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Richard H. Boyd and Grant D. Smith
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Part I

Methodology

The first five chapters deal with the methodology used to study relaxation processes. The first four deal with experimental methods, namely mechanical relaxation, dielectric relaxation, nuclear magnetic resonance and neutron diffraction. The first two are very familiar long-used methods. This is due both to their relevance to practical material properties and to the insights they have led to in understanding the time dependence of material behavior. The NMR method is very selective in probing certain elements based, of course, on the nuclear spins involved. The development of complex pulse techniques has allowed the investigation of relaxational processes over very broad time scales. The availability of sophisticated neutron sources has led to a wealth of data involving dynamic scattering factors for coherent and incoherent scattering. Molecular dynamics (MD) simulations are becoming more and more useful in the interpretation of the various relaxation experiments and Chapter 5 presents the basics of that methodology.

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Mechanical relaxation

1.1 Regimes of behavior

Amorphous polymers tend to behave in an elastic manner at low temperature in the glassy state. The strain at break is usually small (a few percent), they can deform quickly, hold their length at constant load, and recover completely when unloaded (Figure 1.1). The material is *elastic*. In the vicinity of the glass transition temperature when the length of the specimen is held constant the stress decays with time (stress relaxation). Under constant load (creep), in addition to the instantaneous deformation characteristic of the glass, the sample deforms in a time dependent fashion and when released from constant load recovers nearly completely and in a time dependent manner (retarded elasticity) (Figure 1.2). Such a material is called *anelastic*. At higher temperature, in addition to the instantaneous and retarded elasticity a non-recoverable strain appears in the creep experiment due to viscous flow (Figure 1.3). The material is *viscoelastic*.

There is a considerable advantage in being able to describe and summarize the above behavior in terms of a simple model. For example, it would be impractical to perform every type of mechanical test on a sample. Rather it would be much better to perform enough measurements to characterize the material and then predict the results of other tests from a model. Continuum linear elasticity theory is soundly based on the application of classical mechanics to the deformation of solids. However, in order to include time dependent material behavior an independent additional conjecture about how such materials behave must be introduced. Because the conjecture has no obvious molecular or other fundamental derivation the model is said to be a *phenomenological* one. Based on the above comments it is apparent that a first step is to introduce the conjecture upon which linear viscoelastic behavior is based. This is the *superposition* assumption.

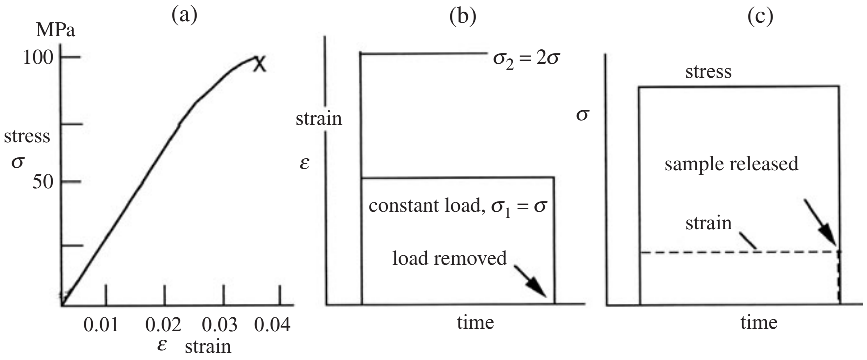

Figure 1.1 Glassy state: (a) stress–strain, (b) creep and (c) stress relaxation curves. For small strains, strain is proportional to stress (see (b)). Recovery from load or strain is complete and rapid. The material is *elastic*.

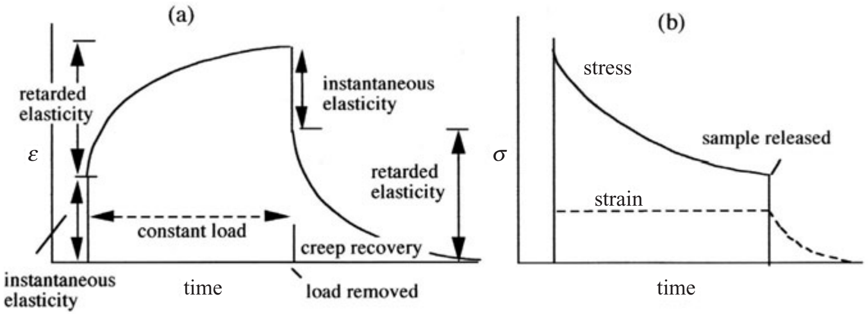

Figure 1.2 Near the glass temperature: (a) in the creep curve there is, in addition to the instantaneous strain of the glassy state, a time dependent strain. It is largely recoverable on removal of the stress. (b) In stress relaxation, the stress decays with time. The material is said to be *anelastic*.

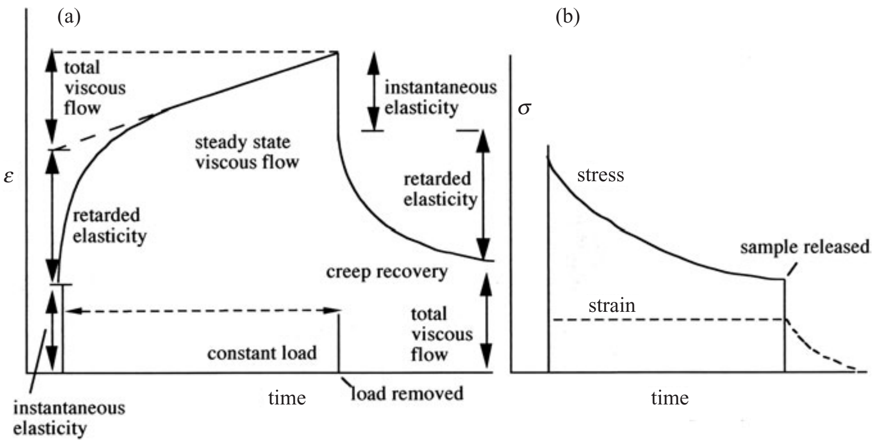

Figure 1.3 Well above glass temperature: (a) creep and (b) stress relaxation curves. In addition to instantaneous and retarded elasticity, a non-recoverable component is important, i.e. viscous flow. The material is *viscoelastic*.

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1.2 Superposition principle

In linear continuum elasticity theory, *linear* means that stress and strain are proportional *and* that strains occasioned by multiaxial stresses and vice versa are additive or superposable (see Appendix A1). In linear viscoelasticity the same linearity is invoked. But in addition and of more significance in the present context is the (Boltzmann [1]) *superposition principle* that describes the time dependence. The central consequence of time dependent behavior is the necessity for the concept of past time *and* current time. In creep, for example (Figure 1.1), when a perfectly elastic material is unloaded, the strain immediately responds. Thus there is only one concept of time necessary, the record of the loading schedule. In Figure 1.2 where time dependence does appear, a plot with only one time axis can still be made. This is because a simple loading history, the sudden application or removal of the load, was invoked. Suppose, however, the load in creep varies slowly over time. For an elastic material this is of no consequence since the strain responds quickly (subject only to inertia). For an anelastic or viscoelastic material this is no longer the case. The strain at the *current* time is still changing from *past* applications of the load. Thus an additional assumption about material behavior is required.

The superposition principle states that the time evolution of a strain response to a past stress is independent of any stresses applied in the intervening period up to the time at which the strain is currently being measured. Thus the present time strain is the *sum* of all strains arising from past applications of stress. The converse applies when the strain history is imposed and stress occurs in response (stress relaxation). The present time stress is the sum of all stresses arising from past applications of strain.

In what follows all of the examples are given in terms of uniaxial tensile stress–strain measurements. Similar formulations and equations follow for shear measurements.

1.3 Relaxation modulus

The superposition principle is easily mathematically quantified. The case of an imposed strain history is used in illustration. The time dependence is embedded in a time dependent modulus that is characteristic of the material. This modulus is a function of the elapsed time between the application of an imposed strain at past time, u, and the current time, t, at which the stress is being measured. The modulus, now called a *relaxation modulus*, is denoted as $E_\mathrm{R}(t-u)$. Suppose a strain increment, $\Delta\varepsilon(u)$ is applied at time u. Then the stress increment at later time, t, arising from this will be

$$\Delta\sigma(t) = E_\mathrm{R}(t-u)\Delta\varepsilon(u). \tag{1.1}$$

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The total stress at the current time, t, from a series of past strain applications at times $u_1, u_2, \ldots, u_i, \ldots$ is, under the superposition principle,

$$\sigma(t) = E_\mathrm{R}(t-u_1)\Delta\varepsilon(u_1) + E_\mathrm{R}(t-u_2)\Delta\varepsilon(u_2) + \cdots + E_\mathrm{R}(t-u_i)\Delta\varepsilon(u_i) + \cdots. \tag{1.2}$$

An arbitrary strain history can be built up by passing to the integral,

$$\sigma(t) = \int_{-\infty}^{t} E_\mathrm{R}(t-u)(\mathrm{d}\varepsilon/\mathrm{d}u)\,\mathrm{d}u, \tag{1.3}$$

where the device of introducing $\mathrm{d}\varepsilon/\mathrm{d}u$ enables the integration to be carried out over past time, u. This equation forms the basis for the description of the stress response under all strain histories. In other words, everything about the material is contained in $E_\mathrm{R}(t-u)$, everything about various possible experiments, tests, etc. is contained in $\varepsilon(u)$. It is obviously presumed that the relaxation modulus $E_\mathrm{R}(t-u)$ is known. The strategy is to determine it experimentally under some standard imposed strain history. Then the results of other strain histories may be predicted from E_R using eq. (1.3).

As a mathematical convenience later, it will be useful to explicitly recognize that at long times the stress generally decays not to zero but to a constant value expressed through the equilibrium fully *relaxed modulus*, E_r. Thus eq. (1.3) becomes

$$\sigma(t) = E_\mathrm{r}\varepsilon(t) + \int_{-\infty}^{t} (E_\mathrm{R}(t-u) - E_\mathrm{r})(\mathrm{d}\varepsilon/\mathrm{d}u)\,\mathrm{d}u. \tag{1.4}$$

The term $(E_\mathrm{R}(t-u) - E_\mathrm{r})$ does approach zero at large values of $t-u$.

1.4 Simple stress relaxation

A common experiment is to impose a sudden finite strain step at $u = 0$ that remains constant at ε^0 and to observe the ensuing stress as a function of time. Under this circumstance eq. (1.3) or eq. (1.4) integrates to

$$\sigma(t) = E_\mathrm{R}(t)\varepsilon^0. \tag{1.5}$$

Thus the relaxation modulus is directly determined by the experiment (for times greater than several times the rise time of the step strain) as $E_R(t) = \sigma(t)/\varepsilon^0$.

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1.5 Dynamic modulus

A common experiment is the imposition of a cyclic stress or strain. It is a mathematical convenience to express such periodic functions in complex notation. Thus an imposed periodic strain of angular frequency ω can be written as

$$\varepsilon^*(\mathrm{i}\omega t) = \varepsilon^0 \mathrm{e}^{\mathrm{i}\omega t} = \varepsilon^0[\cos(\omega t) + \mathrm{i}\sin(\omega t)]. \tag{1.6}$$

It is implied that the actual strain is the real part of $\varepsilon^*(\mathrm{i}\omega\tau)$, or, therefore $\varepsilon^0\cos(\omega t)$. Since eq. (1.4) is linear in ε, σ may be found from the real part of σ^* in

$$\sigma^*(\mathrm{i}\omega t) = E_\mathrm{r}\varepsilon^0\mathrm{e}^{\mathrm{i}\omega t} + \int\limits_{-\infty}^{t} (E_\mathrm{R}(t-u') - E_\mathrm{r})(\mathrm{i}\omega\varepsilon^0\mathrm{e}^{\mathrm{i}\omega u'})\,\mathrm{d}u', \tag{1.7}$$

where past time is labeled u' and where eq. (1.6) has been used to find $\mathrm{d}\varepsilon/\mathrm{d}u'$. Making the substitution, $u = t - u'$ gives

$$\sigma^*(\mathrm{i}\omega t) = \varepsilon^0\mathrm{e}^{\mathrm{i}\omega t}\left[E_\mathrm{r} + \int\limits_0^\infty (E_\mathrm{R}(u) - E_\mathrm{r})(\mathrm{i}\omega\mathrm{e}^{-\mathrm{i}\omega u})\,\mathrm{d}u\right]. \tag{1.8}$$

It is convenient to define a *complex dynamic modulus* $E^*(\mathrm{i}\omega)$ such that

$$\sigma^*(\mathrm{i}\omega t) = E^*(\mathrm{i}\omega)\varepsilon^*(\mathrm{i}\omega t), \tag{1.9}$$

where

$$E^*(\mathrm{i}\omega) = E_\mathrm{r} + \mathrm{i}\omega\int\limits_0^\infty (E_\mathrm{R}(u) - E_\mathrm{r})\mathrm{e}^{-\mathrm{i}\omega u}\,\mathrm{d}u. \tag{1.10}$$

Although only the real part of $\sigma^*(\mathrm{i}\omega t)$ is of physical significance, since the right hand side of eq. (1.9) involves the product of two complex numbers, the imaginary part of $E^*(\mathrm{i}\omega)$ does have physical meaning as it gives rise to a real term in $\sigma^*(\mathrm{i}\omega t)$. The real and imaginary parts of $E^*(\mathrm{i}\omega)$ in

$$E^*(\mathrm{i}\omega) = E'(\omega) + \mathrm{i}E''(\omega) \tag{1.11}$$

are given by

$$E'(\omega) = E_\mathrm{r} + \omega\int\limits_0^\infty (E_\mathrm{R}(u) - E_\mathrm{r})\sin(\omega u)\,\mathrm{d}u, \tag{1.12}$$

$$E''(\omega) = \omega\int\limits_0^\infty (E_\mathrm{R}(u) - E_\mathrm{r})\cos(\omega u)\,\mathrm{d}u. \tag{1.13}$$

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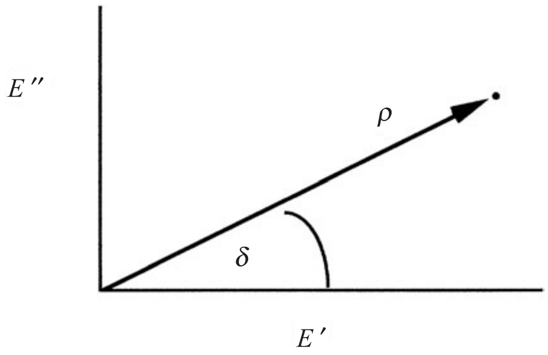

Figure 1.4 Complex plane representation of E^*.

The physical significances of E' and E'' are best seen by writing E^* in polar form (see Figure 1.4) as

$$E^* = \rho \mathrm{e}^{\mathrm{i}\delta}, \tag{1.14}$$

where

$$\rho = (E'^2 + E''^2)^{1/2} \tag{1.15}$$

and

$$\tan\delta = E''/E'. \tag{1.16}$$

Thus,

$$\sigma^*(\mathrm{i}\omega t) = \rho\varepsilon^0 \mathrm{e}^{\mathrm{i}(\omega t+\delta)} \tag{1.17}$$

and

$$\sigma(t) = \rho\varepsilon^0 \cos(\omega t + \delta) = \sigma^0 \cos(\omega t + \delta). \tag{1.18}$$

Therefore it may be seen that the stress in response to an imposed periodic strain of angular frequency ρ is also periodic with the same frequency but leads the strain by an angle δ. See Figure 1.5.

The maximum stress, i.e., its amplitude, is given by $\sigma^0 = \rho\varepsilon^0$. The real component of E^*, E', is called the *dynamic storage modulus* and the imaginary part, E'', is called the *dynamic loss modulus*. The reasons for these designations are the following.

The work done per unit volume, W, in deforming the material by a small strain is given by

$$\mathrm{d}W = \sigma\,\mathrm{d}\varepsilon = \mathrm{Re}(E^*\varepsilon^*)\,\mathrm{d}\varepsilon. \tag{1.19}$$

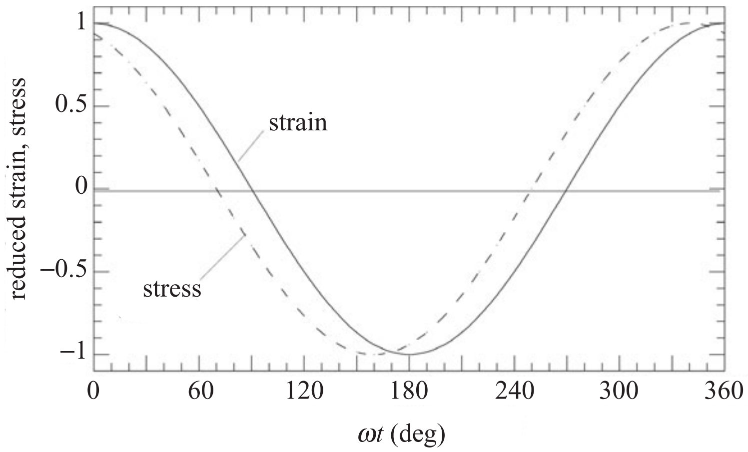

Figure 1.5 The stress and strain over one cycle in a dynamic experiment. Both are normalized to unity as, $\varepsilon/\varepsilon^0$ and σ/σ^0. Phase angle $\delta = 20^\circ$.

The work associated with E' is reversible and is zero over a complete cycle. However, as seen below E'' leads to energy absorption. The work per unit volume per second at frequency, ν, is

$$\dot{W} = \mathrm{d}W/\mathrm{d}t = \nu\,\mathrm{Re}\left[\int_0^{t=1/\nu} E^*\varepsilon^*(\mathrm{d}\varepsilon/\mathrm{d}u)\,\mathrm{d}u\right] \tag{1.20}$$

$$= \frac{\omega}{2\pi}\varepsilon^{0\,2}\mathrm{Re}\left[\int_0^{2\pi/\omega}(E' + \mathrm{i}E'')\mathrm{e}^{\mathrm{i}\omega u}(\mathrm{e}^{\mathrm{i}\omega u} - \mathrm{e}^{-\mathrm{i}\omega u})\frac{\mathrm{i}\omega}{2}\,\mathrm{d}u\right] \tag{1.21}$$

$$= \omega E''\varepsilon^{0\,2}/2. \tag{1.22}$$

1.6 Interconversion of stress relaxation and dynamic modulus

The complex dynamic modulus may be measured directly via the stress magnitude and the phase angle in response to an applied periodic strain of magnitude ε^0. However, it may also be derived indirectly from the results of a stress relaxation experiment using eq. (1.10) or equivalently eq. (1.12) and eq. (1.13). Notice, however, that the limits in these integrations are 0, ∞. The *entire* stress relaxation function over time must in principle be known. Because of the rather slowly varying with time or frequency nature of most polymeric relaxations this latter condition can be relaxed considerably. More on this is introduced later.

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It is also possible to convert the dynamic modulus into the relaxation modulus. This is done by invoking the Fourier transformation properties associated with eq. (1.10) or eq. (1.12), eq. (1.13). That is, if

$$f(x)=\sqrt{\frac{2}{\pi}}\int_0^\infty F_c(y)\cos(xy)\mathrm{d}y=\sqrt{\frac{2}{\pi}}\int_0^\infty F_s(y)\sin(xy)\,\mathrm{d}y, \tag{1.23}$$

then

$$F_c(y)=\sqrt{\frac{2}{\pi}}\int_0^\infty f(x)\cos(xy)\,\mathrm{d}x \tag{1.24}$$

and

$$F_s(y)=\sqrt{\frac{2}{\pi}}\int_0^\infty f(x)\sin(xy)\,\mathrm{d}x, \tag{1.25}$$

from which it follows that

$$E_R(t)=E_r+\frac{2}{\pi}\int_0^\infty [E'(\omega)-E_r]\sin(\omega t)\,\mathrm{d}\omega/\omega \tag{1.26}$$

or

$$E_R(t)=E_r+\frac{2}{\pi}\int_0^\infty E''(\omega)\cos(\omega t)\,\mathrm{d}\omega/\omega. \tag{1.27}$$

Thus interconversion of stress relaxation and dynamic data is possible via numerical Fourier transform methods provided the data cover or can be accurately extrapolated over the entire time or frequency range.

Since both $E'(\omega)$ and $E''(\omega)$ may be expressed in terms of a single function, $E_R(t)$, it is apparent that $E'(\omega)$ and $E''(\omega)$ must be themselves related. A relationship may be found by substituting eq. (1.27) into eq. (1.12),

$$E'(\omega)=E_e+\omega\int_0^\infty \frac{2}{\pi}\left[\int_0^\infty E''(x)\cos(xu)(\mathrm{d}x/x)\right]\sin(\omega u)\,\mathrm{d}u \tag{1.28}$$

$$=E_e+\frac{2}{\pi}\omega\lim_{R\to\infty}\int_0^\infty\left[\int_0^R E''(x)\cos(xu)\sin(\omega u)\,\mathrm{d}u(\mathrm{d}x/x)\right] \tag{1.29}$$

$$=E_e+\frac{2\omega}{\pi}\lim_{R\to\infty}\int_0^\infty E''(x)\left[\frac{1-\cos(\omega-x)R}{2(\omega-x)}+\frac{1-\cos(\omega+x)R}{2(\omega+x)}\right](\mathrm{d}x/x) \tag{1.30}$$