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On internal stress and activation volume in polymers

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The two-site model is developed for the analysis of stress relaxation data. It is shown that the product of d ln $(-\dot{\sigma})/\mathrm{d}\sigma$ and $(\sigma - \sigma_i)$ is constant where σ is the applied stress, σ_i is the (deformation-induced) internal stress and $\dot{\sigma} = \mathrm{d}\sigma/\mathrm{d}t$. The quantity d ln $(-\dot{\sigma})/\mathrm{d}\sigma$ is often presented in the literature as the "(experimental) activation volume", and there are many examples in which the above relationship with $(\sigma - \sigma_i)$ holds true. This is in apparent contradiction to the arguments that lead to the association of the quantity d ln $(-\dot{\sigma})/\mathrm{d}\sigma$ with the activation volume, since these normally start with the premise that the activation volume is independent of stress. In the modified theory presented here the source of this anomaly is apparent. Similar anomalies arise in the estimation of activation volume from creep or constant strain rate tests and these are also examined from the standpoint of the site model theory. In the derivation presented here full account is taken of the site population distribution and this is the major difference compared to most other analyses. The predicted behaviour is identical to that obtained with the standard linear solid. Consideration is also given to the orientation-dependence of stress-aided activation.

1. Introduction

In common with other classes of materials, polymers show a sigmoidal stress relaxation characteristic when stress, σ, is plotted against the logarithm of time, (ln t). This is illustrated in Fig. 1 in which it is seen that the stress decays asymptotically to a limit, σ_i, that is often described as the "internal stress". It will be shown that a non-zero limiting value follows from the two-site theory.

In theories based on the concept of stress-aided thermal activation, deformation or stress relaxation is considered to be the result of a large number of similar events on the molecular level, involving localized motions of segments or possibly side groups of molecules. These events can be thermally activated and the presence of a stress may bias the reaction. This can be illustrated by reference to Fig. 2 which shows a potential well corresponding to the energy state of a particular segment or side group. In the unstressed state the height of the energy barrier is ΔG and the probability that the jumping element will surmount the barrier and move to a new state, (not shown), is proportional to $\exp(-\Delta G/kT)$ where k is the Boltzmann constant and T is the absolute temperature. On application of a stress σ in such a direction that work is done by the force when the segment moves over the barrier, then the barrier is effectively lowered. It is normally assumed that this change in barrier height is proportional to the stress and this is shown in Fig. 2. The constant of proportionality must have the dimensions of

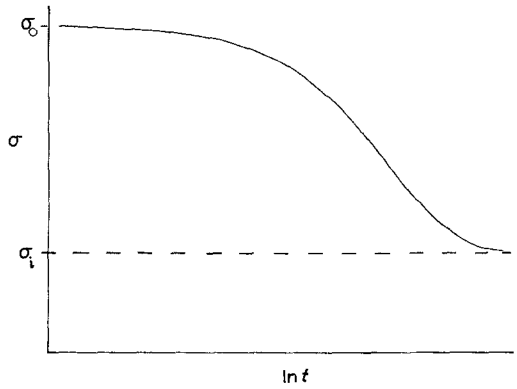

Figure 1 Schematic form of stress relaxation.

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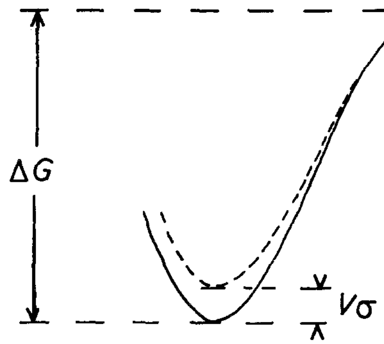

Figure 2 Potential barrier for a segment of a molecule, showing the modification produced by an applied stress, σ.

volume and this quantity, V, is often termed the "activation volume". A physical model that coincides with this definition is developed by associating V with the volume swept out by the moving segment as it proceeds to the top of the energy barrier. The probability that the segment will transform during a given interval will now become proportional to $\exp[(-\Delta G + V\sigma)/kT]$. Each individual conformational change of a particular type, (e.g. Site 1 → Site 2), can be assumed to produce a fixed incremental change in the unstressed dimensions of the body and can be expressed as an overall change in strain, $\Delta\epsilon$. In most of the experimental studies to which this analysis is directed the stresses used are $<20\,\mathrm{MN\,m^{-2}}$ and it is expected that the energy-elastic response will be linear or very nearly linear, and that any non-linearity will be associated with the entropic response, (which is dealt with by the site model theory developed herein). Thus, when a change in conformation (= unit change in site population distribution) takes place, giving a change $\Delta\epsilon$ in the unstressed strain of the test-piece, the stress relief afforded if the test-piece is maintained at constant deformation, (stress relaxation test), will be proportional to $\Delta\epsilon$ and therefore is itself a constant, $(\Delta\sigma)$. In a stress relaxation experiment it thus follows that:

$$\frac{-\mathrm{d}\sigma}{\mathrm{d}t} = A\exp\left(\frac{-\Delta G + V\sigma}{kT}\right) = \dot{\sigma}, \qquad (1)$$

where A is a constant and hence

$$\ln(-\dot{\sigma}) = \ln A - \frac{\Delta G}{kT} + \frac{V\sigma}{kT} \qquad (2)$$

whence

$$\frac{\mathrm{d}\ln(-\dot{\sigma})}{\mathrm{d}\sigma} = \frac{V}{kT}. \qquad (3)$$

In this analysis the following assumptions are implicit:

(1) That the segment will not return to its original state by surmounting the activation barrier in the opposite direction; that is, backward movement is discounted; and

(2) that there is no influence of the population distribution of the different types of site available to the jumping elements.

In the theory that follows both of these factors are taken into account. It is clear that Assumption 1 will be invalid if the potential minima on either side of the activation barrier are closely similar. As for Assumption 2, one way in which the population distribution effect might be deemed unimportant would be if movement over the potential barrier re-created a site of the same kind. Such might be the case in the motion of a dislocation through a large single crystal or in the slip of molecules in a polymer melt. Clearly, in either of these examples Assumption 1 would not be valid. It is expected that in most instances backward motion will be important, while the introduction of the site population dependency is shown to modify the theory to give better accord with experimental observations.

In the analysis presented below it is assumed that the material is homogeneous and free from (residual) moulding stresses.

2. The two-site model

2.1. Basic theory

The two-site model can be explained by reference to Fig. 3. Suppose that sufficient time has elapsed in the unstressed state to enable the establishment of a dynamic equilibrium between Sites 1 and 2 such that the following equation is fulfilled

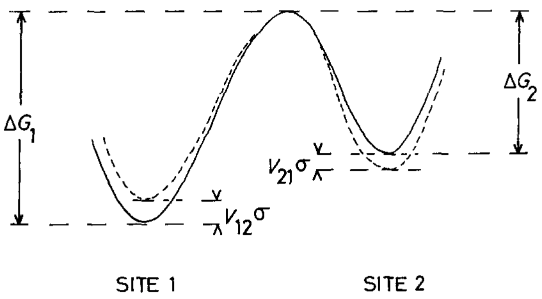

Figure 3 Energy diagram for a molecule segment that can exist in one of two isomeric forms, (Site 1 and Site 2). The energy levels are modified in the presence of an applied stress as shown by broken lines for the case in which the stress favours jumps in the direction 1 → 2.

$$N_1^0\omega_{12}^0 = N_2^0\omega_{21}^0, \tag{4}$$

where N_1^0 and N_2^0 are the populations of Site 1 and Site 2, respectively, and ω_{ij}^0 represents the frequency with which successful attempts are made at surmounting the potential barrier in the direction $i \rightarrow j$. We can therefore write

$$\frac{\omega_{12}^0}{\omega_{21}^0} = \frac{\exp(-\Delta G_1/kT)}{\exp(-\Delta G_2/kT)} = \exp\left\{\frac{-(\Delta G_1-\Delta G_2)}{kT}\right\}$$
$$= \exp\left(\frac{-\delta\Delta G}{kT}\right), \tag{5}$$

where

$$\delta\Delta G = \Delta G_1 - \Delta G_2. \tag{6}$$

In the presence of a stress, σ, jumps in one direction will be assisted, (e.g. by lowering the barrier by $V_{12}\sigma$ for jumps $1 \rightarrow 2$ in the example illustrated in Fig. 3), while those in the opposite direction will be opposed, the barrier increasing by $V_{21}\sigma$. The jump frequencies alter correspondingly and as a consequence the site populations will change. The rate of change of site population distribution can be derived in a straightforward manner as described by Ward [1], and is given by [1, 2]

$$\frac{\mathrm{d}\Delta N}{dt} + \Delta N(\omega_{12}^0 + \omega_{21}^0) = N_1^0\omega_{12}^0(V_{12}+V_{21})\sigma/kT, \tag{7}$$

where ΔN is the change in site population, as referred to the original state, (i.e. $\Delta N = [N_1^0 - N_1(t)]$ for the case shown in Fig. 3 in which the stress causes a reduction in population of Type 1 sites). In arriving at Equation 7 two approximations have been made [1, 2]. Firstly, it has been assumed that the stress is sufficiently small to make the approximation

$$\exp\frac{V\sigma}{kT} \simeq 1 + \frac{V\sigma}{kT}. \tag{8}$$

Secondly, it has been assumed that

$$|\Delta N(V_{12}\omega_{12}^0 - V_{21}\omega_{21}^0)| \ll N_1^0\omega_{12}^0(V_{12}+V_{21}). \tag{9}$$

The validity of these assumptions will be examined in Section 2.5.1.

Ward [1] shows that for creep under constant stress, Equation 7 may be rewritten with strain as the dependent variable by making the assumption that each unit change in site population gives an equal increment of strain. An analogous procedure has been used for the case of stress relaxation [2] leading to the equation

$$\frac{\mathrm{d}\sigma}{\mathrm{d}t} + \sigma\left\{\omega_{12}^0 + \omega_{21}^0 + N_1^0\omega_{12}^0\frac{(V_{12}+V_{21})}{kT}\Delta\sigma\right\}$$
$$= \sigma_0(\omega_{12}^0 + \omega_{21}^0), \tag{10}$$

where σ_0 is the initial stress at $t = 0$, and $\Delta\sigma$ is the increment of stress relaxation per unit site population change. i.e.

$$\sigma = \sigma_0 - \Delta N\Delta\sigma. \tag{11}$$

It is convenient to re-write Equation 10 as

$$\frac{\mathrm{d}\sigma}{\mathrm{d}t} + C\sigma = D\sigma_0, \tag{10a}$$

where C and D are functions of temperature but are independent of stress. The solution is

$$\sigma = \sigma_0\exp(-Ct) + \frac{D}{C}\sigma_0[1-\exp(-Ct)]. \tag{12}$$

This function decays asymptotically to a non-zero value of stress, $(D/C)\sigma_0$, as shown schematically in Fig. 1. This limiting stress σ_i, $[=(D/C)\sigma_0]$, corresponds to a new equilibrium state for which we may write

$$N_{1,\infty}\omega_{12}(\sigma_i) = N_{2,\infty}\omega_{21}(\sigma_i), \tag{13}$$

where

$$\left.\begin{aligned}\omega_{12}(\sigma_i) &= \omega_{12}^0\exp\left(\frac{V_{12}\sigma_i}{kT}\right)\\ \text{and}\qquad \omega_{21}(\sigma_i) &= \omega_{21}^0\exp\left(\frac{-V_{21}\sigma_i}{kT}\right)\end{aligned}\right\} \tag{14}$$

again using the condition represented by Fig. 3 and keeping V_{12} and V_{21} positive.

2.2. The (experimental) activation volume

It is explained above why the quantity $\mathrm{d}\ln(-\dot{\sigma})/\mathrm{d}\sigma$ is often evaluated for stress relaxation tests and used in the estimation of the "(experimental) activation volume." If we allow for backward jumps then we can consider the rate of stress relaxation to be proportional to

$$X = N_1\exp\left(\frac{-\Delta G_1 + V_{12}\sigma}{kT}\right)$$
$$-N_2\exp\left(\frac{-\Delta G_2 - V_{21}\sigma}{kT}\right), \tag{15}$$

where N_1, N_2 and σ are time-varying quantities. Near the beginning of the test $N_1 \simeq N_1^0$ and $N_2 \simeq N_2^0$ and

$$X_0 \simeq N_1^0\exp\left(\frac{-\Delta G_1}{kT}\right)$$

$$\times\left[\exp\left(\frac{V_{12}\sigma}{kT}\right)-\exp\left(\frac{-V_{21}\sigma}{kT}\right)\right]. \quad (16)$$

If $V_{12}=V_{21}$, as might be expected for a symmetrical barrier, then

$$X_0 \simeq N_1^0\exp\left(\frac{-\Delta G_1}{kT}\right)\sinh\left(\frac{V_{12}\sigma}{kT}\right). \quad (17)$$

This is the form commonly associated with Eyring and was originally derived to describe non-Newtonian viscous flow [3]. For this particular case it is probably justified to ignore the site population distribution and to make the symmetrical barrier assumption.

It is apparent that the derived quantity $\mathrm{d}\ln(-\dot{\sigma})/\mathrm{d}\sigma$ has no particular significance in this framework unless σ is sufficiently large to make valid the approximation

$$\sinh\left(\frac{V_{12}\sigma}{kT}\right) \simeq \exp\left(\frac{V_{12}\sigma}{kT}\right). \quad (18)$$

An examination of the activation volume that takes into account backward jumps but not site population changes has been presented by Krausz [4]. The same author has also investigated the effect of having consecutive barriers of differing height [5], and although he includes terms to describe the site population distribution no attempt is made to take into account the change in population that accrues when forward and backward jump frequencies are unequal. Further discussion by the original authors is to be found in their comprehensive review, [6].

It is quite common to find that "(experimental) activation volumes" estimated using the $\mathrm{d}\ln(-\dot{\sigma})/\mathrm{d}\sigma$ formula are strongly dependent on σ [7–12]. Kubât and co-workers show that for a large range of materials, including polymers, the product of σ and $\mathrm{d}\ln(-\dot{\sigma})/\mathrm{d}\sigma$ is approximately constant [7–11]. The values presented for the activation volume derived by this procedure are consequently extremely high at low stress but at high stresses the magnitudes are comparable to estimates of the volume swept out by the jumping element expected to be involved in the relaxation. If it is admitted that the activation volume is not a constant, then Equation 1 is invalidated, so that the significance of $\mathrm{d}\ln(-\dot{\sigma})/\mathrm{d}\sigma$ is clouded still further. Again it must be emphasized that any analysis based on Equation 17 can only apply to the beginning of the test, before the site population distribution has changed significantly. (As discussed above, this restriction may be relaxed in certain cases, as for example that originally addressed by Eyring).

Other experimental techniques for measuring the activation volume share similar drawbacks. Creep results could be analysed by the same procedure, using measurements of strain rate, $\dot{\epsilon}$, at constant stress instead of $\dot{\sigma}$ at constant ϵ. We find by a similar route

$$V = \left(kT\frac{\mathrm{d}\ln\dot{\epsilon}}{\mathrm{d}\sigma}\right)_{T,\epsilon,P}, \quad (19)$$

where tests at constant temperature, T, and pressure, P, are used to obtain strain rates for a series of different stress values and these are compared at a fixed strain, ϵ, to obtain the differential coefficient. This procedure would further require that the "structure" of the material is uniquely determined by the strain, a point discussed below.

Constant strain-rate tests have also been employed, again with the result that the computed value of the activation volume decreases as stress increases [13]. Another variation used in the estimation of the activation volume utilizes a constant strain-rate test in which a sudden change in strain-rate is imposed at a selected point in the test, [14–19]. This point can be the point at which yield occurs, and if the second rate, $\dot{\epsilon}_2$, is higher than the first, $\dot{\epsilon}_1$, the material reverts to pre-yield behaviour [17]. In this way the activation volume at yield is supposed to be measured using the following formula [17]:

$$V = 2kT\frac{\ln(\dot{\epsilon}_2/\dot{\epsilon}_1)}{\sigma_{y,2}-\sigma_{y,1}}, \quad (20)$$

where $\sigma_{y,1}$ and $\sigma_{y,2}$ are the values of yield stress at strain-rates $\dot{\epsilon}_1$ and $\dot{\epsilon}_2$, respectively.

The activation volumes estimated by this method show a similar stress dependence to those discussed above [17] and further analysis of this procedure in terms of the modified site model theory will be presented in Section 5. One of the motives for conducting strain-rate jump experiments is to obtain information at different strain-rates on samples at "constant structure", (i.e. just before and just after the change in strain rate) [17–20]. In the present paper we identify "structure" with site population distribution; earlier workers studying flow in metals identified "structure" with dislocation density. We have not considered the possibility that there is a deformation-dependent multiplication of "sites" in the polymeric materials with which we are concerned here, in contrast to the case met in metals in which dislocation multiplication is an important factor.

Let us now turn to the site theory as developed in Section 2.1 in which full account has been taken of the shift in population. Beginning with Equation 10a we find

$$\frac{\mathrm{d}\ln(-\dot{\sigma})}{\mathrm{d}\sigma} = \frac{C\exp Ct}{(C-D)\sigma_0}; \qquad (21)$$

also, from Equation 10a we have

$$\exp Ct = \frac{(C-D)\sigma_0}{C\sigma - D\sigma_0} \qquad (22)$$

whence

$$\frac{\mathrm{d}\ln(-\dot{\sigma})}{\mathrm{d}\sigma} = \frac{C}{C\sigma - D\sigma_0} \equiv \frac{1}{\sigma-\sigma_\mathrm{i}} = \frac{1}{\sigma^*}, \qquad (23)$$

where $\sigma^* = (\sigma - \sigma_\mathrm{i})$ is sometimes called the "effective stress", [7–11, 20–22]. In practice the product $\sigma^* \cdot \mathrm{d}\ln(-\dot{\sigma})/\mathrm{d}\sigma$ has frequently been found to be constant [7–11] in agreement with the prediction given in Equation 23. This product is claimed by Kubát and co-workers to be much larger than unity, but the data of Pink *et al.* [12], seems to be in good agreement with Equation 23.

2.3. New method of determining activation volume

In this section we will develop a procedure for evaluating $(V_{12} + V_{21})$ which follows from the site theory presented in Section 2.1 and which is free from the objections cited in Section 2.2 in which alternative procedures were discussed.

From Equations 13 and 14 we can write that at the final equilibrium state in a stress relaxation test

$$\frac{N_{1,\infty}\omega_{12}^0}{N_{2,\infty}\omega_{21}^0} = \left[\frac{-(V_{12}+V_{21})\sigma_\mathrm{i}}{kT}\right] = \frac{N_{1,\infty}}{N_{2,\infty}}\exp\left(\frac{-\delta\Delta G}{kT}\right) \qquad (24)$$

To eliminate the unknowns $N_{1,\infty}$ and $N_{2,\infty}$ we can utilize Equation 11 which at the final equilibrium state becomes

$$\sigma_\mathrm{i} = \sigma_0 - \Delta\sigma(N_1^0 - N_{1,\infty}) = \sigma_0 - \Delta\sigma(N_{2,\infty} - N_2^0). \qquad (25)$$

Substitution in Equation 24 gives

$$\left[\frac{N_1^0 - \left(\dfrac{\sigma_0-\sigma_\mathrm{i}}{\Delta\sigma}\right)}{N_2^0 + \left(\dfrac{\sigma_0-\sigma_\mathrm{i}}{\Delta\sigma}\right)}\right]\exp\left(\frac{-\delta\Delta G}{kT}\right) = \exp\left[-\left(\frac{V_{12}+V_{21}}{kT}\right)\sigma_\mathrm{i}\right]. \qquad (26)$$

From Equations 4 and 5 we have

$$N_2^0 = N_1^0\exp\left(\frac{-\delta\Delta G}{kT}\right) \qquad (27)$$

and on substitution into Equation 26 this gives

$$\frac{N_1^0 - [(\sigma_0-\sigma_\mathrm{i})/\Delta\sigma]}{N_1^0\exp\left(\dfrac{-\delta\Delta G}{kT}\right) + \left(\dfrac{\sigma_0-\sigma_\mathrm{i}}{\Delta\sigma}\right)} = \exp\frac{\delta\Delta G}{kT}\exp\left\{\frac{-(V_{12}+V_{21})\sigma_\mathrm{i}}{kT}\right\}. \qquad (28)$$

If the small stress approximation

$$\exp\left\{\frac{-(V_{12}+V_{21})\sigma_\mathrm{i}}{kT}\right\} = 1 - \frac{(V_{12}+V_{21})\sigma_\mathrm{i}}{kT} \qquad (8a)$$

is applied to the right-hand side of Equation 28 then after some rearrangement we obtain

$$\left(\frac{V_{12}+V_{21}}{kT}\right)\sigma_\mathrm{i}\left[N_1^0 + \left(\frac{\sigma_0-\sigma_\mathrm{i}}{\Delta\sigma}\right)\exp\frac{\delta\Delta G}{kT}\right] = \left(\frac{\sigma_0-\sigma_\mathrm{i}}{\Delta\sigma}\right)\left(1+\exp\frac{\delta\Delta G}{kT}\right). \qquad (29)$$

Taking reciprocals and rearranging leads to

$$\frac{1}{\sigma_\mathrm{i}} = \frac{1}{(\sigma_0-\sigma_\mathrm{i})}\left(\frac{V_{12}+V_{21}}{kT}\right)\frac{N_1^0\Delta\sigma}{[1+\exp(\delta\Delta G/kT)]} + \left(\frac{V_{12}+V_{21}}{kT}\right)\frac{\exp\dfrac{\delta\Delta G}{kT}}{\left(1+\exp\dfrac{\delta\Delta G}{kT}\right)} \qquad (30)$$

Hence, for a series of specimens tested at different initial stress values a plot of $1/\sigma_\mathrm{i}$ against $1/(\sigma_0 - \sigma_\mathrm{i})$ would give a straight line with gradient M and intercept c on the $1/\sigma_\mathrm{i}$ axis where

$$M = \left(\frac{V_{12}+V_{21}}{kT}\right)\frac{N_1^0\Delta\sigma}{\left(1+\exp\dfrac{\delta\Delta G}{kT}\right)} \qquad (31)$$

and

$$c = \left(\frac{V_{12}+V_{21}}{kT}\right)\frac{\exp\dfrac{\delta\Delta G}{kT}}{\left(1+\exp\dfrac{\delta\Delta G}{kT}\right)}. \quad (32)$$

Hence,

$$\frac{M}{c} = \frac{N_1^0\Delta\sigma}{\exp\dfrac{\delta\Delta G}{kT}}. \quad (33)$$

From Equation 32 it is therefore possible to deduce that for the case of positive $\delta\Delta G$,

$$\frac{1}{2}\left(\frac{V_{12}+V_{21}}{kT}\right) \leqslant c \leqslant \left(\frac{V_{12}+V_{21}}{kT}\right) \quad (34)$$

while for negative $\delta\Delta G$,

$$\left(\frac{V_{12}+V_{21}}{kT}\right) \geqslant c. \quad (35)$$

While there may be exceptions it is expected that $\delta\Delta G$ will normally be positive, so that Equation 34 holds. To check this, rearrangement of Equation 33 gives

$$\ln\frac{c}{M} = \frac{\delta\Delta G}{kT} - \ln N_1^0\Delta\sigma \quad (36)$$

and a plot of $\ln c/M$ against $1/T$ for tests conducted at different temperatures gives a slope of $(\delta\Delta G/k)$. Preliminary results have confirmed that $\delta\Delta G$ is positive for a set of injection-moulded polymethylmethacrylate bars, [23]. In this case $\delta\Delta G$ is sufficiently large that Equation 34 becomes

$$c \simeq \left(\frac{V_{12}+V_{21}}{kT}\right). \quad (37)$$

If we characterize the process by the mean activation volume

$$\bar{V} = \frac{V_{12}+V_{21}}{2} \quad (38)$$

then

$$\bar{V} = \frac{ckT}{2}. \quad (39)$$

Hence, provided it can be deduced that $\delta\Delta G$ is positive, $\bar{V}$ can be derived by employing the plot suggested by Equation 30.

Returning to the original formulation summarized in Section 2.1 we have

$$\begin{aligned}\sigma_i &= \frac{D}{C}\sigma_0 \\ &= \frac{\sigma_0(\omega_{12}^0+\omega_{21}^0)}{\omega_{12}^0+\omega_{21}^0+N_1^0\omega_{12}^0(V_{12}+V_{21})\Delta\sigma/kT}.\end{aligned} \quad (40)$$

Hence, a plot of σ_i against σ_0 should be a straight line through the origin having as gradient:

$$\begin{aligned}M' &= \left[1+\frac{N_1^0\Delta\sigma(V_{12}+V_{21})}{(1+\omega_{21}^0/\omega_{12}^0)kT}\right]^{-1} \\ &= \left[1+\frac{N_1^0\Delta\sigma(V_{12}+V_{21})}{\left(1+\exp\dfrac{\delta\Delta G}{kT}\right)kT}\right]^{-1} = \frac{1}{1+M}.\end{aligned} \quad (41)$$

The reason why Equations 30 and 40 are apparently in conflict can be traced to the employment of the condition expressed by Equation 9 in the derivation of Equation 40. Equation 30 is not subject to the condition expressed in Equation 9. A σ_i against σ_0 plot can therefore provide only a rough check on the value of M.

2.4. Double loading experiments

On a previous occasion we have employed double loading experiments in which a specimen is allowed to stress-relax to equilibrium then reloaded to the original stress, σ_0 (see Fig. 4) [24]. We are now able to analyse this according to the site model theory.

Suppose that the equilibrium state corresponding to the first deformation is reached when the site population has changed by $\Delta N_{\infty,1}$ so that the Site 1 population has become

$$N_{1,\infty} = N_1^0 - \Delta N_{\infty,1} = N_1^0\frac{(\sigma_0-\sigma_{i,1})}{\Delta\sigma} \quad (42)$$

where $\sigma_{i,1}$ is the deformation-induced internal stress.

By the same process as before we may now derive an equation describing stress relaxation after a second loading in terms of the further site population change, $(\Delta N')$, beginning at the time of re-loading

$$\frac{\mathrm{d}\Delta N'}{\mathrm{d}t} + \Delta N'(\omega_{12}^0+\omega_{21}^0) = N_1^0\omega_{12}^0\left(\frac{V_{12}+V_{21}}{kT}\right)\sigma - \left(\frac{\sigma_0-\sigma_{i,1}}{\Delta\sigma}\right)(\omega_{12}^0+\omega_{21}^0). \quad (43)$$

On substituting $\Delta N' = (\sigma_0-\sigma)/\Delta\sigma$ into Equation 43 we obtain

$$\frac{\mathrm{d}\sigma}{\mathrm{d}t} + \sigma\left[\omega_{12}^0+\omega_{21}^0+N_1^0\Delta\sigma\omega_{12}^0\left(\frac{V_{12}+V_{21}}{kT}\right)\right] = (2\sigma_0-\sigma_{i,1})(\omega_{12}^0+\omega_{21}^0). \quad (44)$$

Hence, when $\mathrm{d}\sigma/\mathrm{d}t \to 0$ we find the new internal stress level is

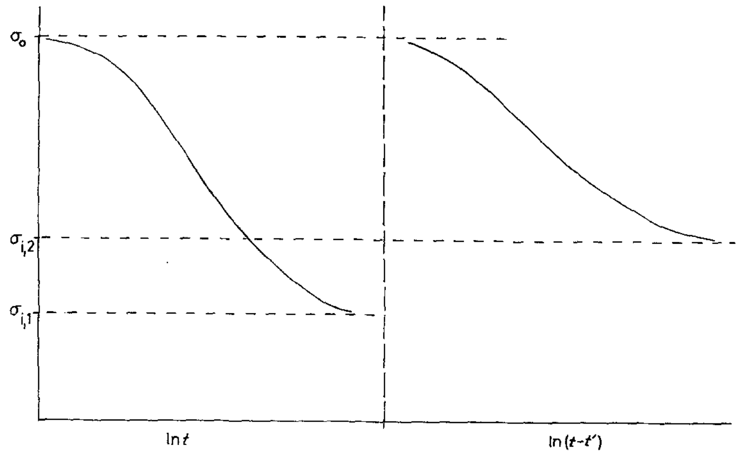

Figure 4 Schematic diagram of a double loading experiment in which stress relaxation from an initial stress, σ_0, is allowed to proceed to equilibrium, $(\sigma = \sigma_{i,1})$, then at $t = t'$ the deformation is suddenly increased to restore the stress to σ_0, and stress relaxation is allowed to proceed to a new equilibrium, $(\sigma = \sigma_{i,2})$.

$$\sigma_{i,2} = \frac{(2\sigma_0 - \sigma_i)(\omega^0_{12} + \omega^0_{21})}{\omega^0_{12} + \omega^0_{21} + N^0_1 \Delta\sigma\omega^0_{12}\dfrac{(V_{12} + V_{21})}{kT}}\,; \qquad (45)$$

therefore,

$$\frac{\sigma_{i,2}}{\sigma_{i,1}} = 2 - \frac{\sigma_{i,1}}{\sigma_0} = 2 - \frac{1}{1+M}\,. \qquad (46)$$

The assumption used previously [24] that the deformation-induced internal stresses $\sigma_{i,2}$ and $\sigma_{i,1}$ are related as $\sigma_{i,2} = 2\sigma_{i,1}$ is therefore only an approximation.

2.5. Limitations and approximations

In this section the several approximations employed in the derivations presented above will be examined.

2.5.1. Range of validity of Equation 7

There are two approximations used in the derivation of Equation 7 that require justification. One is that [1, 2]

$$\left.\begin{aligned} &|\Delta N(\omega^0_{12}V_{12} - \omega^0_{21}V_{21})| \ll N^0_1\omega^0_{12}(V_{12} + V_{21}) \\ &\text{i.e.,} \\ &\left|\Delta N\left\{V_{12} - V_{21}\exp\frac{\delta\Delta G}{kT}\right\}\right| \ll N^0_1(V_{12} + V_{21}) \end{aligned}\right\}. \qquad (9)$$

Even if we retain the possibility that ΔN may be a significant fraction of N^0_1 Condition 9 is seen to hold as long as V_{12} and V_{21} are fairly similar, as expected, and likewise ω^0_{12} and ω^0_{21} are fairly similar. On the other hand if $\delta\Delta G$ is significant Condition 9 may not hold. In this case an additional term containing the product $\sigma\Delta N$ enters Equation 7, leading to a term in σ^2 in Equation 10. The modified equation can be solved in a fairly straightforward manner and will be dealt with elsewhere [25].

The other condition that must be fulfilled is the one given in Equation 8. From the analysis of data obtained in our own laboratory [23, 26] and from a review of data appearing in the literature and appraised according to the viewpoint put forward in this paper, we consider that a reasonable value for $\bar{V}$ is of the order of $300 \times 10^{-30}\,\text{m}^3$ (i.e. $300\,\text{Å}^3$) for polystyrene or for polymethylmethacrylate. For stress relaxation tests conducted at a slightly elevated temperature, (say 320 K), we therefore estimate that

$$\frac{V}{kT} \simeq 70 \times 10^{-9}\,\text{m}^2\text{N}^{-1}. \qquad (47)$$

Hence, if we insist that $\exp(V\sigma/kT)$ must not exceed $(1 + V\sigma/kT)$ by more than 5% then $\sigma \lesssim 5\,\text{MN}\,\text{m}^{-2}$. This lies within the range used in our experiments [23, 27] and might therefore be the source of departure from the linearity which is predicted by the derivation when the approximation given by Equation 8 is employed.

2.5.2. Determination of activation volume

In Section 2.3 a similar approximation to that discussed above is employed, i.e.

$$\exp\left[\frac{-(V_{12} + V_{21})\sigma_i}{kT}\right] \simeq 1 - \frac{(V_{12} + V_{21})}{kT}\sigma_i. \qquad (8a)$$

In this case the stress factor is σ_i rather than the time-variable σ. Since we now have the sum $(V_{12} + V_{21})$ instead of only a single activation volume, the limiting value of σ_i giving a 5% departure from equality in Equation 8a will be approximately $2.5\,\text{MN}\,\text{m}^{-2}$. Some of our tests produced σ_i values higher than this and we conclude that the part of the analysis given in Section 2.3 may show discrepancies especially at very high stresses. The exact shape of the relaxation curve may depart from that predicted by Equations 10 and 12 at σ_0 values as low as $5\,\mathrm{MN\,m^{-2}}$. (All of these computations are based on the value $V = 300 \times 10^{-30}\,\mathrm{m}^3$ and will need revision for activation volumes of different magnitudes.)

3. Comparison with the Kubåt and Rigdahl analysis

Kubåt and Rigdahl have introduced an analysis of stress relaxation in which a series of identical specimens are tested at different deformations and the data plotted as σ against $\ln t$ [21]. The gradient at the steepest point is then plotted against the initial stress σ_0 ("KR plot"). They based their analysis on a power-law description of stress relaxation, namely

$$\dot{\sigma} = -EB(\sigma - \sigma_i)^n, \tag{48}$$

where E is the elastic modulus of the material and B and n are constant material parameters. This leads to the prediction that the KR plot will be a straight line. If σ_i has a "residual" component in addition to the deformation-induced internal stress then this line will intercept the σ_0 axis at a position that is in some way representative of the overall residual stress distribution, [9, 21, 28, 29]. Moreover the gradient of the KR plot is related to n through

$$\frac{\mathrm{d}F}{\mathrm{d}\sigma_0} = n^{-n/(n-1)}, \tag{49}$$

where

$$F = \left(\frac{-\mathrm{d}\sigma}{\mathrm{d}\ln t}\right)_{\max}. \tag{50}$$

Now from Equation 12 we have

$$\frac{-\mathrm{d}\sigma}{\mathrm{d}\ln t} = (\sigma - \sigma_i)\ln\left(\frac{\sigma_0 - \sigma_i}{\sigma - \sigma_i}\right). \tag{51}$$

It can be shown that this has its maximum value when

$$\ln\left(\frac{\sigma_0 - \sigma_i}{\sigma - \sigma_i}\right) = 1 \tag{52}$$

i.e. when $(\sigma - \sigma_i) = 1/e\,(\sigma_0 - \sigma_i)$, therefore

$$F = \frac{1}{e}(\sigma_0 - \sigma_i). \tag{53}$$

Now σ_i is a function of σ_0, so we must write

$$\frac{\mathrm{d}F}{\mathrm{d}\sigma_0} = \frac{1}{e}\left(1 - \frac{\mathrm{d}\sigma_i}{\mathrm{d}\sigma_0}\right)$$

$$= \frac{1}{e} - \frac{(\omega_{12}^0 + \omega_{21}^0)}{e[(\omega_{12}^0 + \omega_{21}^0) + N_1^0\omega_{12}^0\Delta\sigma(V_{12} + V_{21})/kT]}$$

$$= \frac{1}{e} - \frac{1}{e}\left[1 + \frac{N_1^0\Delta\sigma(V_{12} + V_{21})}{kT\left(1 + \exp\dfrac{\delta\Delta G}{kT}\right)}\right]^{-1}. \tag{54}$$

It is of interest to examine the temperature dependence of this expression and to do this two cases must be considered. Firstly, we must consider the case in which the site population is allowed to equilibrate at the test temperature before application of the stress, ("Case I"); in this case it is necessary to take into account the temperature dependence of N_1^0. Secondly, ("Case II"), we assume that N_1^0 is a constant, that is, it is dependent only on the history prior to the stress relaxation test, and that the temperature-dependent shift in population distribution that takes place during the period that the specimen is equilibrating at the test temperature prior to the stress relaxation experiment can be neglected. It is expected that most practical cases will fall between these limits.

3.1. Case I: N_1^0 equilibrates at the test temperature

The temperature dependence of N_1^0 is given by

$$\frac{N_1^0}{N_0} = \frac{\exp(\delta\Delta G/kT)}{1 + \exp(\delta\Delta G/kT)}, \tag{55}$$

where N_0 is the total number of occupied sites ($= N_1^0 + N_2^0$). It follows that

$$\frac{\mathrm{d}}{\mathrm{d}T}\left(\frac{\mathrm{d}F}{\mathrm{d}\sigma_0}\right) = \frac{-ak}{ex^2(1 + a/x)^2} \times \left[2 + \left(1 - \frac{\delta\Delta G}{kT}\right)\exp\left(\frac{\delta\Delta G}{kT}\right) + \left(1 + \frac{\delta\Delta G}{kT}\right) \times \exp\left(\frac{-\delta\Delta G}{kT}\right)\right], \tag{56}$$

where $a = N_0\Delta\sigma(V_{12} + V_{21})$ and $x = \{kT[1 + \exp(\delta\Delta G/kT)]^2\}/\exp(\delta\Delta G/kT)$. $(\mathrm{d}/\mathrm{d}T)(\mathrm{d}F/\mathrm{d}\sigma_0)$ is negative for values of $(\delta\Delta G/kT) \lesssim 1.3$ and positive for $(\delta\Delta G/kT) > 1.31$.

For a test temperature of 40° C it is thus predicted that $(\mathrm{d}/\mathrm{d}T)(\mathrm{d}F/\mathrm{d}\sigma_0)$ will be positive if $\delta\Delta G > 0.035\,\mathrm{eV}$ ($\sim 3.4\,\mathrm{kJ\,mol^{-1}}$). The discussion in Section 2.5.1 is clearly relevant here and the value of $\delta\Delta G$ at which $(\mathrm{d}/\mathrm{d}T)(\mathrm{d}F/\mathrm{d}\sigma_0)$ equals zero may be subject to modification [25].

3.2. Case II: N_1^0 is treated as a constant

In this case

$$\frac{\mathrm{d}}{\mathrm{d}T}\left(\frac{\mathrm{d}F}{\mathrm{d}\sigma_0}\right) = \frac{-bk}{ey^2(1+b/y)^2} \times\left[1+\exp\left(\frac{\delta\Delta G}{kT}\right)-\frac{\delta\Delta G}{kT}\exp\left(\frac{\delta\Delta G}{kT}\right)\right], \quad (57)$$

where $b = N_1^0\Delta\sigma(V_{12}+V_{21})$ and $y = kT[1+\exp(\delta\Delta G/kT)]$. It is evident that the departure from Case I is modest and the value of $\delta\Delta G/kT$ at which this expression changes from negative to positive is very similar (~ 1.28).

Before comparing these results with experimental data it should be noted that the signs and magnitudes derived above all depend on the validity of the particular energy barrier arrangement presented in Fig. 3, for it has been assumed that $(V_{12}+V_{21})$ and $\delta\Delta G$ are both positive and these were originally defined as presented in that diagram. It is now necessary to consider the effect of having the situation depicted in Fig. 5 in which this time Site 1 is a higher energy than Site 2: the stress-aided direction is still 1 → 2, but $\delta\Delta G$ is now negative. For Case I, inspection of Equation 56 shows that the sign of $(\mathrm{d}/\mathrm{d}T)(\mathrm{d}F/\mathrm{d}\sigma_0)$ changes at the same magnitude of $\delta\Delta G$ as for that obtained with the barrier arrangement of Fig. 3. On the other hand the Case II alternative, (Equation 57), is negative for all negative $\delta\Delta G$.

4. Orientation-dependence of stress-aided activation

In the account of stress-aided activation outlined above it is implicit that each jumping element makes the same angle with the stress axis and that each event relieves the stress by the same amount. While it is possible that in certain instances this may be a reasonable description, as for example with highly oriented polymers, it is clearly not applicable to an isotropic material. This has been recognized by Robertson [30] who replaced $V\sigma$ by $V\sigma\cos\theta$ for the work done by the stress σ during a transition between states, where θ is the angle between the stress axis and the displacement vector representing the jump. We will now adapt the theory presented in Section 2.1, taking into account the effects attributable to elements lying at all possible orientations. In addition to the modification to the work term we must also replace $\Delta\sigma$ by an orientation-dependent expression, $\Delta\sigma\cos\theta$, because jumps inclined to the stress axis will be less effective in relieving stress. Finally we must also choose an appropriate description of the distribution of elements as a function of orientation.

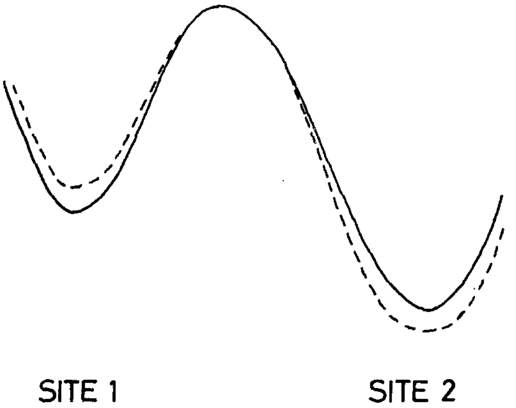

Figure 5 Two-site energy level diagram for the case in which stress aids motion from the site already possessing a higher energy level. The stress aided direction is again 1 → 2, but this time Site 1 has a higher energy in the unstressed state than Site 2, (cf. the case depicted in Fig. 3).

It is convenient to begin with Equation 7. Let us define orientation with reference to the jump vector so that ΔN_θ is the site population change for elements having a jump vector at θ to the stress axis and $N_{1,\theta}^0$ is the initial Site 1 population for elements thus defined. Hence

$$\frac{\mathrm{d}\Delta N_\theta}{\mathrm{d}T}\cdot\mathrm{d}\theta + \Delta N_\theta(\omega_{12}^0+\omega_{21}^0)\mathrm{d}\theta = \frac{N_{1,\theta}^0\omega_{12}^0(V_{12}+V_{21})}{kT}\sigma\cos\theta\,\mathrm{d}\theta. \quad (7a)$$

For an isotropic polymer there will be a constant number of elements, δN_0, per unit solid angle so that the fraction lying within a cone with semi-angle θ within $\mathrm{d}\theta$ will be proportional to $2\pi\sin\theta\,\mathrm{d}\theta$ (Fig. 6). Hence

$$N_1^0 = \int_0^{\pi/2} N_{1,\theta}^0\mathrm{d}\theta = \int_0^{\pi/2}\delta N_0 2\pi\sin\theta\,\mathrm{d}\theta = 2\pi\delta N_0, \quad (58)$$

Hence

$$\delta N_0 = N_1^0/2\pi \quad (59)$$

and

$$N_{1,\theta}^0 = N_1^0\sin\theta; \quad (60)$$

therefore,

$$\frac{\mathrm{d}\Delta N_\theta}{\mathrm{d}T} + (\omega_0^{12}+\omega_{21}^0)\Delta N_\theta = \frac{N_1^0\omega_{12}^0(V_{12}+V_{21})\sin\theta\cos\theta\sigma}{kT}. \quad (61)$$

We also have

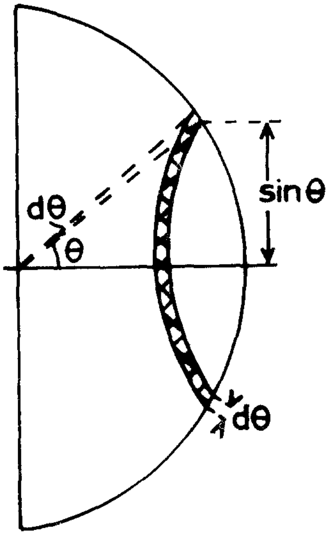

Figure 6 For a spherically symmetric distribution of vectors the probability of finding one inclined at an angle θ within $\mathrm{d}\theta$ to a chosen axis is proportional to the area of the ring element that is defined by this condition, (i.e. $2\pi r \sin\theta\,\mathrm{d}\theta$, where r is the radius of the sphere). i.e. $f(\theta)\mathrm{d}\theta \propto 2\pi r\sin\theta\,\mathrm{d}\theta$. If we normalize such that $\int_0^{\pi/2} f(\theta)\mathrm{d}\theta = 1$, then $f(\theta) = \sin\theta$.

$$\begin{aligned}\sigma &= \sigma_0 - \Sigma(\Delta\sigma\cos\theta)\Delta N_\theta \mathrm{d}\theta \\ &= \sigma_0 - \Delta\sigma\int_0^{\pi/2}\Delta N_\theta\cos\theta\,\mathrm{d}\theta; \qquad (62)\end{aligned}$$

therefore,

$$\frac{\mathrm{d}\Delta N_\theta}{\mathrm{d}t} + D\Delta N_\theta = \sin 2\theta\left(p - q\int_0^{\pi/2}\Delta N_\theta\cos\theta\,\mathrm{d}\theta\right), \qquad (63)$$

where $p = N_1^0\omega_{12}^0(V_{12}+V_{21})\sigma_0/2kT$, $q = N_1^0\omega_{12}^0 \times (V_{12}+V_{21})\Delta\sigma/2kT$ and $D = \omega_{12}^0 + \omega_{21}^0$ as before; (see Equations 10 and 10a). The solution to Equation 63 is

$$\Delta N_\theta = \frac{p\{1-\exp[-(D+2q/3)t]\}\sin 2\theta}{D+2q/3}. \qquad (64)$$

This solution shows that this approach does not predict the existence of a distribution of time constants, for the factor $(D + 2q/3)$ is independent of θ. Thus although the fractional change in site population at equilibrium is very sensitive to the orientation of the sample of jumping elements under consideration, the rate of approach to the stressed equilibrium state is not.

On substituting Equation 64 in Equation 62 we find

$$\sigma = \sigma_0 - \frac{\Delta\sigma p}{D+2q/3}\{1-\exp[-(D+2q/3)]\}. \qquad (65)$$

The stress asymptote at infinite time is once again found to have a magnitude proportional to σ_0, (through its dependency on p); compare with Equation 12. The similarity in the two Equations 12 and 65 can be seen by rewriting as

$$\sigma = \frac{D}{C}\sigma_0 + \sigma_0\left(\frac{C-D}{C}\right)\exp(-Ct) \qquad (12a)$$

and

$$\sigma = \left(\sigma_0 - \frac{\Delta\sigma p}{D+2q/3}\right) + \frac{\Delta\sigma p}{D+2q/3} \times \exp[-(D+2q/3)t] \qquad (65a)$$

and substituting for C, D, p and q.

5. Constant strain-rate tests

5.1. Site model analysis

In this section we examine the constant strain-rate test and derive the stress–strain relationship predicted by the site model theory taking into account site population distribution as before. The starting point is Equation 7, up to which point the analysis does not depend on the loading conditions [1, 2]. For constant strain-rate testing we have

$$\epsilon = \epsilon_\mathrm{u} + \Delta N\Delta\epsilon = \frac{\sigma}{E_\mathrm{u}} + \Delta N\Delta\epsilon, \qquad (66)$$

where ϵ_u is the unrelaxed strain, which is a function of the stress and can be obtained by dividing the stress by the unrelaxed modulus, E_u. $\Delta\epsilon$ is the increment of strain produced per unit change in site population. Therefore

$$\frac{\mathrm{d}\epsilon}{\mathrm{d}t} = \frac{1}{E_\mathrm{u}}\frac{\mathrm{d}\sigma}{\mathrm{d}t} + \Delta\epsilon\frac{\mathrm{d}\Delta N}{\mathrm{d}t}. \qquad (67)$$

Thus on substitution into Equation 7 we find

$$\frac{1}{\Delta\epsilon}\frac{\mathrm{d}\epsilon}{\mathrm{d}t} - \frac{1}{\Delta\epsilon E_\mathrm{u}}\frac{\mathrm{d}\sigma}{\mathrm{d}t} + \frac{1}{\Delta\epsilon}\left(\epsilon - \frac{\sigma}{E_\mathrm{u}}\right)(\omega_{12}^0 + \omega_{21}^0) = \frac{N_1^0\omega_{12}^0(V_{12}+V_{21})\sigma}{kT}. \qquad (68)$$

For a constant strain-rate test $\mathrm{d}\epsilon/\mathrm{d}t = \dot{\epsilon} =$ constant and $\epsilon = \dot{\epsilon}t$, therefore

$$\frac{\mathrm{d}\sigma}{\mathrm{d}t} + \sigma\left[\omega_{12}^0 + \omega_{21}^0 + \frac{N_1^0\omega_{12}^0(V_{12}+V_{21})\Delta\epsilon E_\mathrm{u}}{kT}\right] = E_\mathrm{u}\dot{\epsilon} + E_\mathrm{u}\dot{\epsilon}t(\omega_{12}^0 + \omega_{21}^0). \qquad (69)$$

This is of the form

$$\frac{\mathrm{d}\sigma}{\mathrm{d}t} + C'\sigma = E_\mathrm{u}\dot{\epsilon} + E_\mathrm{u}\dot{\epsilon}Dt. \tag{70}$$

If we solve this equation for the boundary condition $t = 0, \sigma = 0$ we find,

$$\sigma = \frac{DE_\mathrm{u}}{C'}\epsilon + E_\mathrm{u}\dot{\epsilon}\left(\frac{1}{C'} - \frac{D}{C'^2}\right)[1 - \exp(-C't)]. \tag{71}$$

This is identical to the solution for the standard linear solid depicted in Fig. 7 when deformed at a constant strain rate. i.e.

$$\sigma = E_1\epsilon + \mu\dot{\epsilon}\left[1 - \exp\left(\frac{-E_2 t}{\mu}\right)\right]. \tag{72}$$

Thus we identify DE_u/C' with E_1, and C' with E_2/μ. i.e.

$$\frac{E_\mathrm{u}(\omega_{12}^0 + \omega_{12}^0)}{[\omega_{12}^0 + \omega_{21}^0 + N_1^0\omega_{12}^0(V_{12} + V_{21})\Delta\epsilon E_\mathrm{u}/kT]} \equiv E_1 \tag{73}$$

and

$$\omega_{12}^0 + \omega_{21}^0 + N_1^0\omega_{12}^0(V_{12} + V_{21})\Delta\sigma/kT \equiv E_2/\mu. \tag{74}$$

But the unrelaxed modulus is equal to $(\mathrm{d}\sigma/\mathrm{d}\epsilon)_{\epsilon=0}$, i.e.,

$$E_\mathrm{u} = E_1 + E_2 \tag{75}$$

and the incremental form gives

$$\Delta\sigma = E_\mathrm{u}\Delta\epsilon. \tag{76}$$

Hence we can form

$$\frac{\omega_{12}^0 + \omega_{21}^0}{\omega_{12}^0 + \omega_{21}^0 + N_1^0\omega_{12}^0(V_{12} + V_{21})\Delta\sigma/kT} \equiv \frac{E_1}{E_1 + E_2}. \tag{77}$$

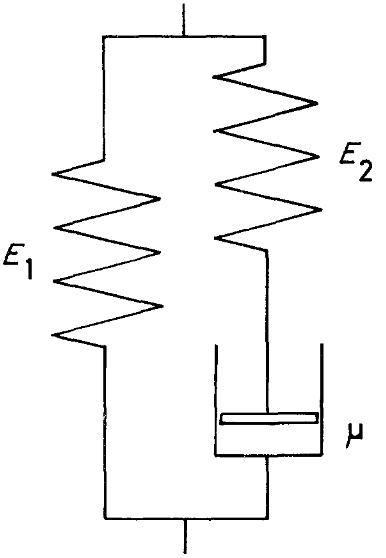

Figure 7 The form of the standard linear solid used in this paper.

On comparing the results of this section with those presented previously for creep and stress relaxation [2] it is found that the standard linear solid gives identical results to the site model theory for creep, stress relaxation and constant strain rate testing. That is, not only is the form of the $\sigma(\epsilon)$, $\sigma(t)$ or $\epsilon(t)$ curves the same but also the same relationships of the parameters in the site model with the spring and dash-pot constants of the standard linear solid must be made in each case [31].

5.2. Estimation of activation volume from constant strain-rate tests

Two methods of estimating the (experimental) activation volume from constant strain-rate tests have been described by Pink and co-workers [16, 18, 19]. In the first a series of tests are conducted at different strain-rates, each on a different specimen. In the second, tests are conducted on a single specimen which is subjected to a sudden change in strain-rate to a new fixed value at some point during the test. These two methods will now be examined in the context of the site model theory.

5.2.1. *First method*

The data can be presented as stress–strain characteristics as shown in Fig. 8. It is convenient to analyse the problem in terms of the standard linear solid, Fig. 7, as introduced above (Section 5.1). The equation of the $\sigma(\epsilon)$ characteristic is therefore given by

$$\sigma = E_1\epsilon + \mu\dot{\epsilon}[1 - \exp(-E_2\epsilon/\mu\dot{\epsilon})]. \tag{78}$$

For a fixed value of ϵ this leads to

$$\left(\frac{\mathrm{d}\ln\dot{\epsilon}}{\mathrm{d}\sigma}\right)_\epsilon = [\sigma - E_1\epsilon - E_2\epsilon\exp(-E_2\epsilon/\mu\dot{\epsilon})]^{-1}. \tag{79}$$

If we now differentiate the right-hand side with respect to ϵ we can determine the behaviour of the quantity $(\mathrm{d}\ln\dot{\epsilon}/\mathrm{d}\sigma)_\epsilon$ evaluated for different deformations. It is easily shown that $(\mathrm{d}/\mathrm{d}\epsilon)(\mathrm{d}\ln\dot{\epsilon}/\mathrm{d}\sigma)_\epsilon$ is always negative and therefore the experimental activation volume, $[\propto (\mathrm{d}\ln\dot{\epsilon})\mathrm{d}\sigma)_\epsilon]$, decreases as the deformation at which it is obtained increases. This is consistent with observations.

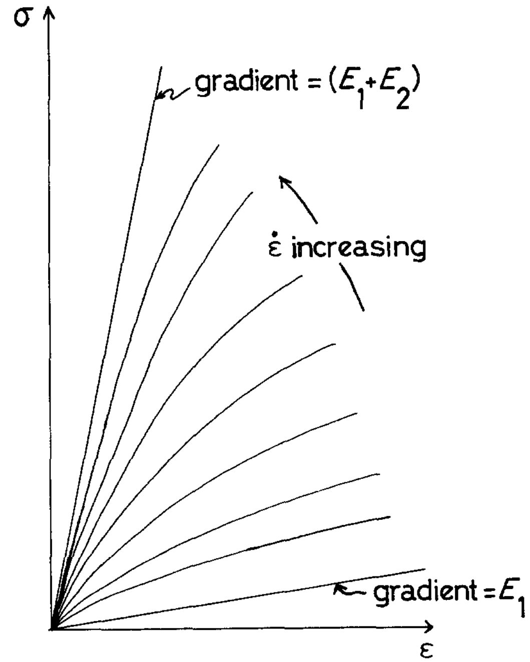

Figure 8 Stress–strain curves for the standard linear solid, showing the strain-rate dependence.

5.2.2. Second method

In the method preferred by Pink and co-workers a sudden change in strain-rate from $\dot{\epsilon}_1$ to $\dot{\epsilon}_2$ is applied at some instant $t = t_1$ during the test, [16, 18, 19]. The activation volume derived from such a strain-rate change (SRC) experiment is taken to be

$$V_{\text{SRC}} = \frac{kT\ln(\dot{\epsilon}_2/\dot{\epsilon}_1)}{\sigma(t_1+\Delta t)-\sigma_1(t_1+\Delta t)}, \quad (80)$$

where $\sigma(t_1 + \Delta t)$ represents the stress a short time, Δt, after the application of the change in strain rate, and $\sigma_1(t_1 + \Delta t)$ is the value the stress would have at this time if the original strain-rate were maintained without change throughout. If we evaluate $\sigma(t_1 + \Delta t) - \sigma_1(t_1 + \Delta t)$ for the standard linear solid of Fig. 7 we find

$$\sigma(t_1+\Delta t)-\sigma_1(t_1+\Delta t) = (\dot{\epsilon}_2-\dot{\epsilon}_1)(E_1+E_2)\Delta t. \quad (81)$$

This predicts that if V_{SRC} is evaluated for different stresses obtained by changing the strain rates then V_{SRC} decreases as stress increases.

6. Discussion

The analysis of deformation behaviour presented here is based upon the two-site model theory and special attention has been paid to the population distribution. When this is taken into account it is found that the expressions commonly computed and called the "(experimental) activation volume" are predicted to be stress-dependent and not constants. The behaviour of these computed constants is generally in agreement with the predictions of the theory. It is seen that the use of expressions like $[\mathrm{d}\ln(-\dot{\sigma})/\mathrm{d}\sigma]\cdot kT$ for the activation volume in the case of stress relaxation, for example, must be based on a false analysis since their derivation is based on the premise that the activation volume is a constant. Once it is found that $\mathrm{d}\ln(-\dot{\sigma})/\mathrm{d}\sigma$ is not a constant the validity of the procedure disappears.

The site model theory presented here does give a reasonable description of the general behaviour observed with polymers. Indeed it is predicted that the product of $\mathrm{d}\ln(-\dot{\sigma})/\mathrm{d}\sigma$ and the effective stress should be a constant, within the limitations imposed by the mathematical approximations made in reaching this conclusion. Therefore this quantity is not material-specific and the data presented by Kubát and co-workers [7–11] becomes less remarkable when viewed from this standpoint. Departures from the predictions of the theory may sometimes be related to the mathematical approximations used and it is important to test these whenever possible. On the other hand it is also true that the model may not always be applicable, as already mentioned in Section 1. The model addresses the case in which there are only two possible sites for each deforming element so that on surmounting the energy barrier in one direction the only possible jump is one in the opposite direction, back to the original state. In certain deformation processes this model is clearly not appropriate. Sometimes another jump of the same kind and in the same direction is possible, while in other cases consecutive energy barriers of different heights may exist.

The theory gives rise to a linear viscoelastic solution, completely compatible with the standard linear solid [31]. As such it provides a theoretical foundation for the standard linear solid but at the same time will suffer from the same limitations. Fitting experimental data to spring and dash-pot model behaviour has long been practised and a simple three-element model is rarely found to be sufficient to imitate observations with any degree of precision, (see, for example, the series of papers by Eyring and co-workers [32–42]). Again it must be emphasized that there are mathematical approximations employed in the site-model derivation of the differential equation that coincides with the equation of motion of the standard linear solid that may not always be valid, particularly at high stress levels. Here, perhaps, then is a source of non-linear behaviour [25].

A clear deficiency of the theory is that it produces a solution possessing a single relaxation time only. This is of course inevitable with a theory in which it is assumed that a single process with a single activation energy is responsible for the deformation. Even taking into account the distribution of orientation of the jumping elements does not alter this. Stress relaxation results obtained in our own laboratory [23–26, 28, 43] give much gentler slopes in σ against $\ln t$ plots than is demanded by a single relaxation process, as is generally found.

Finally it must be emphasized that the theory presented here is not offered as an alternative to those in which it is attempted to quantify the role of free volume. Robertson [44, 45] has indicated how this might be done for relaxation behaviour following a temperature change while Matsuoka and co-workers [46–49] have suggested that stress-induced dilatation has an important effect on the stress relaxation and other mechanical properties of polymers. The purpose of this paper is instead an attempt to tidy up some of the apparent anomalies found in the literature based loosely on the Eyring approach. As pointed out by Macedo and Litovitz [50] a suitable combination of both approaches is probably required to properly account for the viscoelastic properties of real materials.

7. Conclusions

The site model theory has been developed taking into account population distribution, with the following results:

(a) The deformation-induced internal stress follows naturally from the site population imbalance.

(b) The stress dependence of computed values of the "(experimental) activation volume" can be understood. An alternative method has been developed that enables the estimation of an "activation volume" that is in keeping with the original definition for which this term was coined.

(c) A theoretical foundation for the standard linear solid is provided.

(d) The activation parameters and experimental conditions often employed sometimes invalidate approximations made in rate theory analysis and it is always necessary to check critically at each stage.

References

1. I. M. WARD, "Mechanical Properties of Solid Polymers" (John Wiley and Sons, New York, 1971).
2. J. R. WHITE, *Mater. Sic. Eng.* **45** (1980) 35.
3. H. EYRING, *J. Chem. Phys.* **4** (1936) 283.
4. A. S. KRAUSZ, *Z. Naturforsch.* **31a** (1976) 728.
5. *Idem, Mater. Sci. Eng.* **26** (1976) 65.
6. A. S. KRAUSZ and H. EYRING, "Deformation Kinetics" (Wiley-Interscience, New York, 1975).
7. J. KUBÁT and M. RIGDAHL, *ibid.* **24** (1976) 223.
8. *Idem, Phys. Stat. Sol. (a)* **35** (1976) 173.
9. J. KUBÁT, M. RIGDAHL and R. SELDÉN, *J. Appl. Polymer Sci.* **20** (1976) 2799.
10. J. KUBÁT and R. SELDÉN, *Mater. Sci. Eng.* **36** (1978) 65.
11. J. KUBÁT, *Makromol. Chem. Suppl.* **3** (1979) 233.
12. E. PINK, V. BOUDA and H. BÄCK, *Mater. Sci. Eng.* **38** (1979) 89.
13. J. P. CAVROT, J. HAUSSY, J. M. LEFEBVRE and B. ESCAIG, *ibid.* **36** (1978) 95.
14. E. PINK, *Progr. Colloid and Polymer Sci.* **58** (1975) 81.
15. *Idem, Mater. Sci. Eng.* **22** (1976) 85.
16. *Idem, Rev. Deform. Behav. Mater.* **2** (1977) 37.
17. E. PINK, H. BÄCK and B. ORTNER' *Phys. Stat. Sol. (a)* **55** (1979) 751.
18. E. PINK and J. D. CAMPBELL, *Mater. Sci. Eng.* **15** (1974) 187.
19. *Idem, J. Mater. Sci.* **9** (1974) 665.
20. J. C. M. LI, *Can. J. Phys.* **45** (1967) 493.
21. J. KUBÁT and M. RIGDAHL, *Int. J. Polymeric Mater.* **3** (1975) 287.
22. E. PINK, *Mater. Sci. Eng.* **38** (1979) 285.
23. B. HAWORTH and J. R. WHITE, *J. Mater. Sci.* **16** (1981) 3263.
24. L. D. COXON and J. R. WHITE, *ibid.* **14** (1979) 1114.
25. J. R. WHITE, *J. Polymer Sci. Polymer Phys. Ed*, in press.
26. B. HAWORTH, MSc thesis, University of Newcastle upon Tyne (1979).
27. B. HAWORTH, G. J. SANDILANDS and J. R. WHITE, *Plast. Rubber Int.* **5** (1980) 109.
28. L. D. COXON and J. R. WHITE, *Polymer Eng. Sci.* **20** (1980) 230.
29. J. KUBÁT and M. RIGDAHL, *Mater. Sci. Eng.* **21** (1975) 63.
30. R. E. ROBERTSON, *J. Chem. Phys.* **44** (1966) 3950.
31. J. R. WHITE, *Rheol. Acta* **20** (1981) 23.
32. G. HALSEY, H. J. WHITE, Jr and H. EYRING, *Text. Res. J.* **15** (1945) 295.
33. H. EYRING and G. HALSEY, *ibid.* **16** (1946) 13.
34. R. STEIN, G. HALSEY and H. EYRING, *ibid.* **16** (1946) 53.
35. H. EYRING and G. HALSEY, *ibid.* **16** (1946) 124.
36. H. D. HOLLAND, G. HALSEY and H. EYRING, *ibid.* **16** (1946) 201.

37. G. HALSEY and H. EYRING, *ibid.* **16** (1946) 329.
38. S. KATZ, G. HALSEY and H. EYRING, *ibid.* **16** (1946) 378.
39. C. H. REICHARDT and H. EYRING, *ibid.* **16** (1946) 382.
40. C. H. REICHARDT, G. HALSEY and H. EYRING, *ibid.* **16** (1946) 382.
41. G. HALSEY, *J. Appl. Phys.* **18** (1947) 1072.
42. H. EYRING and G. HALSEY, in "High Polymer Physics: a Symposium", edited by H. A. Robinson, (Ramsen Press, NY, 1948) p. 61.
43. G. J. SANDILANDS and J. R. WHITE, *Polymer* **21** (1980) 338.
44. R. E. ROBERTSON, *J. Polymer Sci.-Symp.* **63** (1978) 173.
45. *Idem, J. Polymer Sci – Polymer Phys. Ed.* **17** (1979) 597.
46. S. MATSUOKA, C. J. ALOISIO and H. E. BLAIR, *J. Appl. Phys.* **44** (1973) 4265.
47. S. MATSUOKA, H. E. BLAIR and C. J. ALOISIO, *J. Polymer Sci. – Symp.* **46** (1974) 115.
48. S. MATSUOKA, *Polymer Eng. Sci.* **14** (1974) 162.
49. S. MATSUOKA, H. E. BLAIR, S. S. BEARDER, H. E. KERN and J. T. RYAN, *ibid.* **18** (1978) 1073.
50. P. B. MACEDO and T. A. LITOVITZ, *J. Chem. Phys.* **42** (1965) 245.

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