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Nanjing lectures
Lecture 2: Linear viscoelasticity

1 Isothermal viscoelasticity

Many materials and fluid have properties that are neither completely solid-like or completely fluid-like. These materials are sometimes called soft materials (due to the soft modulus) or complex fluids (due to a complex molecular structure). Examples are polymer melts, polymer solutions or colloidal systems. From the mechanical point of view the materials are called viscoelastic. The complete theory of viscoelastic materials in arbitrary deformations is not yet fully explored. However in small deformations close to equilibrium, the exists a framework called the theory of linear viscoelasticity (LVE). This framework will be described in this chapter. The theory of LVE is frequently used to connect mechanical properties with molecular structure. For simplicity we limit consideration to shear deformations.

Stress relaxation after single step strain

We consider a shear deformation of magnitude γ that occurs at time $t = 0$. By this we mean, that particles are displaced by the amounts:

$$\begin{aligned} u_x &= x(t) - x(0) = \gamma y(0) \\ u_y &= y(t) - y(0) = 0 \\ u_z &= z(t) - z(0) = 0 \end{aligned} \tag{1}$$

If no other deformation takes place one would expect for an ideal solid material that the shear stress at times $t > 0$ is given by

$$\sigma_{xy} = G\gamma(t, 0)$$

where G is the shear modulus. However for viscoelastic materials, the shear stress may decay with time. This is called stress relaxation. The stress may decay to zero (in which case we have a fluid) or to some finite value (in which case we have a solid). For both fluids and solids we define the stress relaxation modulus $G(t)$ by

$$\sigma_{xy}(t) = G(t)\gamma(t, 0) \tag{2}$$

Fluids are characterized by by $G(t) \to 0$ for $t \to \infty$, while $G(t) \to G_0 > 0$ for $t \to \infty$ for solids.
For future reference we assume that the strain may occur not necessarily at time $t = 0$ but at some arbitrary time t_1. Then the deformation may be visualized as in Figure 1, In this illustration we have introduced the function

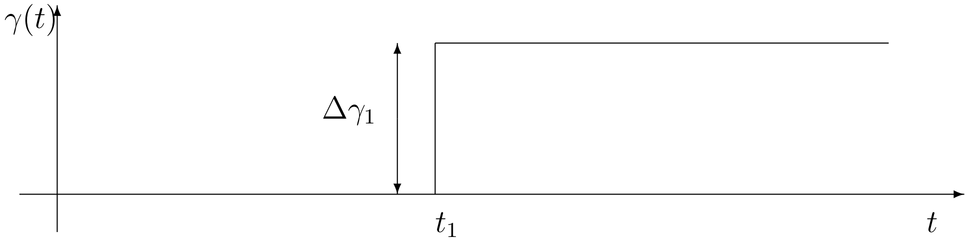

Figure 1: Single step strain at time t_1

$\gamma(t)$ that increases by the amount $\Delta\gamma_1$ at time t_1. Then the stress at time $t > t_1$ is given by

$$\sigma_{xy}(t) = G(t - t_1)\Delta\gamma_1 \tag{3}$$

Stress relaxation after double step strain
Now consider the deformation history illustrated in Figure 2. Here there the total deformation as described by $\gamma(t)$ is composed of two step deformations of magnitudes $\Delta\gamma_1$ and $\Delta\gamma_2$ at two past events at times t_1 and t_2 where $t_1 < t_2$.

By the principle of linear superposition we assume that the shear stress at time $t > t_2$ is given by

$$\begin{aligned} \sigma_{xy}(t) &= G(t - t_1)\Delta\gamma_1 + G(t - t_2)\Delta\gamma_2 \qquad (4) \\ &= \sum_{i=1}^{2} G(t - t_i)\Delta\gamma_i \qquad (5) \end{aligned}$$

The continuous limit
Now consider an more general deformation history composed of many small

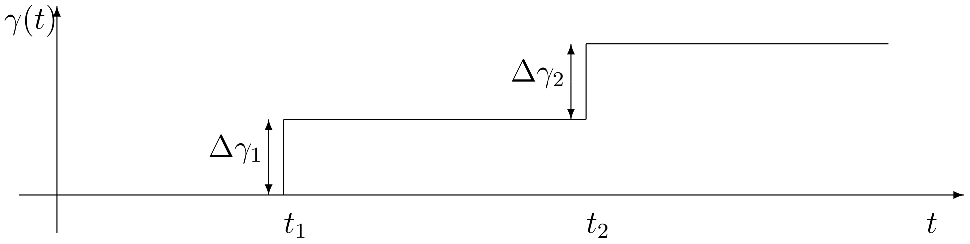

Figure 2: Single step strain at time t_1

incremental deformations $\Delta\gamma_i$ where $i = 1, 2, \cdots N$. The stress then becomes

$$\sigma_{xy}(t) = \sum_{i=1}^{N} G(t - t_i)\Delta\gamma_i \tag{6}$$

In the continuous limit we write this summation as an integral

$$\sigma_{xy}(t) = \int_{t'=-\infty}^{t} G(t - t')d\gamma(t') \tag{7}$$

The lower limit of the integral has for convenience been set to $-\infty$. Equation 7 is the general linear viscoelastic model. It is frequently written in another form in terms of the rate-of-deformation

$$\dot{\gamma}(t') = \frac{d\gamma}{dt}(t')$$

Since $d\gamma$ in Eq. 7 is evaluated at time t' we obtain

$$\sigma_{xy}(t) = \int_{t'=-\infty}^{t} G(t - t')\dot{\gamma}_{xy}(t')dt' \tag{8}$$

We have attached the subscript x and y to the rate-of-deformation in order to clarify that we consider shear deformations. Equation 8 may be used to compute the stress in any viscoelastic material in small deformations. It is called the general linear viscoelastic model.

Small amplitude shear oscillation

By far the most frequently use method to characterize viscoelastic materials in the linear limit is to consider an oscillatory shear deformation of the form

$$\gamma_{xy}(t) = \gamma_0 \sin(\omega t)$$

Here γ_0 is an amplitude of deformation and ω the frequency. The corresponding rate-of-deformation becomes

$$\dot{\gamma}_{xy}(t) = \gamma_0 \omega \cos(\omega t) \tag{9}$$

By insertion of Eq 9 into Eq 8 it may be shown that

$$\sigma_{xy}(t) = G'(\omega)\gamma_0 \sin(\omega t) + G''(\omega)\gamma_0 \cos(\omega t)$$

where

$$\begin{aligned} G'(\omega) &= \omega \int_0^\infty G(s) \sin(\omega s) ds \\ G''(\omega) &= \omega \int_0^\infty G(s) \cos(\omega s) ds \end{aligned}$$

The function $G'(\omega)$ is called the storage modulus, while the function $G''(\omega)$ is called the loss modulus. The definition above are sometimes written in the form

$$G^*(\omega) = G'(\omega) + iG''(\omega) = i\omega \int_0^\infty G(s) e^{-i\omega s} ds \tag{10}$$

where G^* is called the complex modulus.
Two ideal materials are contained in this model:

- **Ideal solid:** A solid of modulus G corresponds to $G' = G$ and $G'' = 0$.
- **Viscous fluid:** A viscous fluid of viscosity η corresponds to $G' = 0$ and $G'' = \eta\omega$.

A **Maxwell fluid** is given by

$$G(t) = \frac{\eta}{\lambda} \exp(-t/\lambda) \tag{11}$$

Here η and λ are two parameters of the Maxwell model (a viscosity in and a time-constant). Show that the viscoelastic moduli for the Maxwell are

$$G'(\omega) = \frac{\eta\lambda\omega^2}{1 + (\lambda\omega)^2} \tag{12}$$

$$G''(\omega) = \frac{\eta\omega}{1 + (\lambda\omega)^2} \tag{13}$$

Problem 1: Find the behavior of G' and G'' for large and small frequency. Make a qualitative drawing of the moduli as function of frequency ω.

Problem 2: Show that one may write the stress as

$$\sigma_{xy}(t) = A(\omega)\gamma_0 \sin(\omega t + \delta)$$

where $A(\omega) = \sqrt{G'^2 + G''^2}$ is related to the stress amplitude, and $\tan\delta = G''/G'$ is called the loss tangent.

Problem 3: Wave transmission in a semi-infinite viscoelastic material

A viscoelastic liquid is located in the region $0 \leq y < \infty$. The velocity v_x at the surface $y = 0$ is $v_x = V\cos(\omega t)$, where V is the amplitude of the velocity and ω is the frequency. Find the velocity distribution in the material when transients have died out. Hint: From DPL Table B.1 show that

$$\rho\frac{\partial v_x}{\partial t} = \int_{-\infty}^{t} G(t-t')\frac{\partial^2 v_x}{\partial y^2}dt' \tag{14}$$

Now assume that after transients have died out the velocity will be of the form:

$$v_x(y,t) = \Re\{v_0(y)e^{\omega t}\} \tag{15}$$

Then show that

$$\frac{d^2 v_0}{dy^2} + \omega^2\frac{\rho}{G^*}v_0 = 0 \tag{16}$$

For simplicity at this stage specialize to a fully elastic material $G^* = G$ to show that the wave is transmitted undamped with wave speed $v_s = \sqrt{G/\rho}$. For a general viscoelastic material let

$$\omega^2\frac{\rho}{G^*} = -(\alpha + i\beta)^2 \tag{17}$$

to show that

$$v_x(y,t) = Ve^{-\alpha y}\cos(\omega t - \beta y) \tag{18}$$

It is now clear that α is the attenuation of the velocity wave and ω/β is the wave speed. The expressions for α and β in terms of G^* may be found in Dynamics of Polymeric Liquids, vol. I, Example 5.4.1.

2 Non-isothermal viscoelasticity

A key concept in non-isothermal viscoelasticity is the time shift factor a_T that describes the way molecular relaxation changes with the temperature. Imagine a step shear experiment, say of shear magnitude γ_0 after which the shear stress relaxes with time. The shear relaxation modulus $G(t)$ is defined such that

$$\sigma_{xy}(t) = \gamma_0 G(t)$$

For the present purpose we may let the relaxation modulus be described by a series of exponentially relaxing modes:

$$G(t) = \sum_i G_i \exp(-t/\lambda_i) \tag{19}$$

Here the λ_i are a set of time-constants for stress relaxation and the G_i are a set of moduli. In the non-isothermal situation these constants are functions of temperature, so that we may write:

$$G(T, t) = \sum_i G_i(T) \exp(-t/\lambda_i(T)) \tag{20}$$

Now the *time shift factor* a_T and the *modulus shift factor* b_T are defined such that:

$$G(T, t) = b_T G(T_r, t_r) \ \text{ for } \quad t_r = \frac{t}{a_T} \tag{21}$$

The modulus shift factor is given in agreement with rubber elasticity as

$$b_T = \frac{\rho T}{\rho_r T_r} \tag{22}$$

For incompressible materials such as polymer melts one may simply use $b_T = T/T_r$. In fact the modulus shift factor is close to unity and is often simply taken to be unity.

The time shift factor is the ratio of the time constants at the given temperature and the time constants at the reference temperature:

$$a_T = \frac{\lambda_i(T)}{\lambda_i(T_r)} \tag{23}$$

This means that the time shift factor is the ratio of the time to reach a particular relative decrease in stress (from time 0) at the given temperature compared to the time t_r it would take at the reference temperature T_r.

WLF equation for time shift factor

The shift factors may be determined from experimental data taken at a series of temperatures by shifting the data vertically and horizontally. However it is convenient to have a functional expression for a_T (corresponding to Eq. 22 for b_T) both for data-fitting but also for predictive purposes. A very important equation for this purpose is the WLF equation named after Williams, Landel and Ferry who applied this equation to polymers in 1955. While the WLF equation is semi-empirical, it may be rationalized in terms of the concept of free volume in polymers as described in the following.

First of all, the fractional free volume f is taken to be linearly increasing with temperature:

$$f = \alpha(T - T_\infty) \tag{24}$$

Here α is a thermal expansion coefficient for the fractional free volume. Also T_∞ is the extrapolated temperature at which the free volume would be zero. Sometimes T_∞ is taken to about 50K below the glass transition temperature (the constant c_2 in the WLF equation below).

Secondly, the free volume is considered important for the flow of polymers. If there is no free volume, the polymer can not flow since there are no empty sites available that polymer segments can move to. This corresponds to an infinite viscosity. Conversely if there is a lot of free volume, it is easier for the polymer to flow, hence the viscosity decreases with increasing free volume. The Doolittle equation captures this behavior as follows:

$$\eta = \eta_0 \exp(B/f) \tag{25}$$

for constants B and η_0.

We know from basic linear viscoelasticity (Session 10-11, 2005 notes) that the viscosity η is related to the relaxation modulus by:

$$\eta = \sum_i G_i \lambda_i \tag{26}$$

Therefore we have that

$$\frac{\eta(T)}{\eta(T_r)} = a_T b_T \tag{27}$$

In the following we let $b_T = 1$. Moreover we choose a reference temperature

T_r with viscosity η_r. Then according to the above:

$$
\begin{aligned}
a_T = \frac{\eta}{\eta_r} &= \exp B \left(\frac{1}{f} - \frac{1}{f_r} \right) && (28) \\
&= \exp \frac{B}{f_r} \left(\frac{f_r - f}{f} \right) && (29) \\
&= \exp \left(-\frac{B}{f_r} \frac{T - T_r}{T - T_\infty} \right) && (30)
\end{aligned}
$$

Hence the logarithm to the base 10 of a_T becomes:

$$\log a_T = \frac{\ln a_T}{\ln 10} = -\left(\frac{B}{f_r \ln 10} \right) \frac{T - T_r}{T - T_\infty} \tag{31}$$

This gives the Williams, Landel, Ferry (WLF) equation in the form:

$$\log a_T = \frac{-c_1 (T - T_r)}{c_2 + T - T_r} \tag{32}$$

where $c_1 = B/f_r \ln 10$ and $c_2 = T_r - T_\infty$. Sample values of c_1 and c_2 may be found in the literature. Often the reference temperature is taken to be the glass temperature, T_g, and the two other constants are then approximated by $c_1 = B/f_g \ln 10 \approx 17.44$ and $c_2 = T_g - T_\infty \approx 51.6\text{K}$.

3 Exercises

3.1 Temperature shift

You are given a sample of polystyrene with viscosity $\eta = 7.88\text{MPa}\,\text{s}$ at 130°C. Estimate the temperature increase needed to decrease the viscosity by a factor of 10. The glass transition temperature is 130°C. A rough estimate will suffice, however you should state any approximations you make.

3.2 Differential Maxwell model

The Maxwell model may be formulated both in integral and differential form. To go from the integral form to the differential form it is convenient to use the Leibnitz formula for differentiating an integral which works as follows: Given a function $f(x,t)$ that depends two variables x and t and the integral:

$$I(t) = \int_{\alpha(t)}^{\beta(t)} f(x,t)dx \tag{33}$$

Then the derivative of $I(t)$ is given as follows:

$$\frac{d}{dt}\int_{\alpha(t)}^{\beta(t)} f(x,t)dx = \int_{\alpha(t)}^{\beta(t)} \frac{\partial}{\partial t} f(x,t)dx + \left(f(\beta,t)\frac{d\beta}{dt} - f(\alpha,t)\frac{d\alpha}{dt} \right) \tag{34}$$

Use this relation to show that the integral form of the Maxwell model in Eq. 11 may be formulated as follows:

$$\boldsymbol{\sigma} + \lambda \frac{d}{dt}\boldsymbol{\sigma} = \eta\dot{\boldsymbol{\gamma}} \tag{35}$$

Use this formulation to discuss how the material will react under the following two limits:

- High Deborah number flow: ($\lambda \frac{d}{dt}\boldsymbol{\sigma} \gg \boldsymbol{\sigma}$)
- Low Deborah number flow: ($\lambda \frac{d}{dt}\boldsymbol{\sigma} \ll \boldsymbol{\sigma}$)

Finally use the two limits to describe the "spring and dashpot" mechanical analog model.

3.3 Meaning of loss modulus

Consider a solid cube of dimensions $l_0 \times l_0 \times l_0$ described in a rectangular coordinate system (x, y, z). The box undergoes a deformation such that a given particle located at (x_0, y_0, z_0) at time $t = 0$ is located at $x(t), y(t), z(t)$ at time t:

$$\begin{aligned} x(t) &= x_0 + u_x(t) \quad (36)\\ y(t) &= y_0 + u_y(t) \quad (37)\\ z(t) &= z_0 + u_z(t) \quad (38) \end{aligned}$$

The functions u_x, u_y and u_z are called displacements. The infinitesimal strain tensor is defined as derivatives of the displacements (see Fall 2005, Problem

session 8, Eq. (2)).
In this problem consider specifically a small amplitude oscillatory deformation in which

$$\begin{aligned} u_x(t) &= y_0\gamma_0 \sin(\omega t) && (39)\\ u_y(t) &= 0 && (40)\\ u_z(t) &= 0 && (41) \end{aligned}$$

In this situation the shear stress $\sigma_{xy}(t)$ is given by

$$\sigma_{xy}(t) = \gamma_0(G'(\omega)\sin\omega t + G''(\omega)\cos\omega t) \qquad (42)$$

Make a drawing of the cube at time 0 and at some later time t. Show that the force on the top plate is given by

$$f_x = l_0^2\sigma_{xy}$$

In a time interval dt the top plate is displaced by the amount dx. Show that the two are related by

$$dx = l_0\gamma_0\omega\cos(\omega t)dt \qquad (43)$$

Now consider the work needed for this displacement. By definition this is given by $dW = f_x dx$. Let the work per unit volume be $dw = dW/l_0^3$. Show that the work per unit volume for an entire cycle is

$$w = \pi\gamma_0^2 G''(\omega) \qquad (44)$$

Finally show that the work per unit volume per unit time is

$$P = \frac{\omega}{2}\gamma_0^2 G''(\omega) \qquad (45)$$

Relate the answer to the naming of G' and G''.

3.4 Creep compliance

Given that

$$\begin{aligned} G' &= \omega\int_0^\infty G(s)\sin\omega s ds && (46)\\ G'' &= \omega\int_0^\infty G(s)\cos\omega s ds && (47) \end{aligned}$$

Show that for small ω:

$$G' = \int_0^\infty sG(s)ds\,\omega^2 + O(\omega^4) \tag{48}$$

$$G'' = \int_0^\infty G(s)ds\,\omega + O(\omega^3) \tag{49}$$

Define the equilibrium compliance J_{eq} with reference to Figure 5.3-3 in DPL such that

$$\gamma_0 = J_{eq}\tau_0 \tag{50}$$

Then show that for small frequencies:

$$G' = \omega^2 \int_0^\infty sG(s)ds + \cdots = \omega^2 \eta_0^2 J_{eq} + \cdots \tag{51}$$

$$G'' = \omega \int_0^\infty G(s)ds + \cdots = \omega\eta_0 + \cdots \tag{52}$$

(See Example 5.3-6 in DPL (result in Eq. 5.3-42))

3.5

Make a qualitative drawing of G' and G'' as function of frequency for a polymer melt and a crosslinked network.

- Do you think that rubber for automobile tyres should have $G' \gg G''$ or $G' \ll G''$. Discuss.
- How do you think the moduli for un-crosslinked polyisoprene would change if the molecules are crosslinked? Is there some way of adjusting the modulus by changing the density of crosslinks?

CHAPTER 5

THE GENERAL LINEAR VISCOELASTIC FLUID

In Chapter 4 we discussed an expression for the stress tensor that is particularly useful for engineers who must solve problems involving large-deformation flows, both without and with heat transfer. In such problems, as we have seen, the predominant feature of the rheological behavior of the macromolecular fluids is their shear-rate-dependent viscosity.

Although the generalized Newtonian fluid has proven to be of great value in solving problems of engineering interest, its use is strictly speaking limited to steady-state shearing flows. It is generally inappropriate for the description of unsteady flow phenomena, where the elastic response of the polymeric fluid becomes important. In this chapter we introduce a constitutive equation that can describe some of the time-dependent motions of macromolecular fluids, albeit only the restricted class of flows with very small displacement gradients.

Why do we spend a whole chapter on such a restricted class of flows? There are several very good reasons for studying this subject, known as "linear viscoelasticity": (1) polymer chemists have evolved several experiments that have enabled them to interrelate structure with the linear mechanical responses; (2) the material functions measured in these experiments have proven useful for characterization and quality control; and (3) some background in linear viscoelasticity is helpful to proceed to the subject of "nonlinear viscoelasticity", which is treated in Chapters 6 through 9 of this volume. It is this last reason that we shall consider the principal motivation here. For the reader interested in the experiments of linear viscoelasticity, their analysis and molecular interpretations, we recommend the outstanding treatise of Ferry,[1] where a wealth of information and an extensive bibliography are to be found.

We begin in §5.1 by comparing and contrasting Newton's "law" of viscosity and Hooke's "law" of elasticity, the two limiting idealizations for viscous liquids and elastic solids. Then in §5.2 we show how Maxwell combined the ideas of viscosity and elasticity to arrive at a simple equation for a "viscoelastic fluid"; after that we show how Maxwell's idea can be extended to obtain the constitutive equation for the *general linear viscoelastic fluid*, which has been widely used for many years to characterize the small-displacement behavior of polymeric liquids. It is this constitutive equation that is the primary subject of study in this chapter.

In §5.3 we use the constitutive equation to obtain expressions for some of the time-dependent material functions defined in Chapter 3. In the highly idealized flows discussed in this section, the velocity distribution is prescribed, and the shear stress is obtained directly from the constitutive equation. By contrast, in §5.4 we solve some linear viscoelastic flow problems that require the simultaneous consideration of the equations of change and the

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[1] J. D. Ferry, *Viscoelastic Properties of Polymers*, 3rd ed., Wiley, New York (1980).

constitutive equation. In the final section, §5.5, we point out the limitations of the constitutive equation studied in this chapter.

§5.1 NEWTONIAN FLUIDS AND HOOKEAN SOLIDS

In Chapter 1 a discussion of the constitutive equation for the Newtonian fluid was given. Here we introduce the constitutive equation for the Hookean solid and point out some similarities and differences between these two "classical" constitutive equations. We do this by considering the two idealized experiments shown in Fig. 5.1-1.

The first experiment (Fig. 5.1-1*a*) is the *shearing motion of a Newtonian fluid* between two planes, the upper one of which moves with a velocity $V(t)$. We assume that the viscosity μ is so large and that the interplane distance B is so small that the velocity distribution $v_x(y, t)$ is a linear function of y. Then the velocity distribution is:

$$v_x(y, t) = \frac{V(t)}{B}\, y = \dot{\gamma}_{yx}(t) y \qquad (5.1\text{-}1)$$

in which $\dot{\gamma}_{yx}$ is the yx-component of the *rate-of-strain tensor*

$$\dot{\boldsymbol{\gamma}} = \nabla \boldsymbol{v} + (\nabla \boldsymbol{v})^\dagger \qquad \left(\text{or } \dot{\gamma}_{ij} = \frac{\partial}{\partial x_i} v_j + \frac{\partial}{\partial x_j} v_i\right) \qquad (5.1\text{-}2)$$

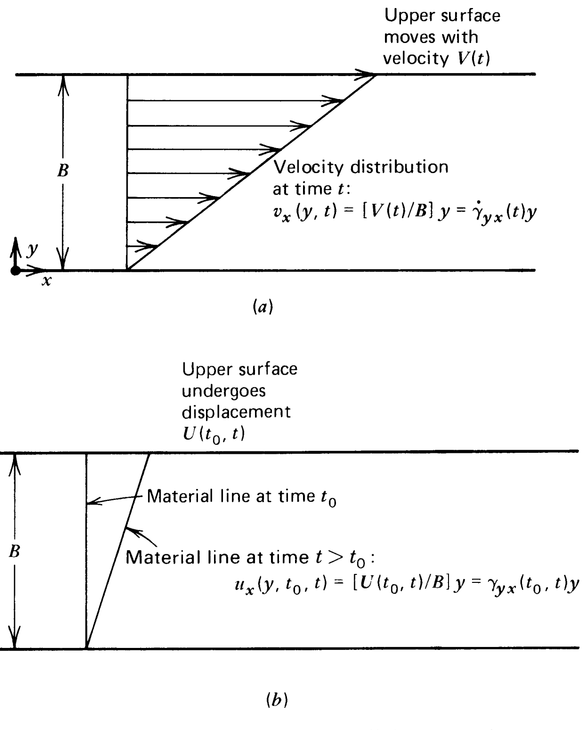

FIGURE 5.1-1. Material being sheared between two parallel planes, the upper one of which moves as a function of time. (*a*) The *velocity* profile for unsteady shear flow of a Newtonian fluid. (*b*) The *displacement* profile for the unsteady shearing motion of a Hookean solid. Note: at time t_0 the solid is at rest with no shear stress.

The shear stress is then given for a Newtonian fluid by

$$\tau_{yx}(t) = -\mu \frac{\partial v_x}{\partial y} = -\mu \dot{\gamma}_{yx}(t) \tag{5.1-3}$$

That is, the stress at time t is proportional to the velocity gradient *at the same time* t.

The second experiment (Fig 5.1-1*b*) is the *shearing motion of a Hookean solid* between two parallel planes. At some time t_0 the solid is in an isotropic stress state with no imposed external stresses other than atmospheric pressure. Then the upper plane undergoes an infinitesimal displacement $U(t_0, t)$. We assume that the displacement of the material in the gap is a linear function of the distance y above the lower plane, so that the displacement at any position is:

$$u_x(y, t_0, t) = \frac{U(t_0, t)}{B} y = \gamma_{yx}(t_0, t) y \tag{5.1-4}$$

Here $\gamma_{yx}(t_0, t)$ is the yx-component of the *infinitesimal strain tensor*, which is defined in terms of the *displacement gradient tensor* $\nabla \boldsymbol{u}$ as follows

$$\boldsymbol{\gamma} = \nabla \boldsymbol{u} + (\nabla \boldsymbol{u})^\dagger \qquad \left(\text{or } \gamma_{ij} = \frac{\partial}{\partial x_i} u_j + \frac{\partial}{\partial x_j} u_i\right) \tag{5.1-5}$$

Note that the strain tensor depends on two times and that $\gamma_{yx}(t_0, t_0) = 0$. Then the shear stress for a Hookean solid is given by

$$\tau_{yx}(t) = -G \frac{\partial u_x}{\partial y} = -G \gamma_{yx}(t_0, t) \tag{5.1-6}$$

where G is the elastic modulus; that is, the stress at time t is proportional to the strain at time t, referred to the isotropic stress state at time t_0. The Hookean solid "remembers" where it was at time t_0, in contrast to the Newtonian fluid which has no memory of past events.

The two discussions above are parallel except for two points: (i) in the discussion of solids we must specify a reference time with respect to which strain is measured; strain tensors always depend on two times, and we establish the convention that the first variable listed denotes the reference state; (ii) the stress relation, Eq. 5.1-6, is restricted to infinitesimally small displacement gradients $\partial u_j/\partial x_i$; for large displacement gradients Eq. 5.1-6 ceases to be valid, whereas Eq. 5.1-3 is valid for flow with arbitrarily large displacement gradients. The restriction that is placed on Eq. 5.1-6 has some important implications to be discussed in §5.5.

The kinematic quantities in the two experiments are related to one another. The velocities and displacements are related by:

$$\begin{cases} v_x(y, t) = \dfrac{\partial}{\partial t} u_x(y, t_0, t) & \text{(5.1-7a)} \\[2ex] u_x(y, t_0, t) = \displaystyle\int_{t_0}^{t} v_x(y, t')dt' & \text{(5.1-7b)} \end{cases}$$

Similarly the components of the rate-of-strain and infinitesimal strain tensors are related by:

$$\begin{cases} \dot{\gamma}_{yx}(t) = \dfrac{\partial}{\partial t}\gamma_{yx}(t_0, t) & \text{(5.1-8a)} \\[2ex] \gamma_{yx}(t_0, t) = \displaystyle\int_{t_0}^{t} \dot{\gamma}_{yx}(t')dt' & \text{(5.1-8b)} \end{cases}$$

We also point out that for the infinitesimal strain tensor

$$\gamma_{yx}(t_0, t) = \gamma_{yx}(t_0, t^*) + \gamma_{yx}(t^*, t) \tag{5.1-9}$$

That is, the infinitesimal strains are additive. These relations are referred to later.

§5.2 LINEAR VISCOELASTIC FLUIDS

In Chapter 2 it was found that *polymeric liquids are viscoelastic.* For example, the photographs of §2.5e show how a polymeric liquid recoils because of its elastic properties. Furthermore in §§3.4 and 3.5 several kinds of transient-response experiments were described in which elastic behavior was evident. For example, delayed stress relaxation after cessation of steady flow is an indication of fluid elasticity as is the large recovery following elongational flow. The main thrust of this chapter is to show how the ideas of viscosity and elasticity may be combined into a single constitutive equation that can describe these various elastic effects.

a. The Maxwell Model

The first attempt to obtain a viscoelastic constitutive equation appears to have been that of Maxwell,[1] who over a century ago developed a theory for viscoelasticity, because he thought that gases might be viscoelastic. He proposed that fluids with both viscosity and elasticity could be described by:

$$\tau_{yx} + \frac{\mu}{G}\frac{\partial \tau_{yx}}{\partial t} = -\mu\dot{\gamma}_{yx} \tag{5.2-1}$$

For steady-state motions this equation simplifies to the Newtonian fluid with viscosity μ. For sudden changes in stress, the time derivative term dominates the left side of the equation, and then integration with respect to time (with the help of Eq. 5.1-8b) gives the Hookean solid with elastic modulus G. This is the simplest expression for the shear stress for a fluid that is both viscous and elastic.

Since Hooke's law is valid only for infinitesimal displacement gradients, it seems reasonable to expect that Maxwell's equation would be subject to the same restriction. We must keep in mind that Newton's and Hooke's "laws" were both proposed empirically; these linear relations were put forward as modest but reasonable suggestions. Subsequent experimentation, coupled with calculations based on the equations of change and the

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[1] J. C. Maxwell, *Phil. Trans. Roy. Soc.*, **A157**, 49–88 (1867).

proposed constitutive equations, showed that the linear relations of Newton and Hooke are indeed useful for a wide range of materials. However, it has long been recognized that these "classical" constitutive equations do have their limitations. Many materials require more complex mathematical descriptions.

Maxwell's proposal was also empirical. Although it turns out that its range of validity is somewhat limited, certain nonlinear generalizations of the Maxwell constitutive equation have proven to be very useful in polymer fluid dynamics, and we will eventually present and evaluate these generalizations in Chapters 7 and 8.

We now look at some alternative forms of the Maxwell model. First we generalize Eq. 5.2-1 to arbitrary, small displacement flows by putting the equation in tensor form. In addition, we adopt new symbols for the constants, since this notation will be more in keeping with subsequent developments: we replace μ by η_0 (the zero-shear-rate viscosity) and μ/G by λ_1 (a time constant, often called the "relaxation time"). Then the *Maxwell model* is:

$$\boxed{\boldsymbol{\tau} + \lambda_1 \frac{\partial}{\partial t}\boldsymbol{\tau} = -\eta_0 \dot{\boldsymbol{\gamma}}} \tag{5.2-2}$$

This is more complicated than Newton's and Hooke's equations since this is a differential equation for $\boldsymbol{\tau}$.

For many purposes it would be preferable to solve Eq. 5.2-2 for the stress tensor. That is easily done by recognizing that Eq. 5.2-2 is a first-order, linear equation[2] for $\boldsymbol{\tau}$ as a function of t, which can be integrated at once to give:

$$\boldsymbol{\tau}(t) = e^{-t/\lambda_1}\left[\int\left(-\frac{\eta_0}{\lambda_1}\dot{\boldsymbol{\gamma}}(t)\right)e^{t/\lambda_1}\,dt + \boldsymbol{\kappa}\right] \tag{5.2-3}$$

We now affix limits on the integral and write:

$$\boldsymbol{\tau}(t) = -\frac{\int_{-\infty}^{t}(\eta_0/\lambda_1)\dot{\boldsymbol{\gamma}}(t')e^{t'/\lambda_1}\,dt'}{e^{t/\lambda_1}} + \boldsymbol{\kappa}e^{-t/\lambda_1} \tag{5.2-4}$$

where primes have been added to t's in the integrand in order to avoid confusion; the choice of $-\infty$ as the lower limit is arbitrary—some other choice would result in a different value for the integration constant $\boldsymbol{\kappa}$. If we prescribe that the stress in the fluid is finite at $t = -\infty$, we must choose $\boldsymbol{\kappa}$ to be zero. But we must also check the first term on the right side of Eq. 5.2-4, since both numerator and denominator tend to zero as t goes to $-\infty$. When we use L'Hôpital's rule we get:

$$\lim_{t\to-\infty}\boldsymbol{\tau}(t) = \lim_{t\to-\infty} -\frac{(\eta_0/\lambda_1)\dot{\boldsymbol{\gamma}}(t)e^{t/\lambda_1}}{(1/\lambda_1)e^{t/\lambda_1}} = -\eta_0\dot{\boldsymbol{\gamma}}(-\infty) \tag{5.2-5}$$

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[2] Recall that the differential equation $dy/dx + P(x)y = Q(x)$ has the solution:

$$y = e^{-\int P(x)dx}\left[\int Q(x)e^{+\int P(x)dx}\,dx + K\right] \tag{5.2-2a}$$

where K is a constant of integration.

Therefore, if $\dot{\gamma}(-\infty)$ is finite, the stress is also finite at $t = -\infty$. Consequently, the Maxwell constitutive equation can be written in the form

$$\boxed{\tau(t) = -\int_{-\infty}^{t} \left\{\frac{\eta_0}{\lambda_1} e^{-(t-t')/\lambda_1}\right\} \dot{\gamma}(t')dt'} \tag{5.2-6}$$

The quantity within the braces is called the *relaxation modulus* for the Maxwell fluid. When written in this form, the Maxwell model says that the stress at the present time t depends on the rate of strain at time t as well as on the rate of strain at all past times t', with a weighting factor (the relaxation modulus) that decays exponentially as one goes backwards in time. Thus we see that this form of the Maxwell equation contains the notion of a "fading memory". The fluid remembers very well what it has experienced in the very recent past but has only a hazy recollection of events in the distant past. Sometimes we say that the stress at time t depends on the "history" of the rate of strain for all past times $-\infty < t' \leq t$.

Next, we want to put the Maxwell model into still another form by doing an integration by parts using Eq. 5.1-8b. However, in using the latter equation we have to specify a reference time (there called t_0). For fluids there is no unique reference state t_0 to use in describing strains, so that *for fluids it is customary to measure the strain at a past time t' relative to the configuration of the fluid at the present time t.* Hence, for fluids we generalize Eq. 5.1-8 thus:

$$\frac{\partial \gamma}{\partial t'} = \dot{\gamma}(t') \quad \text{and} \quad \gamma(t, t') = \int_{t}^{t'} \dot{\gamma}(t'')dt'' \tag{5.2-7}$$

These relations are valid for any flow pattern as long as the displacement gradients are infinitesimally small. Now integration by parts of Eq. 5.2-6 gives

$$\boxed{\tau(t) = +\int_{-\infty}^{t} \left\{\frac{\eta_0}{\lambda_1^2} e^{-(t-t')/\lambda_1}\right\} \gamma(t, t')dt'} \tag{5.2-8}$$

The quantity within the braces is called the *memory function* for the Maxwell fluid. In this form the Maxwell model states that the stress at the present time t depends on the history of the strain for all past times $-\infty < t' \leq t$. The exponential factor in the integrand describes the fading memory.

All three forms of Maxwell's constitutive equation—Eqs. 5.2-2, 6, and 8—are equivalent provided that $\dot{\gamma}$ is finite at $t = -\infty$ and the displacement gradients are infinitesimally small. Equation 5.2-6 looks like a modified Newton's law and Eq. 5.2-8 like a modified Hooke's law. Maxwell's equation played a key role in the development of linear viscoelasticity, and as we shall see in Chapters 7 and 8, it has also been taken as the starting point for the development of nonlinear viscoelastic models. It is therefore important that the material presented in this section be thoroughly understood before continuing.

The two-constant Maxwell model was found to be inadequate for describing linear viscoelastic data. Therefore, through the years more elaborate equations were suggested; let us look at a few of these.

b. The Jeffreys Model

The Maxwell equation in Eq. 5.2-2 is a linear relation between τ and $\dot{\gamma}$. But one can easily invent other linear relations. For example, we can include the time derivative of $\dot{\gamma}$ and get the constitutive equation

$$\tau + \lambda_1 \frac{\partial \tau}{\partial t} = -\eta_0 \left(\dot{\gamma} + \lambda_2 \frac{\partial \dot{\gamma}}{\partial t} \right) \tag{5.2-9}$$

which is known as the *Jeffreys model*. This equation, containing two time constants λ_1 and λ_2 (the "relaxation time" and the "retardation time", respectively), was proposed for the study of wave propagation in the earth's mantle.[3]

The Jeffreys model can also be put into integral form. When Eq. 5.2-9 is integrated as a first-order differential equation, using the initial condition that τ be finite at $t = -\infty$, we find that (if $\dot{\gamma}$ and $\partial\dot{\gamma}/\partial t$ are both finite at $t = -\infty$)

$$\tau(t) = -\int_{-\infty}^{t} \frac{\eta_0}{\lambda_1}\left(1 - \frac{\lambda_2}{\lambda_1}\right) e^{-(t-t')/\lambda_1} \dot{\gamma}(t')dt' - \frac{\eta_0 \lambda_2}{\lambda_1} \dot{\gamma}(t) \tag{5.2-10}$$

From this form of the constitutive equation it can be seen that $\lambda_2 < \lambda_1$; otherwise, in stress relaxation after cessation of steady shear flow τ_{yx} would have the wrong sign.

We would like to put Eq. 5.2-10 into a form that is the same as Eq. 5.2-6, so that we can identify the relaxation modulus. This is done by using the Dirac delta function:[4]

$$\tau(t) = -\int_{-\infty}^{t} \left\{ \frac{\eta_0}{\lambda_1}\left(1 - \frac{\lambda_2}{\lambda_1}\right) e^{-(t-t')/\lambda_1} + 2\frac{\eta_0 \lambda_2}{\lambda_1} \delta(t - t') \right\} \dot{\gamma}(t')dt' \tag{5.2-11}$$

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[3] H. Jeffreys, *The Earth*, Cambridge University Press (1929), p. 265.

[4] P. A. M. Dirac, *The Principles of Quantum Mechanics*, 3rd ed., Oxford University Press (1947), pp. 58–61; M. J. Lighthill, *Fourier Analysis and Generalised Functions*, Cambridge University Press (1964), p. 17. Here we use the definition that:

$$\delta(x) = \lim_{n\to\infty} \sqrt{\frac{n}{\pi}}\, e^{-nx^2} \tag{5.2-10a}$$

From this it follows that:

$$\int_{-a}^{a} f(x)\delta(x)dx = 2\int_{0}^{a} f(x)\delta(x)dx = f(0) \tag{5.2-10b}$$

$$\int_{-a}^{a} f(x)\delta'(x)dx = -f'(0) \tag{5.2-10c}$$

in which $a > 0$, and the prime denotes differentiation with respect to x. Note particularly the occurrence of the factor of 2 in Eq. 5.2-10b when the integral is over the region from 0 to a. This explains the occurrence of the factors of 2 in the δ-function terms in Eqs. 5.2-11 and 12.

The quantity enclosed in the braces is the relaxation modulus for the Jeffreys model. Integration by parts then gives:

$$\tau(t) = +\int_{-\infty}^{t} \left\{\frac{\eta_0}{\lambda_1^2}\left(1 - \frac{\lambda_2}{\lambda_1}\right)e^{-(t-t')/\lambda_1} + \frac{2\eta_0\lambda_2}{\lambda_1}\frac{\partial}{\partial t'}\delta(t-t')\right\}\gamma(t, t')dt' \qquad (5.2\text{-}12)$$

The quantity in braces here is the memory function. The Jeffreys model is also used in Chapters 7 and 8 as a point of departure for proposing nonlinear viscoelastic models. Clearly more time derivatives could be added to the left and right sides of Eq. 5.2-9 thereby generating many more linear relations between τ and $\dot{\gamma}$ (see Problem 5C.1).

c. The Generalized Maxwell Model

Another way to generalize the Maxwell model is to construct a "superposition" of Maxwell models. We can write Eq. 5.2-2 for the kth partial stress τ_k using constants λ_k and η_k; then we get the total stress by summing the partial stresses. This constitutive equation can be integrated to give equations similar in form to Eqs. 5.2-6 and 5.2-8. To summarize, we have for the *generalized Maxwell model*:

$$\tau(t) = \sum_{k=1}^{\infty} \tau_k(t); \qquad \tau_k + \lambda_k \frac{\partial}{\partial t}\tau_k = -\eta_k\dot{\gamma} \qquad (5.2\text{-}13)$$

$$\tau(t) = -\int_{-\infty}^{t} \left\{\sum_{k=1}^{\infty} \frac{\eta_k}{\lambda_k} e^{-(t-t')/\lambda_k}\right\}\dot{\gamma}(t')dt' \qquad (5.2\text{-}14)$$

$$\tau(t) = +\int_{-\infty}^{t} \left\{\sum_{k=1}^{\infty} \frac{\eta_k}{\lambda_k^2} e^{-(t-t')/\lambda_k}\right\}\gamma(t, t')dt' \qquad (5.2\text{-}15)$$

We adopt the convention that $\lambda_1 > \lambda_2 > \lambda_3 \ldots$. This model contains infinitely many constants λ_k and η_k, thus allowing for a spectrum of relaxation times and viscosities. (Of course, one can set $\lambda_k = 0$ and $\eta_k = 0$ for k greater than some finite number K.) For some purposes it may be desirable to reduce the total number of parameters to three by use of the following empiricisms:[5]

$$\eta_k = \eta_0 \frac{\lambda_k}{\sum_k \lambda_k}; \quad \lambda_k = \frac{\lambda}{k^\alpha} \qquad (5.2\text{-}16,17)$$

where η_0 is the zero-shear-rate viscosity, λ is a time constant, and α is a dimensionless quantity, which describes the slope of η' versus ω on a log-log plot at high ω (for large ω, $\eta' \propto \omega^{(1/\alpha)-1}$). The relations above are not entirely empirical. The *Rouse molecular theory for dilute polymer solutions*[6] gives very nearly Eqs. 5.2-16,17 with $\alpha = 2$; in this theory the polymer molecules are modeled as freely jointed chains made up of beads connected linearly by Hookean springs. Experimental data for concentrated polymer situations and polymer melts seem to be portrayed reasonably well by Eqs. 5.2-16,17 with α in the range 2 to 4. On the other hand, the *Doi and Edwards molecular theory for polymer melts*[7] suggests an

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[5] T. W. Spriggs, *Chem. Eng. Sci.*, **20**, 931-940 (1965).

[6] P. E. Rouse, Jr., *J. Chem. Phys.*, **21**, 1272-1280 (1953); see also Chapter 15.

[7] M. Doi and S. F. Edwards, *J. Chem. Soc. Faraday Trans. II*, **74**, 1789-1832 (1978); **75**, 38-54 (1979); see also Chapter 19.

empiricism with λ_k replaced by λ_k^2 in Eq. 5.2-16, and k taking on odd values only. Still other possibilities for describing $G(s)$ are the three-parameter empiricism in Problem 5B.2 and the finite sum of exponentials used in Example 5.3-7.

d. The General Linear Viscoelastic Model

When we compare Eq. 5.2-6 (for the Maxwell model), Eq. 5.2-11 (for the Jeffreys model), and Eq. 5.2-14 (for the generalized Maxwell model) we find that they are all of the same form: an integral over all past times of a relaxation modulus multiplied by a rate-of-deformation tensor. The only physical ideas that have been included in these models of varying degrees of complexity are those of viscosity and elasticity. An equation that includes all of these models, and many more of course, is the *general linear viscoelastic model*, which may be written in either of two equivalent forms:

$$\boxed{\tau = -\int_{-\infty}^{t} G(t-t')\dot{\gamma}(t')dt'} \qquad (5.2\text{-}18)$$

$$\boxed{\tau = +\int_{-\infty}^{t} M(t-t')\gamma(t,t')dt'} \qquad (5.2\text{-}19)$$

in which $G(t-t')$ is the *relaxation modulus* and $M(t-t') = \partial G(t-t')/\partial t'$ is the *memory function*. This model is the starting point for most of the development in this chapter and will be referred to in connection with nonlinear constitutive equations and molecular theories. Of course, for getting quantitative answers to problems we shall have to use some specific expression for $G(t-t')$, such as the expression between braces in Eqs. 5.2-6, 11, or 14. It should be kept in mind that Eqs. 5.2-18 and 19 are equivalent only if $\dot{\gamma}$ is finite at $t = -\infty$ and if the displacement gradients are infinitesimally small.

Equations 5.2-18 and 19 have an important feature: the integrands consist of the product of two functions, *the first depending on the nature of the fluid* (since material parameters, such as η_k and λ_k, appear in $G(t-t')$ or $M(t-t')$) and *the second depending on the nature of the flow* (since the kinematics is described by $\dot{\gamma}(t')$ or $\gamma(t,t')$). In Chapter 8 we discuss nonlinear viscoelastic constitutive equations that have this same "factorized" structure.

In Eqs. 5.2-18 and 19 the functions $G(s)$ and $M(s)$ are positive functions which decrease monotonically to zero as $s = t - t'$ goes to infinity. Such viscoelastic fluids are often said to have "fading memory". If $G(s)$ has the form given by the generalized Maxwell model, the duration of the memory is governed by the largest relaxation time, λ_{max}. Although Eqs. 5.2-18 and 19 are strictly applicable only to flows with infinitesimally small displacement gradients, we can in some instances apply them outside this region because of the rapidly fading memory. For example, in steady shear flow with shear rate $\dot{\gamma} \ll 1/\lambda_{\text{max}}$, the memory of the large strains is negligible and does not contribute to the stress.

The general linear viscoelastic model in Eq. 5.2-18 may also be derived by more formal arguments.[8] One assumes that the stress at time t resulting from a step strain at time t' is linear in the strain and multiplied by a decaying function of the elapsed time $t - t'$. An actual flow history may then be regarded as made up of a number of small step strains. By *Boltzmann's superposition principle*[9] it is assumed that the stress contributions from the

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[8] A. C. Pipkin, *Lectures on Viscoelasticity Theory*, Springer, New York (1972), pp. 7–12.

[9] L. Boltzmann, *Pogg. Ann. Phys.*, 7, 624–654 (1876).

individual small step strains at past times t' may be added to give the stress at time t. This results in the integral in Eq. 5.2-18. In the linear limit considered in this chapter the Boltzmann superposition principle seems reasonable inasmuch as coupling effects between two past deformations must be of second order in the applied deformations and hence negligible.

Equation 5.2-18 (or Eq. 5.2-19) is generally accepted as the correct starting point for the description of the rheology of incompressible viscoelastic fluids for small-displacement-gradient motions. In Chapters 7, 8, and 9 large-displacement-gradient flows are considered and equations more general than Eq. 5.2-18 are given.

§5.3 LINEAR VISCOELASTIC RHEOLOGICAL PROPERTIES

In the foregoing section it was shown that the elementary concepts of viscosity and elasticity can be combined in a number of ways to develop equations of increasing complexity, culminating with Eq. 5.2-18, which is the most general equation of linear viscoelasticity. In this section we illustrate the use of this equation by obtaining expressions for the time-dependent material functions in terms of the relaxation modulus $G(t - t')$.

Before discussing the transient-response phenomena, we mention briefly how Eq. 5.2-18 simplifies for steady-state shear flow. When the fluid has been flowing between parallel plates for a long time with constant velocity gradient $\dot{\gamma}_{yx}$ (where $\lambda_{\max}|\dot{\gamma}_{yz}| \ll 1$), then Eq. 5.2-18 becomes

$$\begin{aligned} \tau_{yx} &= -\int_{-\infty}^{t} G(t - t')\dot{\gamma}_{yx}\,dt' \\ &= -\left[\int_{0}^{\infty} G(s)ds\right]\dot{\gamma}_{yx} \\ &\equiv -\eta_0\dot{\gamma}_{yx} \end{aligned} \tag{5.3-1}$$

Here the change of variables $s = t - t'$ has been made. We see that the viscosity is just equal to the integral over the relaxation modulus. The subscript "0" on η_0 indicates that this is the zero-shear-rate viscosity. In the theory of linear viscoelasticity we are able to obtain the viscosity only in this limit of vanishingly small velocity gradients.

EXAMPLE 5.3-1 Small-Amplitude Oscillatory Motion

A polymeric fluid is located in the space between two parallel plates, the upper one of which is made to oscillate with frequency ω in its own plane in the x-direction. As shown in Figure 3.4-1b the velocity profile is assumed to be instantaneously linear,[1] which is a good assumption for highly viscous materials in very narrow slits (cf. Problem 1D.1). Therefore the velocity gradient is changing with time in the following way:

$$\dot{\gamma}_{yx}(t) = \dot{\gamma}_{yx}^{0} \cos \omega t \tag{5.3-2}$$

in which we take $\dot{\gamma}_{yx}^{0}$ to be real and positive. In order to satisfy the small-displacement-gradient restriction on Eq. 5.2-18, we require that $\dot{\gamma}_{yx}^{0}/\omega \ll 1$. Find the time-dependent shear stress τ_{yx} that is needed to maintain this oscillatory motion, and obtain expressions for the real and imaginary parts of the complex viscosity.

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[1] Inertial effects have been considered by K. Walters and R. A. Kemp in R. E. Whetton and R. W. Whorlow, eds., *Polymer Systems*, Macmillan, London (1968), pp. 237–250, and *Rheol. Acta*, 7, 1–8 (1968).

SOLUTION Substitution of the velocity gradient of Eq. 5.3-2 into the constitutive equation in Eq. 5.2-18 gives:

$$\begin{aligned}\tau_{yx} &= -\int_{-\infty}^{t} G(t-t')\dot{\gamma}_{xy}^{0}\cos\omega t'\,dt' \\ &= -\dot{\gamma}_{yx}^{0}\int_{0}^{\infty} G(s)\cos\omega(t-s)\,ds \\ &= -\left[\int_{0}^{\infty} G(s)\cos\omega s\,ds\right]\dot{\gamma}_{yx}^{0}\cos\omega t \\ &\quad-\left[\int_{0}^{\infty} G(s)\sin\omega s\,ds\right]\dot{\gamma}_{yx}^{0}\sin\omega t\end{aligned} \tag{5.3-3}$$

Comparison of this result with the definitions of $\eta'(\omega)$ and $\eta''(\omega)$ in Eq. 3.4-3b shows that:

$$\eta'(\omega) = \int_{0}^{\infty} G(s)\cos\omega s\,ds \tag{5.3-4}$$

$$\eta''(\omega) = \int_{0}^{\infty} G(s)\sin\omega s\,ds \tag{5.3-5}$$

or, alternatively, we may write the results in terms of the "complex viscosity"

$$\eta^* = \eta' - i\eta'' = \int_{0}^{\infty} G(s)e^{-i\omega s}\,ds \tag{5.3-6}$$

The relaxation modulus $G(s)$ can be eliminated between Eqs. 5.3-4 and 5 to give the Kramers-Kronig relations (see Problem 5D.2), which interrelate $\eta'(\omega)$ and $\eta''(\omega)$. Finally, we note for future reference that:

$$\lim_{\omega\to 0}\frac{\eta''(\omega)/\omega}{\eta'(\omega)} = \frac{\int_0^\infty G(s)s\,ds}{\int_0^\infty G(s)\,ds} \tag{5.3-7}$$

We shall find as we go through this section that several other limiting quantities are also equal to the same ratio of integrals.

Let us now see what the expressions for $\eta'(\omega)$ and $\eta''(\omega)$ look like for the particular choice of relaxation modulus given by the generalized Maxwell model (quantity in braces in Eq. 5.2-14)

$$\eta'(\omega) = \sum_{k=1}^{\infty}\frac{\eta_k}{1+(\lambda_k\omega)^2} \tag{5.3-8}$$

$$\frac{\eta''(\omega)}{\omega} = \sum_{k=1}^{\infty}\frac{\eta_k\lambda_k}{1+(\lambda_k\omega)^2} \tag{5.3-9}$$

If, in addition, we introduce the expressions for η_k and λ_k given in Eqs. 5.2-16 and 17, these results become

$$\frac{\eta'}{\eta_0} = \frac{1}{\zeta(\alpha)}\sum_{k=1}^{\infty}\frac{k^{\alpha}}{k^{2\alpha}+(\lambda\omega)^2} \tag{5.3-10}$$

$$\frac{\eta''}{\eta_0} = \frac{\lambda\omega}{\zeta(\alpha)}\sum_{k=1}^{\infty}\frac{1}{k^{2\alpha}+(\lambda\omega)^2} \tag{5.3-11}$$

in which $\zeta(\alpha)$ is the Riemann zeta function.[2] These expressions are not particularly appropriate for computation of the functions $\eta'(\omega)$ and $\eta''(\omega)$. Instead we have available[3] an alternative pair of expressions useful for low frequencies ($\omega \ll \lambda^{-1}$)

$$\frac{\eta'}{\eta_0} = 1 - \left[\frac{(\lambda\omega)^2}{\zeta(\alpha)} \sum_{k=1}^{\infty} \frac{1}{k^{\alpha}(k^{2\alpha} + (\lambda\omega)^2)}\right] \tag{5.3-12}$$

$$\frac{\eta''}{\eta_0} = \lambda\omega\left[\frac{\zeta(2\alpha)}{\zeta(\alpha)} - \frac{(\lambda\omega)^2}{\zeta(\alpha)} \sum_{k=1}^{\infty} \frac{1}{k^{2\alpha}(k^{2\alpha} + (\lambda\omega)^2)}\right] \tag{5.3-13}$$

and another pair of asymptotic expressions that is excellent for high frequencies ($\omega \gg \lambda^{-1}$)

$$\frac{\eta'}{\eta_0} \sim \frac{1}{\zeta(\alpha)}\left[\frac{\pi(\lambda\omega)^{(1/\alpha)-1}}{2\alpha \sin((\alpha + 1)\pi/2\alpha)}\right] \tag{5.3-14}$$

$$\frac{\eta''}{\eta_0} \sim \frac{1}{\zeta(\alpha)}\left[\frac{\pi(\lambda\omega)^{(1/\alpha)-1}}{2\alpha \sin(\pi/2\alpha)} - \frac{(\lambda\omega)^{-1}}{2}\right] \tag{5.3-15}$$

These large-frequency expressions are obtained by using the Euler–Maclaurin expansion to convert the sums into integrals (see Problem 5B.5). Equations 5.3-10 and 11 (and their low- and high-frequency equivalents) are useful for curve-fitting data for the small-amplitude oscillatory experiment. In addition, in Example 5.3-7 it is shown how η_k and λ_k can be chosen so that Eqs. 5.3-8 and 9 accurately fit experimental data for η' and η''.

We conclude this illustrative example by reminding the reader that for a Newtonian fluid η' is just a constant (the viscosity), and that η'' is zero; that is, for the Newtonian fluid the shear stress is in phase with the velocity gradient.

EXAMPLE 5.3-2 Stress Relaxation after a Sudden Shearing Displacement

The purpose of this example is to show why the function $G(t - t')$ is called the "relaxation modulus". A polymeric liquid is at rest in the region between two parallel plates for time $t < t_0$. At time $t = t_0$ the upper plate is instantaneously moved slightly in the x-direction, as shown in Fig. 3.4-1e. Find the expression for the shear stress at time $t > t_0$, for a sudden shear strain $\gamma_0 \ll 1$.

SOLUTION To solve this problem we first imagine that the displacement actually occurs during the finite time interval from $t_0 - \varepsilon$ to t_0, and then later we let ε go to zero. That is, the yx-components of the infinitesimal strain tensor and of the rate-of-strain tensor are as shown in Fig. 5.3-1.

For the displacement occurring in the finite time interval ε, Eq. 5.2-18 becomes (for $t > t_0$)

$$\begin{aligned} \tau_{yx}(t) &= -\int_{-\infty}^{t_0-\varepsilon} G(t - t')\dot{\gamma}_{yx}(t')dt' - \int_{t_0-\varepsilon}^{t_0} G(t - t')\dot{\gamma}_{yx}(t')dt' - \int_{t_0}^{t} G(t - t')\dot{\gamma}_{yx}(t')dt' \\ &= -\frac{\gamma_0}{\varepsilon}\int_{t_0-\varepsilon}^{t_0} G(t - t')dt' \end{aligned} \tag{5.3-16}$$

---

[2] The Riemann zeta function is defined as:

$$\zeta(\alpha) = \sum_{k=1}^{\infty} k^{-\alpha}, \qquad \alpha > 1 \tag{5.3-11a}$$

a few sample values being $\zeta(2) = \pi^2/6$, $\zeta(4) = \pi^4/90$, $\zeta(6) = \pi^6/945$ (see M. Abramowitz and I. A. Stegun, eds., *Handbook of Mathematical Functions*, Nat. Bur. Stds. Appl. Math. Series No. 55, U.S. Govt. Ptg. Off., Washington, D.C. (1964), p. 807).

[3] T. W. Spriggs, *Chem. Eng. Sci.* **20**, 931–940 (1965).

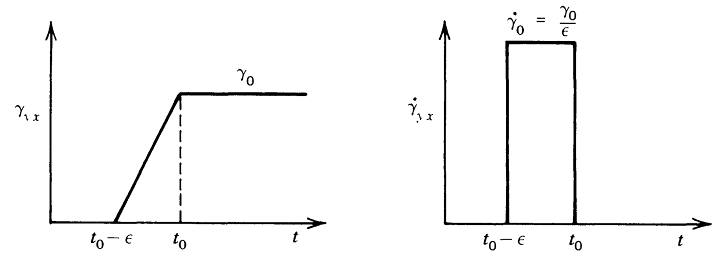

FIGURE 5.3-1. Time-dependent behavior of γ_{yx} and $\dot{\gamma}_{yx}$ in the sudden shear strain stress-relaxation experiment.

since the velocity gradient is zero except during the middle time interval. Now we take the limit as ε approaches zero using L'Hôpital's rule:

$$\begin{aligned}\tau_{yx}(t) &= \lim_{\varepsilon \to 0}(-\gamma_0)\left[\frac{\dfrac{d}{d\varepsilon}\displaystyle\int_{t_0-\varepsilon}^{t_0} G(t-t')dt'}{\dfrac{d}{d\varepsilon}\varepsilon}\right] \\ &= -\gamma_0 G(t - t_0) \end{aligned} \tag{5.3-17}$$

Thus the function $G(t - t_0)$ describes the way in which the shear stress relaxes after the sudden shearing displacement. The top curve in either Fig. 3.4-15 or Fig. 3.4-16a gives a direct experimental measurement of G. If we insert the expression for the relaxation modulus for the generalized Maxwell fluid, we see that the stress dies out as a sum of exponentials. Keep in mind that for a Newtonian fluid there is no delayed stress relaxation—the stress drops instantly to zero as soon as the motion stops.

EXAMPLE 5.3-3 Stress Relaxation after Cessation of Steady Shear Flow

Next we turn our attention to the stress relaxation that occurs in a different type of experiment. Here we envisage a steady shear flow with shear rate $\dot{\gamma}_0 \ll 1/\lambda_{\max}$, for time $t < 0$ (see Fig. 3.4-1d). Then at time $t = 0$ the flow is stopped suddenly. It is desired to describe the way in which the stress decays with time after the cessation of the steady shear flow. It is also desired to find the area under the $\eta^-(t)$ curve.

SOLUTION For this experiment Eq. 5.2-18 gives for $t < 0$ and $t > 0$

$$\tau_{yx}(t < 0) = -\eta_0 \dot{\gamma}_0 = -\dot{\gamma}_0 \int_{-\infty}^{t} G(t - t')dt' \tag{5.3-18}$$

$$\tau_{yx}(t > 0) = -\eta^- \dot{\gamma}_0 = -\dot{\gamma}_0 \int_{-\infty}^{0} G(t - t')dt' \tag{5.3-19}$$

We now take the ratio of the above two expressions and then integrate it from $t = 0$ to $t = \infty$. This gives for the area under the stress-relaxation curve

$$\begin{aligned}\int_0^\infty \frac{\eta^-(t)}{\eta_0}dt &= \int_0^\infty \frac{\int_{-\infty}^0 G(t-t')dt'}{\int_{-\infty}^t G(t-t')dt'}dt \\ &= \frac{\int_0^\infty \int_t^\infty G(s)ds\,dt}{\int_0^\infty G(s)ds} \\ &= \frac{\int_0^\infty \int_0^s G(s)dt\,ds}{\int_0^\infty G(s)ds} \\ &= \frac{\int_0^\infty sG(s)ds}{\int_0^\infty G(s)ds} \end{aligned} \tag{5.3-20}$$

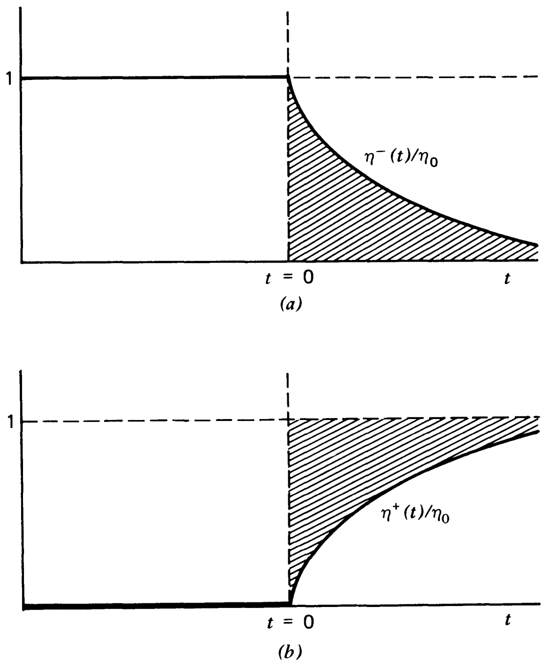

FIGURE 5.3-2. Integrals evaluated in Examples 5.3-3 and 4. (*a*) Integral in Eq. 5.3-20 for stress relaxation is given by the shaded area; (*b*) integral in Eq. 5.3-24 for stress growth is given by the shaded area.

In going from the second to the third line, we interchanged the order of integration so that one integration could be performed. See Fig. 5.3-2*a* for the graphical interpretation of this integral.

Note further that if we use the relaxation modulus for the generalized Maxwell model, then we find

$$\frac{\eta^-}{\eta_0} = \frac{\sum_k \eta_k e^{-t/\lambda_k}}{\sum_k \eta_k} \tag{5.3-21}$$

This result describes the top curve of the set of curves in Fig. 3.4-11, that is, the limiting curve for vanishingly small $\dot{\gamma}_0$. The linear theory cannot describe the dependence of the lower curves on $\dot{\gamma}_0$. To describe those curves we need a nonlinear viscoelastic theory, such as one of those described in Chapters 7 and 8.

EXAMPLE 5.3-4 Stress Growth at Inception of Steady Shear Flow

The next flow situation we examine is that shown in Fig. 3.4-1c where a fluid at rest is suddenly made to undergo steady-state shear flow after $t = 0$. Let the velocity gradient for $t > 0$ be $\dot{\gamma}_0$, where $\lambda_{\max}\dot{\gamma}_0 \ll 1$. Find $\eta^+(t)$ and the area under the curve of $1 - (\eta^+/\eta_0)$.

SOLUTION For this experiment Eq. 5.2-18 gives for $t < 0$ and $t > 0$

$$\tau_{yx}(t < 0) = 0 \tag{5.3-22}$$

$$\begin{aligned} \tau_{yx}(t > 0) &= -\eta^+\dot{\gamma}_0 \\ &= -\dot{\gamma}_0 \int_0^t G(t - t')dt' \end{aligned} \tag{5.3-23}$$

The area between the stress growth curve and its asymptote (see Fig. 5.3-2*b*) is given by

$$\int_0^\infty \left(1 - \frac{\eta^+(t)}{\eta_0}\right) dt = \int_0^\infty \frac{\int_{-\infty}^{0} G(t - t')dt'}{\int_{-\infty}^{t} G(t - t')dt'} dt$$

$$= \frac{\int_0^\infty \int_t^\infty G(s)ds\, dt}{\int_0^\infty G(s)ds}$$

$$= \frac{\int_0^\infty sG(s)ds}{\int_0^\infty G(s)ds} \qquad (5.3\text{-}24)$$

Thus the area between the stress-growth curve and its asymptote is the same as the area between the stress-relaxation curve and its asymptote.

When the relaxation modulus is specified as that for the generalized Maxwell model, then the stress-growth function is

$$\frac{\eta^+}{\eta^0} = \frac{\sum_k \eta_k(1 - e^{-t/\lambda_k})}{\sum_k \eta_k} \qquad (5.3\text{-}25)$$

Note that this curve is monotonically increasing with t; it gives the upper "envelope" in Fig. 3.4-7. We cannot, by means of the linear viscoelastic theory, describe the "overshoot effect" shown in Figs. 3.4-7 and 8.

EXAMPLE 5.3-5 Constrained Recoil after Cessation of Steady Shear Flow

Next we investigate the system depicted in Fig. 3.4-18. Prior to $t = 0$ the fluid between the two parallel plates is undergoing steady shear flow with velocity gradient $\dot{\gamma}_0 \ll 1/\lambda_{\text{max}}$. After $t = 0$, the shear stress is removed so that $\tau_{yx} = 0$. The fluid then recoils and the strain $\gamma_{yx}(0, t)$ can be followed as a function of time. It is presumed that the plate spacing is small enough and the fluid viscous enough that a linear velocity profile is maintained throughout the experiment; that is, inertial effects can be neglected. We wish to find the "ultimate recoil," $\gamma_\infty = \gamma_{yx}(0, t)|_{t=\infty} = \int_0^\infty \dot{\gamma}_{yx}(t)\, dt$ (see Fig. 3.4-18). (*Note*: In this problem it is convenient to take $t = 0$ to be the reference time for the measurement of strain!)

SOLUTION Application of Eq. 5.2-18 to this problem for $t > 0$ gives

$$0 = -\int_{-\infty}^{0} G(t - t')\dot{\gamma}_0\, dt' - \int_0^t G(t - t')\dot{\gamma}_{yx}(t')dt' \qquad (5.3\text{-}26)$$

or, in terms of the variable $s = t - t'$

$$0 = -\dot{\gamma}_0 \int_t^\infty G(s)ds - \int_0^t G(s)\dot{\gamma}_{yx}(t - s)ds \qquad (5.3\text{-}27)$$

Next we integrate over the time from $t = 0$ to $t = \infty$, and this gives

$$0 = -\dot{\gamma}_0 \int_0^\infty \int_t^\infty G(s)ds\, dt - \int_0^\infty \int_0^t G(s)\dot{\gamma}_{yx}(t - s)ds\, dt \qquad (5.3\text{-}28)$$

Next interchange the order of integration to get

$$0 = -\dot{\gamma}_0 \int_0^\infty \left[\int_0^s dt\right] G(s)ds - \int_0^\infty \left[\int_s^\infty \dot{\gamma}_{yx}(t - s)dt\right] G(s)ds \tag{5.3-29}$$

or

$$0 = -\dot{\gamma}_0 \int_0^\infty sG(s)ds - \int_0^\infty \left[\int_0^\infty \dot{\gamma}_{yx}(t')dt'\right] G(s)ds \tag{5.3-30}$$

The quantity in brackets in Eq. 5.3-30 is just the ultimate recoil γ_∞, for which we then have the final result

$$\frac{-\gamma_\infty}{\dot{\gamma}_0} = \frac{\int_0^\infty sG(s)ds}{\int_0^\infty G(s)ds} \tag{5.3-31}$$

Notice that we did not actually solve the integral equation for $\dot{\gamma}_{yx}(t)$ in Eq. 5.3-26, but we were able to extract an integral of the solution, namely the ultimate recoil. This problem can also be solved by using Laplace transforms, as indicated in Problem 5D.1.

A quantity J_e^0, the steady-state compliance, is defined by Eq. 3.4-11

$$\gamma_\infty = J_e^0 \tau_0 \tag{5.3-32}$$

where $\tau_0 = -\eta_0 \dot{\gamma}_0$ is the shear stress prior to recoil. According to the linear viscoelasticity theory, this quantity is given by

$$J_e^0 = \frac{\int_0^\infty sG(s)ds}{[\int_0^\infty G(s)ds]^2} \tag{5.3-33}$$

This is obtained by combining the results in Eqs. 5.3-31 and 32.

EXAMPLE 5.3-6 Creep after Imposition of Constant Shear Stress

The next experiment we consider is that shown in Fig. 3.4-1f. Prior to $t = 0$ the fluid contained between two parallel plates is at rest. After $t = 0$ the fluid sample is subjected to a constant applied shear stress, so that the strain has a response similar to that shown in Fig. 5.3-3. We want to find an expression for the intercept γ_0. Designate the applied shear stress by τ_0 and the ultimate velocity gradient by $\dot{\gamma}_\infty$.

SOLUTION During the creep process, the rate of strain (or velocity gradient) will be (see Eq. 5.1-8a)

$$\dot{\gamma}_{yx} = \frac{d}{dt}\gamma_{yx}(0, t) \tag{5.3-34}$$

and therefore at any time t the strain will be

$$\gamma_{yx}(0, t) = \int_0^t \dot{\gamma}_{yx}(t')dt' \tag{5.3-35}$$

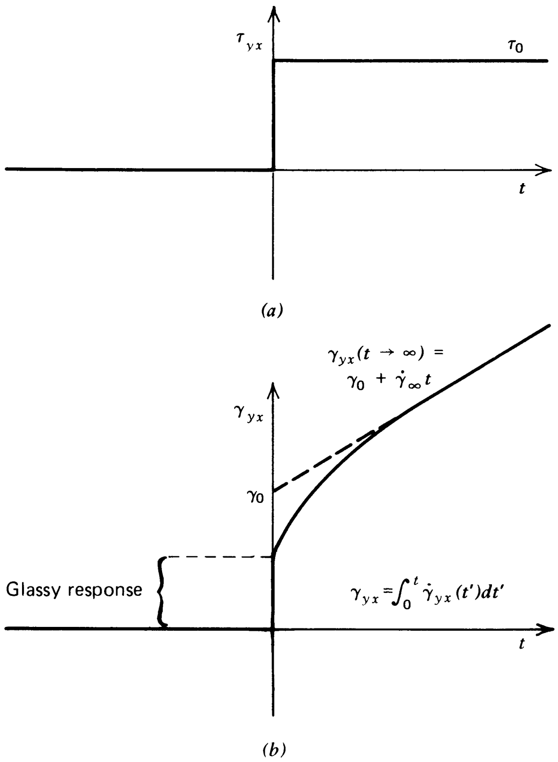

FIGURE 5.3-3. Creep experiment. (*a*) A constant shear stress τ_0 is applied at $t = 0$ and maintained for all times greater than $t = 0$; (*b*) the shear strain measured relative to $t = 0$ in the creep experiment increases with time and approaches an asymptote with slope $\dot{\gamma}_\infty$ for long times.

As in the preceding illustrative example we take $t = 0$ to be the reference time. For very large time, the strain curve will approach the dashed-line asymptote in Fig. 5.3-3, which is given by the equation

$$\lim_{t \to \infty} \gamma_{yx}(0, t) = \gamma_0 + \dot{\gamma}_\infty t \tag{5.3-36}$$

If we write Eq. 5.3-35 for $t \to \infty$ and equate the result to Eq. 5.3-36, then we get for the intercept γ_0

$$\gamma_0 = \int_0^\infty (\dot{\gamma}_{yx}(t') - \dot{\gamma}_\infty)dt' \tag{5.3-37}$$

Now we get an expression for this quantity by using the constitutive equation for the linear viscoelastic fluid.

If we write Eq. 5.2-18 for the creep experiment, we have

$$\tau_0 = -\int_0^t G(t - t')\dot{\gamma}_{yx}(t')dt' \tag{5.3-38}$$

But we can also write Eq. 5.2-18 for the steady-state shear flow with $\tau_{yx} = \tau_0$ and $\dot{\gamma}_{yx} = \dot{\gamma}_\infty$

$$\tau_0 = -\int_{-\infty}^t G(t - t')\dot{\gamma}_\infty \, dt' \tag{5.3-39}$$

We now equate these two expressions for τ_0 to obtain

$$\dot{\gamma}_\infty \int_0^\infty G(s)ds = \int_0^t G(s)\dot{\gamma}_{yx}(t-s)ds \tag{5.3-40}$$

This may be rewritten as

$$\dot{\gamma}_\infty \int_t^\infty G(s)ds = \int_0^t G(s)[\dot{\gamma}_{yx}(t-s) - \dot{\gamma}_\infty]ds \tag{5.3-41}$$

Next we integrate both sides from $t = 0$ to $t = \infty$ and then interchange the order of integration of s and t; this gives finally:

$$\frac{\gamma_0}{\dot{\gamma}_\infty} = \frac{\int_0^\infty sG(s)ds}{\int_0^\infty G(s)ds} \tag{5.3-42}$$

Here again we did not solve the integral equation for the velocity gradient, but extracted from the problem only the integral defined in Eq. 5.3-37.

From the above examples we find that certain quantities measured in different shearing experiments are given by the same ratio of integrals: $\int_0^\infty sG(s)ds/\int_0^\infty G(s)ds$. For future reference we list all of these results in Table 5.3-1. We also include one additional

TABLE 5.3-1

Shear Flow Experiments and "Analogous Quantities"

Experiment	Meaning of Symbols	Measurable Quantity[a] Equal to $\int_0^\infty sG(s)ds/\int_0^\infty G(s)ds$
Small-amplitude oscillatory motion (Eq. 5.3-7)	ω = frequency of oscillation	$\lim_{\omega\to 0} \frac{\eta''/\omega}{\eta'}$
Stress relaxation after cessation of steady shear flow (Eq. 5.3-20)	$\dot{\gamma}_0$ = shear rate before stress relaxation	$\lim_{\dot{\gamma}_0\to 0} \int_0^\infty \frac{\eta^-}{\eta_0} dt$
Stress growth after inception of steady shear flow (Eq. 5.3-24)	$\dot{\gamma}_0$ = shear rate during stress growth	$\lim_{\dot{\gamma}_0\to 0} \int_0^\infty \left(1 - \frac{\eta^+}{\eta_0}\right) dt$
Constrained recoil after cessation of steady shear flow (Eq. 5.3-31)	$\dot{\gamma}_0$ = shear rate before recoil begins	$\lim_{\dot{\gamma}_0\to 0} \frac{-\gamma_\infty}{\dot{\gamma}_0}$
Creep after application of steady shear stress (Eq. 5.3-42)	$\dot{\gamma}_\infty$ = shear rate when steady state is attained	$\lim_{\tau_0\to 0} \frac{\gamma_0}{\dot{\gamma}_\infty}$
Steady-state shear flow (Problem 6B.3)	$\dot{\gamma}$ = shear rate at steady state	$\lim_{\dot{\gamma}\to 0} \frac{\Psi_1}{2\eta}$

[a] Note that this ratio of integrals has the dimensions of time and is often used as the "characteristic time of the fluid" to construct the Deborah number. For the generalized Maxwell model the ratio of integrals is approximately equal to the longest relaxation time λ_1.

entry—that for the normal stress coefficient in steady-state shear flow—for which nonlinear viscoelasticity theory is required; this result will be obtained in Problem 6B.3, but we include it in the table for completeness.[4]

These relations among various experiments have been the subject of considerable experimentation, and they are useful in providing cross-checks of experimental techniques. The establishment of these interrelations requires no assumptions regarding the relaxation modulus. It must be kept in mind that all of the quantities listed in the right column of Table 5.3-1 are limiting values, and for some fluids these may have to be obtained experimentally by tedious extrapolation processes.

EXAMPLE 5.3-7 Determination of the Relaxation Spectrum from Linear Viscoelastic Data

In the preceding six examples we have shown how the response of a viscoelastic fluid to small deformation gradient experiments is related to the relaxation modulus $G(t)$. Here we want to show how this information can be used to find G from linear data. Take the relaxation modulus to be given by the generalized Maxwell model expression in Eq. 5.2-14 and use the storage and loss moduli for low-density polyethylene presented in Fig. 3.4-3 to illustrate the procedure for fitting G. Because time-temperature superposition has been used in obtaining these data, an extremely wide range of frequencies has been covered.

SOLUTION We begin by selecting a set of relaxation times λ_j for the spectrum. The spacing of these is conveniently taken to be decade intervals in order to reduce the amount of computation, but smaller spacings can be taken if more accurate fitting is required. The longest relaxation time λ_j is chosen so that $\lambda_1 \omega_{\min} > 1$, where $\omega_{\min}$ is the lowest frequency for which data are available, unless the zero-frequency region is reached in the experiments. In the latter case take $\lambda_1 \omega_0 \doteq 0.1$ where ω_0 is the critical frequency that marks the end of the zero-frequency regime. Similarly the smallest relaxation time $\lambda_{\min}$ is chosen so that $\lambda_{\min}\omega_{\max} < 1$, where $\omega_{\max}$ is the highest frequency for which data are available. For the low-density polyethylene melt we choose the λ_j to be $10^3, 10^2, \ldots, 10^{-3}, 10^{-4}$ s.

It remains to fit the viscosities η_j for each relaxation time. This is done by minimizing the difference between the measured and predicted moduli at N frequencies ω_j. If we denote the measured properties by G'_j and G''_j and the predicted properties by $G'(\omega_j)$ and $G''(\omega_j)$, then the quantity to be minimized is

$$\sum_{j=1}^{N} \left\{ \left[\frac{G'(\omega_j)}{G'_j} - 1 \right]^2 + \left[\frac{G''(\omega_j)}{G''_j} - 1 \right]^2 \right\}$$

The calculated moduli are obtained from the following truncated forms of Eqs. 5.3-8 and 9:

$$G'(\omega_j) = \sum_{k=1}^{N} \frac{\eta_k \lambda_k \omega_j^2}{1 + (\lambda_k \omega_j)^2} \tag{5.3-43}$$

$$G''(\omega_j) = \sum_{k=1}^{N} \frac{\eta_k \omega_j}{1 + (\lambda_k \omega_j)^2} \tag{5.3-44}$$

For the low-density polyethylene this minimization[5] leads to the values of η_k shown in Table 5.3-2.

It is instructive to look at the spectral decomposition of the dynamic moduli that are predicted by the relaxation spectrum parameters in Table 5.3-2. Figure 5.3-4 shows the contribution of the

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[4] The equality of the entries involving $\eta''/\omega\eta'$ and $\Psi_1/2\eta$ has been verified experimentally by T. Kotaka and K. Osaki, *J. Polym. Sci.*, **C15**, 453–479 (1966).

[5] A. C. Papanastasiou, L. E. Scriven, and C. W. Macosko, *J. Rheol.*, **27**, 387–410 (1983), discuss the use of nonlinear regression methods to determine simultaneously the best set of λ_k and η_k to fit $G(t)$.

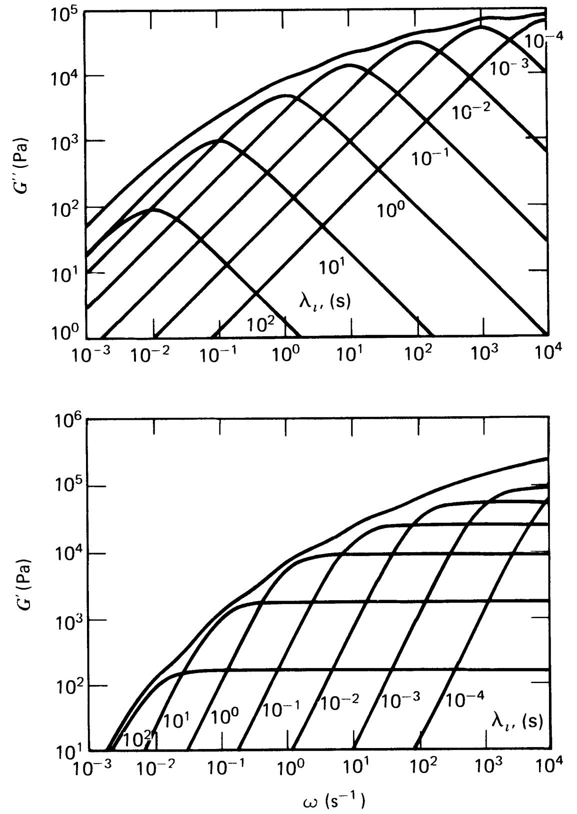

FIGURE 5.3-4. Spectral decomposition of the storage and loss moduli for the low-density polyethylene melt shown in Fig. 3.4-3. The moduli are calculated by Eqs. 5.3-43 and 44 with the λ_k and η_k given in Table 5.3-2. The upper, composite curves are also shown in Fig. 3.4-3 for comparison with the experimental data. Note that the contribution from the longest relaxation time is not shown. [H. M. Laun, *Rheol. Acta*, **17**, 1-15 (1978).]

TABLE 5.3-2

Constants in the Linear Viscoelastic Spectrum for the Low-Density Polyethylene Melt of Fig. 3.4-3

i	$\lambda_i(s)$	η_i (Pa · s)
1	10^3	1.00×10^3
2	10^2	1.80×10^4
3	10^1	1.89×10^4
4	10^0	9.80×10^3
5	10^{-1}	2.67×10^3
6	10^{-2}	5.86×10^2
7	10^{-3}	9.48×10^1
8	10^{-4}	1.29×10^1

Maxwell elements to the moduli. From this figure it is clear that the low-frequency behavior is dominated by the long relaxation times and that the high-frequency response is controlled by the short relaxation times. Once the spectrum is available it is straightforward to calculate other linear viscoelastic material functions by means of the formulas developed in the preceding examples. Predictions made in this way are included in the graphs of low-density polyethylene material functions presented in §§3.4 and 3.5.

§5.4 LINEAR VISCOELASTIC FLOW PROBLEMS

In determining the linear viscoelastic material functions in §5.3, the equations of continuity and motion were not needed because it was assumed there that the velocity profiles are, to a good approximation, linear in properly designed linear viscoelasticity experiments. In this section we turn our attention to the solution of flow problems, in which we are given only the boundary and initial conditions, and we have to solve the equations of continuity and motion along with the constitutive equation.

EXAMPLE 5.4-1 Wave Transmission in a Semi-Infinite Viscoelastic Liquid

A viscoelastic liquid is located in the region $0 \leq y < \infty$. The velocity v_x at the surface $y = 0$ is maintained at $v_x = V \cos \omega t$, where V is the amplitude of the velocity and ω is the frequency. Find the velocity distribution $v_x(y, t)$ throughout the medium, after the initial transients have died out. For the analogous Newtonian fluid problem see Problem 1D.1.

SOLUTION We postulate that the velocity profile has the form $v_x = v_x(y, t)$, $v_y = 0$, $v_z = 0$. Then the equation of continuity is exactly satisfied, and the equation of motion and the constitutive equation give

$$\rho \frac{\partial v_x}{\partial t} = -\frac{\partial}{\partial y} \tau_{yx} \tag{5.4-1}$$

$$\tau_{yx}(y, t) = -\int_{-\infty}^{t} G(t - t') \frac{\partial v_x(y, t')}{\partial y} dt' \tag{5.4-2}$$

Combining these results in an integrodifferential equation for $v_x(y, t)$:

$$\rho \frac{\partial v_x}{\partial t} = \int_{-\infty}^{t} G(t - t') \frac{\partial^2 v_x(y, t')}{\partial y^2} dt' \tag{5.4-3}$$

Inasmuch as we are not interested in the fluid response immediately after the commencement of the wall oscillation, it is appropriate to make a further postulate for $v_x(y, t)$; since the system is linear, it is anticipated that the fluid will execute sinusoidal motion throughout, so that

$$v_x(y, t) = \mathcal{R}e\, \{v_x^0(y) e^{i\omega t}\} \tag{5.4-4}$$

Here $v_x^0(y)$ is a complex amplitude, with $v_x^0(0) = V$ and $v_x^0(\infty) = 0$. When this velocity expression is substituted into the previous equation we get

$$\begin{aligned} \rho\, \mathcal{R}e\, \{i\omega v_x^0(y) e^{i\omega t}\} &= \int_{-\infty}^{t} G(t - t')\, \mathcal{R}e \left\{ \frac{d^2 v_x^0}{dy^2} e^{i\omega t'} \right\} dt' \\ &= \mathcal{R}e \left\{ \frac{d^2 v_x^0}{dy^2} e^{i\omega t} \int_0^\infty G(s) e^{-i\omega s} ds \right\} \end{aligned} \tag{5.4-5}$$

The integral over $s = t - t'$ in the last line is just η^* according to Eq. 5.3-6. When the $\mathscr{R}e$-operator is removed and the factors $e^{i\omega t}$ eliminated, we get the ordinary differential equation for v_x^0

$$\frac{d^2 v_x^0}{dy^2} - \frac{\rho i\omega}{\eta^*} v_x^0 = 0 \qquad (5.4\text{-}6)$$

If we let

$$\frac{\rho i\omega}{\eta^*} = (\alpha + i\beta)^2 \qquad (5.4\text{-}7)$$

where α and β are real functions of ω, then the solution to Eq. 5.4-6 is

$$v_x^0(y) = Ve^{-(\alpha + i\beta)y} \qquad (5.4\text{-}8)$$

and then from Eq. 5.4-4 we get

$$v_x(y, t) = Ve^{-\alpha y} \cos(\omega t - \beta y) \qquad (5.4\text{-}9)$$

It is now clear that α is the attenuation of the velocity wave, and βy is the phase shift at a distance y from the wall; these frequency-dependent quantities are obtained by solving Eq. 5.4-7. After some tedious algebra we get

$$\alpha(\omega) = \frac{1}{|\eta^*|}\sqrt{\frac{\rho\omega}{2}(|\eta^*| - \eta'')} \qquad (5.4\text{-}10)$$

$$\beta(\omega) = \frac{\eta'}{|\eta^*|}\sqrt{\frac{(\rho\omega/2)}{|\eta^*| - \eta''}} \qquad (5.4\text{-}11)$$

where $|\eta^*| = \sqrt{\eta'^2 + \eta''^2}$. For the Newtonian fluid $\eta'' = 0$, $\eta' = |\eta^*| = \mu$, and $\alpha = \beta = \sqrt{\rho\omega/2\mu}$.

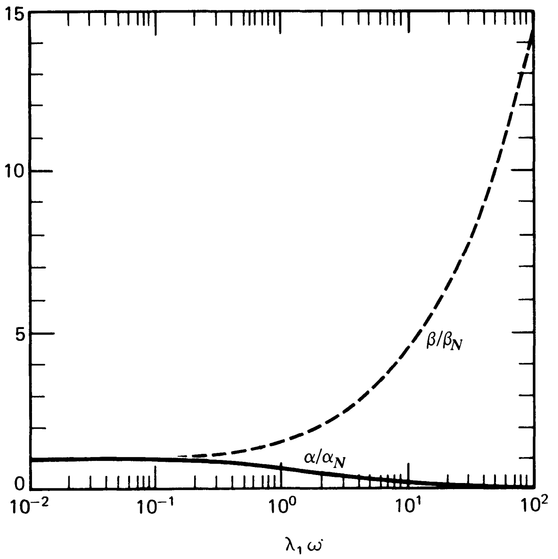

FIGURE 5.4-1. The functions $\alpha(\omega)$ and $\beta(\omega)$, from Eqs. 5.4-10 and 11, for the Maxwell model of Eq. 5.2-2. The functions have been normalized by dividing by the corresponding quantities for a Newtonian fluid with viscosity η_0, namely $\alpha_N = \beta_N = \sqrt{\rho\omega/2\eta_0}$.

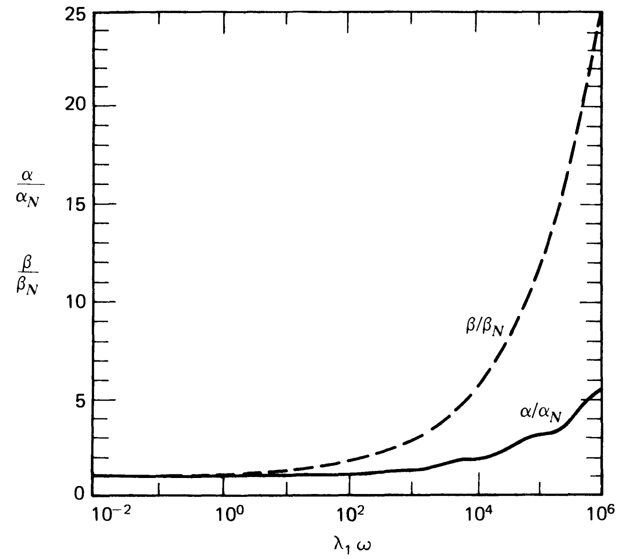

FIGURE 5.4-2. The functions $\alpha(\omega)$ and $\beta(\omega)$ of Eqs. 5.4-10 and 11, obtained from the experimental data on an LDPE melt, as represented by a finite sum of exponentials (see Example 5.3-7). The time constant λ_1 is the longest time constant in the relaxation spectrum; $T = 150°\text{C}$.

The functions $\alpha(\omega)$ and $\beta(\omega)$ are plotted in Fig. 5.4-1 for a Maxwell model; for this model $\alpha(\omega)$ is a monotone decreasing function. For the generalized Maxwell model, Eqs. 15.3-14 and 15 suggest that $\alpha(\omega)$ should increase somewhat with ω for large values of the frequency. This seems to be borne out by the function $\alpha(\omega)$ determined from experimental data on $\eta^*(\omega)$ for a polyethylene melt, as shown in Fig. 5.4-2. Both figures show that $\beta(\omega)$ is a rather rapidly increasing function of ω.

Finally it must be kept in mind that the analysis given here, leading to Eqs. 5.4-9 to 11, is valid only for linear viscoelasticity. This means that the final results can be used only if $V\sqrt{\rho/\omega\eta_0} \ll 1$.

EXAMPLE 5.4-2 Motion of a Viscoelastic Fluid Pulsating in a Tube[1]

A polymeric liquid in a circular tube of radius R is made to oscillate by means of a sinusoidally varying pressure gradient

$$-\frac{\partial p}{\partial z} = \mathcal{R}e\,\{P^0 e^{i\omega t}\} \qquad (5.4\text{-}12)$$

where the magnitude of the complex amplitude P^0 is very small. Obtain an expression for the oscillatory volume flow rate when the "oscillatory steady state" has been reached.

SOLUTION We postulate that the velocity and shear-stress distributions are of the form

$$v_z = \mathcal{R}e\,\{v_z^0(r)e^{i\omega t}\}, \qquad v_r = 0, \qquad v_\theta = 0 \qquad (5.4\text{-}13)$$

$$\tau_{rz} = \mathcal{R}e\,\{\tau_{rz}^0(r)e^{i\omega t}\} \qquad (5.4\text{-}14)$$

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[1] This problem was solved for a Maxwell fluid by L. J. F. Broer, *Appl. Sci. Res.*, **A6**, 226–236 (1957), and for the general linear viscoelastic fluid by A. G. Fredrickson, *Principles and Applications of Rheology*, Prentice-Hall, Englewood Cliffs, NJ (1964), pp. 133 *et seq.*