3   Linear viscoelasticity

A **linear viscoelastic fluid** is a fluid which has a linear relationship between its strain history and its current value of stress:

$$\sigma(t) = \int_{-\infty}^{t} G(t - t')\dot{\gamma}(t') \, \mathrm{d}t'$$

The function $G(t)$ is the relaxation modulus of the fluid. Because a fluid can never remember times in the future, $G(t) = 0$ if $t < 0$.

Physically, you would also expect that more recent strains would be more important than those from longer ago, so in $t > 0$, $G(t)$ should be a decreasing function. There aren't really any other constraints on G.

A few often-used forms for $G(t)$ where $t \geq 0$ are:

$$
\begin{array}{rl}
\text{Single exponential} & G_0 \exp\left[-t/\tau\right] \\
\text{Multi-mode exponential} & G_1 \exp\left[-t/\tau_1\right] + G_2 \exp\left[-t/\tau_2\right] + \cdots \\
\text{Viscous fluid} & \eta\,\delta(t) \\
\text{Linearly elastic solid} & G_0
\end{array}
$$

Let's just check the last two. For the viscous form we have

$$\sigma(t) = \int_{-\infty}^{t} G(t - t')\dot{\gamma}(t') \, \mathrm{d}t' = \int_{-\infty}^{t} \eta\,\delta(t - t')\dot{\gamma}(t') \, \mathrm{d}t' = \eta\dot{\gamma}(t)$$

as we would expect for a Newtonian viscous fluid. For the elastic solid we have

$$\sigma(t) = \int_{-\infty}^{t} G(t - t')\dot{\gamma}(t') \, \mathrm{d}t' = \int_{-\infty}^{t} G_0\dot{\gamma}(t') \, \mathrm{d}t' = G_0 \int_{-\infty}^{t} \dot{\gamma}(t') \, \mathrm{d}t'.$$

The integral on the right is the total strain (or shear) the material has undergone: so this, too, gives the form we expect.

3.1   Creep

Given a sample of material, how would you go about modelling it? Even if you start by assuming it is a linear material (and they all are for small enough strains), how would you calculate $G(t)$?

One way would be to carry out a **step strain** experiment: for shear flow this means you would set up your material between two plates and leave it to settle, so it loses the memory of the flow that put it there. Once it has had time to relax, you shear it through one shear unit (i.e. until the top plate has moved a distance the same as the distance between the plates). Then stop dead. Measure the force required to maintain the plates in position as time passes. The results will look something like this:
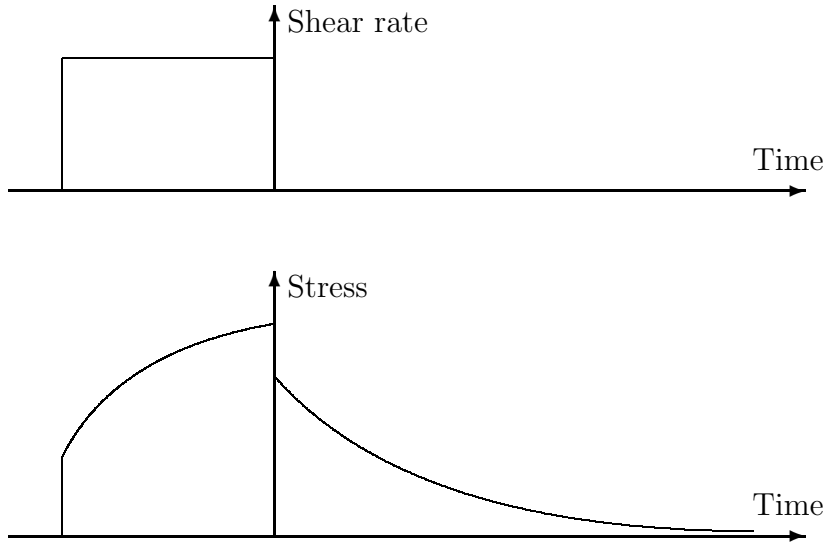
What is the real relationship between the stress function $\sigma(t)$ and the relaxation modulus $G(t)$ in this case?

Suppose the length of time the material is sheared for is T. Then the shear rate during that time must be $1/T$ (to get a total shear of 1):

$$\dot{\gamma}(t') = \begin{cases} 0 & t' < -T \\ 1/T & -T \le t' \le 0 \\ 0 & t' > 0 \end{cases}$$

Then the stress function becomes

$$\sigma(t) = \int_{-\infty}^{t} G(t-t')\dot{\gamma}(t') \, \mathrm{d}t' = \frac{1}{T}\int_{-T}^{0} G(t-t') \, \mathrm{d}t'.$$

Now suppose that we do the shear **very fast** so that T is very small. Then

$$\int_{-T}^{0} G(t-t') \, \mathrm{d}t' \approx TG(t)$$

and so the stress is

$$\sigma(t) \approx G(t).$$

Thus the relaxation modulus is actually the response of the system to an instantaneous unit shear.

3.2   Storage and Loss Moduli

An step shear is very difficult to achieve in practice. Real rheologists, working in industry, are far more likely to carry out an **oscillatory shear** experiment.

The material sample is placed in a **Couette device**, which is essentially a pair of concentric cylinders, one of which is fixed. The material is put in the narrow gap between the cylinders, and the free cylinder is rotated. The flow set up between the two cylinders

is almost simple shear flow (as long as the gap is narrow relative to the radius of the cylinders, and no instabilities occur).

The rotation is set up to be a simple harmonic motion, with shear displacement:

$$\gamma(t) = \alpha \sin(\omega t)$$

where γ is the shear, ω the frequency and α the amplitude. In reality α must be kept small to ensure the material is kept within its linear régime; but if we are dealing with an ideal linear viscoelastic material, α can be any size. Note that the shear rate of the fluid, $\dot{\gamma}(t)$, will be

$$\dot{\gamma}(t) = \alpha \omega \cos(\omega t).$$

Suppose this motion started a long time ago ($t \to -\infty$). Then at time t, the stress profile for a general linear viscoelastic material becomes

$$\sigma(t) = \int_{-\infty}^{t} G(t - t')\dot{\gamma}(t') \, dt' = \int_{-\infty}^{t} G(t - t')\alpha \omega \cos(\omega t') \, dt'$$

We can transform this integral by changing variables using $s = t - t'$:

$$\sigma(t) = \int_{-\infty}^{t} G(t - t')\alpha \omega \cos(\omega t') \, dt' = \alpha \omega \int_{0}^{\infty} G(s) \cos(\omega(t - s)) \, ds$$

and now if we write $\cos(\omega(t - s)) = \Re[\exp[i\omega(t - s)]]$ we get:

$$
\begin{aligned}
\sigma(t) &= \alpha \omega \int_{0}^{\infty} G(s)\Re[\exp[i\omega(t - s)]] \, ds = \alpha \omega \Re\left[\int_{0}^{\infty} G(s) \exp[i\omega(t - s)] \, ds\right] \\
&= \alpha \omega \Re\left[\exp[i\omega t] \int_{0}^{\infty} G(s) \exp[-i\omega s] \, ds\right]
\end{aligned}
$$

and the integral on the right is now a one-sided Fourier transform. Since it has no dependence on t, it is just a complex number. By convention we define the **complex shear modulus**, G^*, as:

$$G^* = i\omega \int_{0}^{\infty} G(s) \exp[-i\omega s] \, ds,$$

and its real and imaginary parts:

$$G^* = G' + iG''$$

are called the **storage modulus** G' and the **loss modulus** G''.

This gives

$$
\begin{aligned}
\sigma(t) &= \alpha \Re[\exp[i\omega t](-iG^*)] = \alpha \Re[(\cos(\omega t) + i\sin(\omega t))(G'' - iG')] \\
&= \alpha[G' \sin(\omega t) + G'' \cos(\omega t)] = G'\gamma(t) + \frac{G''}{\omega}\dot{\gamma}(t).
\end{aligned}
$$

Now a purely viscous fluid would give a response

$$\sigma(t) = \eta\dot{\gamma}(t) = \eta\alpha\omega\cos{(\omega t)}$$

and a purely elastic solid would give

$$\sigma(t) = G_0\gamma(t) = G_0\alpha\sin{(\omega t)}.$$

We can see that if $G'' = 0$ then G' takes the place of the ordinary elastic shear modulus G_0: hence it is called the *storage* modulus, because it measures the material's ability to store elastic energy. Similarly, the modulus G'' is related to the viscosity or *dissipation* of energy: in other words, the energy which is lost.

Since the rôle of the usual Newtonian viscosity η is taken by G''/ω, it is also common to define

$$\eta' = \frac{G''}{\omega}$$

as the effective viscosity; however, the storage and loss moduli G' and G'' are the most common measures of linear rheology.

Let us check a few values:

$$\begin{aligned}
G(t) &= \eta\delta(t) & G^*(\omega) &= i\omega\eta \\
G(t) &= G_0 & G^*(\omega) &= G_0 \text{ NB: By observation \textbf{not} integration} \\
G(t) &= G_0\exp{[-t/\tau]} & G^*(\omega) &= \frac{i\omega G_0\tau}{(1 + i\omega\tau)} = \frac{G_0(\omega^2\tau^2 + i\omega\tau)}{1 + \omega^2\tau^2}
\end{aligned}$$

Let us look more at the single-relaxation-time model. At slow speeds $\omega\tau \ll 1$ we have
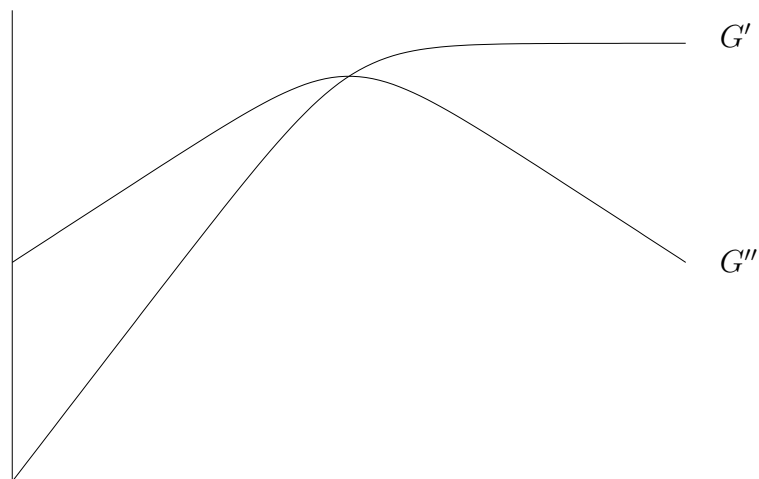
$$G^* \approx iG_0\omega\tau$$

so the material looks like a viscous fluid with viscosity $G_0\tau$. At high speeds $\omega\tau \gg 1$, we have instead

$$G^* \approx G_0$$

and the material looks like an elastic solid with modulus G_0.

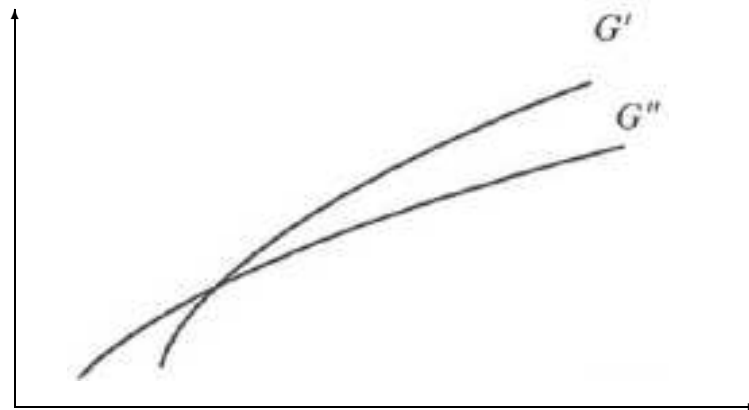If we plot the two moduli, G' and G'' against ω the graph looks like this:

Frequency, ω

14

The point where the two graphs cross is given by:

$$
\begin{aligned}
G' &= G'' \\
\frac{G_0\omega^2\tau^2}{1+\omega^2\tau^2} &= \frac{G_0\omega\tau}{1+\omega^2\tau^2} \\
\omega\tau &= 1.
\end{aligned}
$$

A real fluid has more complex dynamics:

Typical dynamic data for an elastic liquid

G'

G''

Frequency, ω

but a first engineering approximation often used is to take the value of ω_c at which the two curves cross, and use $\tau = \omega_c^{-1}$ as the relaxation time of the fluid. Alternatively, a series of relaxation modes is used to fit the curves as well as possible.