CHAPTER 3

LINEAR VISCOELASTICITY

3.1 Introduction

The word 'viscoelastic' means the simultaneous existence of viscous and elastic properties in a material (cf. §1.2). It is not unreasonable to assume that all real materials are viscoelastic, i.e. in all materials, both viscous and elastic properties coexist. As was pointed out in the Introduction, the particular response of a sample in a given experiment depends on the time-scale of the experiment in relation to a natural time of the material. Thus, if the experiment is relatively slow, the sample will appear to be viscous rather than elastic, whereas, if the experiment is relatively fast, it will appear to be elastic rather than viscous. At intermediate time-scales mixed (viscoelastic) response is observed. The concept of a natural time of a material will be referred to again later in this chapter. However, a little more needs to be said about the assumption of viscoelasticity as a universal phenomenon. It is not a generally-held assumption and would be difficult to prove unequivocally. Nevertheless, experience has shown that it is preferable to assume that all real materials are viscoelastic rather than that some are not. Given this assumption, it is then incorrect to say that a liquid is Newtonian or that a solid is Hookean. On the other hand, it would be quite correct to say that such-and-such a material shows Newtonian, or Hookean, behaviour in a given situation. This leaves room for ascribing other types of behaviour to the material in other circumstances. However, most rheologists still refer to certain classes of liquid (rather than their behaviour) as being Newtonian and to certain classes of solid as being Hookean, even when they know that these materials can be made to deviate from the model behaviours. Indeed, it is done in this book! Old habits die hard. However, it is considered more important that an introductory text should point out that such inconsistencies exist in the literature rather than try to maintain a purist approach.

For many years, much labour has been expended in the determination of the linear viscoelastic response of materials. There are many reasons for this (see, for example, Walters 1975, p. 121, Bird et al. 1987(a), p. 225). First there is the possibility of elucidating the molecular structure of materials from their linear-viscoelastic response. Secondly, the material parameters and functions measured in the relevant experiments sometimes prove to be useful in the quality-control of industrial products. Thirdly, a background in linear viscoelasticity is helpful before proceeding to the much more difficult subject of *non*-linear viscoelasticity (cf. the relative simplicity of the mathematics in the present chapter with that in Chapter 8 which essentially deals with non-linear viscoelasticity). Finally, a further motivation for some past studies of viscoelasticity came from tribology, where knowledge of the steady shear viscosity function $\eta(\dot{\gamma})$ discussed in §2.3 was needed at high shear rates ($10^6\ s^{-1}$ or higher). Measurements of this function on low-viscosity "Newtonian" lubricants at high shear rates were made difficult by such factors as viscous heating, and this led to a search for an analogy between shear viscosity and the correspond- ing dynamic viscosity determined under linear viscoelastic conditions, the argument being that the latter viscosity was easier to measure (see, for example, Dyson 1970).

Many books on rheology and rheometry have sections on linear viscoelasticity. We recommend the text by Ferry (1980) which contains a wealth of information and an extensive list of references. Mathematical aspects of the subject are also well covered by Gross (1953) and Staverman and Schwarzl (1956).

3.2 The meaning and consequences of linearity

The development of the mathematical theory of linear viscoelasticity is based on a "superposition principle". This implies that the response (e.g. strain) at any time is directly proportional to the value of the initiating signal (e.g. stress). So, for example, doubling the stress will double the strain. In the linear theory of viscoelas- ticity, the differential equations are linear. Also, the coefficients of the time differentials are constant. These constants are material parameters, such as viscosity coefficient and rigidity modulus, and they are not allowed to change with changes in variables such as strain or strain rate. Further, the time derivatives are ordinary partial derivatives. This restriction has the consequence that the linear theory is applicable only to small changes in the variables.

We can now write down a general differential equation for linear viscoelasticity as follows:

$$\left(1+\alpha_1\frac{\partial}{\partial t}+\alpha_2\frac{\partial^2}{\partial t^2}+\ldots+\alpha_n\frac{\partial^n}{\partial t^n}\right)\sigma$$
$$=\left(\beta_0+\beta_1\frac{\partial}{\partial t}+\beta_2\frac{\partial^2}{\partial t^2}+\ldots+\beta_m\frac{\partial^m}{\partial t^m}\right)\gamma, \quad (3.1)$$

where $n=m$ or $n=m-1$ (see for example, Oldroyd 1964). Note that for simplicity we have written (3.1) in terms of the shear stress σ and the strain γ, relevant to a simple shear of the sort discussed in Chapter 1, except that we now allow σ and γ to be functions of the time t. However, we emphasise that other types of deformation could be included without difficulty, with the stress and strain referring to that particular deformation process. Mathematically, this means that we could replace the scalar variables σ and γ by their tensor generalizations. For example, σ could be replaced by the stress tensor σ_{ij}.

3.3 The Kelvin and Maxwell models

We now consider some important special cases of eqn. (3.1). If β_0 is the only non-zero parameter, we have

$$\sigma=\beta_0\gamma, \quad (3.2)$$

which is the equation of Hookean elasticity (i.e. linear solid behaviour) with β_0 as the rigidity modulus. If β_1 is the only non-zero parameter, we have

$$\sigma=\beta_1\frac{\partial\gamma}{\partial t}, \quad (3.3)$$

or

$$\sigma=\beta_1\dot{\gamma} \quad (3.4)$$

in our notation. This represents Newtonian viscous flow, the constant β_1 being the coefficient of viscosity.

If $\beta_0\ (=G)$ and $\beta_1\ (=\eta)$ are both non-zero, whilst the other constants are zero, we have

$$\sigma=G\gamma+\eta\dot{\gamma}, \quad (3.5)$$

which is one of the simplest models of viscoelasticity. It is called the 'Kelvin model', although the name 'Voigt' is also used. If a stress $\bar{\sigma}$ is suddenly applied at $t=0$ and held constant thereafter, it is easy to show that, for the Kelvin model,

$$\gamma=(\bar{\sigma}/G)[1-\exp(-t/\tau_K)], \quad (3.6)$$

where τ_K has been written for the ratio η/G. It has the dimension of time and controls the rate of growth of strain γ following the imposition of the stress $\bar{\sigma}$. Figure 3.1 shows the development of the dimensionless group $\gamma G/\bar{\sigma}$ diagrammati- cally. The equilibrium value of γ is $\bar{\sigma}/G$; hence $\gamma G/\bar{\sigma}=1$, which is also the value for the Hooke model. The difference between the two models is that, whereas the

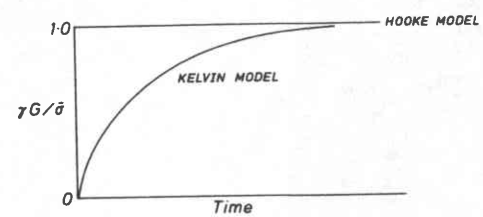

Fig. 3.1 Growth of strain γ following the application of stress $\bar{\sigma}$ at time $t=0$ for a Kelvin model and Hooke model.

Hooke model reaches its final value of strain "instantaneously", in the Kelvin model the strain is retarded. The time constant τ_K is accordingly called the 'retardation time'. The word instantaneously is put in quotation marks because in practice the strain could not possibly grow in zero time even in a perfectly elastic solid, because the stress wave travels at the speed of sound, thus giving rise to a delay.

It is useful at this stage to introduce "mechanical models", which provide a popular method of describing linear viscoelastic behaviour. These one-dimensional mechanical models consist of springs and dashpots so arranged, in parallel or in series, that the overall system behaves analogously to a real material, although the elements themselves may have no direct analogues in the actual material. The correspondence between the behaviour of a model and a real material can be achieved if the differential equation relating force, extension and time for the model is the same as that relating stress, strain and time for the material, i.e. this method is equivalent to writing down a differential equation relating stress and strain, but it has a practical advantage in that the main features of the behaviour of a material can often be inferred by inspection of the appropriate model, without going into the mathematics in detail.

In mechanical models, Hookean deformation is represented by a spring (i.e. an element in which the force is porportional to the extension) and Newtonian flow by a dashpot (i.e. an element in which the force is porportional to the rate of extension) as shown in Fig. 3.2. The analogous rheological equations for the spring and the dashpot are (3.2) (with $\beta_0 = G$) and (3.4) (with $\beta_1 = \eta$), respectively. The behaviour of more complicated materials is described by connecting the basic elements in series or in parallel.

The Kelvin model results from a parallel combination of a spring and a dashpot (Fig. 3.3(a)). A requirement on the interpretation of this and all similar diagrams is that the horizontal connectors remain parallel at all times. Hence the extension (strain) in the spring is at all times equal to the extension (strain) in the dashpot. Then it is possible to set up a balance equation for the forces (stresses) acting on a connector. The last step is to write the resulting equation in terms of stresses and strains. Hence, for the Kelvin model the total stress σ is equal to the sum of the stresses in each element. Therefore

$$\sigma = \sigma_E + \sigma_V \tag{3.7}$$

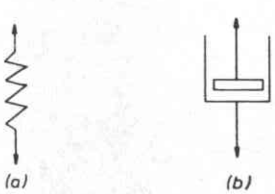

Fig. 3.2 Diagrammatic representations of ideal rheological behaviour: (a) The Hookean spring; (b) The Newtonian dashpot.

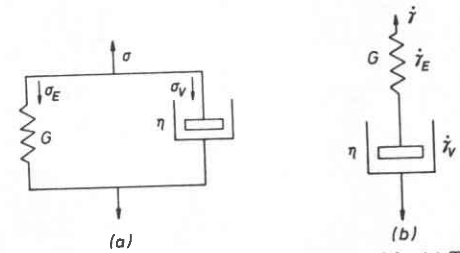

Fig. 3.3 The simplest linear viscoelastic models: (a) The Kelvin model; (b) The Maxwell model.

in the obvious notation, and using eqns. (3.2) and (3.4) (with $\beta_0 = G$ and $\beta_1 = \eta$) we have

$$\sigma = G\gamma + \eta\dot{\gamma}. \tag{3.8}$$

This is identical to eqn. (3.5), which was a very simple case of the general linear differential equation (3.1). It is readily seen from the diagram of the Kelvin model that after sudden imposition of a shear stress $\bar{\sigma}$, the spring will eventually reach the strain given by $\bar{\sigma}/G$, but that the dashpot will retard the growth of the strain and, the higher the viscosity, the slower will be the response.

Another very simple model is the so-called 'Maxwell model' *. The differential equation for the model is obtained by making α_1 and β_1 the only non-zero material parameters, so that

$$\sigma + \tau_M\dot{\sigma} = \eta\dot{\gamma}, \tag{3.9}$$

where we have written $\alpha_1 = \tau_M$ and $\beta_1 = \eta$.

If a particular strain rate $\bar{\gamma}$ is suddenly applied at $t = 0$ and held at that value for subsequent times, we can show that, for $t > 0$,

$$\sigma = \eta\bar{\gamma}\left[1 - \exp(-t/\tau_M)\right], \tag{3.10}$$

which implies that on start-up of shear, the stress growth is delayed; the time constant in this case is τ_M. On the other hand, if a strain rate which has had a constant value $\bar{\gamma}$ for $t < 0$ is suddenly removed at $t = 0$, we can show that, for $t \geqslant 0$,

$$\sigma = \eta\bar{\gamma}\exp(-t/\tau_M). \tag{3.11}$$

Hence the stress relaxes exponentially from its equilibrium value to zero (see Fig. 3.4). The rate constant τ_M is called the 'relaxation time'.

* Recall the discussion in §1.2 concerning the influence of J.C. Maxwell on the introduction of the concept of viscoelasticity in a fluid.

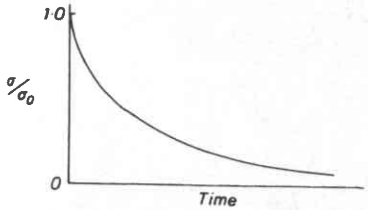

Fig. 3.4 Decay of stress σ following the cessation of steady shear at time $t = 0$ for a Maxwell model, where $\sigma_0 = \eta\bar{\gamma}$.

The pictorial Maxwell model is a spring connected in series with a dashpot (see Fig. 3.3(b)). In this case, the strains, or equally strain-rates, are additive; hence the total rate of shear $\dot{\gamma}$ is the sum of the rates of shear of the two elements. Thus

$$\dot{\gamma} = \dot{\gamma}_E + \dot{\gamma}_V, \tag{3.12}$$

which leads to

$$\dot{\gamma} = \frac{\dot{\sigma}}{G} + \frac{\sigma}{\eta} \tag{3.13}$$

or, after rearrangement,

$$\sigma + \tau_M\dot{\sigma} = \eta\dot{\gamma}, \tag{3.14}$$

in which τ_M has been written for η/G. This equation is the same as eqn. (3.9) which arose as a special case of the general differential equation.

The next level of complexity in the linear viscoelastic scheme is to make three of the material parameters of eqn. (3.1) non zero. If α_1, β_1 and β_2 are taken to be non-zero we have the "Jeffreys model". In the present notation, the equation is

$$\sigma + \tau_M\dot{\sigma} = \eta(\dot{\gamma} + \tau_J\ddot{\gamma}), \tag{3.15}$$

which has two time constants τ_M and τ_J. With a suitable choice of the three model parameters it is possible to construct two alternative spring–dashpot models which correspond to the same mechanical behaviour as eqn. (3.15). One is a simple extension of the Kelvin model and the other a simple extension of the Maxwell model as shown in Fig. 3.5.

We note with interest that an equation of the form (3.15) was derived mathematically by Fröhlich and Sack (1946) for a dilute suspension of solid elastic spheres in a viscous liquid, and by Oldroyd (1953) for a dilute emulsion of one incompressible viscous liquid in another. When the effect of interfacial slipping is taken into account in the *dilute* suspension case, Oldroyd (1953) showed that two further non-zero parameters (α_2 and β_2) are involved.

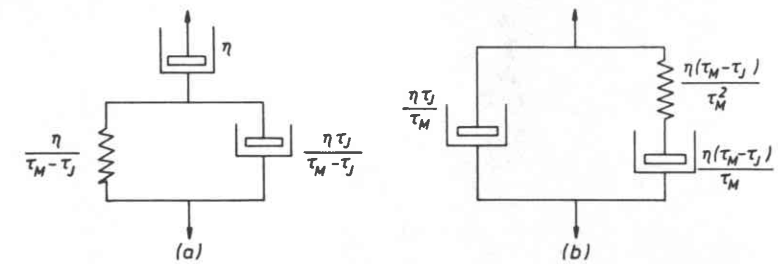

Fig. 3.5 Spring–dashpot equivalents of the Jeffreys model. The values of the constants of the elements are given in terms of the three material parameters of the model (eqn. 3.15).

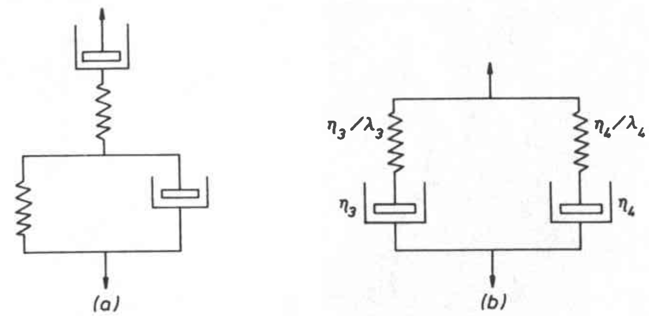

Fig. 3.6 The Burgers model: (a) and (b) are equivalent representations of this 4-parameter linear model.

Finally, in this preliminary discussion of the successive build-up of model complexity, we draw attention to the so-called "Burgers model". This involves four simple elements and takes the mechanically-equivalent forms shown in Fig. 3.6.

In terms of the parameters of the Maxwell-type representation (Fig. 3.6(b)), the associated constitutive equation for the Burgers model has the form

$$\sigma + (\lambda_3 + \lambda_4)\dot{\sigma} + \lambda_3\lambda_4\ddot{\sigma} = (\eta_3 + \eta_4)\dot{\gamma} + (\lambda_4\eta_3 + \lambda_3\eta_4)\ddot{\gamma}. \tag{3.16}$$

In this equation the λs are time constants, the symbol λ being almost as common as τ in the rheological litrature.

3.4 The relaxation spectrum

It is certainly possible to envisage more complicated models than those already introduced, but Roscoe (1950) showed that all models, irrespective of their complexity, can be reduced to two canonical forms. These are usually taken to be the generalized Kelvin model and the generalized Maxwell model (Fig. 3.7). The generalized Maxwell model may have a finite number or an enumerable infinity of Maxwell elements, each with a different relaxation time.

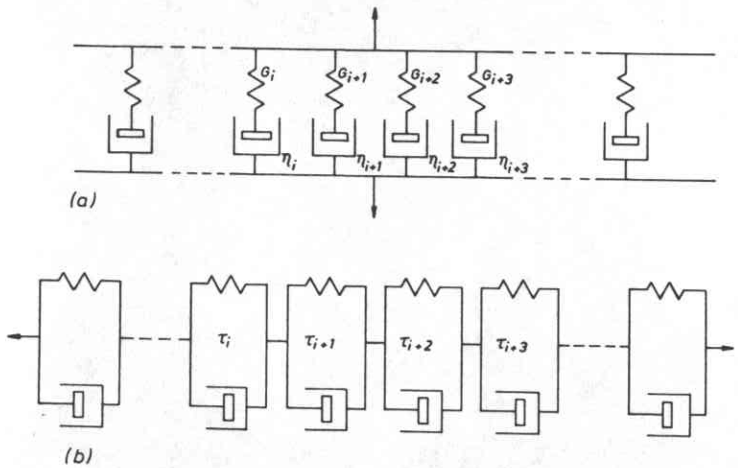

Fig. 3.7 Canonical spring–dashpot models: (a) Distribution of Maxwell relaxation processes; (b) Distribution of Kelvin retardation processes.

By a suitable choice of the model parameters, the canonical forms themselves can be shown to be mechanically equivalent and Alfrey (1945) has given methods for computing the parameters of one canonical form from those of the other. In the same paper, Alfrey also showed how a linear differential equation can be obtained for either of the canonical forms and vice versa. In other words, the three methods of representing viscoelastic behaviour (the differential equation (3.1) and the two canonical forms of mechanical model of Fig. 3.7 are equivalent and one is free to choose any one of them as a basis for generalization to materials requiring a continuous infinity of parameters to specify them.

In order to generalize from an enumerable infinity to a continuous distribution of relaxation times, we choose to start with the simple Maxwell model, whose behaviour is characterized by the differential equation (3.9) or what is equivalent

$$\sigma(t) = \frac{\eta}{\tau}\int_{-\infty}^{t} \exp[-(t-t')/\tau]\,\dot{\gamma}(t')\,\mathrm{d}t', \tag{3.17}$$

where we have dropped the subscript M in τ_M to enable us to generalize eqn. (3.17) without introducing a clumsy notation. *

Considering next, a number, n, of discrete Maxwell elements connected in parallel as in Fig. 3.7(a), we can generalize eqn. (3.17), with the aid of the

* The integral equation (3.17) is obtained by solving the differential equation (3.9) by standard techniques.

superposition principle, to give

$$\sigma(t) = \sum_{i=1}^{n} \frac{\eta_i}{\tau_i}\int_{-\infty}^{t} \exp[-(t-t')/\tau_i]\,\dot{\gamma}(t')\,\mathrm{d}t', \tag{3.18}$$

where η_i and τ_i now correspond to the ith Maxwell element.

The theoretical extension to a continuous distribution of relaxation times can be carried out in a number of ways. For example, we may proceed as follows.

The "distribution function of relaxation times" (or "relaxation spectrum") $N(\tau)$ may be defined such that $N(\tau)\,\mathrm{d}\tau$ represents the contributions to the total *viscosity* of all the Maxwell elements with relaxation times lying between τ and $\tau + \mathrm{d}\tau$. The relevant equation then becomes (on generalizing (3.18))

$$\sigma(t) = \int_{0}^{\infty} \frac{N(\tau)}{\tau}\int_{-\infty}^{t} \exp[-(t-t')/\tau]\,\dot{\gamma}(t')\,\mathrm{d}t'\,\mathrm{d}\tau, \tag{3.19}$$

and if we introduce the "relaxation function" ϕ, defined by

$$\phi(t-t') = \int_{0}^{\infty} \frac{N(\tau)}{\tau} \exp[-(t-t')/\tau]\,\mathrm{d}\tau, \tag{3.20}$$

eqn. (3.19) becomes

$$\sigma(t) = \int_{-\infty}^{t} \phi(t-t')\,\dot{\gamma}(t')\,\mathrm{d}t'. \tag{3.21}$$

We remark that we could have immediately written down an equation like (3.21) on the basis of Boltzmann's superposition principle.

It is also possible to proceed from eqn. (3.18) by introducing a distribution function $H(\tau)$ such that $H(\tau)\,\mathrm{d}\tau$ represents the contribution to the *elasticity modulus* of the processes with relaxation times lying in the interval τ and $\tau + \mathrm{d}\tau$. Further, other workers have used a spectrum of relaxation frequencies $\overline{H}(\log F)$ where $F = 1/(2\pi\tau)$. The relationships between these functions are

$$(N(\tau)/\tau)\,\mathrm{d}\tau = H(\tau)\,\mathrm{d}\tau = \overline{H}(\log F)\,\mathrm{d}(\log F). \tag{3.22}$$

In a *slow steady* motion which has been in existence indefinitely (i.e. $\dot{\gamma}$ is small, and independent of time) eqn. (3.21) reduces to

$$\sigma = \eta_0\dot{\gamma}, \tag{3.23}$$

where

$$\eta_0 = \int_{-\infty}^{t} \phi(t-t')\,\mathrm{d}t' = \int_{0}^{\infty} \phi(\xi)\,\mathrm{d}\xi,$$

in which ξ has been written for the time interval $(t-t')$. The variable ξ is the one which represents the time-scale of the rheological history. It is also easy to show from eqns. (3.19), (3.21) and (3.22) that

$$\eta_0=\int_0^{\infty} N(\tau)\,\mathrm{d}\tau=\int_0^{\infty}\tau H(\tau)\,\mathrm{d}\tau=\int_{-\infty}^{\infty}\frac{\overline{H}(\log F)}{2\pi F}\,\mathrm{d}(\log F). \tag{3.24}$$

We see from eqn. (3.23) that η_0 can be identified with the limiting viscosity at small rates of shear, as observed in steady state experiments. Thus, the equations in (3.24) provide useful normalization conditions on the various relaxation spectra. It is also of interest to note that η_0 is equal to the area under the $N(\tau)$ spectrum, whilst it is equal to the first moment of the $H(\tau)$ spectrum.

3.5 Oscillatory shear

It is instructive to discuss the response of viscoelastic materials to a small-amplitude oscillatory shear, since this is a popular deformation mode for investigating linear viscoelastic behaviour.

Let

$$\gamma(t')=\gamma_0\exp(\mathrm{i}\omega t'), \tag{3.25}$$

where $\mathrm{i}=\sqrt{-1}$, ω is the frequency and γ_0 is a strain amplitude which is small enough for the linearity constraint to be satisfied. The corresponding strain rate is given by

$$\dot\gamma(t')=\mathrm{i}\omega\gamma_0\exp(\mathrm{i}\omega t'),$$

and, if this is substituted into the general integral equation (3.21), we obtain

$$\sigma(t)=\mathrm{i}\omega\gamma_0\exp(\mathrm{i}\omega t)\int_0^{\infty}\phi(\xi)\exp(-\mathrm{i}\omega\xi)\,\mathrm{d}\xi. \tag{3.26}$$

In oscillatory shear we define a 'complex shear modulus' G^*, through the equation

$$\sigma(t)=G^*(\omega)\gamma(t) \tag{3.27}$$

and, from eqns. (3.25), (3.26) and (3.27), we see that

$$G^*(\omega)=\mathrm{i}\omega\int_0^{\infty}\phi(\xi)\exp(-\mathrm{i}\omega\xi)\,\mathrm{d}\xi. \tag{3.28}$$

It is customary to write

$$G^*=G'+\mathrm{i}G'' \tag{3.29}$$

and G' and G'' are referred to as the 'storage modulus' and 'loss modulus', respectively. G' is also called the dynamic rigidity. If we now consider, for the purpose of illustration, the special case of the Maxwell model given by eqn. (3.9) or eqn. (3.14) (with $\tau_M=\tau$) we can show that

$$G^*=\frac{\mathrm{i}\omega\eta}{1+\mathrm{i}\omega\tau},\quad\text{or alternatively}\quad G^*=\frac{\mathrm{i}\omega\tau G}{1+\mathrm{i}\omega\tau}, \tag{3.30}$$

and

$$G'=\frac{\eta\tau\omega^2}{1+\omega^2\tau^2},\quad\text{or alternatively}\quad G'=\frac{G\omega^2\tau^2}{1+\omega^2\tau^2}, \tag{3.31}$$

$$G''=\frac{\eta\omega}{1+\omega^2\tau^2},\quad\text{or alternatively}\quad G''=\frac{G\omega\tau}{1+\omega^2\tau^2}. \tag{3.32}$$

To some readers, the use of the complex quantity $\exp(\mathrm{i}\omega t)$ to represent oscillatory motion may be unfamiliar. The alternative procedure is to use the more obvious wave-forms represented by the sine and cosine functions, and we now illustrate the procedure for the simple Maxwell model.

Let

$$\gamma=\gamma_0\cos\omega t. \tag{3.33}$$

Thus, the strain rate is

$$\dot\gamma=-\gamma_0\omega\sin\omega t, \tag{3.34}$$

and if this is substituted into the equation for the Maxwell model, a first order linear differential equation is obtained, with solution

$$\sigma=\frac{\eta\omega\gamma_0}{(1+\omega^2\tau^2)}(\omega\tau\cos\omega t-\sin\omega t). \tag{3.35}$$

The part of the stress *in phase* with the applied strain is obtained by putting $\sin\omega t$ equal to zero and is written $G'\gamma$. The part of the stress which is *out of phase* with the applied strain is obtained by setting $\cos\omega t$ equal to zero and is written $(G''/\omega)\dot\gamma$. Hence

$$G'=\frac{\eta\tau\omega^2}{1+\omega^2\tau^2}, \tag{3.36}$$

$$G''=\frac{\eta\omega}{1+\omega^2\tau^2}, \tag{3.37}$$

in agreement with (3.31) and (3.32) as expected.

Returning now to the more convenient complex representation of the oscillatory motion, we remark that as an alternative to the complex shear modulus, we can define 'complex viscosity' η^*, as the ratio of the shear stress σ to the rate of shear $\dot{\gamma}$. Thus

$$\sigma(t) = \eta^* \dot{\gamma}(t), \tag{3.38}$$

and it follows that, for the general integral representation,

$$\eta^*(\omega) = \int_0^\infty \phi(\xi)\exp(-i\omega\xi)\,d\xi. \tag{3.39}$$

We now write

$$\eta^* = \eta' - i\eta'', \tag{3.40}$$

noting that η' is usually given the name 'dynamic viscosity'. The parameter η'' has no special name but it is related to the dynamic rigidity through $G' = \eta''\omega$. It is also easy to deduce that $G'' = \eta'\omega$.

It is conventional to plot results of oscillatory tests in terms of the dynamic viscosity η' and the dynamic rigidity G'. Figure 3.8 shows plots of the normalized dynamic functions of the Maxwell model as functions of $\omega\tau$, the normalized, or reduced, frequency. The notable features are the considerable fall in normalized η' and the comparable rise in normalized G' which occur together over a relatively narrow range of frequency centred on $\omega\tau = 1$. The changes in these functions are virtually complete in two decades of frequency. These two decades mark the viscoelastic zone. Also, in the many decades of frequency that are, in principle, accessible on the low frequency side of the relaxation region, the model displays a viscous response ($G' \sim 0$). In contrast, at high frequencies, the response is elastic ($\eta' \sim 0$). From Fig. 3.8, the significance of τ as a characteristic natural time for the Maxwell model is clear.

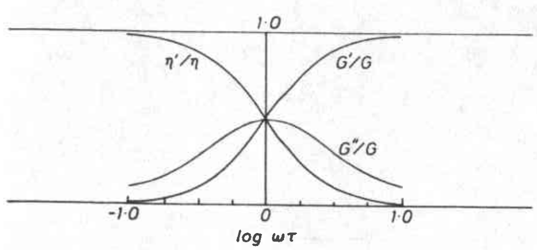

Fig. 3.8 The Maxwell model in oscillatory shear. Variation of the normalized moduli and viscosity with normalized frequency ($\tau = \eta/G$).

In the literature, other methods of characterizing linear viscoelastic behaviour are to be found. For example, it is possible to define a 'complex shear compliance' J^*. By definition

$$\gamma(t) = J^*(\omega)\sigma(t) \tag{3.41}$$

in an oscillatory shear, with

$$J^* = J' - iJ''. \tag{3.42}$$

It is important to note that, although $J^* = 1/G^*$, the components are not similarly related. Thus $J' \neq 1/G'$ and $J'' \neq 1/G''$.

The second alternative method of characterizing linear viscoelastic response is to plot G' and the 'loss angle' δ. In this method, it is assumed that for an applied oscillatory strain given by eqn. (3.25), the stress will have a similar form, but its phase will be in advance of the strain by an angle δ. Then,

$$\sigma(t) = \sigma_0 \exp[i(\omega t + \delta)]. \tag{3.43}$$

It is not difficult to show that

$$\tan\delta = G''/G'. \tag{3.44}$$

Figure 3.9 shows how δ and G'/G (where $G = \tau\eta$) vary with the normalized frequency for the Maxwell model. At high values of the frequency, the response, as already noted, is that of an elastic solid. In these conditions the stress is in phase with the applied strain. On the other hand, at very low frequencies, where the response is that of a viscous liquid, the stress is 90° ahead of the strain. The change from elastic to viscous behaviour takes place over about two decades of frequency. This latter observation has already been noted in connection with Fig. 3.8. In Fig. 3.10, we show the wave-forms for the oscillatory inputs and outputs. Figure 3.10(a) represents an experiment in the viscoelastic region. Figure 3.10(b) represents very high and very low frequency behaviour where the angle δ is 0° or 90°, respectively.

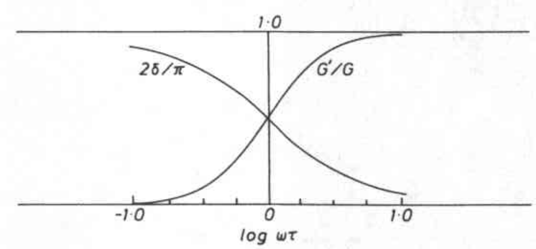

Fig. 3.9 The Maxwell model in oscillatory shear. Variation of the normalized storage modulus and phase angle with normalized frequency.

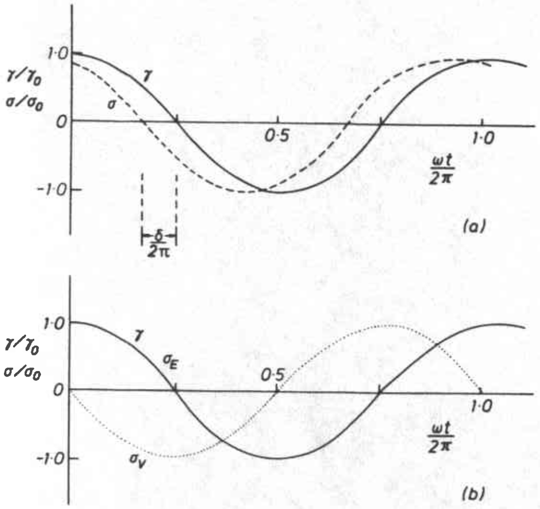

Fig. 3.10 Wave-forms for oscillatory strain input and stress output: (a) Solid line (———) strain according to eqns. (3.25) and (3.33); dashed line (- - - - -) stress in advance by angle δ, according to eqn. (3.43); (b) Solid line (———) strain input and also stress output for elastic behaviour; dotted line (· · · · · ·) stress output for viscous behaviour.

Note that although the stress is 90° in advance of the shear strain for the viscous liquid, it is in phase with the rate of shear.

3.6 Relationships between functions of linear viscoelasticity

In previous sections we have introduced a number of different functions which can all be used to characterize linear viscoelastic behaviour. These range from complex moduli to relaxation function and spectra. They are not independent, of course, and we have already given mathematical relationships between some of the functions. For example, eqn. (3.28), which is fairly typical of the complexities involved, relates the complex shear modulus G^* to the relaxation function ϕ. Equation (3.28) is an integral transform and the determination of ϕ from G^* can be accomplished by inverting the transform. There is nothing sophisticated, therefore, in determining one viscoelastic function from another: although this is a statement "in principle", and much work has been carried out on the non-trivial problem of inverting transforms when experimental data are available only over a limited range of the variables (like frequency of oscillation). The general problem of determining one viscoelastic function from another was discussed in detail by Gross (1953) and practical methods are dealt with by, for example, Schwarzl and Struik (1967).

Nowadays most experimental data from linear viscoelasticity experiments are presented in the form of graphs of components of the dynamic parameters (such as

complex modulus) and are rarely transformed into the relaxation function or the relaxation spectrum.

3.7 Methods of measurement

Two different types of method are available to determine linear viscoelastic behaviour: *static* and *dynamic*. Static tests involve the imposition of a step change in stress (or strain) and the observation of the subsequent development in time of the strain (or stress). Dynamic tests involve the application of a harmonically varying strain.

In this section we shall be concerned with the main methods in the above classification. Attention will be focussed on the principles of the selected methods and none will be described in detail. The interested reader is referred to the detailed texts of Walters (1975) and Whorlow (1980) for further information.

An important point to remember is that, whatever the method adopted, the experimenter must check that measurements are made in the linear range; otherwise the results will be dependent on experimental details and will not be unique to the material. The test for linearity is to check that the computed viscoelastic functions are independent of the magnitude of the stresses and strains applied.

3.7.1 Static methods

The static methods are either 'creep' tests at constant stress or relaxation tests at constant strain (see Figs. 3.11 and 3.12). In theory, the input stress or strain, whether it is an increase or a decrease, is considered to be applied instantaneously. This cannot be true in practice, because of inertia in the loading and measuring systems and the delay in transmitting the signal across the test sample, determined by the speed of sound. As a general rule, the time required for the input signal to reach its steady value must be short compared to the time over which the ultimate varying output is to be recorded. This usually limits the methods to materials which have relaxation times of at least a few seconds. A technique for estimating whether apparatus inertia is influencing results is to deliberately change the inertia, by

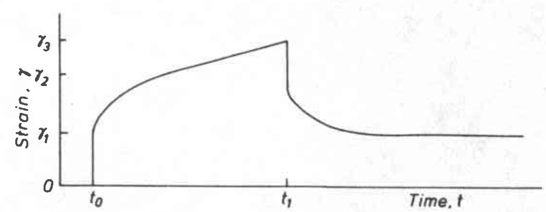

Fig. 3.11 Typical creep curve of strain γ plotted against time t. A constant stress was applied at $t = t_0$ and removed at $t = t_1$. The strain comprises three regions: instantaneous (0 to γ_1); retardation (γ_0 to γ_2); constant rate (γ_2 to γ_3). In linear behaviour the instantaneous strains on loading and unloading are equal and the ratio of stress to instantaneous strain is independent of stress; the constant-rate strain (γ_2 to γ_3) is not recovered.

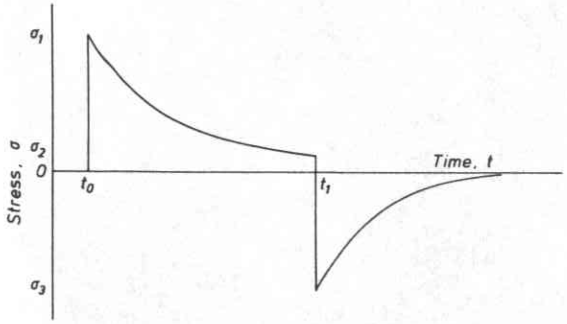

Fig. 3.12 Typical relaxation curve of stress σ plotted against time t. A constant strain was applied at $t = t_0$ and reversed at $t = t_1$. In linear behaviour the instantaneous changes of stress from 0 to σ_1 and σ_2 to σ_3 are equal and the ratio of instantaneous stress to strain is independent of strain. The incomplete relaxation at $t = t_1$ may indicate either that further relaxation would occur in a longer time, or, that the material at very low deformation behaves like a Hookean solid and a residual stress would persist indefinitely.

adding weights for example, and checking the effect on the derived viscoelastic functions.

The basic apparatus for static tests is simple. Once the shape and means of holding the specimen have been decided upon, it is necessary to apply the input signal and measure, and record, the output. It is easier to measure strain, or deformation, than stress. Hence, creep tests have been much more common than relaxation tests.

The geometry chosen for static tests depends largely on the material to be tested. For solid-like materials, it is usually not difficult to fashion a long slender specimen for a tensile or torsional experiment. Liquid-like material can be tested in simple shear with the concentric-cylinder and cone- and-plate geometries and constant-stress rheometers are commercially available for carrying out creep tests in simple shear. Plazek (1968) has carried out extensive experiments on the creep testing of polymers over wide ranges of time and temperature.

3.7.2 *Dynamic methods: oscillatory strain*

The use of oscillatory methods increased considerably with the development of commercial rheogoniometers, and a further boost was given when equipment became available for processing the input and output signals to give in-phase and out-of-phase components directly. With modern instruments it is now possible to display automatically the components of the modulus as functions of frequency.

A general advantage of oscillatory tests is that a single instrument can cover a very wide frequency range. This is important if the material has a broad spectrum of relaxation times. Typically, the frequency range is from 10^{-3} to 10^3 s^{-1}. Hence a time spectrum from about 10^3 to 10^{-3} s can be covered. If it is desired to extend the limit to longer times, static tests of longer duration than 3 hr (10^4 s) would be

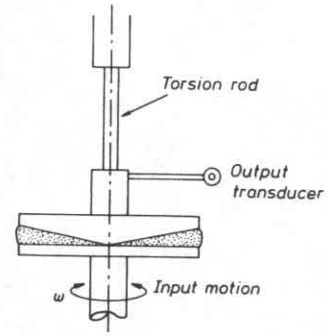

Fig. 3.13 Representation of the cone-and-plate apparatus for oscillatory tests. The specimen is positioned between the input motion and the output stress.

needed. The lower relaxation time limit of oscillatory methods can be extended by wave-propagation methods (see § 3.7.3).

The conventional oscillatory methods involve the application of either free or forced oscillatory strains in conventional tensile and shear geometries. An advantage possessed by the free vibration technique is that an oscillator is not required and the equipment can be fairly simple. On the other hand, the frequency range available is no more than two decades. The reason for this is that a change of frequency relies on a change in moment of inertia of the vibrating system and the scope for this is limited. The method is readily adaptable to torsional deformation with solid-like materials.

The wide frequency range quoted above is achieved with forced oscillations. We show in Fig. 3.13 the most common example of the forced-oscillation experiment, although the geometry could equally well be a parallel-plate or concentric-cylinder configuration. The test material is contained between a cone and plate, with the angle between the cone and plate being small ($< 4°$). The bottom member undergoes forced harmonic oscillations about its axis and this motion is transmitted through the test material to the top member, the motion of which is constrained by a torsion bar. The relevant measurements are the amplitude ratio of the motions of the two members and the associated phase lag. From this information it is relatively simple to determine the dynamic viscosity η' and the dynamic rigidity G', measured as functions of the imposed frequency (see Walters 1975 for the details of this and related techniques).

3.7.3 *Dynamic methods: wave propagation*

A number of books are available which describe in detail the theory and practice of wave-propagation techniques. Kolsky (1963) has dealt with the testing of solids, Ferry (1980) has reviewed the situation as regards polymers and Harrison (1976) has covered liquids. The overall topic is usefully summarized by Whorlow (1980).

Basically, the waves are generated at a surface of the specimen which is in contact with the wave generator and the evaluation of the viscoelastic functions requires the measurement of the velocity and the attenuation through the specimen. One significant advantage of wave-propagation methods is that they can be adapted to high frequency studies: they have been commonly used in the kHz region and higher, even up to a few hundred GHz. This is invaluable when studying liquids which behave in a Newtonian manner in other types of rheometer. Such liquids include, as a general rule, those with a molecular weight below 10^3. They include most of the non-polymeric liquids. Barlow and Lamb have made significant contributions in this area (see, for example, Barlow et al. 1967).

3.7.4 Dynamic methods: steady flow

In the oscillatory experiments discussed above, instrument members are made to oscillate and the flow is in every sense unsteady. A relatively new group of instruments for measuring viscoelastic behaviour is based on a different principle. The flow in these rheometers is steady in the sense that the velocity at a fixed point in the apparatus is unchanging. (Such a flow is described in fluid dynamics as being "steady in an Eulerian sense".) However, the rheometer geometry is constructed in such a way that individual fluid elements undergo an oscillatory shear (so that the flow is "unsteady in a Lagrangian sense"). A typical example of such an instrument is the Maxwell orthogonal rheometer which is shown in Fig. 3.14 (Maxwell and Chartoff 1965). It comprises two parallel circular plates separated by a distance h, mounted on parallel axes, separated by a small distance d. One spindle is rotated at *constant* angular velocity Ω. The other is free to rotate and takes up a velocity close to that of the first spindle.

The components of the force on one of the plates are measured using suitable transducers. In the interpretation of the data it is assumed that the angular velocity of the second spindle is also Ω. It can then be readily deduced that individual fluid elements are exposed to a sinusoidal shear and that the components of the force on each plate (in the plane of the plates) can be directly related to the dynamic viscosity and dynamic rigidity.

The Maxwell orthogonal rheometer and other examples of the steady-flow viscoelastic rheometers are discussed in detail by Walters (1975).

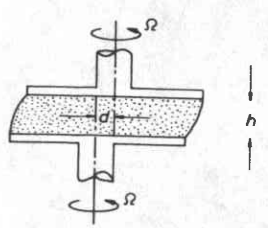

Fig. 3.14 Arrangement of rotating plates in a Maxwell orthogonal rheometer. Plate separation h; axis displacement d. One shaft rotates at constant velocity Ω and the second shaft takes up (nearly) the same velocity.

CHAPTER 4

NORMAL STRESSES

4.1 The nature and origin of normal stresses

We have already stated in §1.5 that, for a steady simple shear flow given by

$$v_x = \dot{\gamma} y, \quad v_y = v_z = 0, \tag{4.1}$$

the relevant stress distribution for non-Newtonian liquids can be expressed in the form

$$\left.\begin{aligned} &\sigma_{xy} = \sigma = \dot{\gamma}\eta(\dot{\gamma}), \quad \sigma_{xz} = \sigma_{yz} = 0, \\ &\sigma_{xx} - \sigma_{yy} = N_1(\dot{\gamma}), \quad \sigma_{yy} - \sigma_{zz} = N_2(\dot{\gamma}). \end{aligned}\right\} \tag{4.2}$$

The variables σ, N_1 and N_2 are sometimes called the viscometric functions. A useful discussion of the importance of these functions is given by Lodge (1974, p. 212). In this chapter, we shall be concerned with the normal stress differences N_1 and N_2 or, equivalently, the so-called normal stress coefficients Ψ_1 and Ψ_2, where

$$N_1 = \dot{\gamma}^2 \Psi_1, \quad N_2 = \dot{\gamma}^2 \Psi_2. \tag{4.3}$$

In principle, it is possible for a non-Newtonian *inelastic* model liquid to exhibit normal-stress effects in a steady simple shear flow. The so called Reiner–Rivlin fluid, which is a general mathematical model for an inelastic fluid (see §8.4), can be used to demonstrate this. However, all the available experimental evidence is that the theoretical normal stress distribution predicted by this model, viz. $N_1 = 0$, $N_2 \neq 0$ is not observed in any known non-Newtonian liquid. In practice, normal-stress behaviour is always that to be expected from models of viscoelasticity, whether they be mathematical or physical models.

The normal stress differences are associated with non-linear effects (cf. §1.3). Thus, they did not appear explicitly in the account of linear viscoelasticity in Chapter 3. In the experimental conditions of small-amplitude oscillatory shear, in which linear viscoelasticity is demonstrated and the parameters measured, the three normal stress components have the same value. They are equal to the ambient pressure, which is isotropic. Similarly, in steady flow conditions, provided the flow is slow enough for second-order terms in $\dot{\gamma}$ to be negligible, the normal stresses are