change. This means that if we replace $y$ with $-y$ everywhere, the only changes we would expect to see would be changes of sign. Any physical quantity can either be unchanged or exactly reversed[1] but not a mixture of the two. Looking at the form of $\sigma_{12}$, the $K$ term will be reversed but the $A$ term is unchanged: so $A$ must be zero.

We are now working with $\sigma_{12} = -Ky$ over the range $-H \le y \le H$.

If $KH < \sigma_c$, then $|\sigma_{12}| < \sigma_c$ throughout the flow, so $\dot\gamma = 0$ and there is no flow.

If $KH > \sigma_c$, there will be three regions to consider:

$$\begin{array}{llcl} \sigma_{12} > \sigma_c & \text{where} \quad -H < y < -\sigma_c/K & \text{and} & \dot\gamma = (-Ky - \sigma_c)/\mu \\ |\sigma_{12}| < \sigma_c & \text{where} \quad -\sigma_c/K < y < \sigma_c/K & \text{and} & \dot\gamma = 0 \\ \sigma_{12} < -\sigma_c & \text{where} \quad \sigma_c/K < y < H & \text{and} & \dot\gamma = (\sigma_c - Ky)/\mu \end{array}$$

We can now integrate up from $y = -H$, where $U = 0$: for $-H < y < -\sigma_c/K$ we have

$$\frac{\mathrm{d}U}{\mathrm{d}y} = -\frac{K}{\mu}y - \frac{\sigma_c}{\mu} \qquad U = -\frac{K}{2\mu}y^2 - \frac{\sigma_c}{\mu}y + C_1$$

and using the condition that $U(-H) = 0$,

$$U = \frac{K}{2\mu}(H^2 - y^2) - \frac{\sigma_c}{\mu}(y + H)$$

Now between $-\sigma_c/K < y < \sigma_c/K$, $\dot\gamma = 0$ so the velocity is constant:

$$U = \frac{K}{2\mu}\left(H - \frac{\sigma_c}{K}\right)^2$$

and finally, between $\sigma_c/K < y < H$, we have

$$\frac{\mathrm{d}U}{\mathrm{d}y} = -\frac{K}{\mu}y + \frac{\sigma_c}{\mu} \qquad U = -\frac{K}{2\mu}y^2 + \frac{\sigma_c}{\mu}y + C_2$$

and matching velocities at $y = \sigma_c/K$ fixes:

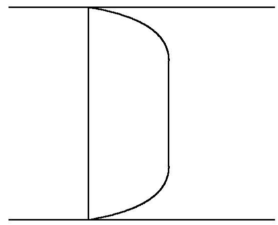
$$U = \frac{K}{2\mu}(H^2 - y^2) + \frac{\sigma_c}{\mu}(y - H).$$

Summarising the velocity profile:

$$U = \frac{1}{2\mu}\left\{ \begin{array}{ll} K(H^2 - y^2) - 2\sigma_c(y + H) & -H < y < -\sigma_c/K \\ K\left(H - (\sigma_c/K)\right)^2 & -\sigma_c/K < y < \sigma_c/K \\ K(H^2 - y^2) + 2\sigma_c(y - H) & \sigma_c/K < y < H \end{array} \right.$$

which looks like this:

[1] depending on whether its definition depended on the $y$-axis



The central region is unyielded and flows in a solid **plug**: this flow profile is called a **plug flow**.

The yield fluid is a good model for fluids like toothpaste. Look at your toothpaste as you squeeze it out of the tube: it comes out more or less as a solid cylinder, but in fact it is lubricated by a thin layer near the walls.

**Exercise 1**: Calculate the Poiseuille flow profile for a power law fluid. What do the flow profiles look like for different values of $n$?

## 2.3 Inconsistent experimental results

In real experiments with polymer fluids, it is almost always observed that the response to the shear rate is not reproducible: if you hold one shear rate for a long time, you may always reach the same stress, but often this stress is not obtained quickly. It takes some time for the fluid to fully adjust to the new flow happening to it: in other words, the fluid has a **memory** of its previous flow history.

The most extreme version of this is an elastic or rubber solid, which always remembers the shape it was to start with. When the stress applied to it is released, it will **relax** back to its original shape.

In terms of shear flows, a linearly elastic solid can be modelled using

$$\sigma = G_0 \gamma(t) = G_0 \int_0^t \dot{\gamma}(s)\,\mathrm{d}s.$$

It is not directly related to the shear rate: it doesn't care how fast it's moving, only how far it has moved.

A standard polymeric fluid won't remember its shape forever; but because its molecules can be stretched by a flow, it will remember what has happened to it until the molecules have had time to relax. It is a cross between a viscous liquid (which forgets instantly) and an elastic solid (which never forgets): a **viscoelastic liquid**. To model a viscoelastic liquid, we really need something that exhibits a decaying **memory**. If we just allow a linear dependence on the flow history, we get the **linear viscoelastic fluid**, which we will see next time.