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Co-operative effects in non-linear relaxation

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A many-body, co-operative, theory of relaxation recently presented by the authors is extended to the case of non-linear response in the time domain to the application of high force fields. It is shown that the characteristic fractional power law time decay of the initial perturbation is an essential feature of co-operative relaxation. The application of the theory to experimental situations is considered.

1. Introduction

A theory describing the dynamics of relaxation in co-operative, many-body, systems has recently been presented [1]. The co-operative nature of the system generates a relaxation rate equation which is non-linear in the deviation from equilibrium. The equilibrium, itself, being a non-linear function of the external perturbation causing the deviation. A simple, linearized, form for the solutions to the non-linear functions has been successfully applied to a derivation of the frequency dependent dielectric susceptibility and its temperature dependence [1, 2].

Non-linear relaxation is observed experimentally when a large deviation from equilibrium is produced by a suitable force field. Examples of such time dependent recovery would be the relaxation of ordered electric systems after the removal of a large static electric field [3], or the relaxation of mechanical stress under the application of a large mechanical strain [4]. A common feature of such experiments is a time region in which the deviation in the property being monitored, M', is proportional to the logarithm of the time since the initiation of the perturbation, i.e.

$$M' = -a \ln(t). \tag{1}$$

Earlier experimental investigation has indicated a value of one tenth for the parameter a [5], when M' is normalized in terms of its zero time value.

A development of the present authors' work [1, 2] to describe non-linear relaxation is presented here. It will be shown that the observed behaviour of Equation 1 is the result of a time power law of the form t^{-n}, characteristic of a co-operative relaxation mechanism. Furthermore it will be shown that the parameter a, can be expressed as

$$(1-n)\cdot F'_{\mathrm{m}}(b, x_0) \tag{2}$$

where the exponent n can be simply interpreted as the degree of correlation of the relaxation mechanism in the response of the material to an external perturbation, just as in the case of dielectric relaxation, and the function $F'_{\mathrm{m}}(b, x_0)$ depends only on the initial and final states of the system.

2. Theory

The theory presented here is based on a picture of a material in which small, local, groups of atoms, ions or molecules have two alternative positions which they can occupy. Such a situation is already implicit in the standard Debye approach to relaxation [6] and is the basis of much work of our present understanding of mechanical loss [4]. These local systems can be represented by a local double minima potential in the potential energy of the system, with a well defined potential barrier between the minima. The minima are not, in general, of identical energies although the difference in the minima energies may be small. The properties of glassy materials have been extensively discussed in terms of local states such as these, with allowance made for quantum mechanical tunnelling between the local minima [7–9].

Such systems relax exponentially in time *only* if the individual local systems are non-interacting, which is not the case for solids or liquids. Interactions between the local systems can occur through an exchange of virtual phonons [10] and can be represented in the form of a spin–spin interaction in which the two alternative local minima play the

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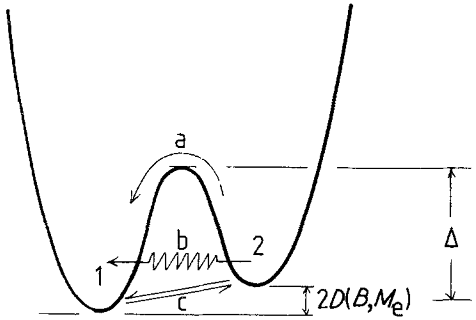

Figure 1 Diagrammatic representation of a double minima potential energy for the average local system. The symbols are defined in the text. Process (a) is the thermally activated relaxation mechanism, process (b) is the co-operative tunnelling mechanism and process (c) is the exchange fluctuation mechanism. The minima are labelled 1 and 2 for clarity.

part of the spin orientations in a spin 1/2 system. Non-exponential relaxation in time results from a consideration of the implications of the various contributions to the interactions [1, 2].

Firstly there is an interaction dependent only on the longitudinal component of the interacting local spins which contributes a mean field term to the total free energy of the whole system. The energy eigenstates of such a system are no longer those appropriate to the individual local systems but are states in which the orientations of all the spins must be simultaneously specified. That is they are configuration states. The system can therefore be described by the macroscopic potential energy diagram of Fig. 1, in which the minima refer to configurations in which all the orientations are in one of two alternative directions.

The average longitudinal component of the spin is the thermal population difference between the configurations of the two minima of Fig. 1, and is given when normalized to unity by

$$M_e = \tanh \frac{D(B, M_e)}{kT} \qquad (3)$$

where the energy difference $D(B, M_e)$ is a function of the mean field energy, which is itself proportional to M_e, and B, which is the average value of the local energy difference, and is equivalent to a local field.

The thermal average value of M_e is established either by activation over the minimum potential barrier Δ between the two sets of configurations or by thermally assisted tunnelling through the potential barrier. A deviation from equilibrium will occur when an external strain is applied to the system. The field of the strain, F, contributing an extra term to the energy difference B, the magnitude of the extra term being dependent on the average local coupling constant d. In the dielectric context, F is the applied electric field and the coupling constant is the local dipole moment. Upon removal of the external field the system relaxes towards equilibrium. The non-linear (in M_e) form of Equation 3 ensures that in general the relaxation will also be non-linear. The detailed form of Equation 3 is determined by $D(B, M_e)$ and will be general for specific classes of interactions. For simplicity here the form appropriate to a material which undergoes alignment of the interacting systems is chosen, that is

$$D(B, M_e) = B + kT_c M_e \qquad (4)$$

where B and the mean field interaction, kT_c, are system parameters. It should be pointed out that the *form* of the time development is independent of the choice of $D(B, M_e)$ which only determines such factors as the detail of the temperature dependence.

The relaxation of a deviation in such a system as that defined by Fig. 1 and Equation 4 is given by [1, 11]

$$\frac{dM(t)}{dt} = -\nu_E \cdot \cosh \left[\frac{B + kT_c M(t)}{kT}\right] \times \left\{M(t) - \tanh\left[\frac{B + kT_c M(t)}{kT}\right]\right\} \qquad (5)$$

where $M(t)$, which is a function of the time t, is the instantaneous value of the normalized population difference,

$$M(t) = \frac{n_1(t) - n_2(t)}{n_1(t) + n_2(t)} \qquad (6)$$

and ν_E is the activated rate constant given by

$$\nu_E = \nu_0 \cdot \exp - (\Delta/kT) \qquad (7)$$

with ν_0 the quantum mechanical transition rate at the top of the barrier and of the order of 10^{-13} $\sec^{-1}$ or less. In some systems, particularly at low temperatures, a thermally assisted quantum mechanical tunnelling rate may be more appropriate, but again this does not affect the *form* of the time development.

A linearized version of Equation 5 has been investigated previously [1, 2]. In the linear form the instantaneous deviation from equilibrium

$M'(t)$ is given by

$$\frac{\mathrm{d}M'(t)}{\mathrm{d}t} = -\omega_\mathrm{p} \cdot M'(t) \tag{8}$$

in which the rate constant ω_p is a function only of the equilibrium conditions, and thus of temperature. The rate of thermal relaxation is then determined solely by the equilibrium system parameters and the relaxation is therefore an isothermal dynamic process.

The general non-linear expression, Equation 5, is one in which the instantaneous population difference $M(t)$ and the instantaneous equilibrium population difference $M_\mathrm{i}\{M(t)\}$ given by

$$M_\mathrm{i}\{M(t)\} = \tanh\left[\frac{B + kT_\mathrm{c}M(t)}{kT}\right] \tag{9}$$

approach each other asymptotically, and both satisfy Equation 3 at equilibrium. This process is thus still an isothermal form of relaxation and the rate Equation 5 can be written as

$$\frac{\mathrm{d}M(t)}{\mathrm{d}t} = -\nu_\mathrm{E} \cdot \cosh\left[\frac{B + kT_\mathrm{c}M(t)}{kT}\right] \times \{M(t) - M_\mathrm{i}[M(t)]\} \tag{10}$$

which can be solved by integration to give

$$\int_{M(0)}^{M(t)} \mathrm{d}M \, |Z(M)|^{-1} = -\nu_\mathrm{E} \cdot t \tag{11}$$

in which

$$Z(M) = \left\{\cosh\left[\frac{B + kT_\mathrm{c}M(t)}{kT}\right](M(t) - M_\mathrm{i}[M(t)])\right\}. \tag{12}$$

$M(0)$ is the initial value of $M(t)$ immediately after the removal of the external force field. It is therefore given by

$$M(0) = \tanh\left[\frac{B + F \cdot d + kT_\mathrm{c}M(0)}{kT}\right] \tag{13}$$

with d the coupling constant of the system to the field F.

The integral over M can be written symbolically as

$$\int_{M(0)}^{M(t)} \mathrm{d}M \, |Z(M)|^{-1} = Y\{M(t)\} - Y\{M(0)\} \tag{14}$$

in which case the rate equation, Equation 5, assumes the form

$$\frac{\mathrm{d}Y\{M(t)\}}{\mathrm{d}t} = -\nu_\mathrm{E}. \tag{15}$$

Before obtaining an expression for $Y\{M(t)\}$ the other processes which affect the rate must be introduced. These are co-operative tunnelling and fluctuation mechanisms. The time development due to these two processes assumes a unique form as a consequence of the co-operative nature of the interacting system. It has been pointed out already that the eigenstates of the system are macroscopic configuration states and Ngai *et al.* [12] have recently established computationally, that for a wide variety of materials such states have a continuum of energy eigenvalues up to a cut-off value ζ, with a constant number density per unit energy. The presence of such a spectrum of states has been established experimentally in the case of glasses [9]. It was recognized by Ngai *et al.* [12] that this property was one of the two requirements for a time power law decay of the form observed in the infrared divergence effect [13, 14]. The second requirement is that the excitations within the system should be between states that have either full or zero thermal population.

This second criterion is met automatically by the co-operative system described by Fig. 1, at any temperature. Consider a configuration in one of the minima in this diagram, the configuration being defined by a set of local systems with their orientation simultaneously in the direction chosen. Each of these orientations is thus fully occupied while the alternative orientation, which belong to a configuration in the opposite minima, are completely unoccupied.

The two co-operative mechanisms affecting the relaxation process and the generation of the power law decay in time have been described in detail previously [2], but, as they bring together a completely new concept, they will be surveyed in some depth here. The co-operative tunnelling mechanism arises from the presence of local tunnelling which splits the energy levels in the local double potential minima. The atoms in one state must now be considered to oscillate between the minima at a rate determined by the tunnelling matrix element. Relaxation to the lower state can only occur when the excess energy is emitted by the state. It is usual to consider this to occur by means of phonon emission, in which case the energy is released to the phonon bath, and thermally assisted tunnelling takes place [15]. In the system described here however there is an alternative process which can absorb the excess energy. An oscillating local system describes the movement of a configuration from one minima to the other. This represents a state of the system in which each minima is excited by the occupation of a previously unoccupied state of higher energy than would be appropriate to the instantaneous equilibrium. This transient is degenerate with the excitation of a large number of alternative configurations, all of which may be excited by the same local tunnelling process. Given the energy spectrum and population properties of the configuration states the excess energy of a local tunnelling state can be distributed among the alternative excitations of the system leading to a relaxation decay of the form

$$\cos(n\pi/2)\cdot(\zeta t)^{-n} \tag{16}$$

for the initial system. Here n is the square of the distortion occurring for the *average* tunnelling event, normalized with respect to the *maximum* possible distortion for the system. The average property requires that

$$0 \leqslant n \leqslant 1 \tag{17}$$

furthermore n can be regarded as the degree of correlation of tunnelling process in the system [1].

The excess energy is redistributed throughout the correlated energy system and is eventually released into the phonon bath. The release however may take place from any one of the number of local systems correlated with the initial system out of equilibrium, rather than only from the initial state.

This decay competes with the thermal process described by the rate equation, Equation 5, and relaxes the system towards its instantaneous equilibrium value. The deviation therefore has the correlated relaxation rate

$$\frac{\mathrm{d}Y\{M(t)\}}{\mathrm{d}t} = -\nu_{\mathrm{E}}\cdot\cos(n\pi/2)\cdot(\zeta t)^{-n}. \tag{18}$$

The second process that affects the rate of relaxation is the fluctuation mechanism and results from the part of the interaction between local systems which corresponds to spin exchange. The mechanism synchronously exchanges local systems between configurations in the two minima of Fig. 1 and can be termed a flip-flop process. After an exchange has taken place the population difference is unchanged. This form of exchange is only possible between systems whose local value of B, B_1, differ by an amount varying from zero up to the magnitude of the exchange energy itself. When the difference in B is not zero a new average value of B results. Because of this the state in each of the minima correspond to an excitation with respect to the new value of B, and the system evolves towards the new state following a different time power law t^{-m}, where m is defined in a similar manner as n and describes the correlation of the flip-flop processes. However the values of B and M_{e} are equilibrium system averages and must be restored. The restoration occurs because all possible pairs of local systems are coupled by this interaction and *any* disturbance generates the restoration through other flip-flop pairs which restores a new macroscopic state satisfying the initial conditions. The restoration is not independent of the decay and its initiation is therefore delayed by the initial decay. As the time average of the fluctuations is independent of time the complete time dependence of the fluctuations has the form

$$t_1^{-m}\cdot(t-t_1)^{+m} \tag{19}$$

which has a time average value of

$$\Gamma(1-m)\cdot\Gamma(1+m) \tag{20}$$

where Γ( ) is the gamma function.

These fluctuations take place throughout the decay process and continue as a power law noise [16] when the system attains equilibrium. Since the magnitude of $M(t)$ is not affected they do not have a direct effect on the relaxation Equation 18. However their destruction of the instantaneous configuration as t_1^{-m} competes with the relaxation decay, while the restoration starting at time t_1 and following the power law $(t-t_1)^m$ produces a new configuration at time t_1 which satisfies the original conditions and which will relax as described by Equation 18 with the new time zero being t_1. The observed relaxation rate is thus a composite of all the fluctuation–restoration initiated rates and requires to be averaged over this process. The observed rate is thus

$$\left\langle\frac{\mathrm{d}Y\{M(t)\}}{\mathrm{d}t}\right\rangle = -\nu_{\mathrm{E}}\cdot\cos\left(\frac{n\pi}{2}\right)\cdot(\zeta)^{-n}\,\frac{\int_0^t (t-t_1)^{-n}\cdot(t-t_1)^{m}\cdot t_1^{-m}\cdot \mathrm{d}t_1}{\int_0^t (t-t_1)^{m}\cdot t_1^{-m}\,\mathrm{d}t_1} \tag{21a}$$

$$= -\nu_{\mathrm{E}}\cdot\cos\left(\frac{n\pi}{2}\right)\cdot(\zeta t)^{-n}\cdot\Gamma(1+m-n)\cdot[\Gamma(2-n)\cdot\Gamma(1+m)]^{-1}. \tag{21b}$$

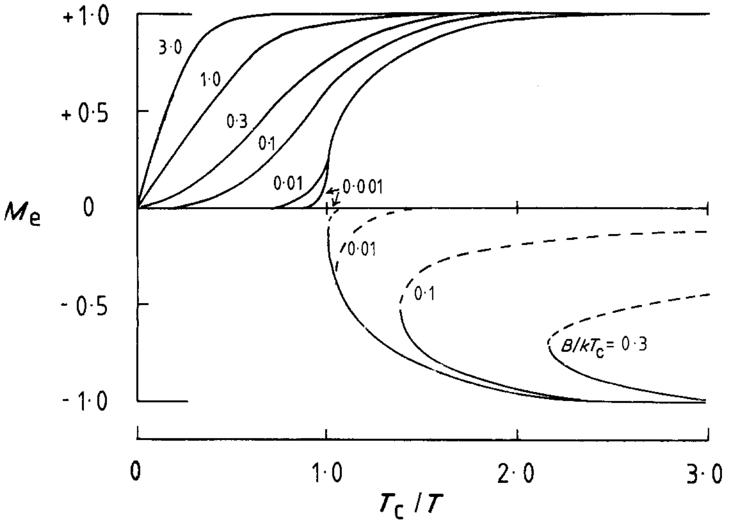

Figure 2 A plot of the solutions to Equation 3 using Equation 4 for the form of $D(B, M_e)$. A parametric variable, $B/(kT_c)$, has been used and the inverse temperature scale normalized in terms of T_c. The dashed region indicates unstable solutions.

It is usual to observe $M(t)$ or the deviation of $M(t)$ from the equilibrium values of M_e given by Equation 3. This can be obtained from Equation 21 by integrating the non-linear relaxation current over the time t and solving the resulting equation for $M(t)$. Thus

$$\langle Y\{M(t)\}\rangle - \langle Y\{M(0)\}\rangle = -\nu_E \cos\left(\frac{n\pi}{2}\right) \cdot (\zeta t)^{-n} \times \frac{t}{(1-n)} \cdot \frac{\Gamma(1+m-n)}{\Gamma(2-n)\Gamma(1+m)} \qquad (22)$$

which is a completely general expression containing all the time dependence involved in non-linear relaxation. In order to complete the solution an expression for $M(t)$ must be obtained which will in detail depend on the form of $D(B, M_e)$, however a general form can be generated and will be examined here.

3. Non-linear deviation from equilibrium

The form of $Y\{M(t)\}$ defined by the integral expression, Equation 11, will be illustrated with reference to the form of $D(B, M_e)$ given in Equation 4 and appropriate to a material undergoing an alignment transition. At temperatures greater than the critical temperature T_c Equation 3 has only one solution. However when T is less than T_c three solutions are possible, as shown in Fig. 2. Two of the solutions correspond to alignment of the system and have values at zero temperature of + 1 and − 1. The third solution, with a zero temperature asymptotic value of $-B/kT_c$, is unstable with respect to *small* deviations from equilibrium. When the normalized variable $B/(kT_c)$ is greater than unity only one solution exists and the system is always in the positive alignment direction. The effect of a large external field at a given temperature is to cause the state of the system, defined by one of the solutions, to relax to the state appropriate to the new value of B, that is

$$B \rightarrow B + F \cdot d. \qquad (23)$$

On removal of the field F the system will recover the nearest state appropriate to the original value of B, showing an identical form of relaxation as it does so.

The detail of the relaxation can be determined by defining a deviation from equilibrium $M'(t)$ as

$$M'(t) = M(t) - M_e \qquad (24)$$

with the zero time value, $M'(0)$, given by

$$M'(0) = M_e(B + F \cdot d) - M_e(B) \qquad (25)$$

where $M_e(B)$ is

$$M_e = \tanh\left(\frac{B + kT_c M_e}{kT}\right). \qquad (26)$$

The function $Z(M)$ then becomes

$$Z(M) = \cosh\left(\frac{B + kT_c M_e}{kT}\right) \cdot \frac{e^{M'T_c/T}}{2} \times [M'(1 + e^{-2M'T_c/T}) + (1 - e^{-2M'T_c/T})(M'M_e - 1 + M_e^2)]. \qquad (27)$$

In order to proceed further it is necessary to approximate the function in square brackets in Equation 27 to the second order in M', which is valid when M' is a large deviation, a term which we

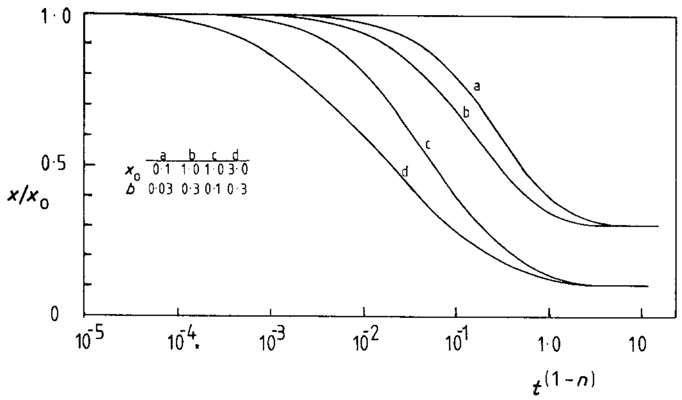

Figure 3 The relaxation characteristics of the co-operative system described by Equation 32. The plots have been normalized in terms of the initial deviation and the values of the parameters b and x_0 for the curves are given in the figure.

shall define later. Thus

$$Z(M') = \cosh\left[\frac{B + kT_c M_e}{kT}\right] M' \cdot e^{M'T_c/T} \times G\left[1 - M'\frac{T_c}{T}\left(1 - \frac{M_e}{G}\right)\right] \tag{28}$$

where

$$G = \left[1 - \frac{T_c}{T}(1 - M_e^2)\right] \tag{29}$$

and Equation 14 becomes

$$Y\{M'(t)\} - Y\{M'(0)\} = = \frac{\nu_E}{\omega_p}\int_{M'(0)}^{M'(t)} \frac{dM'\, e^{-(M'T_c/T)}}{M'[1 - (1 - M_e/G)M'T_c/T]} \tag{30a}$$

where ω_p is the rate constant for the linearized rate Equation 1 and is given by

$$\omega_p = \nu_E \cdot \cosh\left(\frac{B + kT_c M_e}{kT}\right)\left[1 - (1 - M_e^2)\frac{T_c}{T}\right]. \tag{31}$$

Equation 30 is derived assuming a large *positive* deviation, M', which implies that the equilibrium value, M_e, in the absence of the field F is a negative quantity for $T < T_c$. When M' is a large negative deviation, M_e has a positive value in the same temperature range and Equation 14 becomes

$$Y\{|M'(t)|\} - Y\{|M'(0)|\} = \frac{\nu_E}{\omega_p}\int_{|M'(0)|}^{|M'(t)|} \frac{d|M'|\exp - (|M'|T_c/T)}{|M'|[1 - (1 + M_e/G)|M'|T_c/T]} \tag{30b}$$

where the integral is over the modulus of the deviation. Here the sign of M_e in the denominator has been changed with respect to that in Equation 30a. If the branch of the solutions of Equation 3 with the asymptotic value $-B/(kT_c)$ at zero temperature is neglected as a possible equilibrium value for the recovery process of the system Equation 30b can be taken as the general result with M_e in the denominator regarded as $|M_e|$ for temperatures less than the critical temperature T_c.

Equation 30b is integrable. For convenience we set

$$x = |M'(t)| \cdot T_c/T; \quad x_0 = |M'(0)| \cdot T_c/T$$

and

$$b = G/(G + |M_e|)$$

to obtain Equation 22 in the form

$$E_1(x) - E_1(x_0) + e^{-b}[E_1(x_0 - b) - E_1(x - b)] = -\omega_p \cdot t \cdot (\zeta t)^{-n} \cdot \frac{\cos(n\pi/2) \cdot \Gamma(1 + m - n)}{(1 - n) \cdot \Gamma(2 - n) \cdot \Gamma(1 + m)} \tag{32}$$

where $E_1(\ )$ is the exponential integral [17]. This expression is shown diagramatically in Fig. 3 as a plot of the normalized deviation x/x_0 against the logarithm of the left hand side of Equation 32, that is against $\log t^{1-n}$. A range of x_0 and b have been used to show that the limiting value of x at infinite time is b. The condition that $b < x_0$, which can be expressed in the form

$$M'(0) > \frac{T}{T_c}\,\frac{[T - T_c(1 - M_e^2)]}{[T - T_c(1 - M_e^2) + |M_e|]} \tag{33}$$

defines a large deviation.

Two general statements can be made with regard to Equation 32. Firstly the appearance of the exponential integral function arises because of the large deviation approximation of Equation 3 and is therefore independent of the exact form of $D(B, M_e)$. Equation 32 is a quite general result for all materials behaving as described by the double minima macroscopic potential shown in Fig. 1.

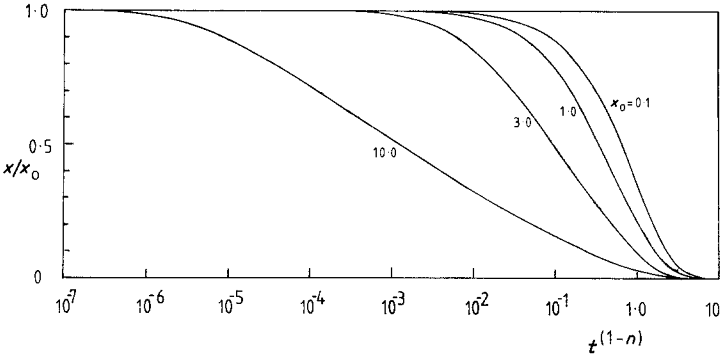

Figure 4 The relaxation characteristics of the co-operative system described by Equation 35 and applicable at temperatures much less than T_c. The plots have been normalized in terms of the initial deviation x_0, the magnitude of which is given for each curve.

Secondly the functions G and b have the properties

$$\left.\begin{array}{l} G \to 0+ \\ b \to 0+ \end{array}\right. \text{for } T \cong T_c \text{ and } \left.\begin{array}{l} G \to 1 \\ b \to \frac{1}{2} \end{array}\right. \text{for } T \ll T_c. \tag{34}$$

Hence for temperatures close to T_c, but less than T_c, the second set of exponential integrals, in parenthesis, dominate the behaviour of the system. As the temperature decreases this term decreases in importance. The exact detail of the contribution clearly depends on the form of $D(B, M_e)$. In the higher temperature range the magnitude of $M'(0)$ has to be greater than G/M_e and at low temperatures greater than $\frac{1}{2}(T/T_c)$ so that in either case quite small magnitudes can be considered as large deviations.

For temperatures in excess of the critical temperature the large deviation approximation derived here is inapplicable because there is only one solution to the transcendental Equation 3 and the linearized approach derived earlier [2] is applicable, even at very large magnitude deviations. Experimental measurements are seldom made under this condition as most materials are approaching a phase transition. For temperatures in the region of T_c the full form of Equation 32 is applicable but at lower temperatures x_0 becomes large and Equation 32 can be approximated by

$$E_1(x) - E_1(x_0) \propto -\omega_p \cdot (\zeta)^{-n} \cdot t^{1-n} \cdot b^{-1}. \tag{35}$$

Fig. 4 shows this function, in a similar presentation to that of Fig. 3. The asymptotic value of the deviation at large times is now zero, effectively as the ratio b/x_0 has gone to zero.

It should be noted that in both Figs 3 and 4 a region does exist, in the neighbourhood of the mean deviation, for which the relationship

$$x = M'(t)\frac{T_c}{T} \propto -(1-n) \cdot \ln(t) \tag{36}$$

applies, as discussed earlier. The gradient in this region, the transition between the two limiting values at short and long times, is directly related to the characteristic parameter n and extremely slow responses could be observed if n were to approach unity. In this case the experimental observation of the approach to equilibrium becomes difficult because of the extended time scale. The curves representing the solution to Equation 35 are symmetric about the value $x_0/2$ for $x_0 \geqslant 3$, which is a convenience if only part of the complete relaxation has been observed experimentally. This symmetry is lost when the higher temperature, more general form of solution, is applicable as shown in Fig. 3. The presence of the fluctuations of the system, governed by the characteristic parameter m, appear as power law noise on the observations [16], and may be identified most clearly at long times when the signal to noise ratio is small.

4. Application to experiment

In the previous sections we described the non-linear relaxation of the normalized population difference $M(t)$ for a system of interacting, bistable, units. These units are regions of disorder embedded in an ordered matrix the units of which vibrate within single minima potential wells. The tunnelling transfer between the local bistable minima of the disordered regions corresponds to many minute adjustments of the vibrational origins of the surrounding matrix, which allow an effective removal of the potential barrier to re-orientation during the transfer. The value of M_e represents the average displacement of the disordered regions from their median positions at the top of the potential barrier, Fig. 1.

The variation of $M(t)$ with time thus represents the relaxation of a physical dimension of the system after removal of an external force. The most common experimental situation is, however, one of constant strain, the stress reducing as the system relaxes. This stress relaxation is related to the relaxation of $M(t)$ in the following manner. The external stress does work on the matrix causing a fixed strain which alters the local potentials of the bistable units. The changed potential is equivalent to a field F conjugate to the bistable displacement and favouring one of the orientations over the other. The average displacement relaxes in order to come into equilibrium with the new total field, and in doing so internal energy is transferred from the matrix to the bistable system. The energy transferred in time t is

$$\begin{aligned} &F\cdot d[M(t)-M_e(B)] \\ &= F\cdot d\{[M(t)-M_e(B+F\cdot d)] \\ &\quad +M_e(B+F\cdot d)-M_e(B)\} \\ &= F\cdot d[-M'(t)+M_e(B+F\cdot d)-M_e(B)]. \end{aligned} \tag{37}$$

The internal energy within the elastic matrix is correspondingly reduced, allowing a reduction of the externally applied stress, σ, maintaining the constant strain ϵX. Thus

$$\begin{aligned} &F\cdot d[M_e(B+F\cdot d)-M_e(B)-M'(t)] \\ &\quad = \epsilon X[\sigma(0)-\sigma(t)] \end{aligned} \tag{38}$$

which allows the time behaviour of $M'(t)$ to be equated with that of $\sigma(t)$. It should be noted that the field F remains constant because the external strain is held fixed. The internal energy of the elastic matrix is regarded as being totally recoverable and in balance with the external stress, whereas the relaxation of the bistable system involves exchange of energy with the heat bath and is thus not recoverable in a coherent manner.

Equations 32 and 35, and the corresponding diagrams, show that the relaxation characteristic is dependent on the magnitudes of the initial perturbation, x_0, the equilibrium value after infinite time, b, and the characteristic parameter for the system, n. In general the absolute values of these will not be known for a particular case under investigation and hence direct comparison between theory and experiment is difficult. A convenient method of determining the magnitudes of the system parameters is given here.

As the experimental results are commonly presented in an initial deviation normalized form we set $z = x/x_0$ and let $z(m)$ be the mean value of the normalized variation, i.e. $(x_0+b)/2x_0$. The gradient of the relaxation characteristic can then be derived from Equation 32, as (c.f. Equation 2),

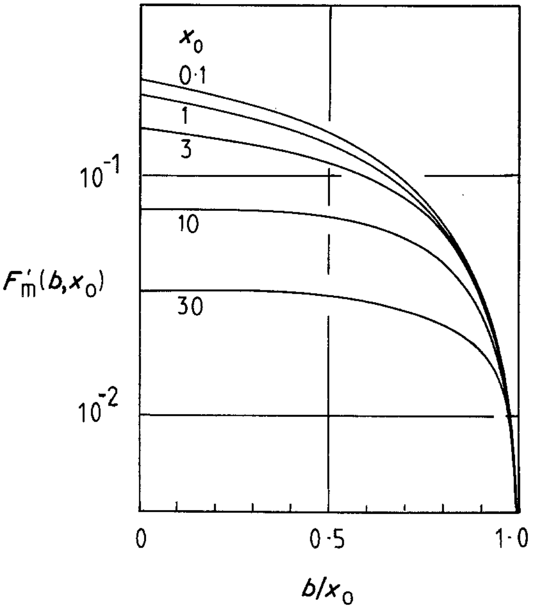

Figure 5 A plot of the function $F'_m(b, x_0)$, Equation 38, against b/x_0 for a range of values of x_0.

$$\left(\frac{dz}{d\ln t}\right)_{z(m)} = -(1-n)\cdot F'_m(b,x_0) \tag{39}$$

with

$$\begin{aligned} F'_m(b,x_0) = &\left\{E_1(x_0)-E_1\left(\frac{x_0+b}{2}\right)\right. \\ &\left.+\,e^{-b}\left[E_1\left(\frac{x_0-b}{2}\right)-E_1(x_0-b)\right]\right\} \\ &\times e^{(x_0+b)/2}\cdot(x_0^2-b^2)\cdot(4bx_0)^{-1} \end{aligned} \tag{40}$$

which is shown in Fig. 5. If now the experiment is carried out with a different value of the initial perturbation x_0 the rate of change of the gradient at the mean value will also contain the term $(n-1)$, but the logarithmic rate of change will not. Furthermore the ratio b/x_0 is accessible from the relaxation characteristic and hence x_0 can be determined. Two cases, however, have to be considered. Either b is independent of x_0, and the ratio b/x_0 changes with x_0 or the ratio stays constant as x_0 is altered. Examination of experimental results indicates that the latter case is

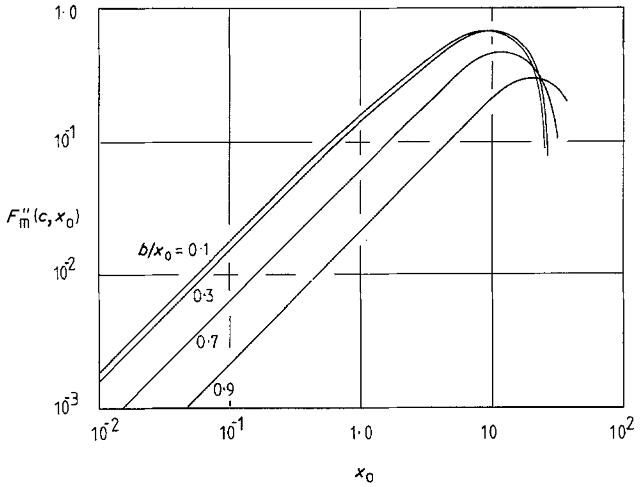

Figure 6 A plot of the function $F''_m(cx_0, x_0)$, Equation 41, against x_0 for a range of values of b/x_0.

applicable in which case

$$\frac{\mathrm{d}\ln[F'_m(b, x_0)]}{\mathrm{d}\ln x_0} = \frac{\left[E_1(x_0 - b) - E_1\left(\frac{x-b}{2}\right)\right] \mathrm{e}^{(x_0-b)/2} \cdot (x_0^2 - b^2)}{4 \cdot x_0 \cdot F'_m(b, x_0)} - \frac{(x_0 + b)}{2}$$

$$= F''_m(cx_0, x_0). \tag{41}$$

The equivalent function for constant b is

$$F''_m(b, x_0) = \frac{(x_0 + b) \cdot \exp\left[-\frac{1}{2}(x_0 - b)\right]}{4 \cdot x_0 \cdot F'_m(b, x_0)} + \tfrac{1}{2}x_0 + \frac{(x_0^2 + b^2)}{(x_0^2 - b^2)} \tag{42}$$

and both $F''_m(cx_0, x_0)$ and $F''_m(b, x_0)$ are independent of the function $(n - 1)$. Fig. 6 gives the function $F''_m(cx_0, x_0)$ for a range of values of b/x_0 as a function of x_0.

The equivalent expressions for the approximation leading to Equation 35 are

$$F'_m(x_0) = E_1(\tfrac{1}{2}x_0) - E_1(x_0) \cdot \tfrac{1}{2}\mathrm{e}^{x_0/2} \tag{43}$$

and

$$F''_m(x_0) = -\tfrac{1}{2}x_0 - (1 - \mathrm{e}^{-\frac{1}{2}x_0}) \cdot [2 \cdot F'_m(x_0)]^{-1} \tag{44}$$

which are the limiting cases of Equations 40 and 41 as b becomes small, and are shown in Fig. 7.

A particular set of measurements by Kubat, Selden and Rigdahl [18] on high density polyethyelene under uniaxial extension with a useful range of initial strains have been reported. The strain, and gradients of the relaxation characteristics, are given in columns 1 and 2 of Table I. The analysis has been carried out in terms of the mean values of the strains and these are listed in column 3. As b/x_0 was, experimentally, constant Equation 41 applied and in deriving the gradients given in column 4 it was necessary to make use of the power relationship between stress and strain given in the original paper. From the gradients the normalized strains were determined in column 6. Making use of Fig. 6 of this paper the gradients $F'_m(cx_0, x_0)$ were found to be essentially constant at -0.24. These values gave the magnitudes of n listed in column 9, with a well defined average of 0.65_6.

The constant value of b/x_0 observed in these results implies that b is a function of the parameter n. In general physical terms this can be understood in the following manner. The parameter n has been ascribed to the correlation index of single re-orientations as affected through the tunnelling relaxations. This behaviour transfers energy from the

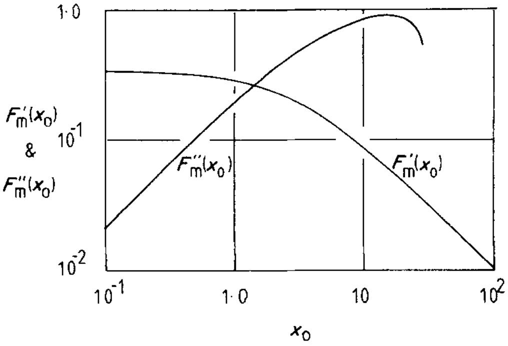

Figure 7 Plots of the functions $F'_m(x_0)$ and $F''_m(x_0)$, Equations 41 and 42, against x_0.

TABLE I Analysis of uniaxial extension relaxation in high density polyethylene

(1) ϵ_0	(2) $d(\sigma/\sigma_0)/d(\ln t)$	(3) ϵ_0 (mean)	(4) $\dfrac{d}{d\ln(\sigma/\sigma_0)}\dfrac{d(\sigma/\sigma_0)}{d(\ln t)}$	(5) b/x_0 (from Fig. 6)	(6) x_0 (from Fig. 6)	(7) $F'_{\mathrm{m}}(b, x_0)$	(8) $(n-1)$ $= (2)/(7)$	(9) n
$5.7\ 10^{-3}$	$-7.8\ 10^{-2}$							
		$1.0\ 10^{-2}$	$2.7\ 10^{-2}$	0.2	0.17	-0.23	-0.35	0.65
$1.54\ 10^{-2}$	$-8.1\ 10^{-2}$							
		$2.0\ 10^{-2}$	$2.76\ 10^{-2}$	0.2	0.17	-0.23	-0.35	0.65
$2.64\ 10^{-2}$	$-8.3\ 10^{-2}$							
		$3.5\ 10^{-2}$	$1.88\ 10^{-2}$	0.2	0.11	-0.25	-0.34	0.66
$4.45\ 10^{-2}$	$-8.5\ 10^{-2}$							

Columns 1 and 2 contain the numerical information taken from the published curves [18]. The second derivative in column 4 has been obtained by interpolation and hence corresponds to the interpolated ϵ_0 values presented in column 3. In determining column 4 as $\sigma/\sigma_0 \propto (\epsilon/\epsilon_0)^{1.7}$, $d/d\ln(\sigma/\sigma_0) = 1/1.7[d/d\ln(\epsilon/\epsilon_0)] = 1/1.7(d/d\ln\epsilon)$.

re-orienting bistable units to the matrix connecting these units, and is reflected in the dielectric relationship established by Jonscher [19]

$$\chi''(\omega)/\chi'(\omega) = \cot(n\pi/2); \quad \omega \gg \omega_{\mathrm{p}} \quad (45)$$

in which the energy transferred irretrieviably to the system, $\chi''(\omega)$, is in a fixed ratio to that which can be coherently recovered, $\chi'(\omega)$. A non-zero value of b is similar in that it implies an irremovable fraction of the original work that is not coherently recoverable.

The values of x_0 determined from the experimental analysis, and listed in Table I, are surprisingly constant over the range of initial strains applied to the sample. It is possible that this may indicate that the actual strains used were not sufficiently large to give strong non-linear behaviour, c.f. Equation 33. In view of this it is gratifying that the parameter n determined in the analysis does not vary significantly, as this indicates that the method developed here is applicable to small strain values. It is worth noting that the value of the parameter n obtained, 0.66, is similar to that obtained more directly from the examination of the frequency dependence of the susceptibility of polyethylene [20], which affords further confirmation of the validity of the approach presented here.

5. Discussion

The many-body, co-operative, theory of relaxation previously applied to the determination of the linear dielectric susceptibility [1, 2] has been extended to describe, quantitatively, non-linear relaxation under large deviations from equilibrium. The time development has been derived as a time average composite non-linear relaxation current in which the system attempts to achieve an instantaneous thermal equilibrium with its population differences. It should be appreciated that the average linear relaxation current determined earlier [2], which is $(dM'(y)/dt)$ in the notation used here, cannot be obtained by solving the average non-linear current for the deviation $M'(t)$ and differentiating with respect to time, that is

$$\left\langle \frac{d[Y(M')]}{dt} \right\rangle \neq \frac{d[Y(M')]}{dM'} \cdot \left\langle \frac{dM'}{dt} \right\rangle. \quad (46)$$

A formal solution has been obtained which has been illustrated with references to a system undergoing an alignment transition. It has been shown that the general result divides into two contributions. One of these is associated with the alignment transition region and the other dominates at low temperatures. The latter is dependent on the general features of the system rather than on its particulars as regards the nature of the transition. The general result shows a relaxation characteristic with a slow move out and approach to equilibrium, on a logarithmic time scale, and an intermediate region in which the deviation is proportional to $(n-1)\ln(t)$, as has been commonly observed in mechanical relaxation and other investigations. This feature is the most important result presented here and is perfectly general for the basic model developed being completely independent of any details of the co-operative interactions involved in the transition. The exponential integral decay function, Equation 35, has been proposed as a relaxation characteristic [4] but is shown here to be a particular limiting case of behaviour.

The rate constant, ω_{p}, presented here is identical, in all respects, to that obtained for the linearized rate equation [1, 2]. On normalizing the time scale with respect to the inverse of ω_{p}, which is equivalent to scaling the experimental results, a non-dimensional factor $(\omega_{\mathrm{p}}/\zeta)^{-n}$ appears on the right hand side of Equation 32. This indicates the presence of a dynamical scaling law [21] similar to that predicted and observed for the linear susceptibility [2, 22].

For small values of the normalized strain, x_0, the parameter $F'_m(b, x_0)$ can be determined from the information contained in Fig. 5 to have a magnitude of about 0.3. The parameter n, for the particular relaxation system examined in detail here, has been determined as 0.66. Hence the product $(1-n)\cdot F'_m(b, x_0)$ has the value of 0.10 in complete agreement with Kubat's observation [5] of a general value of 0.1 for the parameter a, as defined by Equation 1.

It has been shown that the theory developed here is applicable to experimental observations under constant strain and stress relaxation. In particular it has been shown that the co-operative characteristic parameter n is an essential descriptor of the system and cannot be neglected in a full analysis of experimental measurements.

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