

# Viscoelastic behaviour of glass and “fictive temperature” – Pilkington

## 1 Introduction

At relatively high temperatures, glass is known to be very well characterised as an incompressible Newtonian liquid with temperature-dependent viscosity. (A simple empirical relation between viscosity and temperature, called Fulcher’s law, gives remarkably good agreement over many orders of magnitude.) Similarly, at rather lower temperatures, it behaves very much like a linear elastic solid. In this report we are concerned with the intermediate range, in the neighbourhood of the “glass transition temperature” (defined later) in which glass has some rather unusual properties. In particular, it has a complex molecular structure that changes gradually as the temperature varies, rather than the traditional picture of (say) a metal that abruptly solidifies into a periodic crystalline structure at the melting temperature. To model the evolution of a piece of glass during an experiment that involves temperature fluctuations, it is vital to include these structural changes, since the material properties depend crucially on the structure.

Glass scientists frequently attempt to describe this internal structure using a “fictive temperature” (defined later). At present, it is far from clear to what extent fictive temperature is a well-defined concept, and the models that have been proposed for its evolution are somewhat speculative; some of these are described briefly in Section 2. It is highly desirable to put fictive temperature and the modelling thereof on a firm theoretical basis. Unfortunately, although viscoelasticity and temperature effects (such as thermoelasticity) are quite familiar to applied mathematicians, fictive temperature is almost entirely unknown. One aim of this report is to expose this fascinating area of materials science modelling to the applied mathematics community.

A fundamental assumption in all previous modelling efforts in this area has been that the evolution of the microstructure towards its equilibrium

state obeys some kind of relaxation law. Associated with any such law is a relaxation time or a distribution thereof. Equally, in the temperature range of interest glass is known to be viscoelastic, so the stress also satisfies a relaxation law. Intuitively one might expect these two relaxation processes to be related, since internal stress and internal structure are intimately related. The second aim of this report is to attempt to obtain a model that unites structural and stress relaxation, and in particular predicts how the time-scales for each might be related. In Section 3 we propose such a model. We begin with a simple one-dimensional spring/dashpot element which is then used as the basis of a three-dimensional continuum theory. In Section 4 we suggest some simple experiments that might be used to validate the model and to determine some of the parameters therein. Finally we draw our conclusions in Section 5.

## 2 Background

In this section we outline the concept of fictive temperature and give some examples of empirical equations for its evolution that have been suggested previously. The material is largely taken from Scherer (1986), where more details and references can be found.

### 2.1 Vibrational and structural changes

It is well known that most materials, be they solid or fluid, have measurable physical properties, (*e.g.*, specific heat, density, refractive index) which depend on temperature. However, when the temperature is changed, there may be an appreciable delay before any such property adjusts to its equilibrium value. Thus the physical properties depend on the thermal history and not just on the instantaneous temperature. The explanation for this behaviour in glass is that, as the temperature varies, two basically different types of internal change occur in the material:

- **Vibrational changes** (*i.e.*, changes in the vibrational modes of molecules) are the familiar effects that cause (for example) the density of a solid to depend on temperature, even though its molecular structure is fixed;
- **Structural changes** occur because the preferred molecular structure of the material depends on temperature.

The important distinction is that the latter of these occur much more slowly than the former, which for our purposes can be considered to be effectively instantaneous.

In a complicated material like glass there are many structural changes that can be identified with the breaking and reformation of various atomic bonds, and occur over a wide range of temperatures and time-scales. Fortunately, the details of these need not concern us here, except for the experimental observation that the time-scale (say  $t_{st}$ ) for structural changes is strongly temperature-dependent:

- At **high temperatures**, glass behaves very much like a Newtonian liquid with temperature-dependent viscosity. Here  $t_{st}$  is small compared with any other time-scales of interest so that structural changes are effectively instantaneous;
- At **low temperatures**, glass behaves like a linear thermoelastic solid. Now  $t_{st}$  is very large (maybe millennia!) so that the structure is effectively “frozen in”. Any thermal effects in this regime are purely vibrational;
- At **intermediate temperatures**, at which glass is mechanically viscoelastic,  $t_{st}$  is about the same as the time-scales of interest in glass processing. Only in this regime is the thermal history, rather than just the instantaneous temperature, important in determining the structure, and thus the physical properties, of glass.

In the first two regimes, the behaviour of glass is fairly easy to model. In this report we concentrate on the third, in which there are modelling issues that do not seem to have been satisfactorily addressed at present.

## 2.2 The concept of fictive temperature

One way to approach the behaviour outlined above is to characterise the state of the glass at any moment in time by its temperature  $T$  and an “order parameter” that describes the internal structure. Order parameters mean different things to different people; they may be scalar, vector or even tensor functions, which somehow quantify the departure of the material from thermodynamic equilibrium. Many glass scientists use the scalar so-called “fictive temperature”, introduced by Tool (1946), as such a parameter. A detailed exposition on the subject can be found in Scherer (1986). Put crudely, the idea is as follows:

*During an experiment, we measure the instantaneous value of some property  $P$  and the instantaneous temperature  $T$ . If the temperature has varied during the experiment,  $P$  will not be at its*

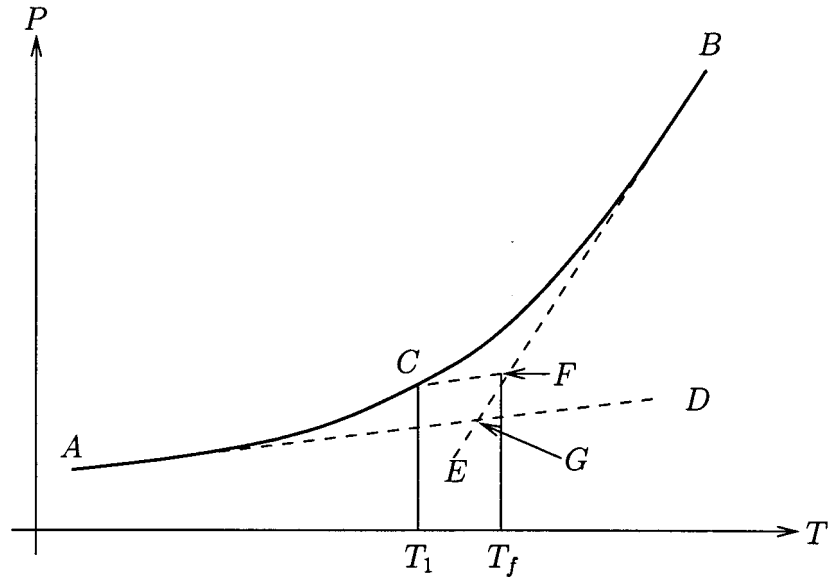


Figure 1: Schematic of the dependence of a property  $P$  on temperature  $T$  during a typical experiment, showing the derivation of the fictive temperature  $T_f$  at a point  $T_1$ . (After Scherer 1986.)

*equilibrium value for the temperature  $T$ . Now we instantaneously change the temperature — too rapidly for any structural changes to occur — to such a value that  $P$  is now at equilibrium. The new value of  $T$  required for this is the **fictive temperature**  $T_f$  of the material.*

The typical behaviour of a property  $P$  with  $T$  is shown in Figure 1. Here the solid line  $BCA$  shows how  $P$  varies as the temperature is reduced, say at a constant rate. Notice that at large  $T$ , the curve asymptotes to the straight line  $EB$ : this is the behaviour corresponding to vibrational and structural changes. However, at low values of  $T$ , the curve asymptotes to a different straight line  $AD$ , which has somewhat smaller slope. Here no structural changes occur and the variations in  $P$  are due purely to vibrational effects. Now consider the point  $C$  midway through the experiment, at which  $T = T_1$ , say. Because  $C$  does not lie on  $EB$ , the structure of the glass is not at equilibrium at this point: if  $T$  were held constant at  $T_1$  then we would expect  $P$  to decrease gradually until equilibrium was reached. However, if we were to increase  $T$  abruptly, (*i.e.*, too rapidly for any structural changes), then  $P$  would follow the dotted line  $CF$  (whose slope, due to vibrational changes, is parallel to  $AD$ ). At the point  $F$  where  $CF$  intersects  $EB$ , the glass would be at equilibrium. The value of  $T$  at  $F$  is called the fictive temperature  $T_f$

of the point  $C$ .

At high temperatures,  $T_f$  is equal to  $T$  since the structure has sufficient time to relax as the material cools. As  $T$  decreases further,  $T_f$  starts to lag behind  $T$  as the structure can no longer keep pace with the cooling rate. Hence, as in the idea of an order parameter, the difference between  $T_f$  and  $T$  measures the distance of the structure from equilibrium, and so the relaxation of the structure towards equilibrium is mirrored by the relaxation of  $T_f$  towards  $T$ .

Notice that at low temperatures,  $T_f$  approaches a limiting value corresponding to the intersection  $G$  between  $AD$  and  $EB$ . This limiting value is commonly called the *glass transition temperature* and denoted  $T_g$ . By the argument given above,  $T_g$  in some sense corresponds to the structure that is “frozen in”. However,  $T_g$  is not a material property of the glass but depends on the cooling rate, as shown in Figure 2. Here we sketch the variation of a property  $P$  with temperature  $T$  for different cooling rates  $q = dT/dt$ . At the faster cooling rate, the glass has less time to relax and so is further from equilibrium: this corresponds to a higher value of  $T_g$ .

The most fundamental question concerning fictive temperature is:

### **Is fictive temperature a well-defined concept?**

If the structure of glass were described completely by the fictive temperature, then *all* the properties  $P$  of the glass should depend on  $T_f$  in the same way. Careful experiments have shown that this is not quite true. Effectively, one obtains different values of  $T_f$ , depending on what property  $P$  one is measuring. It has been proposed to remedy this by characterising the structure by a number of different fictive temperatures corresponding to different properties.

Of course, this begs the question of whether fictive temperature is a useful way of characterising the structure. If we have to define a different fictive temperature for each physical property, why not just use the property itself as an order parameter?

Another question that arose at the Study Group is:

### **Why are the lines $AD$ and $EB$ in figure 1 straight?**

This is really just for ease of illustration. Of course in practice a property  $P$  need not be linear in  $T$ , but an appropriate function of  $P$  can always be taken that *is* linear as  $T \rightarrow 0$  and as  $T \rightarrow \infty$ .

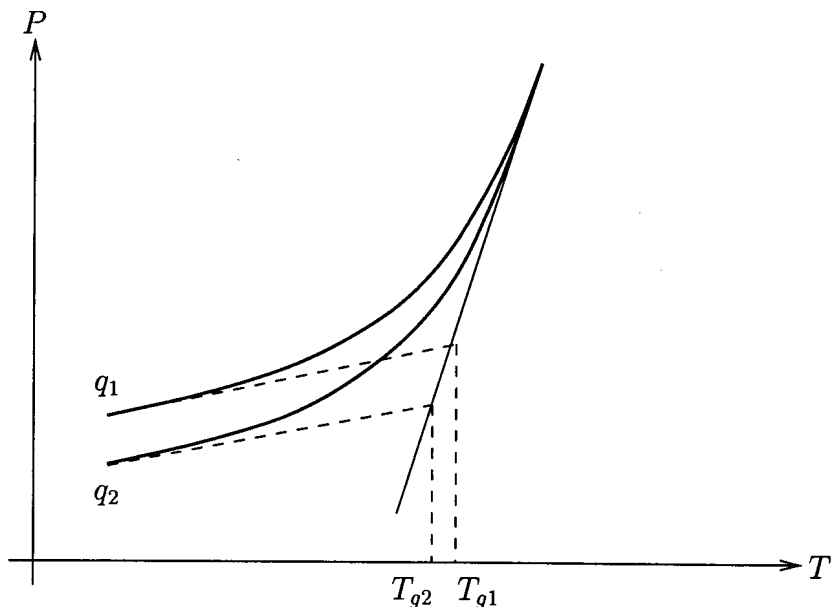


Figure 2: The variation of a property  $P$  with temperature for two different cooling rates  $q_1$  and  $q_2$  with  $|q_1| > |q_2|$ , showing the glass transition temperature  $T_g$  in each case. (After Scherer 1986.)

## 2.3 Empirical equations for $T_f$

### 2.3.1 Tool's equation

Tool (1945) supposed that the property  $P$  satisfied a relaxation law of the form

$$\frac{dP}{dt} = \frac{P_{\text{eq}}(T) - P(T, t)}{\tau_P}, \quad (1)$$

where  $P_{\text{eq}}(T) = P(T, \infty)$  is the equilibrium value, and the relaxation time  $\tau_P$  depends on the property being measured, the temperature,  $T$ , and the structure. From this, and assuming behaviour like that shown in figure 1, he arrived at **Tool's equation**:

$$\frac{dT_f}{dt} = \frac{T - T_f}{\tau_P}. \quad (2)$$

It only remains to determine  $\tau_P$ . By analogy with stress relaxation, it is natural to assume

$$\tau_P = \frac{\mu}{K_P}, \quad (3)$$

where  $\mu$  is the dynamic viscosity and  $K_P$  is a constant with the dimensions of elastic modulus. Now it would seem that we simply have to use one of the

many empirical relations for  $\mu$  as a function of  $T$  (e.g., Arrhenius, exponential or Fulcher's law) to close (2). This approach does not match experimental data since it fails to take account of the variation of  $\mu$  with structure. Tool (1946) obtained good agreement with experiments by *evaluating the empirical relation for  $\mu$  at some weighted average of  $T$  and  $T_f$  rather than at  $T$* , that is

$$\mu = \mu(\theta T + (1 - \theta)T_f), \quad 0 \leq \theta \leq 1. \quad (4)$$

There is no theoretical justification for this step. Neither is there (at present) any systematic argument for how the relaxation time in (2) ought to depend on  $T$  and  $T_f$ .

### 2.3.2 Narayanaswamy's model

Tool's equation (2), which assumes that structural relaxation is characterised by a single relaxation time  $\tau_P$ , was generalised by Narayanaswamy (1971) to allow the material to have a distribution of relaxation times. The variation of  $\tau_P$  over time is captured by using the *reduced time*  $\zeta$ , defined as

$$\zeta = \int_0^t \frac{dt'}{\tau_P}. \quad (5)$$

Under certain assumptions, notably that of *thermorheological simplicity* (TRS), Narayanaswamy (1971) proposed that the evolution of  $T_f$  is given by the integral equation

$$T_f = T - \int_0^\zeta M_P(\zeta - \zeta') \frac{dT}{d\zeta'} d\zeta', \quad (6)$$

where the *relaxation function*  $M_P$  must be found by fitting experimental data (TRS is effectively the assumption that  $M_P$  depends only on  $\zeta$ ). Tool's equation is recovered from (6) if  $M_P$  is a single exponential,

$$M_P = e^{-\zeta}.$$

Better agreement with experiments has been found by taking  $M_P$  to be a sum of exponentials or (more commonly) a stretched exponential:

$$M_P = \exp(-\zeta^b).$$

Notice that closure of the model still requires a relation for  $\tau_P$  in terms of  $T$  and  $T_f$ . Narayanaswamy (1971) proceeded in the same vein as Tool (1945) to assume a functional form of  $\tau_P$  as a function of a weighted average of  $T$  and  $T_f$ . Again, some theoretical justification for such an assumption is sorely needed.

### 3 A unified model for structural and stress relaxation

In this section, we develop an idea due to David Gelder in an attempt to relate stress and structural relaxation. The idea is based on experimental evidence that stress relaxation in glass is fairly well modelled by the superposition of a moderate number (maybe two or three) of exponential decays. It is reasonable to regard each of these decay processes as being associated with the relaxation of a particular bond. This motivates the analysis of a simple one-dimensional spring/dashpot system that is supposed to represent two bonds with different relaxation times. We find that the system possesses many of the glass properties described in the previous section, and that it predicts a relation between structural relaxation, *i.e.*, fictive temperature effects, and stress relaxation. Then, based on this simple system, a three-dimensional model is proposed.

#### 3.1 A one-dimensional model

Consider the one-dimensional element shown in Figure 3. Here we have two Maxwell-type spring/dashpot elements in parallel, with different elastic moduli  $E_i$  and relaxation times  $\tau_i$  (and hence viscosities  $\mu_i = \tau_i E_i$ ). The idea is that these represent two different types of molecular bond. This could be generalised to include more such bonds, or more complicated arrangements of springs and dashpots, but for the sake of simplicity, in this report we concentrate on the system in Figure 3. Notice that the ends of the elements are joined so that they must always have the same length  $l$ .

We assume a simple Maxwell law for each element so that the two stresses  $\sigma_i$  satisfy

$$\sigma_1 + \tau_1 \dot{\sigma}_1 = \tau_1 E_1 \dot{l}, \quad (7)$$

$$\sigma_2 + \tau_2 \dot{\sigma}_2 = \tau_2 E_2 \dot{l}, \quad (8)$$

where  $\dot{\phantom{x}}$  denotes time derivative. The *total* stress in the system is

$$\sigma = \sigma_1 + \sigma_2. \quad (9)$$

If either  $l$  or  $\sigma$  is specified (one can envisage simple experiments in which either the stress is fixed and the strain measured or vice versa) then (7)–(9), along with suitable initial conditions, are sufficient to determine all the remaining dependent variables. Alternatively, for the moment treating  $E_i$  and



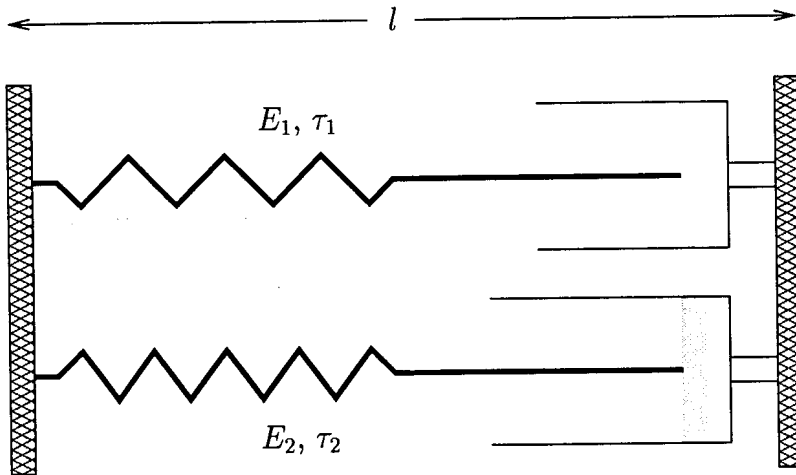


Figure 3: Schematic of two coupled spring/dashpot elements.

$\tau_i$  as constants, by eliminating  $\sigma_1$  and  $\sigma_2$ , we obtain a single o.d.e. relating  $l$  and  $\sigma$ :

$$\tau_1\tau_2(E_1 + E_2)\ddot{l} + (\tau_1E_1 + \tau_2E_2)\dot{l} = \tau_1\tau_2\ddot{\sigma} + (\tau_1 + \tau_2)\dot{\sigma} + \sigma. \quad (10)$$

This elucidates one interesting property of the system, namely that if  $l$  is specified then  $\sigma$  relaxes over the two time-scales  $\tau_1$  and  $\tau_2$ , while if  $\sigma$  is specified,  $l$  relaxes over the single time-scale

$$\tau_l = \frac{\tau_1\tau_2(E_1 + E_2)}{\tau_1E_1 + \tau_2E_2}. \quad (11)$$

The most important property of the system as far as this report is concerned is that it can continue to evolve even when its net stress is zero. If a single element of the type modelled by (7) is in mechanical equilibrium ( $\sigma_1 = 0$ ) then its state is necessarily fixed ( $\dot{l} = 0$ ). However, our two-element system can have  $\sigma_1 = -\sigma_2 \neq 0$  so that, although the element as a whole is in mechanical equilibrium, the individual bonds are not. The residual stress in  $\sigma_1$  and  $\sigma_2$  could be identified with the *structure* of the element, and their relaxation towards zero with the structural relation towards its preferred state. Thus, the state of the system at any time can be described by the stress  $\sigma = \sigma_1 + \sigma_2$ , and a *scalar order parameter*, which characterises the structure, and could be any conveniently chosen function of  $\sigma_1$  and  $\sigma_2$  that is linearly independent of  $\sigma$ . If we make this identification, then the *structural relaxation time* is exactly  $\tau_l$  given in (11).

This simple argument suggests that we may indeed be able to combine both stress and structural relaxation in a simple framework such as (7–9),

and that the time-scales for the two processes may thereby be related. To compare these ideas with those of the previous section, we must now include thermal effects. In terms of the simple element in Figure 3, changes in the temperature  $T$  can broadly be expected to affect:

*i* the material parameters  $E_i$  and  $\tau_i$  and

*ii* the natural lengths of the springs.

If the latter are denoted by  $l_{0i}$  then the natural generalisation of (7, 8) is

$$\sigma_1 + \tau_1 \dot{\sigma}_1 = \tau_1 E_1 (\dot{l} - \dot{l}_{01}), \quad (12)$$

$$\sigma_2 + \tau_2 \dot{\sigma}_2 = \tau_2 E_2 (\dot{l} - \dot{l}_{02}). \quad (13)$$

If we imagine an experiment in which the temperature of an *unstressed* piece of glass is varied, then we have  $\sigma_2 = -\sigma_1$ , and so the structural relaxation is given by

$$\sigma_1 + \tau_1 \dot{\sigma}_1 = \left( \frac{\tau_1 \tau_2 E_1 E_2}{\tau_1 E_1 + \tau_2 E_2} \right) (\dot{l}_{02} - \dot{l}_{01}). \quad (14)$$

If during the experiment we were to measure the length as a function of time, we would find that it satisfies

$$\begin{aligned} (\tau_1 - \tau_2) \frac{d}{dt} \left\{ \frac{\tau_1 \tau_2}{\tau_1 - \tau_2} \left[ (E_1 + E_2) \dot{l} - (E_1 \dot{l}_{01} + E_2 \dot{l}_{02}) \right] \right\} + \\ (\tau_1 E_1 + \tau_2 E_2) \dot{l} - (\tau_1 E_1 \dot{l}_{01} + \tau_2 E_2 \dot{l}_{02}) = 0. \end{aligned} \quad (15)$$

Hence for rapid fluctuations in temperature, (*i.e.*,  $t \ll \tau_i$ ), we would get an elastic response, with

$$l \sim \frac{E_1 l_{01} + E_2 l_{02}}{E_1 + E_2}, \quad (16)$$

while for slower fluctuations ( $t \gg \tau_i$ ) the response would be viscous:

$$l \sim \frac{\tau_1 E_1 l_{01} + \tau_2 E_2 l_{02}}{\tau_1 E_1 + \tau_2 E_2}. \quad (17)$$

Notice that in the special case  $\tau_1 = \tau_2$ , in which the material is characterised by a single relaxation time, (16) and (17) are identical. Also, we could not possibly obtain two different behaviours like (16) and (17) from a single element such as (12)—if  $\sigma_1 = 0$  then (12) necessarily implies  $l \sim l_{01}$ . Different limiting behaviours *could* be obtained by using an alternative, (*e.g.*, Jeffreys) constitutive law in (12), but this would contradict the experimental

evidence that glass *is* basically Maxwellian, *i.e.*, elastic over short times and viscous over long times.

We could use  $l$  as the property  $P$ , as shown in Figure 1. Then the two behaviours (16) and (17) correspond to the slopes of  $AD$  and  $EB$  respectively, that is (16) represents *vibrational* effects, while (17) represents *vibrational and structural* effects. Before we can look at solutions of (15) and draw comparisons with figure (1), we need to know the material parameters  $E_i$ ,  $\tau_i$  and  $l_{0i}$ . In general, all of these are temperature-dependent. Also, recall that the properties, particularly the relaxation times, are known to be dependent on structure. Since in our model structure is described by the internal stresses  $\sigma_i$ , we should make the Maxwell elements in (12) and (13) nonlinear, with parametric dependence on  $\sigma_i$ .

### 3.2 A three-dimensional model

Extending this simple model to three dimensions is a non-trivial task. Firstly, the scalar stress must be replaced with a symmetric stress tensor  $\boldsymbol{\sigma}$ . Secondly, when taking the time derivative of such quantities, one must ensure that the operator is suitably invariant under axis transformations. For large-amplitude motions one of the so-called *co-deformational* or *co-rotational derivatives* should be employed, but under conditions of small deformation, all of these can be approximated by the normal partial time derivative.

For a two-component Maxwell material, the obvious extension of the standard model is

$$\left(\tau_i \frac{\partial}{\partial t} + 1\right) \boldsymbol{\sigma}_i = \lambda_i \nabla \cdot \mathbf{u} \mathbf{I} + \mu_i (\nabla \mathbf{u} + \nabla \mathbf{u}^T), \quad i = 1, 2, \quad (18)$$

where  $\mathbf{u}$  is the velocity field and  $\lambda_i$  and  $\mu_i$  are the bulk and shear viscosities. In the one-dimensional model considered previously, it was assumed that the length  $l$  was the same for each of the elements. In the present three-dimensional scenario, the equivalent assumption is that both viscoelastic species experience the same strain field. That is why the same velocity vector  $\mathbf{u}$  appears in each of the cases  $i = 1, 2$  of (18).<sup>1</sup> Conservation of mass requires that

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{u}) = 0 \quad (19)$$

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<sup>1</sup>In a classical two-phase approach, one would associate a velocity  $\mathbf{u}_i$  with each phase, and then pose a law for inter-phasic motion. From this viewpoint our assumption is effectively that of no slip between the phases.

(again, for small deformations this would typically be linearised), while a stress balance, assuming inertia is negligible, leads to

$$\nabla \cdot \boldsymbol{\sigma} = \mathbf{0}. \quad (20)$$

As in the one-dimensional model, the net internal stress is

$$\boldsymbol{\sigma}_1 + \boldsymbol{\sigma}_2 = \boldsymbol{\sigma}. \quad (21)$$

Once the parameters have been specified, these equations form a closed model for a two-component viscoelastic material and are a natural generalisation of (7)–(9). Recall that in the one-dimensional model we supposed that the two stresses  $\sigma_i$  could describe both the net stress  $\sigma = \sigma_1 + \sigma_2$  and the structure, and proposed the use of a scalar function of the  $\sigma_i$  as an *order parameter* that measures the departure of the structure from equilibrium. If we make the same identification in the current three-dimensional model, then in general *the structure must be described by a symmetric order tensor rather than a scalar*.

### 3.3 Temperature effects

The above model is derived for an isothermal material, and can adequately predict two time-scale decay of stress. Many cases of interest in the glass processing industry occur across a range of temperatures, and the model must be modified to include such situations. Inspired by the one-dimensional case, we could proceed by adding a term to (18), relating to the change in internal bond lengths. Assuming our glass to be isotropic, this would be a term such as

$$\dots = \dots + \tau_i \frac{d}{dt} l_i(T), \quad (22)$$

and would allow a strain to be introduced through heating of the material. The following simple thought experiment suggests that this however is insufficient:

*Consider a block of glass filling a rigid box of fixed dimensions, and held at temperature  $T_0$  sufficiently long that it has reached equilibrium. The glass is now heated at a steady rate until it reaches the new temperature  $T_1$ , where it is then held. Throughout the heating, the stress exerted on the box is measured, and the size of the box held constant (so that  $\mathbf{u} = \mathbf{0}$ ). The model implied by (22) would predict that the stress increases while the temperature changes, and then relaxes to zero as the material reaches equilibrium. Despite being heated, the equilibrium density of the glass would remain unchanged.*

The absence of a preferred size for the glass is a consequence of the spring/dashpot model we have chosen, which allows all stresses to relax to zero. To make our model more physically realistic we introduce a pressure-like term (in much the same way as a partial pressure is used in two-phase flow) that both allows a change in temperature to drive the system from equilibrium and gives a preferred density for the material at each temperature. The exact form this should take is the subject of much debate, as is the “best” way in which to add it to the isothermal equation (18). As a starting point we use the analogy with thermoelasticity to modify (18) thus

$$\left(\tau_i \frac{\partial}{\partial t} + 1\right) (\boldsymbol{\sigma}_i + \alpha_i P \mathbf{I}) = \lambda_i \nabla \cdot \mathbf{u} \mathbf{I} + \mu_i (\nabla \mathbf{u} + \nabla \mathbf{u}^T), \quad (23)$$

with the exact form for  $P(T, \rho, \dots)$  to be determined subsequently. Here  $\alpha_i$  represents the relative susceptibility to thermal effects of each viscoelastic component, with  $\alpha_1 + \alpha_2 = 1$ .

This modified model certainly has some of the desired properties, including:

- the system is sensitive both to temperature and its rate of change;
- at each  $T$  there is a residual stress that cannot relax away if the material is not at its equilibrium density.

One questionable consequence of this choice for the dependence on  $P$  is the natural equilibrium state that can emerge when the block is not allowed to expand ( $\mathbf{u} = \mathbf{0}$ ). Once the block is in equilibrium then changing the temperature will never force it from this state — the stress exerted by the block ( $\boldsymbol{\sigma} = -P\mathbf{I}$ ) depends only on the current temperature and not on the route taken to reach it. This might be remedied by using a different viscoelastic law (one possible suggestion was to use a Maxwell law for shear stress and a Kelvin law for isotropic stress). However, since the whole concept of using coupled viscoelastic laws to model glass is rather speculative, it seems prudent to use a relatively simple viscoelastic law like (23) as a first stab. Once the usefulness of our two-phase approach has been evaluated, more modelling effort should certainly go into deciding exactly the right form for the stress law to replace (23).

Once the physical parameters are known, (19), (20), (21) and (23), along with suitable boundary and initial conditions, are sufficient to determine the unknowns  $\rho$ ,  $\mathbf{u}$ ,  $\boldsymbol{\sigma}_1$  and  $\boldsymbol{\sigma}_2$ , *if the temperature  $T$  is given*. In practice, it is difficult to control the temperature directly in an experiment. It is more natural to supply heat at a given rate, and heating is likely to take place only

at the boundary of a sample. If such issues are to be addressed by our model, we must write down an energy equation. In doing so, on physical grounds it does not seem necessary to associate a different temperature field with each phase. Instead we assume that the glass as a whole has a temperature  $T$ , and thermal capacity and conductivity  $c_p$  and  $k$ .

The schematic form of the energy equation is

$$\begin{aligned} & \frac{d}{dt}(\text{thermal energy}) + \frac{d}{dt}(\text{elastic energy}) \\ & = \text{mechanical work done} + \text{heat flux} + \text{heat source}, \end{aligned}$$

where we must include the elastic energy stored in and work done by each phase. For a single component, the strain energy density is

$$\mathcal{F} = \frac{1}{2E} \left[ (1 + \nu) \boldsymbol{\sigma} : \boldsymbol{\sigma} - \nu (\text{tr } \boldsymbol{\sigma})^2 \right],$$

where the Young's modulus  $E$  and Poisson ratio  $\nu$  are defined as usual by

$$E = \frac{\mu(3\lambda + 2\mu)}{\tau(\lambda + \mu)}, \quad \nu = \frac{\lambda}{2(\lambda + \mu)},$$

while the work done per unit volume is  $\boldsymbol{\sigma} : \nabla \mathbf{u}$ . Hence we obtain the energy equation in the form

$$\rho_0 c_p \frac{\partial T}{\partial t} = \nabla \cdot (k \nabla T) + q + \mathcal{M}_1 + \mathcal{M}_2, \quad (24)$$

where  $q$  is the rate of heating per unit volume, and  $\mathcal{M}_i$  is the mechanical contribution from each phase, given by

$$\mathcal{M} = \frac{1}{\tau E} \left\{ \alpha(1 - 2\nu) (\tau \dot{P} + P) \text{tr } \boldsymbol{\sigma} + (1 + \nu) \boldsymbol{\sigma} : \boldsymbol{\sigma} - \nu (\text{tr } \boldsymbol{\sigma})^2 \right\}.$$

### 3.4 Modelling questions

In the discussion so far, we have concentrated on the equations that describe the evolution of the stress and flow with time. However, before we can begin to solve the problem, we must answer a series of key questions concerning the interdependence of the parameters.

- What functional form should we take for our pressure term,  $P(T, \rho, \dots)$ ?

In particular, what experiments could one carry out to determine the dependence of  $P$ ?

- The relaxation times and viscosities are observed experimentally to depend on the temperature. How should this be modelled?

The standard approach would be to assume a functional (for example exponential) relationship, with the constants determined experimentally. In our two-phase approach, it is not immediately clear how the flow parameters for each of the two phases might be determined independently.

- The internal structure ( $\sigma_1$  and  $\sigma_2$ ) may also affect the relaxation times. If this is the case, what form should the dependence take?

With a dependence of  $\tau_i$  upon  $\sigma_i$  the problem becomes nonlinear. The findings of Tool (1945) and subsequent authors suggest that *the relaxation time decreases with increasing fictive temperature*. In terms of our “two-element” picture, this translates to saying that *the relaxation time decreases with increasing tension in the elements*, and thus implies that our Maxwell elements should be shear-thinning. However, this will be difficult to confirm experimentally since the stresses  $\sigma_i$  cannot be measured independently. This demands the following question, which is the most fundamental so far as the utility of our model is concerned.

- Can the stresses  $\sigma_i$  be related to any measurable physical properties?

First we must decide in what sense the  $\sigma_i$  can be identified with physical bonds and hence with the internal structure. In particular, can we define a symmetric tensor that describes the molecular structure, and then relate such a tensor to the stress tensors? Then, if we could devise an experiment to measure the internal structure, (*e.g.*, polarization or IR spectroscopy) we could determine the  $\sigma_i$  independently.

## 4 Suggested experiments

In this section we suggest experiments that might be used to answer some of the questions raised above. We concentrate on a few scenarios that are particularly simple from both the modelling and the experimental points of view. Some more elaborate and ingenious experiments may have to be devised to overcome the fundamental problem of isolating the internal stresses  $\sigma_1$  and  $\sigma_2$ .

### 4.1 Unidirectional stretching

A particularly simple experiment to carry out is the stretching of a uniform cylinder of glass under an applied axial load. Then symmetry suggests that

the stress tensors should be of the form

$$\boldsymbol{\sigma}_i = \begin{pmatrix} f_i & 0 & 0 \\ 0 & g_i & 0 \\ 0 & 0 & g_i \end{pmatrix}, \quad (25)$$

with

$$f_1 + f_2 = F, \quad g_1 + g_2 = 0, \quad (26)$$

where  $F$  is the applied load. Similarly, the velocity components are simply

$$\mathbf{u} = \begin{pmatrix} \dot{a}x \\ \dot{b}y \\ \dot{b}z \end{pmatrix}, \quad (27)$$

for some time-dependent functions  $a$  and  $b$ , which represent the stretch in the axial and transverse directions respectively. Then, given the load  $F$ , (23) provides four o.d.e.'s for  $f_1$ ,  $g_1$ ,  $a$  and  $b$ , namely

$$\mathcal{D}_1[f_1 + \alpha P] = \lambda_1(\dot{a} + 2\dot{b}) + 2\mu_1\dot{a}, \quad (28)$$

$$\mathcal{D}_1[g_1 + \alpha P] = \lambda_1(\dot{a} + 2\dot{b}) + 2\mu_1\dot{b}, \quad (29)$$

$$\mathcal{D}_2[F - f_1 + (1 - \alpha)P] = \lambda_2(\dot{a} + 2\dot{b}) + 2\mu_2\dot{a}, \quad (30)$$

$$\mathcal{D}_2[-g_1 + (1 - \alpha)P] = \lambda_2(\dot{a} + 2\dot{b}) + 2\mu_2\dot{b}, \quad (31)$$

where

$$\mathcal{D}_i = \tau_i \frac{d}{dt} + 1,$$

and for simplicity  $\alpha_1 = \alpha$ ,  $\alpha_2 = 1 - \alpha$ . Hence information about the parameters can be obtained by measuring how  $a$  and  $b$  change as  $F$  and  $P$  (e.g., by changing the temperature) are varied. The density, assumed to be of the form

$$\rho = \rho_0 + \tilde{\rho}(t),$$

satisfies

$$\tilde{\rho} + (a + 2b)\rho_0 = 0, \quad (32)$$

which may be coupled with (28)–(31) if  $P$  depends on  $\rho$ .

Particularly useful experiments involve either very rapid or very gradual changes, since in those limits elastic and viscous effects respectively can be isolated. In either case, the theory is greatly simplified if *the two viscoelastic species are assumed to have equal Poisson ratio  $\nu$* . Then for rapid changes, with  $\mathcal{D}_i \sim \tau_i d/dt$  we obtain

$$a \sim \frac{F + (1 - 2\nu)P}{E_1 + E_2}, \quad b \sim -\frac{\nu F - (1 - 2\nu)P}{E_1 + E_2}, \quad t \ll \tau_i, \quad (33)$$



while for gradual changes,  $\mathcal{D}_i \sim 1$  and

$$\dot{a} \sim \frac{F + (1 - 2\nu)P}{\tau_1 E_1 + \tau_2 E_2}, \quad \dot{b} \sim -\frac{\nu F - (1 - 2\nu)P}{\tau_1 E_1 + \tau_2 E_2}, \quad t \gg \tau_i, \quad (34)$$

where  $E_i$  are the Youngs moduli of the two phases. Whether the assumption of equal Poisson ratio is reasonable physically is open to question. However, given the other fairly gross assumptions that have been made thus far, and the great simplification that ensues, it appears to be a good first approximation.

## 4.2 Constrained isotropic heating/cooling

Assuming that our model (23) is correct, we can exploit its trivial solution

$$\mathbf{u} = \mathbf{0}, \quad \rho = \text{const.}, \quad \sigma_i = -\alpha_i P \mathbf{I}, \quad (35)$$

noted at the end of the last section, to probe the dependence of  $P$  on  $T$ . We simply have to take a piece of glass in equilibrium, clamp it so that it is unable to move (of course this may be rather difficult in practice!) and then measure the stress as the temperature is varied.

## 4.3 Unconstrained isotropic heating/cooling

Here we simply heat or cool an unstressed piece of glass uniformly and measure the response of its volume. This scenario can be obtained from the theory of Section 4.1 by setting  $F = 0$ ,  $b = a$ ,  $g_i = f_i$ , which leads to

$$\mathcal{D}_1 [f_1 + \alpha P] = \frac{\tau_1 E_1 \dot{a}}{1 - 2\nu}, \quad (36)$$

$$\mathcal{D}_2 [-f_1 + (1 - \alpha)P] = \frac{\tau_2 E_2 \dot{a}}{1 - 2\nu}, \quad (37)$$

$$\tilde{\rho} = -3a\rho_0. \quad (38)$$

The dimensionless volume is given to this approximation by  $1 - \tilde{\rho}/\rho_0$ . As in Section 4.1, the elastic and viscous responses can be isolated by considering very rapid or gradual changes.

## 4.4 Measurement of effective heat capacity

Now suppose that during a uniform heating or cooling experiment like that just described we monitor the heating rate  $q$  as well as the temperature  $T$ . Then we can define an *effective heat capacity*

$$c_{\text{eff}} = \frac{q}{\rho \dot{T}}.$$

The difference between  $c_{\text{eff}}$  and  $c_p$  reflects the mechanical energy, including energy that can be “frozen in” to the structure at low temperatures to be released when the temperature is raised again.

Using (24) and the same solution ansatz as in Section 4.3, we obtain

$$\begin{aligned} c_{\text{eff}} - c_p &= -\frac{\mathcal{M}_1 + \mathcal{M}_2}{\rho_0 \dot{T}} \\ &= -\frac{3(1-2\nu)f_1 \dot{f}_1}{\rho_0 \dot{T}} \left( \frac{1}{E_1} + \frac{1}{E_2} \right). \end{aligned} \quad (39)$$

## 4.5 Numerical results

Before we can expect to obtain realistic predictions from our model we must obtain values for all the parameters, all of which may in general be functions of temperature, density, stress, *etc.*. Nevertheless, we would like to carry out some simple tests to check that it admits solutions with the right qualitative behaviour. Therefore in this section we give some preliminary numerical solutions, where very simple forms for the model parameters have been assumed.

We consider the isotropic cooling of a cube of glass with no applied stresses, as described in section 4.3. The ordinary differential equations (36–38) are easily solved as an initial-value problem once the parameters have been specified. If we are considering relatively small changes in  $T$  and  $\rho$  then it is reasonable to write

$$P = A(T - T_0) + B\tilde{\rho}, \quad (40)$$

for some constants  $A$  and  $B$ . In the calculations to follow we assume that the temperature is reduced at a constant rate:

$$T = T_0 - \epsilon t \quad (41)$$

and that the Youngs moduli  $E_i$  are constant, and use a simple exponential law for the relaxation times

$$\tau_i = \tau_{i0} e^{k_i(T_0 - T)}. \quad (42)$$

Initially the glass is assumed to be in equilibrium:

$$T = T_0, \quad \sigma_i = 0, \quad \text{at } t = 0. \quad (43)$$

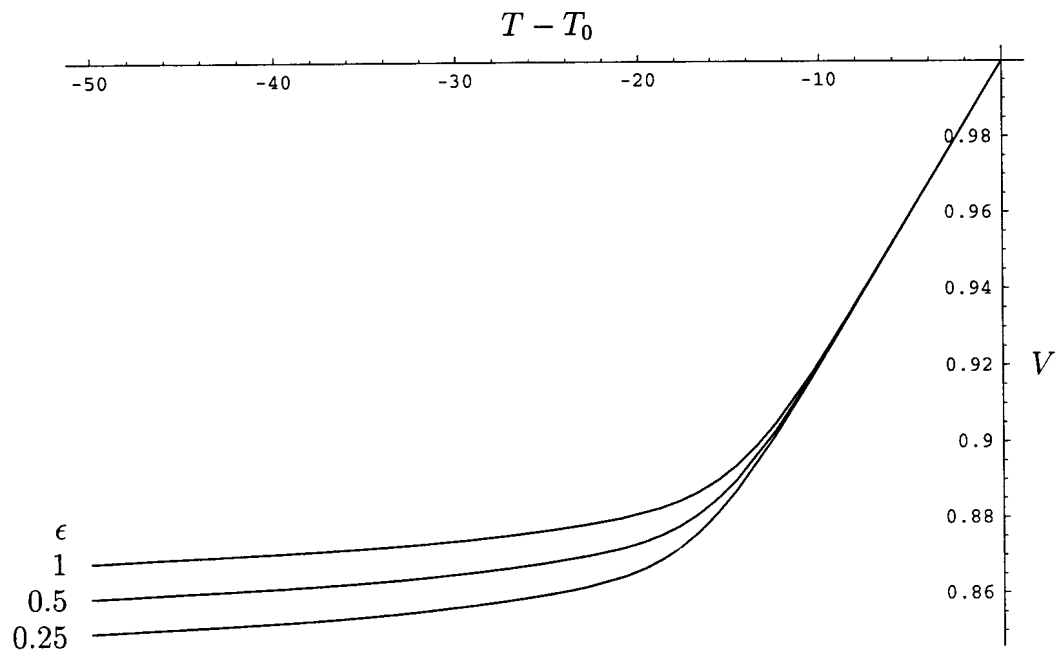


Figure 4: Dimensionless volume  $V = 1 - \tilde{\rho}/\rho_0$  of a glass block versus temperature change  $T - T_0$  (measured in K). The temperature is varied according to  $T = T_0 - \epsilon t$  with  $\epsilon = 1, 0.5, 0.25 \text{ K s}^{-1}$ ; the other parameter values are given in the text.

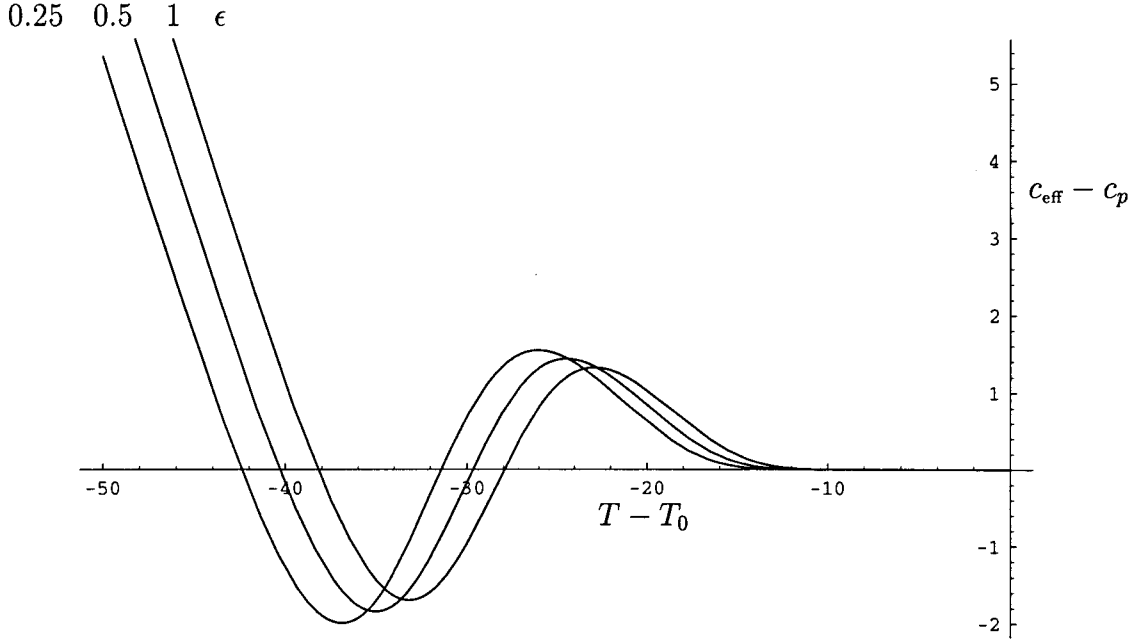


Figure 5: Change in effective heat capacity  $c_{\text{eff}} - c_p$  (measured in  $\text{J kg}^{-1} \text{K}^{-1}$ ) of a glass block versus temperature change  $T - T_0$  (measured in K). The temperature is varied according to  $T = T_0 - \epsilon t$  with  $\epsilon = 1, 0.5, 0.25 \text{ K s}^{-1}$ ; the other parameter values are given in the text.

Figure 4 shows the results of integrating (36–38) numerically, using the parameter values

$$\begin{aligned} \alpha &= 0.25, & \nu &= 0.25, & E_1 &= 4 \times 10^{10} \text{ Pa s}, & E_2 &= 2 \times 10^{10} \text{ Pa s}, \\ \tau_{10} &= 10^{-5} \text{ s}, & \tau_{20} &= 4 \times 10^{-5} \text{ s}, & k_1 &= 0.4 \text{ K}^{-1}, & k_2 &= 0.6 \text{ K}^{-1}, \\ \rho_0 &= 2500 \text{ kg m}^{-3}, & A &= 10^7 \text{ Pa K}^{-2}, & B &= 5 \times 10^5 \text{ m}^2 \text{ s}^{-2}, \end{aligned}$$

and varying the cooling rate:  $\epsilon = 1, 0.5, 0.25 \text{ K s}^{-1}$ . We plot the dimensionless volume of the sample,

$$V = 1 - \tilde{\rho}/\rho_0 = 1 + 3a,$$

versus temperature change  $T - T_0$ ; in each case the calculation was run up to  $t = 50/\epsilon$  so that the temperature was reduced by 50 K. The qualitative agreement with Figures 1 and 2 is encouraging, and if  $V$  were chosen as the measured property  $P$  we could certainly associate fictive temperatures and glass transition temperatures with graphs such as Figure 4.

In Figure 5 we plot the change in effective heat capacity  $c_{\text{eff}} - c_p$ , given by (39), versus temperature change for the same parameter values and cooling

rates. The oscillatory behaviour appears somewhat outlandish, but it is known experimentally that  $c_{\text{eff}}$  *does* behave nonmonotonically with  $T$ . Notice also that the variations (at least with this rather speculative set of parameter values) are small, given that we can expect  $c_p$  to be of order  $10^3 \text{ J kg}^{-1} \text{ K}^{-1}$ .

## 5 Conclusions

In Section 2 we gave a brief description of some of the existing theories for modelling glass in the viscoelastic range. Central to such theories is the fact that the molecular structure of glass changes continuously with temperature, rather than passing through a sudden phase transition. A successful model must take account of this structure, since the material properties depend crucially on it, and the most popular way to do so is via the so-called fictive temperature, which we defined in Section 2. This is a macroscopic property of glass that is fairly easy to measure and is known to be related to the internal structure. However, at present it is far from clear how the two are related, or how the material parameters should vary with fictive temperature.

A greater understanding of the effect of structure on the properties of glass, including fictive temperature, will require more detailed microscopic modelling. Here we have taken a first step in that direction by attempting to model glass as a two-phase viscoelastic material, the idea being that the two components represent different molecular bonds. Such an approach is suggested by experimental evidence that stress relaxation in glass is very well described by a moderate number of exponential decays. Our hypothesis is that *stress and structural relaxation arise from essentially the same molecular processes, and hence can be described by a single unified model.*

We started with a simple one-dimensional spring/dashpot model, which was then generalised to a three-dimensional continuum model. The model was applied to several experimental configurations that might be used to measure the parameters. Some simple numerical solutions showed behaviour encouragingly similar to that observed in experiments. However, many approximations and idealisations were made, some of which may have to be re-assessed in the future. These include:

- It was noted that great simplifications ensue if the viscoelastic components are assumed to have equal Poisson ratio. However, it may be that this assumption misses important structural effects;
- Inertia has thus far been neglected, although it can be incorporated in the theory with little difficulty. It will be important in modelling experiments involving elastic waves;

- If our model is to apply to the viscous range, where large deformations can be expected, then neglected nonlinear terms (such as those arising in an objective time-derivative) must be included;
- The forcing pressure term introduced in Section 3.3 to describe thermal stresses is highly idealised. There seems to be little consensus about the best way to model such effects in general.

Perhaps the greatest challenge for the future lies in linking a phenomenological model like the ones in this report with some more concrete microscopic description of structure. A great deal of physical insight and mathematical ingenuity will be required if this is to be done successfully.

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