# Stochastic defect diffusion model for relaxation effects in crystalline polyethylene

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It is suggested that some relaxation processes observed in crystalline polyethylene are consequences of the diffusive motion of a particular defect called a point dislocation or twist dispiration loop along the polyethylene stems in lamellar crystals. The motion of the defect, characterized by a diffusion coefficient and a mobility, is described by solutions of the Smoluchowski diffusion equation with boundary conditions that constrain the defect to move along routes that produce experimentally observable results. The fact that passage of the defect causes both a 180° rotation of the chain and moves an extra $CH_2$ group in the direction of the chain axis is important to the interpretation of the data according to this model. The diffusion coefficient for a defect is estimated to be around $2 \times 10^{-9}$ cm$^2$ s$^{-1}$ at 70°C. This value is shown to be reasonable both from the viewpoint of detailed computer modelling of defect motion and contemporary ideas about scaling.

**Keywords** Mechanical behaviour; bent lamella; crystal defects; defect mobility; dielectric relaxation; diffusion equation; diffusion mechanical relaxation; dispiration; first passage; molecular rotation; polyethylene; polymers; relaxation

## INTRODUCTION

It is suggested that some relaxation processes and other effects are consequences of the motion of a particular defect in a polyethylene crystal. The defect of interest here is called a point dislocation[1] or a twist dispiration loop[2]. In this paper the word 'defect' is used not in its general sense but as a short name for a point dislocation in a polyethylene crystal.

The passage of a point dislocation along a stem of a polyethylene molecule in a crystal causes two important changes in the part of the stem through which the defect passes.* The part of the chain traversed by the defect is moved in the same direction as the defect travels by a distance of one-half the *c*-axis dimension of the unit cell. This axial transfer provides an elemental mechanism for lamellar thickening[1] and for deformation processes that require a chain to move through a crystal.

The second change produced by the passage of a defect is a 180° rotation of the part of the molecule traversed by the defect. This defect-induced rotation has some consequences similar to a rigid rod rotation but it avoids intermediate setting angles for the chain since most of the time most of the chain is in either one of two positions about 180° apart. Such a discontinuous or restricted rotation is observable in certain carbon-13 nuclear magnetic resonance data[3]. Rotation may also be inferred from dielectric measurements on polyethylene samples which contain a low concentration of electric dipoles such as can be produced by lightly oxidizing polyethylene[4]. Chain rotation has been related to dielectric and mechanical relaxation phenomena[5].

This paper shows how the chain rotation produced by the passage of a defect can account for nuclear magnetic resonance and dielectric data. Additionally, it is shown how changes in the position of the defect which are coupled to mechanical deformation (for example, to lamellar bending) can lead to mechanical relaxation in the temperature and time region in which mechanical relaxation processes are observed.

The model adopted in this paper deals for simplicity with the case of one defect per stem. The actual defect concentration as a function of temperature is not well established. Longitudinal acoustic mode intensity data interpreted as proposed by Reneker and Fanconi[6] suggest that at 70°C $\frac{1}{6}$, and at 120°C $\frac{3}{4}$ of the 30 nm long stems contain one or more defects. More recent longitudinal acoustic mode intensity data[7] also lead to defect concentrations in this range. The defect concentration appears to be controlled more by the relatively small energy difference between a defect and a fold than by the somewhat larger energy required to place a defect in a perfect lattice.

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* A few additional properties of point dislocations (defects) which may be of interest although they are not all essential to this paper are: Defects may be absorbed or emitted from folds. A defect absorbed into a fold from one stem may be emitted from the same fold into the adjacent stem A defect entering or leaving a fold moves the fold and so may lead to interactions with folds in an adjacent lamella. Defects may be created or annihilated at chain ends. Row vacancies at chain ends may be avoided by screw dislocation-like features that extend from a particular chain end to another end or to the surface of a lamella. Defects have a parity that is important in the details of interactions with folds, twist boundaries, or other chain conformations that may occur in interlamellar regions. The energy required to emit a defect from a fold may be significantly smaller than the excess energy of a defect in an otherwise perfect lattice. Point dislocations or twist dispiration loops can occur generally in polymer crystals. The twist and the amount of extra mass associated with a defect will depend upon the symmetry of the molecule and the crystal. The amount of extra mass may be positive (one $CH_2$ for polyethylene) or negative for the vacancy-like defects that can be created in some helical molecules by short-cutting across a turn of the helix.

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Measurements[8] of the intensities of two infra-red bands in a five percent doubly deuterated polyethylene, which are known from normal mode analysis to be associated with bond dihedral angle sequences which are approximately *trans–trans* or *trans–gauche*, also provide qualitative information about the temperature range in which defects are thermally generated.

The defect is a localized region less than 1 nm long which has a conformation that changes in complicated ways as the defect region diffuses along a chain. Some reasonably realistic examples of this motion were modelled using interatomic potentials and the known geometry of polyethylene crystals[9]. Adjacent chains are slightly distorted but remain close to the planar zig-zag conformation. Interactions between defects in adjacent stems are ignored.

In this paper, little attention is paid to the internal features of the defect. The defect is treated as a point which may move along the chain. The motion of the defect is characterized by a diffusion coefficient $D$ and a mobility $\mu$ which is the ratio of the drift velocity of the defect to the force causing the drift. The mobility is related to the reciprocal of the parameter called the friction constant, a term widely used in the literature dealing with the motion of polymer molecules in solutions or melts. The diffusion coefficient and the mobility are connected by the Einstein relation $D = \mu kT$ where $k$ is Boltzmann's constant and $T$ is the absolute temperature.

The defect motion is considered to be stochastic. A defect jumps from one minimum energy site to an adjacent one under the influence of thermal fluctuations and other forces which may result from macroscopic electric or strain fields. These jumps have lengths which are small compared to the length of the stem along which the defect moves. The jumps occur in times that are small compared with the time required for the defect to move through a significant part of the stem length. The Smoluchowski diffusion equation[10] is used to describe the motion of defects. It will also be shown that the value of the diffusion coefficient that characterizes the defect motion is consistent with the microscopic parameters used in the modelling of defect motion by the use of computer simulation[9]. The characteristic time associated with the microscopic motion will be related to the time scale for defect motion along a stem by application of the general scaling ideas put forward by deGennes[11].

This paper is divided into five sections. The first describes the stochastic motion of a defect as the general solution of the diffusion equation. In the second section, special solutions are derived for the interpretation of dielectric relaxation and nuclear magnetic resonance data. Both these experiments provide information about the rotation rate of the chain. The defects must traverse routes which cause the experimentally observed rotations. A particular route is defined by a set of boundary conditions. The time for a defect to traverse the route is called the 'first passage time'[12]. The average of these first passage times over all possible starting positions $x_0$ of the defect is taken as a measure of the rotation rate of the parts of the chain relevant to a particular experiment. The third section shows how defect translation can produce mechanical relaxation. Here the defect energy, which is a function of the position of the defect in a particular strain field, is of central interest as are the times required for defects to diffuse distances of order of the thickness of lamellar crystals. The fourth section compares the detailed computer model of defect motion[9] with the larger scale model of defect diffusion described in the earlier sections. The last section applies the techniques of scaling theory to defect motion.

## GENERAL SOLUTIONS OF THE DIFFUSION EQUATION

The defect motion in a single stem of a polyethylene crystal is described by the Smoluchowski diffusion equation:

$$\frac{\partial w}{\partial t} = \frac{D}{L^2}\frac{\partial^2 w}{\partial x^2} - \frac{\mu F}{L}\frac{\partial w}{\partial x} \tag{1}$$

Here $x$ is the position of the centre of the defect in the stem measured in units in which the stem length, $L$, is unity, $t$ is time, and $w(x,x_0,t)$ is the distribution function of the probabilities of finding the defect near $x$ at time $t$ when the defect starts at $x_0$ at $t = 0$. The external forces parallel to the stem axis are represented by $F$. If the external forces are absent or negligibly small, the last term in equation (1) may be omitted. Forces with oscillatory time dependence or with a step function dependence upon time are useful for relating this model to particular experiments. Forces with a step function dependence on time are characterized by the conditions: $\frac{\mathrm{d}F}{\mathrm{d}t} = \infty$ at $t = 0$, the time at which the step occurs and $\frac{\mathrm{d}F}{\mathrm{d}t} = 0$ for $t > 0$. Solution of equation (1) for $t > 0$ with a constant $F$ may therefore be used to describe the response to a step function force.

The diffusion model can be applied to a variety of interesting physical situations by a judicious choice of the boundary conditions. The folds at the ends of a stem can either partially or totally reflect or absorb a defect. The physical process of emitting a defect from a fold can also be modelled by appropriate boundary conditions. Absorption and emission of defects at folds is believed to be an important part of the process[1], not discussed in detail here, by which stem length changes during annealing. General solutions of the diffusion equation for partially reflecting, partially absorbing barriers can be derived easily only when the applied forces are independent of space and time. For time dependent forces only reflecting barriers will be discussed and perturbation methods based on expansion of the distribution function in powers of the applied force will be employed.

Let $\alpha_1$ be the probability of defect absorption at a fold located at $x' = 0$ and $\alpha_2$ that for a fold at $x' = L$. In this paper, $\alpha_1$ and $\alpha_2$ are either zero or one. Intermediate values would be useful for the description of lamellar thickening and some kinds of interactions between adjacent lamellae. The variable $x'$ ranges from 0 to $L$, the stem length. The general boundary conditions are written as follows:

$$\begin{aligned} \alpha_1 w \pm (1-\alpha_1)\left[\frac{\partial w}{\partial x} - 2Bw\right] &= 0 \quad \text{at } x' = 0 \\ \alpha_2 w \pm (1-\alpha_2)\left[\frac{\partial w}{\partial x} - 2Bw\right] &= 0 \quad \text{at } x' = L \end{aligned} \tag{2}$$

The dimensionless force parameter $B$ used throughout this paper is defined as

$$B = FL\mu/2D \tag{3}$$

or, using Einstein's relation, as $FL/2kT$. To simplify the equations, $x'$ is expressed in dimensionless form as $x = x'/L$ so that $0 \leqslant x \leqslant 1$.

The following transformation[10] is employed to solve the diffusion equation (1):

$$w = u(x,t)e^{B(x-x_0)}e^{-B^2Dt/L^2} \tag{4}$$

so that equation (1) reduces to the Fickian form:

$$\frac{\partial u}{\partial t} = \frac{D}{L^2}\frac{\partial^2 u}{\partial x^2} \tag{5}$$

The boundary conditions for equation (5) are readily obtained from equation (2). Also

$$u \to \delta(x - x_0) \text{ as } t \to 0,$$

since $\quad w \to \delta(x - x_0)$ as $t \to 0$.

Define $h_1$ and $h_2$ as follows:

$$h_1 = \alpha_1 - (1 - \alpha_1)B \tag{6}$$

$$h_2 = \alpha_2 + (1 - \alpha_2)B \tag{7}$$

The solution of equation (5) obtained using Green's function is[13]

$$u = \sum_{n=1}^{\infty} A_n Z_n(x) Z_n(x_0) e^{-Dt\beta_n^2/L^2} \tag{8}$$

where

$$Z_n(x) = (1 - \alpha_1)\beta_n \cos(\beta_n x) - h_1 \sin(\beta_n x)$$

and

$$A_n{}^{-1} = -h_1(1 - \alpha_1) + (1 - \alpha_1)^2\beta_n^2 + h_1^2$$
$$-(1 - \alpha_2)h_2\frac{(1 - \alpha_1)^2\beta_n^2 + h_1}{(1 - \alpha_2)^2\beta_n^2 + h_2^2}$$

$\pm\beta_n$ for $n = 1,2\ldots$ are the $n$ roots of the transcendental equation

$$\tan\beta = \frac{\beta[h_2(1 - \alpha_1) + h_1)1 - \alpha_2)]}{-h_1h_2 + (1 - \alpha_1)(1 - \alpha_2)\beta^2}$$

The solution of the diffusion equation (1) is then found by substituting $u$ from equation (8) into equation (4).

To describe mechanical relaxation, reflecting boundary conditions with $\alpha_1 = \alpha_2 = 0$ are needed for reasons described later. For these boundary conditions the solution of the diffusion equation is

$$w(x,x_0,t) =$$
$$2\sum_{n=1}^{\infty}\frac{[n\pi\cos(n\pi x) + B\sin(n\pi x)]\,[n\pi\cos(n\pi x_0) + B\sin(n\pi x_0)]}{(n^2\pi^2 + B^2)}$$
$$\times\,[e^{-Dt/L^2(\pi^2n^2 + B^2) + B(x - x_0)}] + w(x,\infty) \tag{9}$$

The term $w(x,\infty)$ is the steady-state solution at long times,

$$w(x,\infty) = 2Be^{2B(x-1)}/(1 - e^{-2B})$$

This last term is absent unless $\alpha_1$ and $\alpha_2$ are both zero in which case the defect is never absorbed. In this case, the condition (10) must be satisfied[14]:

$$\int_0^1 w(x,x_0,t)\mathrm{d}x = 1 \tag{10}$$

It is useful to integrate over all the initial positions of the defect to obtain $w(x,t)$:

$$w(x,t) = \int_0^1 w(x,x_0,t)\mathrm{d}x_0. \tag{11}$$

If the oscillatory time dependence of $F$ is written

$$F = F_0 e^{i\omega t} \tag{12}$$

then solutions to the diffusion equation are obtained in the following way. The distribution function is expanded as a power series in the force term $B$:

$$w(x,t) = w_0 + 2Bw_1(x)e^{i\omega t} + \text{terms of order } (2B)^p, p \geqslant 2 \tag{13}$$

This expansion implies a random distribution of defect starting positions $x_0$. Since $Bw_1(x,t) = 0$ for the unstressed state, $w_0 = 1$. The time independent factor $w_1(x)$ is the solution of

$$\frac{D}{L^2}\frac{\partial^2 w_1}{\partial x^2} = i\omega w_1 \tag{14}$$

The boundary conditions for $w_1(x)$ are

$$\frac{\partial w_1}{\partial x} = 1 \text{ at } x = 0 \text{ and } x = 1.$$

The solution of equation (14) is

$$w_1(x) = \left\{\frac{(1 - e^{-C})(e^{Cx} + e^{-Cx})}{e^C - e^{-C}} - e^{-Cx}\right\}\frac{1}{C} \tag{15}$$

where $C = \sqrt{i\omega L^2/D}$. The higher-order expressions for $w_p(x)$ can be obtained from the iterative equation

$$\frac{D}{L^2}\frac{\partial^2 w_p(x)}{\partial x^2} = i\omega w_p(x) - \frac{D}{L^2}\frac{\partial w_{p-1}(x)}{\partial x} \tag{16}$$

For the bent lamella problem described below, $w_p$ for $p$ even make no contribution to the bending moment, since $w_p(x)$ is symmetric with respect to the $x = \frac{1}{2}$ axis when $p$ is even. For odd $p$, $w_p$ is antisymmetric with respect to the $x = \frac{1}{2}$ axis, passing through zero value there. The contributions of terms with $p$ odd decrease at least as fast as $[(2p - 1)]^{-1}$. Equation (13) with $p = 1$ therefore provides usefully precise values of $w(x,t)$ for values of $B$ as large as 2.

## STOCHASTIC DEFECT MOTION AND ASSOCIATED CHAIN ROTATION

It is suggested that both the narrowing of satellite lines in nuclear magnetic resonance data and the dielectric relaxation phenomena are consequences of the distribution of 'first passage times' of a defect along a particular route. In the n.m.r. experiment complete narrowing of the satellite lines requires that all the $CH_2$ groups are rotated at a rate faster than a minimum rate deduced from the linewidth. To rotate all the $CH_2$ groups in a stem, a defect must traverse the entire stem length at least once. The satellite line width is observed to narrow when all the $CH_2$ groups are rotated approximately 180° at a rate of 700 times per second[3]. The observed line narrowing is interpreted to indicate that a defect passes completely through each stem more often than once every 1/700 of a second at about 70°C.

The question to be addressed is, 'What is the average first passage time for a defect route starting at an arbitrary position $x_0$ and passing each $CH_2$ group in a stem of length $L$?' The answer is derived from the solution of the diffusion equation with appropriate boundary conditions to define the relevant set of defect routes. In the n.m.r. experiments no external forces act on the defect so the force parameter $B$ is zero.

The route the defect must travel to rotate an entire stem is defined in the following way. An absorbing boundary is placed at one end of the stem and a reflecting barrier is placed at the other end. The time for a defect starting at $x_0$ to make a first passage to the absorbing boundary is calculated. The defect may touch the reflecting boundary from zero to an arbitrary number of times. The paths which go from $x_0$ to the absorbing boundary without touching the reflecting boundary (and which therefore do not rotate the entire stem) are, in a certain sense, completed and accounted for by interchanging the absorbing and reflecting boundaries and then repeating the calculation. The time for a defect to traverse the entire stem is taken as the sum of these two first passage times. The sum is then averaged over all possible starting positions. This average is the time to be compared with that deduced from the n.m.r. satellite line narrowing observation[3].

The computational algorithm for the first passage problems can now be formulated as follows. For the route that defect travels to narrow the n.m.r. satellite lines, first set $\alpha_1=0$ and $\alpha_2=1$, $B=0$ (equation 8). The probability distribution function for defects diffusing within these boundaries is:

$$w(x,x_0,t)=\sum_{n=0}^{\infty}\cos[(n+\tfrac{1}{2})\pi x]\cos[(n+\tfrac{1}{2})\pi x_0]\,e^{-(n+\frac{1}{2})^2\pi^2 Dt/L^2} \tag{17}$$

Equation (17) is integrated over all $x_0$ to obtain $w(x,t)$:

$$w(x,t)=\int_0^1 w(x,x_0,t)\,\mathrm{d}x_0 \tag{18}$$

$\rho(t)$, the distribution of first passage times to the boundary at $x=1$ is obtained from

$$\rho_{x=1}(t)=-\frac{D}{L^2}\frac{\partial w(x,t)}{\partial x}\bigg|_{x=1} \tag{19}$$

To this, a solution obtained by interchanging boundaries, that is by setting $\alpha_1=1$ and $\alpha_2=0$ and evaluating the derivative in equation (19) at $x=0$, is added. Hence $\rho(t)$, the distribution of first passage times that insure at least one 180° rotation of every $CH_2$ group in a stem is

$$\rho(t)=\frac{2D}{L^2}\sum_{n=0}^{\infty}e^{-(n+1/2)^2\pi^2 Dt/L^2} \tag{20}$$

$\rho(t)$ is normalized, since $\int_0^\infty \rho(t)\mathrm{d}t=1$.

Therefore

$$\langle t\rangle=\int_0^\infty t\rho(t)\mathrm{d}t=\frac{32L^2}{D\pi^4}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^4}=\frac{L^2}{3D} \tag{21}$$

This is almost four times the result that would be obtained if both boundaries were absorbing, i.e., if $\alpha_1=\alpha_2=0$. Absorbing boundaries would follow from the question, 'What is the average time for routes on which the defect reaches either of the two boundaries without previously reaching the other?' The first passage time for absorbing boundaries can be considered as a lower bound on $\langle t\rangle$ for a concentration of one defect per stem.

In a dielectric relaxation experiment such as in the lightly oxidized polyethylene used by Ashcraft and Boyd[4] an applied electric field $\vec{E}$ acts on the dipole moment $\vec{p}$ of an isolated polar group attached to a polyethylene stem to produce an interaction energy $\vec{p}\cdot\vec{E}$. This generally results in a small torque on the molecule. In other words, the force $F$ in the Smoluchowski diffusion equation is not exactly zero as in the n.m.r. experiment. Calculation of the relationship between this torque and the resulting force $F$ which tends to move the defect along the chain axis is rather involved. As will be shown in the section dealing with mechanical relaxation, the influence on the relaxation times of the force parameter $B$ is small. At electric fields up to the dielectric strength, the magnitude of the force parameter $\vec{p}\cdot\vec{E}/kT$ which replaces the parameter $B$, is estimated to be smaller than the mechanical force parameter $B$ term for reasonable strain. For the evaluation of $\langle t\rangle$ it was found that the last term in the diffusion equation (1) can be set equal to zero in the treatment of dielectric relaxation presented here, since $\vec{p}\cdot\vec{E}/kT\ll 1$. It is also assumed that there is one randomly located polar group per stem.

The question to be answered in the interpretation of the dielectric data is, 'What is the average time required for a defect starting at an arbitrary position in a stem to diffuse past a polar group at the arbitrary position $x=l$, assuming that the defect is reflected at the ends of the stem?' This is the average time required for the polar group to rotate and coincides with the reciprocal of the frequency of the applied field at the peak of the dielectric loss curve.

For the route that the defect travels to cause dielectric relaxation, the first passage problem is formulated along the same general lines as in the interpretation of the n.m.r. experiment with modifications as described below.

The defect starting position $x_0$ may be between $l$ and either end of the stem. A first passage calculation is done first with a reflecting boundary placed at the end of the

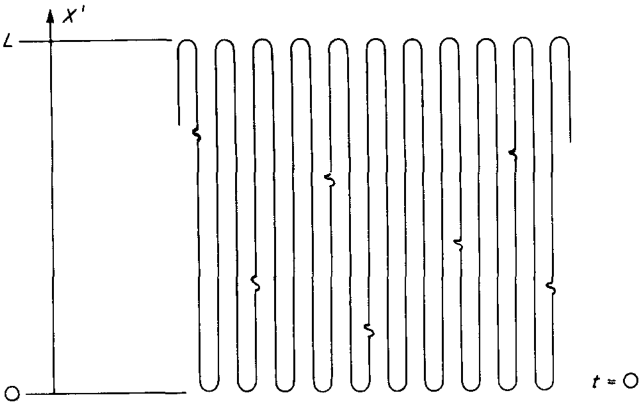

*Figure 1* Population of thermally generated defects in a lamellar crystal of polyethylene an instant before the step-function bending moment is applied. The lamella is not yet bent and the defects are randomly distributed. A concentration of less than one defect per stem is shown to avoid complicating the figure

stem that is on the same side of $l$ as $x_0$. The defect path can touch the reflecting barrier from zero to an arbitrary number of times. The first passage ends when the defect encounters an absorbing boundary placed at $x=l$. Then the calculation is repeated for the cases where $x_0$ lies between $x=l$ and the other end of the stem. Each case contributes amounts proportional to $l$ and $1-l$, respectively, to the average time. For $x_0<l$, the probability distribution function, equation (17) is replaced by

$$w(x,x_0,t)=\sum_{n=0}^{\infty}\cos\left[(n+\tfrac{1}{2})\pi\frac{x}{1}\right]\cos\left[(n+\tfrac{1}{2})\pi\frac{x_o}{l}\right]e^{-(n+\frac{1}{2})^2\pi^2Dt/l^2L^2} \tag{22}$$

Following the same procedure as employed for the n.m.r. case, the distribution of first passage times is

$$\rho_l(t)=\frac{2D}{l^2L^2}\sum_{n=0}^{\infty}e^{-(n+\frac{1}{2})^2\pi^2Dt/l^2L^2} \tag{23}$$

Equation (23) is integrated over all values of $l$ for $0<l<1$. The average time required for a defect to traverse a route that rotates a polar group is

$$\langle t\rangle=\frac{L^2}{9D} \tag{24}$$

which is one-third of the result obtained for the route appropriate for n.m.r.

In summary, the interpretation of chain rotation rate data is based on estimates of the average time required for the random diffusive motion of a defect to rotate all (n.m.r.) or part (dielectric) of the stem by 180°. The theory of first passages of a randomly moving defect which rotates the chain as the defect diffuses along a stem provides a basis for the calculation of the average rotation rates. It is then possible to calculate the diffusion constant $D$ that describes the diffusive motion of the defect from the rotation times deduced from n.m.r. or dielectric relaxation experiments.

The stem length $L$, which can be independently determined from low angle X-ray measurements, is assumed to be 30 nm. Using either equation (21) with $\langle t\rangle=1/700$ [3] or equation (24) with $\langle t\rangle=1/2f_{\max}$, where $f_{\max}$ is the frequency at the dielectric loss peak (see Figure 13 of ref. 4), the values of $D$ obtained are

$$D(\text{n.m.r.})=2\times10^{-9}\,\text{cm}^2\,\text{s}^{-1}$$
$$D(\text{dielectric})=1.3\times10^{-9}\,\text{cm}^2\,\text{s}^{-1}.$$

## MECHANICAL RELAXATION

### *Introduction to the bent lamellar crystal model*

The energy of a defect in a crystal depends upon the strain of the crystal at the location of the defect. Application of most, but not all, types of strains tend to cause the defects to diffuse towards more energetically favourable locations. Since the diffusion process requires some time to occur, the crystal requires a significant time to relax to the state in which the defects are in their new, lower energy positions.

It is possible to model this process in detail for a defect in a polyethylene crystal. The bent lamella provides an inhomogeneous strain field which is straightforward to calculate. The elementary relaxation process in the strain field of a bent lamella does not require either that the defect move through folds or that it interact with chain ends. A single defect in a single stem in a bent lamellar crystal thus illustrates the mechanical relaxation associated with defect diffusion.

*Figure 1* shows a population of thermally generated defects in a lamellar crystal of polyethylene. Application of a step function bending moment, as shown in *Figure 2*, causes the lamella to bend elastically. For a very short time after the bending moment is applied the defects remain near their original location. Calculations of defect energy show that the defects in the part of the crystal which is in compression have a higher energy than the defects in the part of the crystal that is expanded. The defects will, therefore, tend to move from the compressed to the expanded side of a bent crystal. After a time the defects will be closer to the expanded side as shown in *Figure 3*. The tendency for the defect to further expand the lattice causes the crystal to bend more as the defects arrive. When this additional bending has occurred the crystal is 'relaxed'.

The internal motions of a defect which were modelled in ref. 9 enable the defect to diffuse to the lower energy

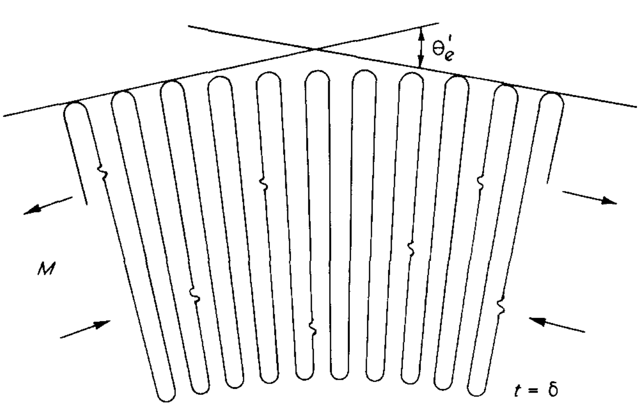

*Figure 2* Similar population of defects an instant after a segment of the lamella is elastically bent by a small angle $\theta_e'$. The defects retain the same random distribution since they have not had time to diffuse toward lower energy positions. The elastic part of the bending angle between adjacent stems, called $\theta_e$ in the text, is obtained by dividing $\theta_e'$ by the number of stems in the segment of the lamella

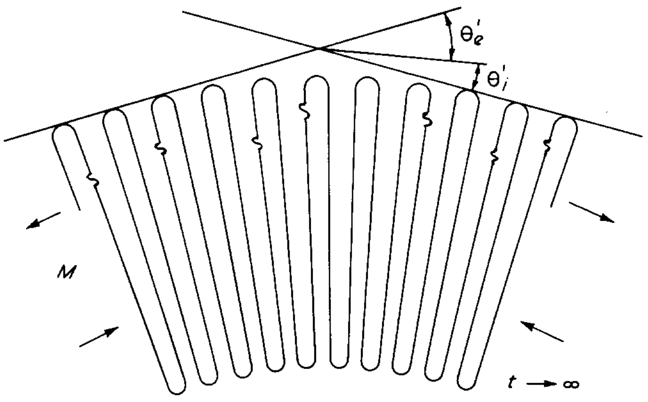

*Figure 3* At very long times the defects tend to accumulate near the lamella surface that is expanded by the bending since the defect energy is lower in an expanded crystal. This causes an inelastic increase in the bending angle $\theta_i'$. The relation between $\theta_i'$ and $\theta_i$ is the same as for $\theta_e'$ and $\theta_e$

positions. The difference in defect energy at different levels in a bent crystal is associated with an effective force. For the small strains ordinarily used in mechanical relaxation experiments this force is not large. The defect moves stochastically, with only a small drift velocity in the direction of lower defect energy. The solutions of the diffusion equation for a defect moving in response to this force were obtained both for the case when $F$ is the result of a step function applied moment and for the case when $F$ results from an applied moment which alternates with a frequency of $\omega/2\pi$. In the following sections an estimate of the magnitude of $F$, the average force in the chain direction acting on a defect, will be obtained. Expressions for the loss tangent and relaxation strength will be derived for the alternating force.

### *Estimation of forces on a defect from changes in unit cell dimensions*

The dependence of the total energy of a crystal containing a defect on the dimensions of a strained unit cell was calculated[9]. Starting with a model for a crystal containing a defect described in ref. 9, the '$a$' and '$b$' axes of the orthorhombic crystal cell were incremented by small amounts $\Delta a$ and $\Delta b$. For each increment a minimum energy conformation was sought by employing the computational algorithm described in ref. 9. The change in the total energy from that of the perfect crystal, $\Delta E_0$, was obtained as a function of $\Delta a$. $\Delta E$ as a function of $\Delta b$ is similar. The following equation for $\Delta E$ as a function of $\Delta a$ was obtained.

$$\Delta E = \Delta E_0 + E_1\left(\frac{\Delta a}{a}\right) + \tfrac{1}{2}E_2\left(\frac{\Delta a}{a}\right)^2 \tag{25}$$

where $E_1 = -314$ kJ mol$^{-1}$, $E_2 = 2720$ kJ mol$^{-1}$, and $a = 0.725$ nm. See ref. 9. The results for $\Delta E$ as a function of $\Delta a$ are shown in *Figure 4*. For $\Delta a/a = 0.01$, which is a typical magnitude for the strain in a mechanical relaxation experiment, the quadratic term can be neglected. For simplicity, the crystal will be considered to be bent around the $b$ axis (i.e., the bending axis is parallel to the $b$ axis) so that changes in the $b$ axis unit cell dimension can be ignored.

For a bent beam[15] the strain, $\Delta a/a$, can be expressed as a function of position as follows:

$$\frac{\Delta a}{a} = \frac{(x - \frac{1}{2})LM}{GI}. \tag{26}$$

Here $G$ is the elastic modulus of the crystal in the direction of the $a$ axis and $I$ is the moment of inertia of the cross sectional area of the crystal with respect to the neutral axis. $M$ is the applied bending moment.

The gradient of the defect energy in the chain axis direction can be regarded approximately as an effective force $F$ on the defect, $F_x = \dfrac{-\partial\Delta E}{L\partial x}$. If one assumes that the strain is 0.01 at $x = 1$, i.e., at the expanded surface, then for $L = 30$ nm

$$F_x = \frac{0.02E_1}{L} = 3.3 \times 10^{-8} \text{ dyne.}$$

The force parameter, $B$, [equation (3)] therefore has a value of 1.25 at $T = 70$°C. It should be remarked that in a bent lamella $B$ is independent of $L$, since $F_x$ is inversely proportional to $L$. In the following analysis $B$ is retained as an adjustable parameter and the consequences of assigning values in the range from 0.5 to 2.0 are investigated.

In order to get a general picture of the geometry of the bent lamella, estimates of the bending moment and the radius of curvature are provided for a lamella of width $y$.

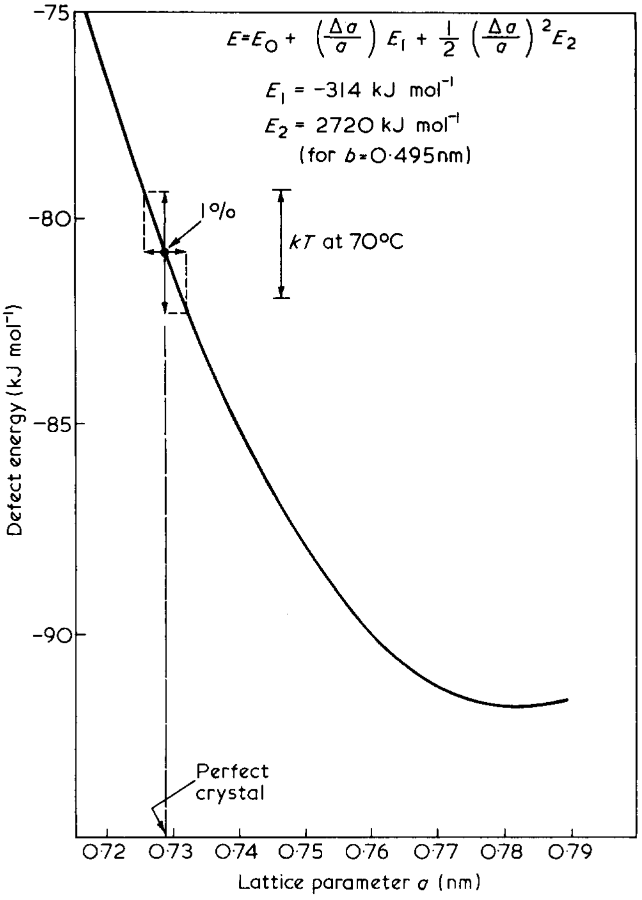

*Figure 4* Defect energy as a function of the $a$-axis lattice parameter. For this calculation the $b$-axis lattice parameter was held constant at its minimum energy value in a perfect crystal. The crossed arrows show that for a lattice strain of 1% the defect energy is changed by an amount commensurate with $kT$ at 70°C

In a lamella with a rectangular cross-section[15], $I=\frac{yL^3}{12}$. A one percent strain in a lamella with $L=30$ nm, $y=100$ nm and a modulus perpendicular to the chain equal to $3\times10^9$ dyne cm$^{-2}$ implies a bending moment $M=5\times10^{-10}$ dyne cm and a radius of curvature of $1.5\times10^{-4}$ cm which is about 50 times the lamellar thickness.

### *Mechanical relaxation time from defect drift velocities*

When a step function bending moment is applied to the crystal, the defects begin to drift in the direction of the force $F$ described above. Reflecting boundary conditions keep the number of defects in the crystal lamella constant. After a time the defect population will diffuse to a new average position and the net drift velocity will be zero. A measure of the mechanical relaxation time is $\tau_v$, the time required for the average drift velocity to decrease by a factor of $1/e$.

The drift velocity $v(x,t)$ is calculated from the solution of the diffusion equation using equation (27),

$$v(x,t)=-\frac{D}{L}\frac{\mathrm{d}\ln w(x,t)}{\mathrm{d}x}+F\mu \tag{27}$$

The quantity sought is the ratio of the drift velocities at time $t$ to the initial drift velocity, averaged over all defect positions:

$$\langle v^*(t)\rangle=\int_0^1\frac{v(x,t)}{v(x,0)}\mathrm{d}x \tag{28}$$

This quantity was evaluated numerically for a range of values for the two dimensionless parameters $B$ and $Dt/L^2$. The results of the computation are given in *Figure 5*. Within the reasonable range of values for $B$ (see above), it turned out that $\langle v^*(t)\rangle$ is insensitive to $B$, showing only a slight increase as $B$ increased. In order to obtain $\tau_v$ the value of $Dt/L^2$ for which $\langle v^*(t)\rangle=1/e$ is calculated, leading to the relation $\tau_v=L^2/(8D)$. Using the estimate of $D$ obtained from the n.m.r. and the dielectric relaxation data, and with $L=$ 30 nm a value of $4.5\times10^{-3}$ s is obtained for $\tau_v$, the mechanical relaxation time. A very slight decrease in the relaxation time as $B$ increases is predicted only for large stresses and implies a virtual independence of $\tau_v$ on strain amplitude. The mechanical relaxation times may be very slightly shorter than dielectric relaxation times. There are some indications in the published data[16] that this occurs, but since the predicted differences are so small, these data probably reflect other differences in the samples.

### *Complex modulus*

In mechanical relaxation experiments in which the lamella is deformed by an alternating applied moment, the strain is found to lag behind the applied stress. In this section the phase lag is derived directly from the defect diffusion model by solving the diffusion equation with appropriate boundary conditions for the bent lamella model.

Assume that the stress $\sigma(x,t)$ is related to the modulus $G$ of a defect free crystal, the unperturbed strain $\varepsilon(x,t)$, the defect concentration and the defect location by the following expression:

$$\sigma(x,t)=G[\varepsilon(x,t)-K\,w(x,t)] \tag{29}$$

Here $w(x,t)$ is the defect distribution function averaged over all defect starting positions and $K$ is a constant. The last term in equation (29) is small enough to be treated as a perturbation. Equation (29) expresses the idea that if a stress that tends to expand the lattice is placed on a crystal and then at some later time defects arrive in the region of interest (in the present case by diffusion), there will be a reduction in the stress, or if the stress is held constant, the strain will increase. The first situation is often referred to as stress relaxation and the second as creep.

It remains convenient to use the same bent lamella model described elsewhere in this paper to provide a specific illustration of the connection between defect diffusion and the complex modulus, although the ideas apply to other strain fields. In a bent lamella the moment $M$ can be considered as the generalized stress and the bending angle $\theta$ as the generalized strain. Following Timoshenko[15], the bending angle is replaced by the reciprocal of the radius of curvature $\rho$. If $z$ denotes a direction perpendicular to the chain axis, in the plane of curvature, then $\rho^{-1}=\mathrm{d}\theta/\mathrm{d}z$. The resulting moment–radius of curvature relationship is found to be simpler and more convenient than the moment–angle relationship.

The bending moment in a beam is connected to the

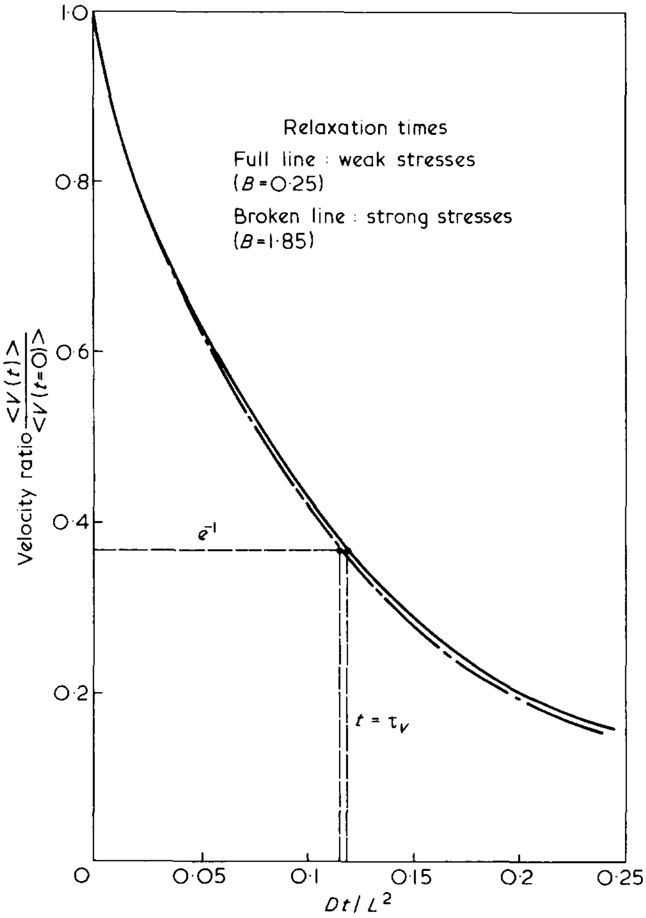

*Figure 5* Reduced drift velocity $\langle v^*(t)\rangle=\langle v(t)\rangle/\langle v(0)\rangle$ as a function of $Dt/L^2$ for a weak force on the defect ($B$ = 0.25) and for a stronger force ($B$ = 1.85). The relaxation time $\tau_V$, which is defined from the value of $\tau_V D/L^2$ at which $\langle v^*(t)\rangle=e^{-1}$, is not affected much by the magnitude of the force on the defect

stress as follows:

$$M=L\int\sigma(x,t)x\mathrm{d}A=L^2y\int_0^1\sigma(x,t)x\mathrm{d}x \qquad (30)$$

In equation (30), $y$ is the width of the lamella in the direction of the bending axis and $\mathrm{d}A$ is an element of the cross sectional area of the lamella. The right hand side of equation (30) implies a beam of rectangular cross section.

The strain, $\varepsilon$, from equation (29) for the uniform defect distribution that persists for a short interval immediately after the step function moment is applied, is expressed as a function of the position along the $x$ axis as follows[15]:

$$\varepsilon(x)=(x-\tfrac{1}{2})L/\rho_e \qquad (31)$$

where $\rho_e$ is the elastic radius of curvature of the beam.

As time evolves, the defects drift along the chain in response to the forces described earlier. Since the region in which the defects accumulate tends to expand (and *vice versa*) the radius of curvature of the beam decreases with time by an amount $\Delta\left(\frac{1}{\rho}\right)$, causing the strain in the sample to change as follows:

$$\varepsilon(x,t)=(x-\tfrac{1}{2})L\left[\frac{1}{\rho_e}+\Delta\left(\frac{1}{\rho}\right)\right] \qquad (32)$$

Equations (31) and (32) express the fact that the bent lamella possesses a neutral axis, located at $x=\frac{1}{2}$ where strains and stresses are zero. Since the increment in the radius of curvature is small, it is useful to replace $\Delta 1/\rho$ by $\Delta\rho/\rho_e^2$. Equation (29) becomes

$$\sigma(x,t)=(x-\tfrac{1}{2})GL\left[1-\frac{K\rho_e}{L}w(x,t)\right]\left[\frac{1}{\rho_e}+\frac{\Delta\rho}{\rho_e^2}\right] \qquad (33)$$

The following expression for $M$ is derived from equations (30) and (33):

$$M=\frac{GyL^3}{12}\left\{1-\frac{12K\rho_e}{L}\frac{\int_0^1(x-\frac{1}{2})w(x-\frac{1}{2},t)\mathrm{d}x}{\int_0^1 w(x-\frac{1}{2},t)\mathrm{d}x}\right\}\left[\frac{1}{\rho_e}+\frac{\Delta\rho}{\rho_e^2}\right]. \qquad (34)$$

Since the response to a step function applied moment is being derived, the moment must remain constant at

$$M=\frac{GyL^3}{12}\rho_e^{-1}.$$

Substitution of this value for $M$ into equation (34) yields

$$\frac{\Delta\rho}{\rho_e}=\frac{12K\rho_e}{L}\int_0^1(x-\tfrac{1}{2})w(x-\tfrac{1}{2},t)\,\mathrm{d}x\Big/\int_0^1 w(x-\tfrac{1}{2},t)\,\mathrm{d}x \qquad (35)$$

which shows the time dependence of $\Delta\rho$. The generalized time-dependent modulus $\mathscr{G}$ in the relationship

$$M(t)=\mathscr{G}\rho^{-1}(t) \qquad (36)$$

between the generalized stress, $M$, and the generalized strain,

$$\rho^{-1}\equiv\rho_e^{-1}\left(1+\frac{\Delta\rho}{\rho_e}\right),$$

is, from equation (34),

$$\mathscr{G}=\frac{L^3yG}{12}\left\{1-\frac{12K\rho_e}{L}\frac{\int_0^1(x-\frac{1}{2})w(x-\frac{1}{2},t)\,\mathrm{d}x}{\int_0^1 w(x-\frac{1}{2},t)\,\mathrm{d}x}\right\} \qquad (37)$$

The term $L^3yG/12$ in equation (37) is recognized in pertinent literature[15] as the flexibility constant. Expressions for both the relaxation strength $\eta$ and the mechanical loss tangent, tan $\delta$, can be obtained from equation (37), as follows.

The relaxation strength $\eta$ does not depend on the functional form of the applied moment since $\eta$ is derived from the limiting values of the relaxed ($t=\infty$ or $\omega=0$) and unrelaxed ($t=0$ or $\omega=\infty$) elasticity moduli.

For the unrelaxed state,

$$\int(x-\tfrac{1}{2})w(x-\tfrac{1}{2},t)\mathrm{d}x=0.$$

Hence $\mathscr{G}_{(t=0)}=\mathscr{G}_{(\omega=\infty)}=L^3yG/12$.

For a relaxed state, that is for $t=\infty$ or $\omega=0$,

$$w_{\omega=0}(x)=w(x,t=\infty)=2Be^{2B(x-1)}/(1-e^{-2B}).$$

Performing the integrations in equation (37) yields an expression for $\mathscr{G}_{(t=\infty)}=\mathscr{G}_{(\omega=0)}$ which leads to the following expression for the relaxation strength $\eta$

$$\eta=\frac{\mathscr{G}_{(t=0)}-\mathscr{G}_{(t=\infty)}}{\mathscr{G}_{(t=0)}}\equiv\frac{\mathscr{G}_{(\omega=\infty)}-\mathscr{G}_{(\omega=0)}}{\mathscr{G}_{(\omega=\infty)}}=6K\rho_e\beta(B)/L \qquad (38)$$

where $\beta(B)$ is the Langevin function,

$$\beta(B)=\coth(B)-\frac{1}{B}. \qquad (39)$$

In the limit of $B\rightarrow 0$, $\eta=2BK\rho_e/L$. For large $B$,$\eta$ approaches $6K\rho_e/L$, independent of the force parameter $B$. This is because, as $B$ increases, all the defects concentrate quickly in the expanded region of the bent crystal but cannot move further because of the boundary.

The dependence of $\eta L/(6K\rho_e)$ on the force parameter $B$ is of the same functional form as the well-known dependence of the average dipole moment on the strength of the applied electric field. In either case, high field strength produces a saturation effect. In the dielectric case, the saturation means that dipoles are oriented in the direction of the field. This saturation is rarely achieved in dielectric relaxation experiments on polymers because the required electric fields exceed the dielectric strength. However, for mechanical relaxation, one encounters situations which are closer to saturation.

An expression for the mechanical loss tangent, tan $\delta$, is derived from the equation that describes the response to a periodic stress, [equation (1) with $F$ periodic]. The solution of the diffusion equation for alternating forces, equations (13)–(16), has these interesting properties: if $p$ is the order of the perturbation [see equation (13)] then for all odd $p$'s

$$\int_0^1 w_p(x)\mathrm{d}x = 0$$

while for all even $p$'s, $p>0$

$$\int_0^1 xw_p(x)\mathrm{d}x = 0$$

For odd $p$, $w_p(x) = -w_p(1-x)$ and $w_p(\tfrac{1}{2}) = 0$. Considering only the zeroth and first perturbation terms, $p=0$ and $p=1$, leads to a simplified version of equation (34) for the complex bending moment:

$$M(t) = \frac{L^3 yG}{12}\left[1 - 24BK\rho_e L^{-1}\int_0^1 xw_1(x)\mathrm{d}x\right]\rho^{-1}e^{i\omega t} \qquad (40)$$

In equation (40) and the following ones use is made of the symmetry properties of $w_1(x)$ already described [see also equation (15)]. The complex modulus, obtained from equation (37) is

$$\mathscr{G} = \frac{L^3 yG}{12}\left[1 - 24BK\rho_e L^{-1}\int_0^1 xw_1(x)\mathrm{d}x\right] \qquad (41)$$

with $w_1$, a complex quantity, given by equation (15).

The mechanical loss factor, tan $\delta$, is obtained directly from equation (41).

$$\tan\delta = \frac{12\eta\,\mathrm{Imaginary}\int_0^1 xw_1(x)\mathrm{d}x}{1 - 12\eta\,\mathrm{Real}\int_0^1 xw_1(x)\mathrm{d}x} \qquad (42)$$

In deriving equation (42), use is made of equation (38), with $\beta(B)$ being replaced by its linear value, i.e., $\beta(B) = B/3$. It is evident that tan $\delta$ is a function of $(L^2\omega/D)$, i.e., the reduced variable $C$ which appears in equation (15). Equation (42) is unwieldy to analyse so it was solved numerically using a computer programmed for complex variable arithmetic for a range of values of $L^2\omega/D$.

Computations showed that tan $\delta$ has its maximum value at $\omega L^2/D = \pi^2$. If $\omega_{\max} \equiv \tau_M^{-1}$, then $D\tau_M/L^2 = \pi^2$, which provides another definition of $\tau_M$, the mechanical relaxation time. This value is close to $\tau_v$, the relaxation time obtained from the defect drift velocities: as seen from calculations described above that produced *Figure 5*, $\tau_v = L^2/8D$. Hence, $\tau_M \cong 0.8\ \tau_v$.

In *Figure 6*, two plots of $\eta^{-1}\tan\delta$ *versus* $\log_{10}\left(\frac{\omega L^2}{\pi^2 D}\right)$ are presented, one for $\eta = 0.1$, the other for $\eta = 0.01$. The plot of $\tan\delta$ vs. $\log_{10}\left(\frac{\omega L^2}{\pi^2 D}\right)$ is seen to be almost, but not exactly, symmetric around its maximum value. The asymptotic behaviour for $\omega \rightarrow 0$ and $\omega \rightarrow \infty$ are obtained from equation (42): As $\omega \rightarrow 0$, $\tan\delta = \omega L^2/10D$ and as $\omega \rightarrow \infty$, $\tan\delta = 12D/\omega L^2$. Hence, approximately, these two limiting values are $\omega\tau_M$ and $(\omega\tau_M)^{-1}$, respectively, a well-known result. *Figure 6* shows that for low $\eta$, $\tan\delta = \eta/2$ at $\omega_{\max}$, in agreement with the well-known result for $\tan\delta$ at the frequency at maximum loss. For $L = 30$ nm and $D = 2\times10^{-9}$ cm$^2$ s$^{-1}$, $\omega_{\max} = 2.2\times10^3$ s$^{-1}$.

*Numerical estimate of relaxation strength*

A lamella bent elastically so that adjacent stems make an angle of $\theta_e$ with each other will bend further by an angle $\theta_i$ as the defects it contains diffuse to lower energy positions. This 'creep' process is analysed to provide a basis for the estimate of $\eta$ from available information. The elastic bending angle, $\theta_e$ is equal to $aM/GI$ and is therefore a function of the elastic modulus and lamellar geometry.

A rigorous calculation of $\theta_i$ is beyond the scope of this paper so a simplified model is adopted. Each defect is considered to cause a local expansion $\delta a$ or $\delta b$ along the corresponding axis of the unit cell. The expansion in the $c$ axis direction is assumed to be zero. The values of $\delta a$ and $\delta b$ can be estimated from the change in volume $V$ of a chain containing a defect using the following relation

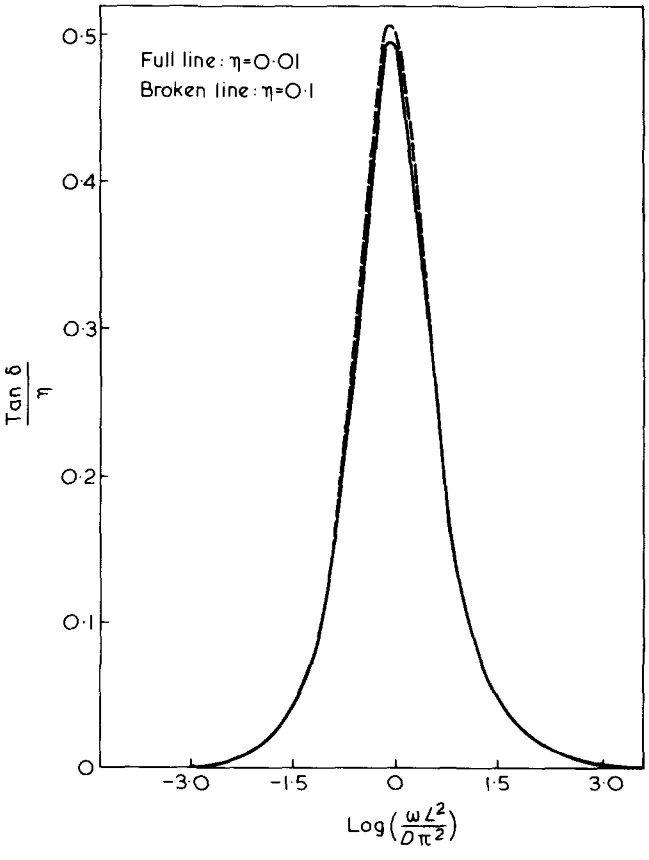

*Figure 6* Plot of the ratio of the mechanical loss tangent to the relaxation strength as a function of $\log_{10}(\omega L^2/D\pi^2)$. For an experiment with alternating moments the mechanical relaxation time, $\tau_{\mathrm{mech}}$, is defined as $\tau_{\mathrm{mech}} = 1/\omega_{\max} = L^2/D\pi^2$

$$\frac{\delta V}{V}=\left(1+\frac{\delta a}{a}\right)\left(1+\frac{\delta b}{b}\right)-1 \tag{43}$$

Computations performed in conjunction with the defect modelling work reported in ref. 9 showed that $\delta a/a \cong \delta b/b$, so that $\delta a/a = \delta V/2V$. A somewhat similar approach was used by Farmer and Eby[18] in polyethylene crystals containing an occasional $CH_3$ group in place of an H atom.

It is assumed that when a defect is at the end of a stem the angle between that stem and adjacent ones increases by $\delta a/\rho$. This intuitive concept can be generalized as follows to account for the dependence of the inelastic part $\theta_i$ of the angle between stems on the time and space variation of the defect distribution:

$$\theta_i(x,t)=\frac{2\delta a}{\rho}(x-\tfrac{1}{2})w(x-\tfrac{1}{2},t)\Big/\int_0^1 w(x-\tfrac{1}{2},t)\mathrm{d}x \tag{44}$$

The mechanical relaxation strength $\eta$ is defined as the ratio of the inelastic bending at long times to the total bending.

$$\eta=\frac{\theta_i}{\theta_e+\theta_i} \tag{45}$$

Since the inelastic bending is relatively small it can be ignored in the denominator of equation (45). The inelastic bending is calculated from equation (44) by replacing $w(x-\tfrac{1}{2},t)$ with $w(x-\tfrac{1}{2},\infty)$ and integrating over $x$ from 0 to 1. Substitution into equation (42) leads to

$$\eta=\frac{\delta a}{a\rho}\beta(B)\frac{GI}{M} \tag{46}$$

where $\beta(B)$ is the Langevin function introduced earlier.

An interesting simplification of equation (46) results if the value of $2\Delta a/aL$ evaluated at $x=1$ is substituted for the ratio $M/GI$ according to equation (26). (Note that $\delta a$ is the lattice expansion associated with a defect while $\Delta a$ introduced in equation (25) is determined by the elastic strain. For a bent lamella $\Delta a$ is a function of position in the lamella.) Therefore,

$$\eta=\frac{L}{2\rho}\frac{\delta a}{\Delta a(x=1)}\beta(B) \tag{47}$$

Timoshenko[15] noted that $L/2\rho$ is approximately equal to the strain $\frac{\Delta a}{a}$ at $x=1$, that is

$$\frac{L}{2\rho}=\frac{\Delta a(x=1)}{a}$$

Substitution into equation (47) produces

$$\eta=\frac{\delta a}{a}\beta(B) \tag{48}$$

Equation (48) indicates that the relaxation strength is essentially independent of the elastic strain amplitude except through the force parameter $B$ which appears in the argument of the Langevin function $\beta$. Equation (48) can also be used to estimate the perturbation parameter $K$ which was defined, but not evaluated, in the preceding section.

The computations performed in conjunction with the work reported in ref. 9 lead to an estimate of $\delta V/V=0.086$. Assuming that the change in lattice parameter $a$ is distributed uniformly along the $C_{15}H_{32}$ oligomer used in the calculation leads to a value of $\delta a/a$ of 0.043. In fact the change in lattice parameter $a$ may be as much as a factor of two larger since the region that is significantly expanded by the defect is only six or seven repeat units long. We therefore estimate

$$\eta=0.04\ \beta(B) \text{ to } 0.08\ \beta(B)$$

For a lamella 30 nm thick with a strain of one percent at $x=1$, $B=1.25$, and $\beta(1.25)=0.38$, an estimate of the relaxation strength in the range of 1.5 to 3% is obtained. This estimate assumes a concentration of one defect per stem. As noted earlier, the defect concentration inferred from the longitudinal acoustic mode intensity measurements[6,17] ranges from 1/6 defect per stem at 70°C to 3/4 defect per stem at 120°C so the above estimates of $\eta$ could be improved by multiplying by the number of defects per stem at a particular temperature.

The value of the relaxation strength derived from this analysis is lower than observed relaxation strengths in crystalline polyethylene in spite of the fact that the relaxation times predicted are in reasonable agreement with those observed. This leads to the suggestion that the relaxation strengths are increased by processes which involve larger scale structures which move on a time scale governed by defect diffusion. There are many structures and processes which may behave in such a manner. An example is the slippage of a lamella past an adjacent lamella with tie molecules connecting the two. It is possible that the rate controlling step is the movement of the tie molecule through the lamella by the diffusion of a series of defects through the part of the tie molecule that is inside the lamellae.

## COMPARISON OF DEFECT DIFFUSION MODEL AND COMPUTER SIMULATED DEFECT MOTION

The macroscopic model of defect motion described in this paper can be compared with the more microscopic computer simulation of defect motion described earlier[9]. In the microscopic model the defect is considered to move over potential barriers separating a series of potential wells. The rate of passage of a defect over these barriers is related to the diffusion constant $D$ used in this paper through models developed by Zener[20] which are summarized by Kittel[21]. These models lead to the relation

$$D=ca^2\nu e^{-E/kT} \tag{49}$$

In equation (49) the probability that the defect occupies the site adjacent to a particular potential barrier is $c$, which is proportional to the defect concentration. In the case of a defect containing six $CH_2$ groups and extending about 0.6 nm along the chain in a stem of length 30 nm, $c=0.02$. The height of the barrier $E$ was calculated[9] as about 17 kJ mol$^{-1}$. The distance $a$ that the centre of the defect moves in travelling from one well to the next is about 0.125 nm, which is half the crystallographic repeat distance along the chain axis direction in a polyethylene crystal. The rate, $v$, at which the defect impacts the barrier is estimated from the mass of a defect containing six $CH_2$ groups and from the apparent force constant ($0.9 \times 10^5$ dyne cm) described by McCullough *et al.*[22] The rate was found to be around $1.7 \times 10^{12}$ $s^{-1}$.

The values of these parameters which describe the rate of motion of a defect over a barrier yield a value of $D$ from equation (49) which is around $5 \times 10^{-9}$ $cm^2$ $s^{-1}$, in satisfactory agreement with the values of $D$ obtained from the n.m.r. and dielectric relaxation data.

## SCALING APPLIED TO DEFECT MOTION

Scaling theory as described by deGennes[11] leads to a simple connection between the relaxation time, $\tau_0$, of a single $CH_2$ unit, the probable time for a defect to move a crystallographic repeat unit (0.25 nm) along the chain, and the probable time for a defect to move a distance of approximately $L$ which is required to produce mechanical relaxation according to the mechanisms described above.

The scaling approach suggests that the relaxation time associated with a process involving $N$ links of a chain is $N^3\tau_0$. The defect considered here involves approximately six $CH_2$ units. The relaxation time for a single unit of a chain[11] is around $10^{-10}$ s so scaling gives a defect relaxation time of $6^3 \times 10^{-10} = 2.2 \times 10^{-8}$ s. The diffusion coefficient of around $2 \times 10^{-9}$ $cm^2$ $s^{-1}$ estimated from n.m.r. and dielectric relaxation data indicates that a defect will move a distance of one repeat unit in a probable time of $(2.5 \times 10^{-8})^2/D = 3 \times 10^{-7}$ s which is within an order of magnitude of the value predicted by scaling. In this argument the defect displays some properties of the 'blob' described by deGennes[11].

Now consider the mechanical relaxation process in a stem 30 nm long which contains 240 $CH_2$ units. The scaling arguments predict a relaxation time for the stem of $(240)^3 \times 10^{-10} = 1.4 \times 10^{-3}$ s. This is the time scale in which observed mechanical relaxation processes occur. It was shown earlier in this paper that the stochastic diffusion of a particular well-defined defect along routes of lengths commensurate with the stem length also can lead to mechanical and dielectric relaxation processes with relaxation times in the millisecond range.

## SUMMARY

The chain rotation effects and mechanical relaxation processes associated with the motion of a single point dislocation (defect) were determined by Brownian molecular dynamics simulations. The defect motion in polyethylene is diffusive and characterized by a diffusion coefficient and a mobility (the drift velocity divided by the average force on the defect). The defect concentration as a function of time and position, that is the probability of finding a defect in a particular region at a particular time, was calculated by solving the Smoluchowski diffusion equation with appropriate boundary conditions. The average times required for a defect to diffuse along a route that produced observed chain rotation effects were then determined by calculating first passage times for the defects along the required routes. Data on polyethylene chain rotation from dielectric relaxation or carbon-13 nuclear magnetic resonance experiments independently lead to a reasonable value for the diffusion coefficient for a defect. The average defect velocity was determined by adding the drift velocity caused by external forces to the diffusional or Brownian motion velocities. A mechanical relaxation time associated with the decay of average drift velocity was described. Using the already determined diffusion coefficient the relaxation time calculated falls in the range of those observed experimentally. It is suggested that defect diffusion plays a central role in the determination of mechanical and dielectric relaxation times although other processes must be involved to account for the magnitude of the observed relaxation strengths. The mobility of a defect is directly involved in the coupling between a strain field and the mechanical relaxation process, but the mobility plays only a small role in the determination of the relaxation time for strains of the order of a few percent.

The diffusion coefficient was connected to the parameters involved in modelling the internal motions of a defect as it moves over the barriers that separate minimum energy conformations at adjacent sites along the chain using the ideas of Zener[20,21]. The scaling method connects the relaxation time associated with a single repeat unit to both the relaxation time of a defect and that of a complete stem which in the model presented here is closely related to the dielectric and mechanical relaxation processes.

Although the model developed in this paper deals only with linear polyethylene the ideas presented seem to have more general applicability. Certainly the specific defect considered here, the point dislocation or twist dispiration loop, can be described in other crystalline polymers and will have a reasonable diffusion coefficient and mobility in many of them. It appears reasonable to suggest that even in glassy polymers where there is no periodic translational structure somewhat similar relaxation processes may occur as consequences of the motion of a reptating chain segment in response to an external electric or strain field.

The concentration of defects depends upon temperature and other factors. Two kinds of experiments, namely, the decrease in intensity of the longitudinal acoustic mode with increasing temperature[6] and the increase in the concentration of *trans–gauche* sequences observed in partially doubly deuterated polyethylene by the relative intensities of reliably assigned rocking mode vibrations[8] suggest that 0.1 to 1 defect per stem is the correct order of magnitude for the temperature range between 70°C and 120°C. Detailed analysis of the effects of defect concentration must await more quantitative measurement of the variation of defect concentration with temperature. Also, the problems associated with the interactions of the specific defect analysed in this paper with folds, chain ends, ordinary crystallographic dislocations, localized chain twist, tie molecules, and other geometrical features of polyethylene chains often referred to collectively as the amorphous component, must be left to a future time when these are modelled in greater detail.

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