10.7 Temperature-dependent Viscoelastic Materials

Many materials, for example polymeric materials, have a response which is strongly temperature-dependent. Temperature effects can be incorporated into the theory discussed thus far in a simple way by allowing for the coefficients of the differential constitutive equations to be functions of temperature. Thus, Eqn. 10.3.19 can be expressed more generally as

$$p_o(\theta)\sigma + p_1(\theta)\dot{\sigma} + p_2(\theta)\ddot{\sigma} + \cdots = q_o(\theta)\varepsilon + q_1(\theta)\dot{\varepsilon} + q_2(\theta)\ddot{\varepsilon} + \cdots \qquad (10.7.1)$$

where θ denotes temperature. Equivalently, one can allow for the creep and relaxation functions to be functions of temperature in the hereditary integral formulation. Thus Eqns. 10.4.20-21 read

$$\begin{aligned} \varepsilon(t,\theta) &= \sigma(0)J(t,\theta) + \int_0^t J(t-\tau,\theta)\frac{d\sigma(\tau)}{d\tau}d\tau \\ \sigma(t,\theta) &= \varepsilon(0)E(t,\theta) + \int_0^t E(t-\tau,\theta)\frac{d\varepsilon(\tau)}{d\tau}d\tau \end{aligned} \qquad (10.7.2)$$

10.7.1 Example: The Maxwell Model

Consider a Maxwell material whose dash-pot viscosity η is a function of temperature θ. The differential constitutive equation is then

$$\sigma + \frac{\eta(\theta)}{\overline{E}}\frac{d\sigma}{dt} = \eta(\theta)\frac{d\varepsilon}{dt} \qquad (10.7.3)$$

where $\overline{E}$ is the temperature-independent spring stiffness. This equation is a function of both temperature and time. With temperature a function of time, $\theta = \theta(t)$, it is a linear differential equation with non-constant coefficients. For constant temperature, it has constant coefficients.

Consider first the case of constant temperature. The relaxation modulus and creep compliance functions can be evaluated by applying unit strain and unit stress. From the previous work, one has

$$\begin{aligned} E(t,\theta) &= \overline{E}e^{-t/t_R(\theta)}, \quad t_R(\theta) = \frac{\eta(\theta)}{\overline{E}} \\ J(t,\theta) &= \frac{1}{\overline{E}} + \frac{t}{\eta(\theta)} \end{aligned} \qquad (10.7.4)$$

Thus any given material has temperature-dependent relaxation and creep functions.

Consider now the change of variable

$$\xi = A\frac{t}{\eta(\theta)} \tag{10.7.5}$$

where *A* is any constant (which can be chosen arbitrarily for convenience – see later). This transforms Eqn. 10.7.3 into

$$\sigma(\xi) + \frac{A}{\overline{E}}\frac{d\sigma}{d\xi} = A\frac{d\varepsilon}{d\xi} \tag{10.7.6}$$

This is now an equation with dependence on only one variable, ξ. From this equation, one obtains relaxation and creep functions

$$\begin{aligned} E(\xi) &= \overline{E}e^{-\xi/t_R}, \quad t_R = \frac{A}{\overline{E}} \\ J(\xi) &= \frac{1}{\overline{E}} + \frac{\xi}{A} \end{aligned} \tag{10.7.7}$$

These equations generate **master curves** from which the different temperature-dependent curves 10.7.4 can be obtained.

Example Data

For example, consider a viscosity which varies linearly over the range $-100^{\circ}\mathrm{C} < \theta < 100^{\circ}\mathrm{C}$ according to the relation

$$\eta(\theta) = \eta_0\left[1 - A_\eta\left(\frac{\theta}{\theta_0} - 1\right)\right] \tag{10.7.8}$$

where η_0 is a constant viscosity, $A_\eta = 0.2$ and $\theta_0 = 20^{\circ}\mathrm{C}$ (a reference temperature at which $\eta(\theta) = \eta_0$. This function is plotted in Fig. 10.7.1 below.

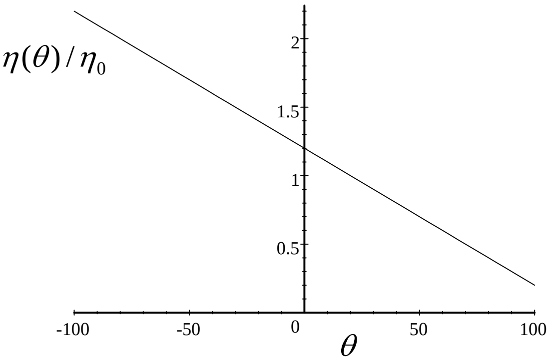

Figure 10.7.1: linear dependence of viscosity on temperature

Also, let $\eta_0 / \overline{E} = m$. The resulting relaxation and creep functions of Eqn. 10.7.4 are plotted in Fig. 10.7.2 below (for $m = 5$).

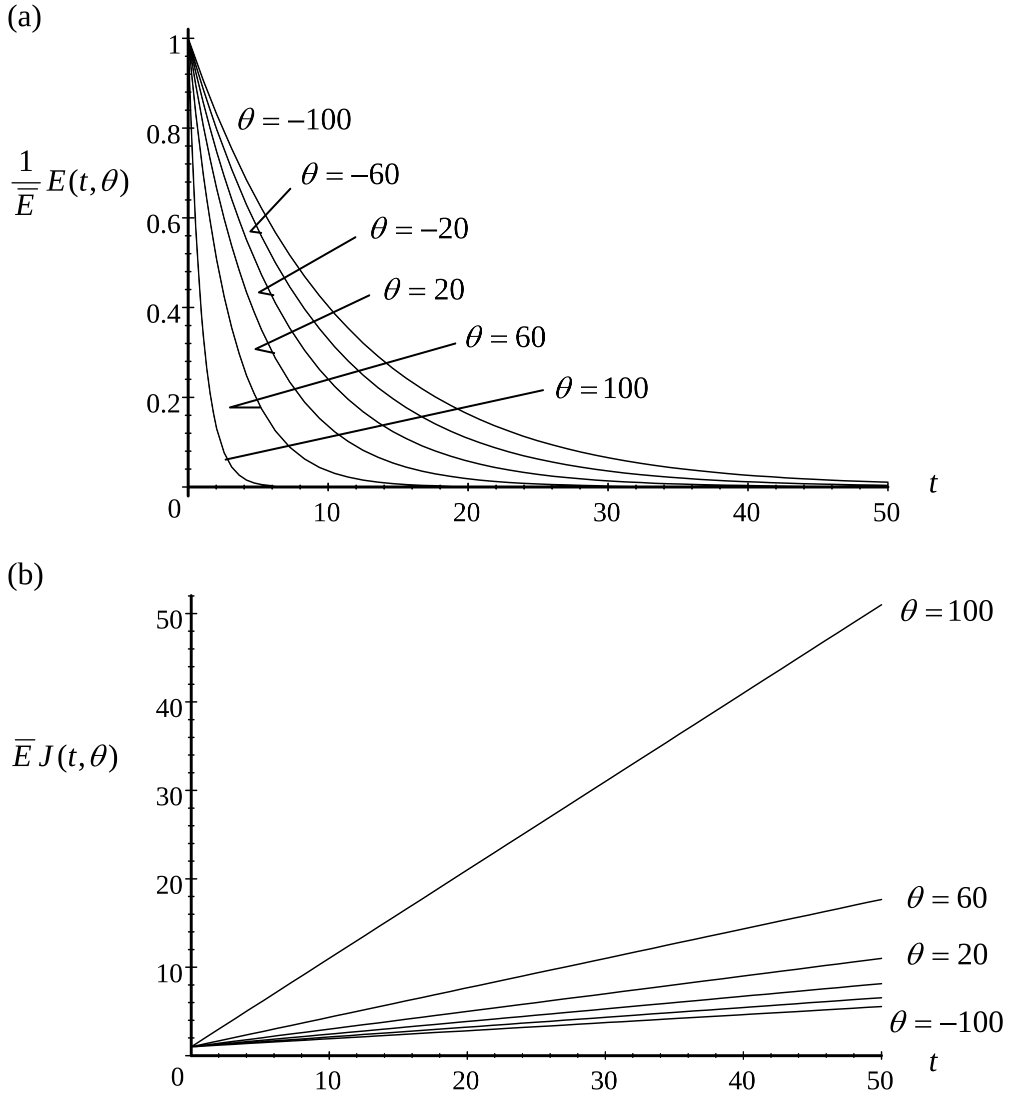

Figure 10.7.2: temperature-dependent functions; (a) relaxation modulus, (b) creep compliance

Note the following, referring to Fig. 10.7.2:

(i) for temperatures greater than the reference temperature $\theta = \theta_0 = 20^{\circ}$ (see Eqn. 10.7.8), the viscosity is $\eta(\theta) < \eta_0$. This implies that, for $\theta > \theta_0$, the relaxation times are shorter than for $\theta = \theta_0$ (see Eqn. 10.7.4a), Fig. 10.7.2a, and the slope of the creep curves is greater than for $\theta = \theta_0$ (see Eqn. 10.7.4b)., Fig. 10.7.2b.

(ii) for temperatures smaller than the reference temperature, $\eta(\theta) > \eta_0$. Thus, for $\theta < \theta_0$, the relaxation times are longer than for $\theta = \theta_0$ and the slope of the creep curves is smaller than for $\theta = \theta_0$.

Now choose the constant *A* in Eqn. 10.7.5 to be equal to η_0. This ensures that $\xi = t$ at the reference temperature θ_0 (see 10.7.8). In other words, the master curves of Eqn. 10.7.7 and the functions 10.7.4 corresponding to θ_0 coincide (with the *t* axis and ξ axis coincident).

The master relaxation and creep curves of Eqn. 10.7.7 are now $E(\xi)/\overline{E} = e^{-\xi/m}$ and $\overline{E}J(\xi) = 1 + \xi/m$. These are plotted in Fig. 10.7.3 below (for $m = 5$).

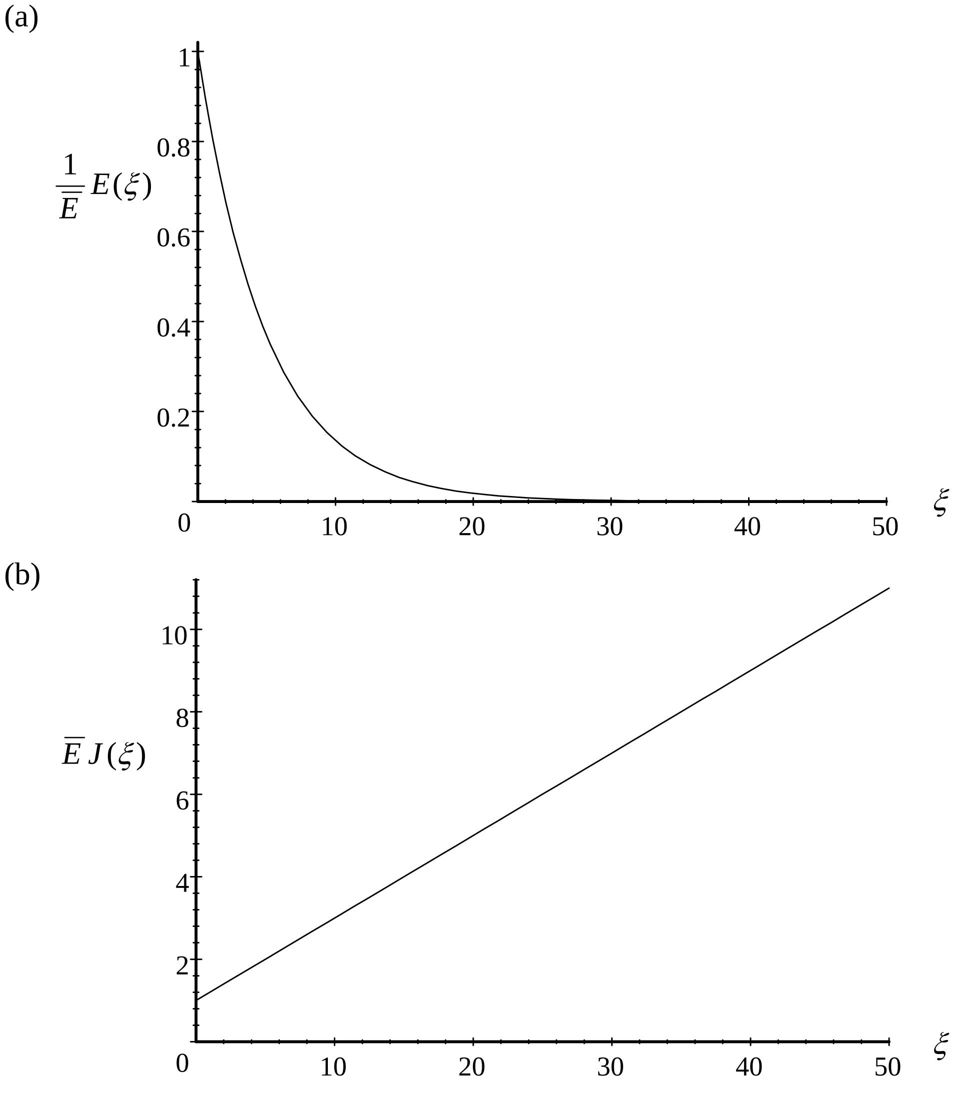

Figure 10.7.3: master curves; (a) relaxation modulus, (b) creep compliance

All the curves of Fig. 10.7.2 collapse onto the master curve of Fig. 10.7.3 as follows:

(i) the curves corresponding to the reference temperature, $\theta = \theta_0 = 20^\circ$, in Figs. 10.7.2 lie on the master curves (with the *t* axis and ξ axis coincident)

(ii) for a curve with $\theta > \theta_0$, if the time axis of Fig. 10.7.2a,b is "stretched" (according to 10.7.5), the curve will come to lie along the $\theta = \theta_0$ curve (and hence on the master curve); for a curve with $\theta < \theta_0$, if the time axis of Fig. 10.7.2a is "shrunk" (according to 10.7.5), the curve will come to lie along the $\theta = \theta_0$ curve (and hence on the master curve)

10.7.2 Thermorheologically Simple Materials

The fact that the relaxation and creep curves of Fig. 10.7.2 collapsed onto the master curves of Fig. 10.7.3 relied on the change of variable, Eqn. 10.7.5, reducing the time and temperature dependent constitutive relation 10.7.3 to an equation in one variable, ξ, only, Eqn. 10.7.6. This in turn depended critically on the form of the differential equation 10.7.3. For example, if the spring stiffness $\overline{E}$ in the Maxwell model is temperature-dependent, the collapsing of curves is not possible.

Temperature-dependent viscoelastic materials for which this collapsing of curves is possible are called **thermorheologically simple** materials. In this context, the parameter ξ is called the **reduced time**. More generally, the transformation 10.7.5 is expressed in the form

$$\xi = \frac{t}{a_\theta(\theta)} \tag{10.7.9}$$

and the function $a_\theta(\theta)$ is called the **shift factor** function. The shift factor is chosen so that the relaxation and creep curves corresponding to the chosen reference temperature θ_0 coincide (as in the Maxwell model example above), i.e. so that $a_\theta(\theta_0) = 1$.

The relaxation and creep functions now transform as

$$E(t,\theta) \;\; \rightarrow \;\; E(\xi,\theta_0), \qquad\qquad J(t,\theta) \;\; \rightarrow \;\; J(\xi,\theta_0) \tag{10.7.10}$$

For temperatures below the reference temperature, $\theta < \theta_0$, $a_\theta(\theta_0)$ will be greater than 1, and the corresponding relaxation/creep curves collapse onto the master curve by "shrinking" the time axis *t*, which looks like a "shifting" of the curve "to the left" onto the $\theta = \theta_0$ curve. On the other hand, for $\theta > \theta_0$, $a_\theta(\theta_0) < 1$, and the corresponding curves collapse by a "stretching" of the time axis, which looks like a "shifting" of the curves "to the right" onto the master curve. This is summarised in Fig. 10.7.4 below.

The result of this is that materials at high temperatures and high strain rates behave similarly to materials at low temperatures and low strain rates.

The method discussed can also be used when the temperature is time-dependent, for then the transformation can be expressed as

$$\xi(t) = \int_0^t \frac{d\tau}{a_\theta(\theta(\tau))} \tag{10.7.11}$$

so that

$$\frac{d\xi}{dt} = \frac{1}{a_\theta(\theta(t))} \tag{10.7.12}$$

leading to the same reduced differential equation.

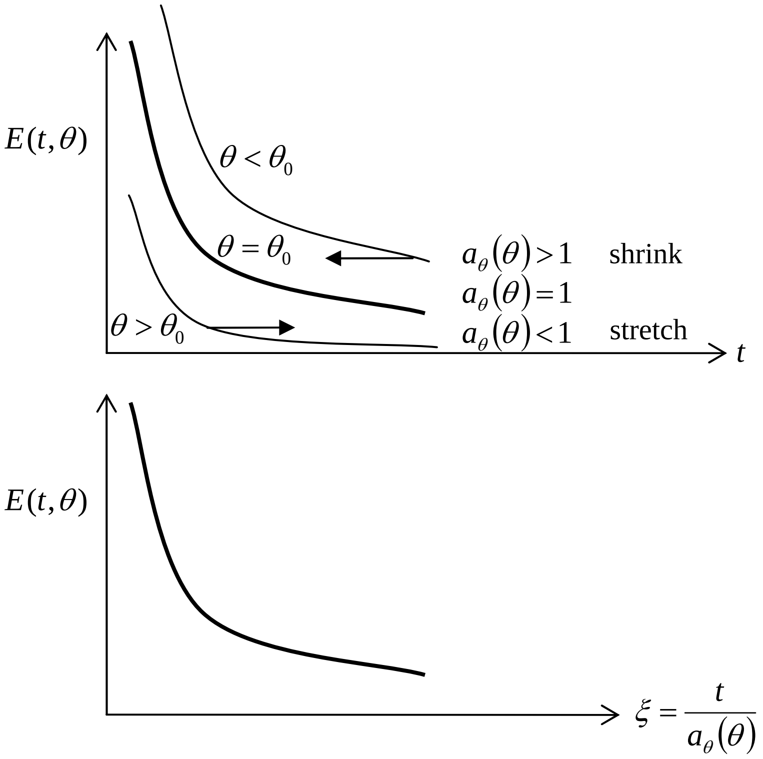

Figure 10.7.4: Relaxation modulus, as a function of (a) time, (b) reduced time

The above discussion has related to the differential constitutive equation 10.7.1. The analysis can also be expressed in terms of hereditary integrals of the form 10.7.2. For example, the equivalent hereditary integral in terms of reduced time, corresponding to the reduced differential equation (see Eqn. 10.7.6 for the Maxwell model equation) is

$$\sigma(\xi) = \int_{-\infty}^{\xi} E(\xi - \tau)\frac{d\varepsilon(\tau)}{d\tau}d\tau \tag{10.7.13}$$

where $E(\xi)$ is as before (see Eqn. 10.7.7 for the Maxwell model expression).