polymer papers

Dispirations, disclinations, dislocations, and chain twist in polyethylene crystals

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It is proposed that the twist in polyethylene chains that can result from crystallization and subsequent deformation aggregates at boundaries and becomes a template for further reorganization that results in the long period observed in polyethylene fibres. The observed lower density at the boundaries requires the transport of free volume to the twist boundaries. Dispirations, disclinations and dislocations are crystallographic defects that are involved in the necessary transport mechanism. Twist and bend, derived from the Eulerian angles which are computed from the sets of chain internal coordinates, relate the orientation of different segments of a chain. Twist and bend are useful for the characterization of both crystallographic defects and arbitrary confomations of polymer chains. Defects, along with folds, chain ends, and ordinary edge and screw dislocations provide a basis for interpretation of structure–property relationships in solid polyethylene.

Keywords Chain twist boundary; crystallographic defect; disclination; dislocation; dispiration; polyethylene; polymer diffusion

INTRODUCTION

The lowest energy conformational defect in a single molecule which forms a crystallographic defect in a polyethylene crystal is a twist dispiration loop[1] which was also called a point dislocation[2], and for brevity is referred to in this paper simply as a dispiration. Computer modelling[3,4] of a dispiration in polyethylene showed that it can diffuse along the chain as is required to thicken lamellar crystals. It is the essential nature of a dispiration to both rotate and translate the part of the molecule along which the dispiration passes. As a result, observations of the rotation rate of polyethylene chains in the crystal permit the deduction of the diffusion coefficient for the dispiration[5]. The interaction of a dispiration with the strain field in a lamellar crystal was shown to lead to a mechanical relaxation which occurred in the region of time and temperature appropriate for the alpha relaxation process[6], but the calculated changes in the magnitude of both the real and imaginary parts of the mechanical modulus were much smaller than the changes observed experimentally.

There are two other small conformational defects in a single molecule that can fit within a polyethylene crystal. Both of these have higher energies than a dispiration. One of these defects is the edge dislocation loop which surrounds only a single stem of a polyethylene molecule in a crystal, contains two extra CH_2 groups, and has no net twist. This dislocation loop can dissociate into two dispirations of opposite sense of twist. The other defect is the twist disclination loop which surrounds a single stem, contains a twist of 360° and has no extra CH_2 groups. If a twist disclination is permitted sufficient mobility, the entire 360° twist can accumulate in a single dihedral angle and the disclination will disappear. In this paper these defects are referred to as a dislocation and a disclination.

Figure 1 shows the three crystallographic defects and the two partial defects schematically in a flat ribbon which represents the planar zig-zag backbone of polyethylene. The ribbon at the top of the figure shows the extended length of all the ribbons in the Figure. The vertical line at the right provides a reference that shows that the bent segments of the dispiration and the partial dislocation contain one extra CH_2 group while the dislocation contains two extra CH_2 groups.

Two partial defects are also considered here. These are the partial disclination and the partial dislocation. In polyethylene partial disclinations that contain a twist of 180° and partial dislocations that contain one extra CH_2 group are of most interest. These partial defects have lower conformational energy than the three defects described above which fit into the crystal. This energy advantage is lost because the chain cannot fit into the lattice on one side of the defect. The resultant necessary rejection of partial disclinations to crystal boundaries requires the development of boundaries in crystals that contain partial disclinations as a result of mechanical deformation or other processes.

Other crystallographic defects can exist in chain folded lamellar crystals of polymers. Keith and Passaglia[7] described edge and screw dislocations which can move inside lamellar crystals. Some of these have strong interactions with fold surfaces. Predecki and Statton[8] suggested that screw dislocation loops provide a way to accommodate chain ends inside a polymer crystal. A chain fold can be accommodated in a similar way. The fold is simply viewed as two chain ends at adjacent points in the crystal. Clark and Muus[9] postulated a helix reversal defect in polytetrafluoroethylene which in the terms used here is a partial disclination with crystallographic twist of opposite sense on either side of the defect.

The schematic model of *Figure 1* represents the

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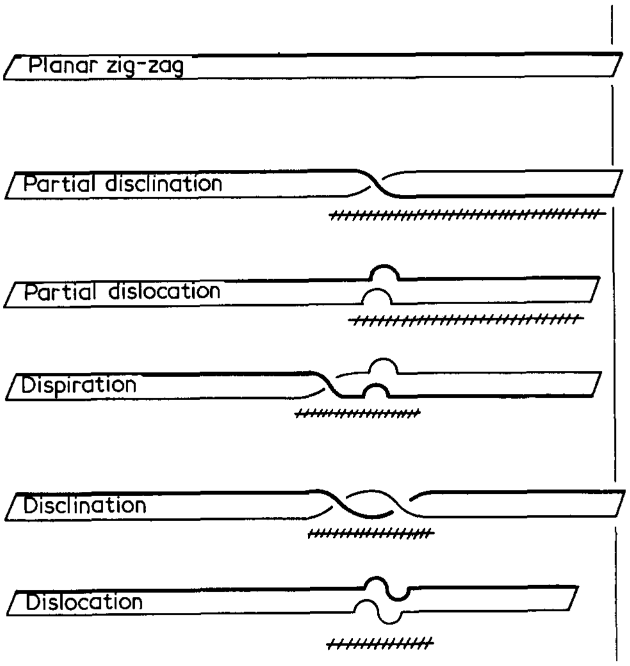

Figure 1 Schematic illustration of crystallographic and partial defects in a polyethylene molecule

planar zig-zag backbone of the molecule by a flat ribbon which can twist around its long axis or bend around a transverse axis. The net amount of twist in each defect is indicated by the crossing of the edges of the ribbon. The bent segments indicate the presence of one extra CH_2 group in the dispiration and partial dislocation or two extra CH_2 groups in the dislocation. The presence of the extra CH_2 groups shortens the ribbon by a corresponding amount indicated at the right end. The regions where the packing energy of the molecule significantly exceeds the packing energy of a planar zig-zag molecule in a perfect crystal are indicated by a cross hatched line. Note that the partial defects force the part of the molecule on one side of the defect to a higher energy position that extends indefinitely while the complete defects have a finite extent. The ribbon model is used in later figures to portray actual minimum energy conformations of various defect structures.

This paper describes an algorithm by which the amount of twist and bend in a polyethylene molecule can be calculated from the sequential values of the dihedral angles. It is observed that twist is a general feature of chain folding which is particularly evident in (110) fold planes. Twist may accumulate as a molecule folds into a crystal. The amount of twist may change, but some persists as the molecule is drawn into a fibre. Twists of 90° and 180° inside a polyethylene crystal are partial disclinations which cause long segments of the molecule to lie off the minimum energy position. Crystal forces therefore tend to localize 90° or 180° twists in adjacent chains into twist boundaries which can play an important role in the establishment of the long period usually observed in drawn fibres. After the twist boundaries are established, other noncrystallographic chain conformations tend to accumulate there. Diffusion of dispirations along the chains plays an important role in this transport process. The interactions between dispirations and twist boundaries are modelled in this paper.

This paper contains three main sections. The first section develops the concept of quantitative parameters called twist and bend which are useful in the description of the conformations of polymer molecules. The calculation of twist and bend from the conformational coordinates of polyethylene is described.

The next section describes some consequences of twist in the crystallization and mechanical drawing of polyethylene. It deals with the twist that is associated with folds and deformation. Twist from folds and from processes that occur during mechanical drawing can persist and create twist boundaries in the drawn fibre. Twist boundaries may play a special role in determining the long period of a drawn fibre. The transport of free volume to the twist boundaries in order to create the regions of observed low density is discussed.

The third section is devoted to the description of the minimum energy conformations and the interactions of defects that primarily involve only single stems in polyethylene crystals. It deals with the 90° and 180° twist boundaries that can occur in polyethylene crystals, describes the interaction of a dispiration with those twist boundaries, and the minimum energy conformations of a disclination, a dislocation, and a dispiration, in that order.

DISCUSSION

Calculation of twist and bend

Two planar zig-zag segments, labelled A and B, of a polyethylene molecule are connected by a series of bonds $(i, i+1, \ldots)$ having dihedral angles labelled τ_i. The planar zig-zag segments may be as short as two adjacent bonds (which always define a plane) or of arbitrary length. The intervening dihedral angles may have any values that connect the two planar zig-zag segments. The orientation of the x', y', z' coordinate system attached to segment B with respect to the x, y, z coordinate system attached to segment A can be specified in terms of Eulerian angles (ϕ,θ,ψ) using the conventions described by Goldstein[10]. *Figure 2*, which is adapted from a Figure in ref. 10, shows how twist and blend are related to the Eulerian angles.

If the plane of the zig-zag ribbon lies initially in the x–z plane then the amount of bend is equal to the Eulerian angle θ. The amount of twist in the chain is given by the algebraic sum of the angles ϕ and ψ. The exact conformation of the chain depends upon the order in which the rotations ϕ, θ and ψ are applied, but the magnitude of the total bend and twist is independent of their order. The circled segments of the chain in *Figure 2* in which bend and twist occur can be as short as one bond or of arbitrary length. In general, rotation of a single dihedral angle affects both bend and twist. The defect segments of interest in this paper involve from five to ten adjacent dihedral angles, the twist associated with each defect never exceeds 360° and the bend never exceeds 180°. A general sequence of dihedral angles contributes to the Eulerian angles in a complicated way that can be calculated with the straightforward rotation matrix algorithm given below.

The concept of twist associated with a defect is used in this paper as a quantity that adds algebraically to the regular twist of a helical molecule. Specifically, twist is the 'additional' twist associated with defects in the ribbon-like, two residues per turn helix of polyethylene. The same concept can be generalized to the more cyclinder-like helices encountered in other polymers. The total twist calculated from the algorithm given below includes a contribution from the regular helix which must be subtracted to arrive at the twist that is associated with defect structures. See *Figure 3* which includes the helical twist and *Figure 4* which shows only the 'additional' twist characteristic of each of three crystallographic defects.

The subtraction of 360° per turn of the regular helix is straightforward but it depends upon details of the conventions used to specify the signs of the bond dihedral angle. The algorithm is not described here in detail. Suffice it to say that the completion of a turn is easily assessed from the inequalities between amounts of twist $(\phi+\psi)$ at successive dihedral angles. If the calculated $(\phi+\psi)$ is increasing at each successive dihedral angle and a sudden decrease is encountered at the next dihedral angle (or *vice versa*), a turn was completed between those two successive dihedral angles and a new turn started.

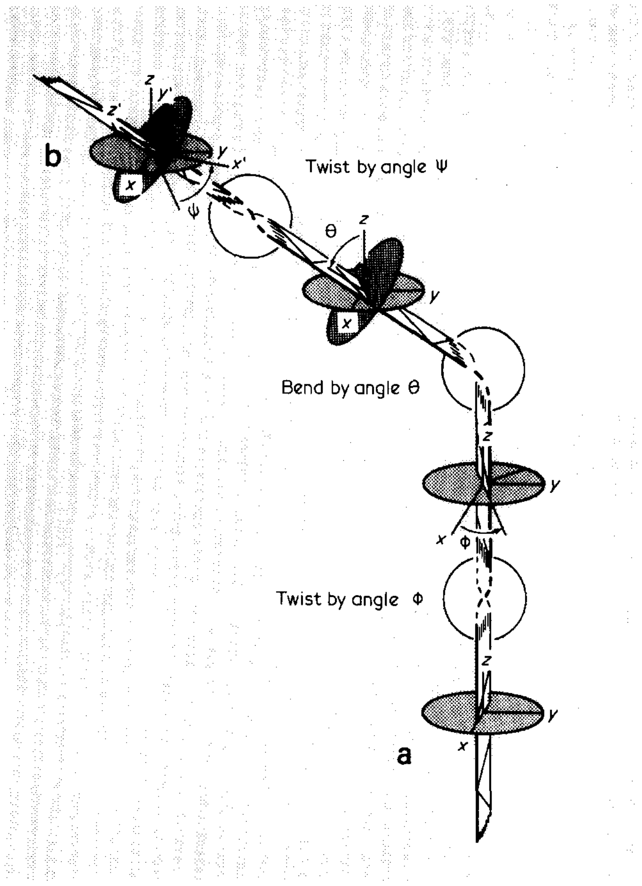

Figure 2 Schematic illustration of the relationship between the Eulerian angles ϕ, θ, ψ, and the amounts of twist and bend. The chain based Cartesian coordinares are shown after each rotation. The circled segments of the chain can be arbitrarily long, but the defects considered here typically involve five to seven bonds

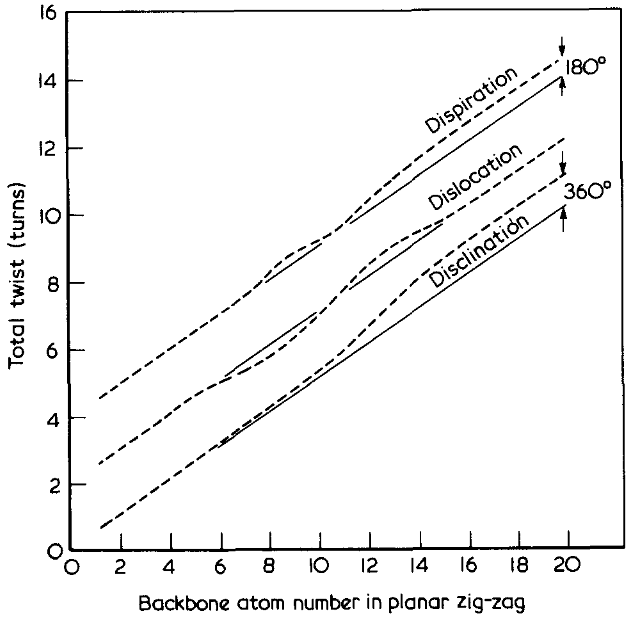

Figure 3 Calculated total twist in polyethylene chains with three different crystallographic defects. The curves are displaced upward for clarity. The planar zig-zag backbone of polyethylene is conventionally described as a two-fold helix with two CH_2 groups per turn. The algorithm described in the text calculates the total twist from the helix and any defect. The total twist therefore increases in proportion to the chain length. The twist associated with a defect, which is called 'twist' in this paper, is determined by subtracting the twist of the regular helix.

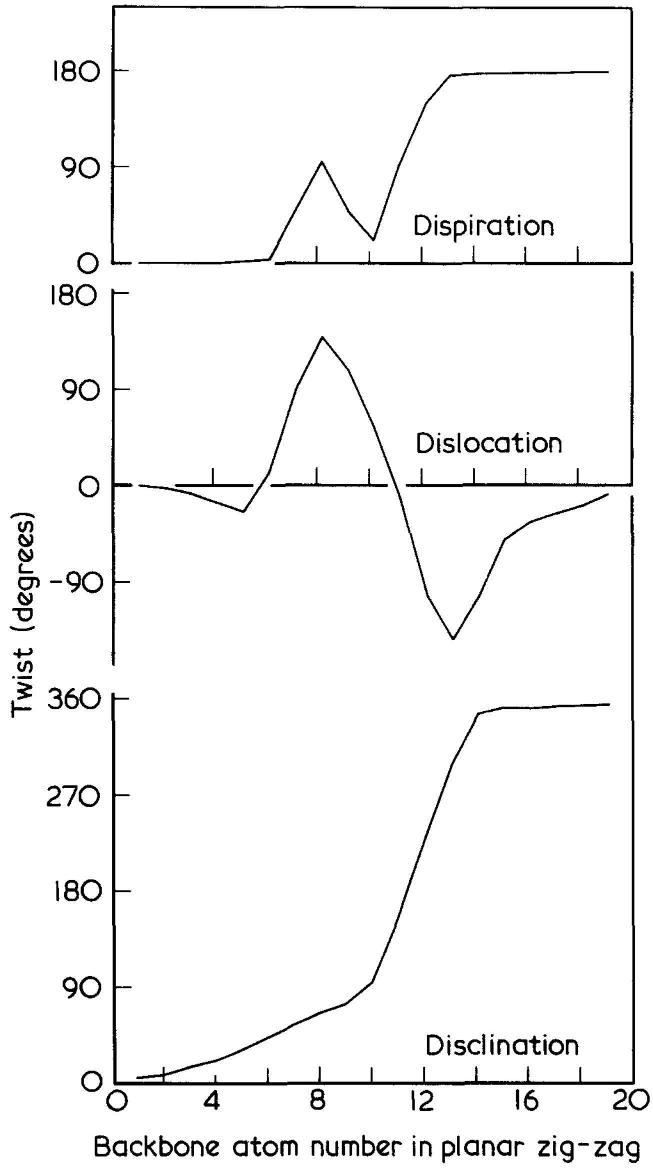

Figure 4 Characteristic features of the twist associated with minimum energy conformations of crystallographic defects in polyethylene crystals. The regular twist of the helix has been subtracted. The twist of a dispiration oscillates as it accumulates to 180°. The twist of the dislocation increases in one sense, then reverses, and finally comes to zero. The twist of the disclination increases to 360° in two parts, a gentle twist of less than 180° and a more rapid twist of over 180° in a region containing *gauche* bonds

The Eulerian angles are related to the bond oriented coordinate system in which the dihedral angle associated with the ith bond is τ_i as described below. By convention, the bond labelled i connects carbon atom i with carbon atom $i+1$. In crystalline polyethylene the dihedral angles τ_i are defined in such a way that if all $\tau_i = 180$, the molecule is in the planar zig-zag conformation which can also be described as a helix with two residues per turn, conventionally written as a 2_1 helix.

The approach is almost idential to that used by McMahon, McCullough and Schlegel[11] except that they chose for the planar zig-zag to lie in the y–z plane while we place it in the x–z plane in order to identify bend with the value of θ. A matrix $\underline{T}$ rotates the coordinate system into a bond based system. The orientation of the bond based system depends only on τ_i if the variations in the C–C–C bond angle and the bond length are ignored. (In the calculations reported below these variations were included and were seen to be small.) A series of N matrices A_i^{i+1} are defined at each intervening bond which rotate $x_{i+1}, y_{i+1}, z_{i+1}$, into x_i, y_i, z_i. It is then possible to express the orientation of the x', y', z' coordinate system attached to segment B at the end of the N-sequence bond system through the Eulerian orientation matrix $\underline{C}_N$ which is given by:

$$\underline{C}_N = \underline{T}_1 \prod_{i=1}^{N} A_i^{i+1} \underline{T}_N$$

In the computations which follow, N is an integer starting with $N=2$. Generally, $\underline{T}_N \neq \underline{T}_1$ unless segments A and B are colinear and fit into the same crystal, in which case these matrices are identical. By calculating the elements of the matrix $\underline{C}_N$ and equating them to the matrix elements in equations (4–46) of ref. 10 the Eulerian angles, which measure twist and bend, can be calculated for the particular sequence of N dihedral angles represented by the set of A matrices. For $\theta = 0°$ and $180°$, that is for a straight chain or a folded chain, ϕ and ψ are indeterminate although a linear combination of these angles can be defined. A convention can be used to assign a value to one of these angles and then the other one can be calculated, for these special cases, in such a way that $\phi + \psi$ always measures the amount of twist. A simple approximate method for calculating twist[3] produces reasonably accurate results but no similar approximate method is available to calculate the bend. Investigation of the properties of the A matrix product provides an explanation for this finding. Twist is a helical property and its amount is practically independent of the sequence in which the dihedral angles occur. The additivity of twist (in the absence of bend) can also be indirectly deduced from the approximate expression for the amount of helical turning per monomer unit given by Hopfinger in equations (1–32) of ref. 12. On the other hand, the amount of bend depends strongly on the sequence in which the dihedral angles occur.

Occurrence of chain twist in folds and during fibre formation

Most chain folds require that the planar zig-zag ribbon twists. The twist in (110) folds is represented schematically in *Figure 5*. The intersections of some neighbouring chains with the surfaces of the crystal are shown to depict the orientation of the a and b axes of the crystal. The twist of approximately 90° associated with each fold results in only one crossover of the edges of the ribbon as it is viewed from any particular viewpoint. The viewpoint chosen for this Figure causes the crossover to occur near the top fold. The twist associated with the bottom fold is evident only as a slight narrowing of the ribbon as it enters the fold.

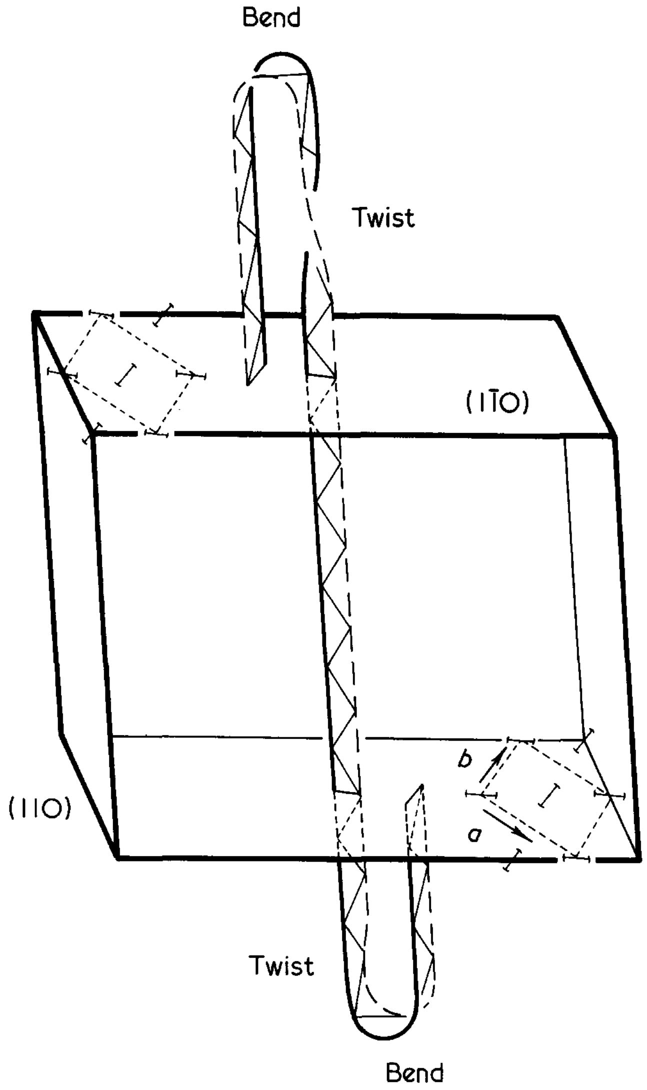

Figure 5 A segment of a polyethylene crystal folded in a (110) plane. The fold conformation is represented schematically to emphasize the twist and bend characteristic of this type of fold

A ribbon emerging from the top of the crystal must bend 180° and then twist so that ribbon plane is correctly oriented to reenter the crystal. The amount of twist required depends upon the sense of the twist, being either twice the setting angle or twice the difference between 90° and the setting angle. The setting angle for polyethylene crystals is approximately 48° with respect to the b axis. For the low energy conformation of the (110) folds, the twist calculated is 84°. In *Figure 5* and elsewhere in this paper the bend and twist of a fold are drawn separately for clarity. In the minimum energy conformation of a (110) fold each of the dihedral angles contribute to both twist and bend so that the shape of the ribbon is more difficult to discern in a sketch of the fold. When the twisted ribbon reaches the bottom surface of the lamellar crystal the ribbon must first twist (or untwist) by approximately 90° so that a bend will return the chain to a proper lattice position. *Figure 6a* shows a ribbon in which the sense of the twist is the same at the top and bottom so that each fold adds approximately 90° of net twist to the ribbon.

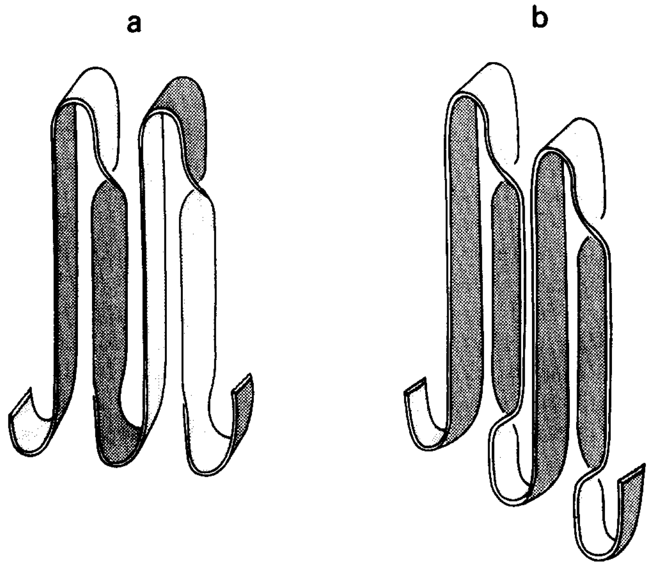

Figure 6 Folded ribbons with 90° twist that approximates that required for a (110) fold plane in polyethylene. In (a) the twist is in the same sense at the top and bottom of the stem so the net twist per stem is 90°. In (b) the stem twists at the top and untwists at the bottom so the net twist is zero

Figure 6b shows the alternative in which the twist at the top fold cancels the twist at the bottom leaving zero twist. The energy differences between the two possibilities appear to be small so the general case may involve some cancelling but leave the ribbon with a reasonable amount of twist.

It is interesting to recall that to produce a hollow pyramidal crystal[13] with a uniform thickness the folds at the top and bottom of the lamellae must cooperate[14]. It is possible that the communication upon which this cooperation rests occurs as the top fold disturbs the setting angle of the entire stem just enough to bias the sense of twist the molecule chooses as it forms the bottom fold.

A folded chain ribbon with (110) folds and 90° non-cancelling twist are incorporated into a lamellar crystal in *Figure 7*. Consider a mechanical deformation process that draws the folded ribbons into a fibre. Since electron micrographs[15] indicate that adjacent lamellae generally cooperate in such a process, fibres from five adjacent lamellae are shown schematically in *Figure 8* as they are incorporated into a polyethylene fibre. Peterlin[16] suggested that this drawing process, often called 'necking', can be described as a combination of slip on crystallographic planes, bending of chains and stress-induced crystallographic transformations. Although all these processes contribute in important ways to drawing, it is not necessary to describe them in greater detail here in order to describe the possible role twist plays in setting the long period. It is sufficient to assume that some or all of the twist persists through the process.

The drawing process creates a necked region in which short, randomly spaced segments are not in the planar zig-zag conformation. A simplified diagram of the neck is shown in *Figure 8*. Defects other than twist are not shown. The irregular distribution of lengths of the planar zig-zag segments causes the longitudinal acoustic mode to be unobservable, as noted by Capaccio, Ward and Wilding[17]. As the molecules pack together in the fibre the twist aggregates into boundaries. The twist boundaries interact with other defects to establish low density boundaries by transporting free volume to the boundary. An interaction between a twist boundary and a dispiration will be described below. Other measurements[18,19] show that the long period observed in fibres depends upon the temperature at which the drawing occurs but not upon the lamellar thickness of the starting material. It is therefore necessary that if the long period is caused by aggregation of twist, at least some of the processes involved in deforming the lamellar crystal into a fibre produce changes in the amount of twist in the chains. The twist bearing defects described here play a role discussed below in adjusting the amount of twist. There are probably also larger scale mechanisms driven by deformation that twist or untwist the molecules.

Twist boundaries in fibres

Severe packing problems occur as twisted polyethylene molecules pack together in a fibre during cold drawing. The cost in terms of packing energy of accommodating the twist can be minimized if the twist in all the adjacent chains is segregated into a transverse plane not necessarily perpendicular to the chain axis. This arrangement does not affect the excess energy of the twist significantly, but it does minimize the lengths of the chain segments that are not at the lowest packing energy value of the setting angle. In its perfect form, a twist boundary can be regarded as a type of twin boundary, that is, a boundary that establishes a specific and recurrent noncrystallographic geometric relationship between two crystal lattices. Twist boundaries with either 180° or 90° of twist in each chain as it passes through the boundary are both possible in polyethylene. *Figure 9*, which is an enlargement of part of *Figure 8*, shows a small fibre containing four 180° twist boundaries. The separation between these boundaries is determined by the amount of twist that is present in the polyethylene molecules as they emerge from the drawing process and are incorporated into the crystalline fibre. A repulsive force between boundaries that is transmitted elastically through the intervening planar zig-zag segments would tend to produce a periodic separation of the boundaries. If the twist boundaries contain only 90° of twist, either for dynamic reasons or because of lower energy, then twice as many boundaries are required to accommodate a given amount of twist.

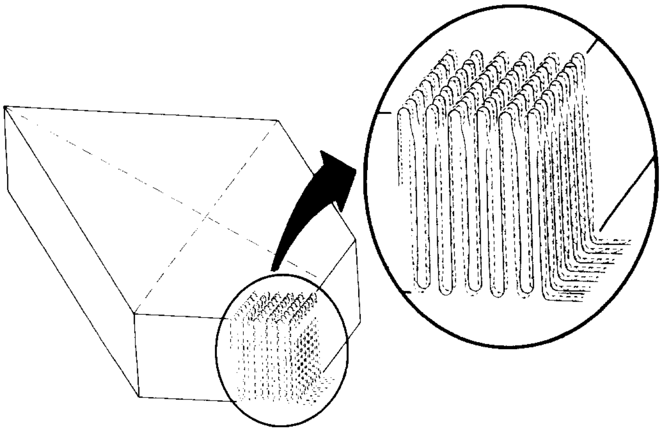

Figure 7 A lamellar crystal of polyethylene with (110) fold planes in which the molecules have a net twist as indicated in *Figure 6a*

It is proposed that the twist boundary separation is an important parameter in establishing the long period in a fibre. Chain ends, vacancies, folds and other defects may be trapped at the twist boundaries or subsequently migrate there.

The importance attached to twist as the primary determinant of the long period in fibres is based upon the following considerations. The amount of twist in a polyethylene molecule tends to be conserved. That is, except during drawing, it is improbable for a molecule in a crystal to find a sequence of accessible conformations that concentrate 360° of twist at a single bond dihedral angle and thereby make the net twist increase or decrease. Twists of 90° or 180° cannot migrate through a crystal since such twists do not restore a chain in the crystal back into the lattice as the twist passes. These twists can disappear only at chain ends or by interaction with other twist-bearing defects such as dispirations, disclinations and twist boundaries.

Proper crystallographic defects associated with a single polymer chain such as twist dispiration loops, dislocation loops and disclination loops do not associate into boundaries for several reasons. Unlike twist, such crystallographic defects are probably not conserved in the drawing process where the translational periodic symmetry needed to define a crystallographic defect is severely disrupted. Dispirations and dislocations contain extra material which leads to repulsive interactions between defects even on adjacent chains. More importantly, in a boundary composed of dislocations, all the chains could simply straighten out, making the fibre one repeat unit (0.25 nm) longer and leaving a perfect crystal. The molecules passing through a boundary composed of partial dislocations would also straighten out if the boundary extended completely across the fibre. If the perimeter of the partial dislocation boundary is inside the fibre, the required crystallographic slip of amount $c/2$ on planes containing the chain axes would lead to a strained region in the vicinity of the perimeter which could stabilize partial dislocation boundaries of small areas. In a hypothetical boundary composed of dispirations each dispiration would straighten out by half a repeat unit (0.125 nm) and leave 180° of twist. That is, a dispiration boundary would decompose into a 180° twist boundary plus a 0.125 nm thick additional layer on the crystal.

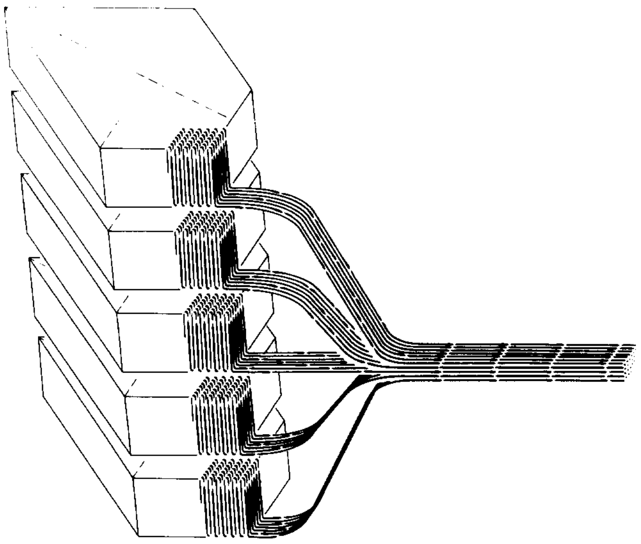

Figure 8 Schematic of the conversion of lamellar crystals into a fibre. Most of the details of the deformation process have been omitted to emphasize the behaviour of twist. Processes, yet to be described, that change the amount of twist during deformation are postulated. Some net twist emerges from the deformation and is trapped in the fibre. The segregation of this net twist into boundaries in the fibre serves as a template for the establishment of the observed long period

As noted above, a boundary composed of twist disclinations could also be called a 360° twist boundary. A disclination boundary would be more costly in packing energy than a 180° or 90° twist boundary. Another powerful argument against the aggregation of disclinations into boundaries also applies to dislocations and dispirations. By their very nature all these crystallographic defects can be incorporated into the crystal with a disturbance to only the immediately adjacent lattice. As a result the crystal gains little or no packing energy by forcing crystallographic defects into a plane. On the other hand, if defects such as a 180° twist, which can be viewed as a partial disclination, or a partial dislocation containing only one extra CH_2 group, were forced into the lattice, long segments of molecules in high energy, noncrystallographic positions would result. Such noncrystallographic defects should aggregate at crystal boundaries to conserve packing energy. The partial disclinations form a twist boundary and the partial dislocations disappear as described above.

(*a*) *Accumulation of free volume at twist boundaries.* In a polyethylene fibre the X-ray or electron diffraction experiments indicate a lower density in the vicinity of the

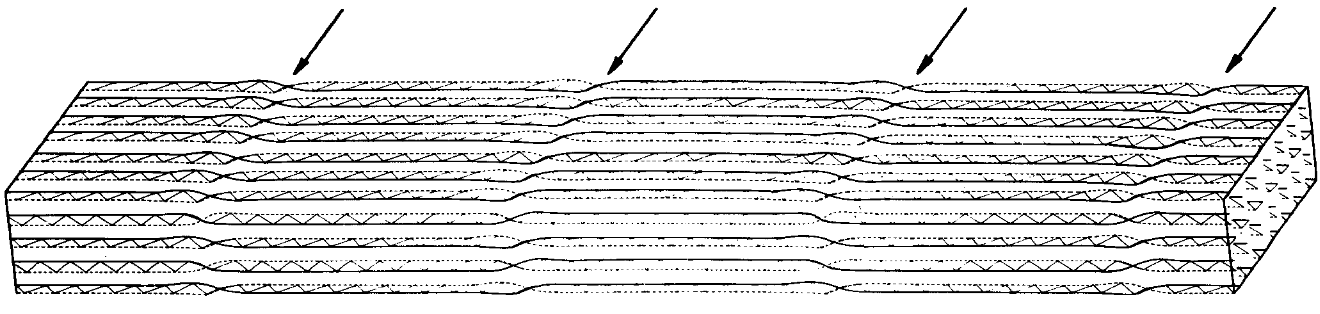

Figure 9 The fibre shown in *Figure 8*, enlarged to show the 180° twist boundaries indicated by arrows

boundaries with respect to the density of the planar zig-zag crystal regions. A perfect twist boundary has nearly the same density as the crystal so it is necessary that mechanisms exist for the transport of free volume to the vicinity of twist boundaries. In polyethylene crystals, free volume is associated with chain ends or folds embedded in the crystal. Without examining the processes in detail, we suggest that it is likely that dispirations (and some dislocations, although their energy is much higher, as will be shown below) in concert with the screw dislocation loops of Predecki and Statton[8], transport folds, chain ends and associated free volume (vacancies) to the twist boundaries.

(*b*) *Motion of twist boundaries.* The long period observed in fibres drawn at low temperatures is relatively short. Annealing at temperatures above the temperature of drawing increases the long period. In this model, the twist boundaries move apart. The net twist per unit length of chain is therefore reduced. Twist can disappear if a twist boundary passes a chain end. Dispirations can reduce the twist either by transporting 180° of twist from the boundary to a chain end or fold or by transporting twist opposite in sense to that in a twist boundary from an end or a fold to the boundary. Examples of the second possibility are modelled in detail in this paper. Disclinations emitted from a boundary can carry away 360° of twist or a disclination arriving at a boundary can cancel twist of opposite handedness in the boundary. A disclination that encounters a region with sufficient free volume can disappear by concentrating all its twist into a 360° rotation around one bond. The non-crystallographic chain conformations that concentrate at the twist boundaries can diffuse along with the twist boundary through a series of dihedral angle rotations analogous to those that permit diffusion of dispirations.

Packing energy calculations for twist boundaries

(*a*) *The 180° twist boundary.* The packing energy program described earlier[3] was used to calculate the energy of a twist boundary near the middle of alkane molecules 21 carbon atoms long. A central chain, six close neighbours and 12 more distant neighbours were included in the calculations. The twist boundary created a bicrystal with the two parts of the crystal in a twin relationship. An approximate conformation was established for the twisted region and used in all the molecules. The conformation of the central molecule was adjusted to minimize the packing energy. Then the adjusted conformation was placed in all the molecules and the minimization process repeated at each of the six neighbouring chains in turn until a stable low energy conformation was reached.

The total energy from all inter and intramolecular interactions of the central chain containing a 180° twist boundary and surrounded by chains with identical twist boundaries is $-38.81\,\mathrm{kcal\,mol^{-1}}$. To determine the excess energy associated with the twist it is necessary to subtract the total energy calculated for a $C_{21}H_{44}$ chain packed in crystallographic register in the planar zig-zag conformation, which is $-54.23\,\mathrm{kcal\,mol^{-1}}$. This leaves $15.42\,\mathrm{kcal\,mol^{-1}}$ of twists as the excess energy to be associated with the 180° twist boundary.

The results of these calculations are shown in *Figure 10* and *Table 1*. Note that the 180° twist involves about five bond dihedral angles which depart significantly from 180° plus others with much smaller departures. The packing forces exerted by the lattice tend to keep the distorted region short, even at the cost of a few dihedral angles being forced into higher energy values between *trans* and *gauche*. *Figure 10* shows a single molecule as it passes through a 180° twist boundary whose minimum energy conformation was calculated as described above. In *Figure 10* and the Figures that follow, the molecule is drawn as a ribbon composed of flat, triangular segments defined by adjacent carbon–carbon bonds. The dihedral angle around a bond thus corresponds exactly to the dihedral angle between adjacent triangular planar segments separated by that bond. The ribbon is shown in perspective projection inside a box with transverse dimensions that are proportional to the *a* and *b* axes of the orthorhombic unit cell, and whose four long edges are at the positions of the *c*-axes of the corner molecules in the usual projection of the unit cell along the *c*-axis. The adjacent molecules (not shown) lie along the long edges of the box. Each box accommodates a planar zig-zag chain of 20 carbon atoms, but since half of the first and last atom are outside the ends of the box, only 19 carbon atoms are within the box. Light lines corresponding to the intersection of planes perpendicular to the chain with the faces of the box are drawn at the position of each of the carbon atoms in a planar zig-zag chain. These lines are numbered to provide a distance scale along the chain axis. The central ribbon has the usual crystallographic setting angle of 48° with respect to the *b*-axis. The molecule and surrounding box are drawn in perspective from a reasonably distant view-point. The faces of the box nearest the viewer are surrounded by heavy lines. The interior faces of the box are shaded. A graph showing the accumulated bend is plotted on one face of the box and the accumulated twist is shown on another face. The accumulated bend and twist were computed as described earlier. One edge of the ribbon that represents the molecule is also drawn with a heavy line. In cases in which one edge of the ribbon passes behind the other, the line passing behind is broken. On one surface of the ribbon the triangular segments are marked with dashed lines parallel to the non-bond edge of the triangle while the opposite surface of the ribbon has no such lines.

(*b*) *The 90° twist boundary.* The directions of the *a*-axis and the *b*-axis of the unit cell are interchanged. In the same way as described for the 180° twist boundary, the excess energy of the 90° twist boundary given by subtracting the total planar zig-zag energy in *Table 1* from the total energy of a chain with 90° twist in *Table 1* was found to be $8.91\,\mathrm{kcal\,mol^{-1}}$. The 90° twist boundary has a group of five bonds with dihedral angles that depart significantly from 180°. This group is flanked by a series of bond dihedral angles with small departures from 180°. The departures from 180° approach zero a few bonds away from the twisted group. A drawing of a planar zig-zag ribbon with a 90° twist boundary is shown in *Figure 11* along with plots of twist and bend.

Interaction of twist dispiration loops with twist boundaries

Since there is no low energy vacancy-like defect that can diffuse along a polyethylene chain to bring free volume to the twist boundary, it is necessary to transport CH_2 groups away from this boundary. The dispiration provides a low energy vehicle for this process, but the

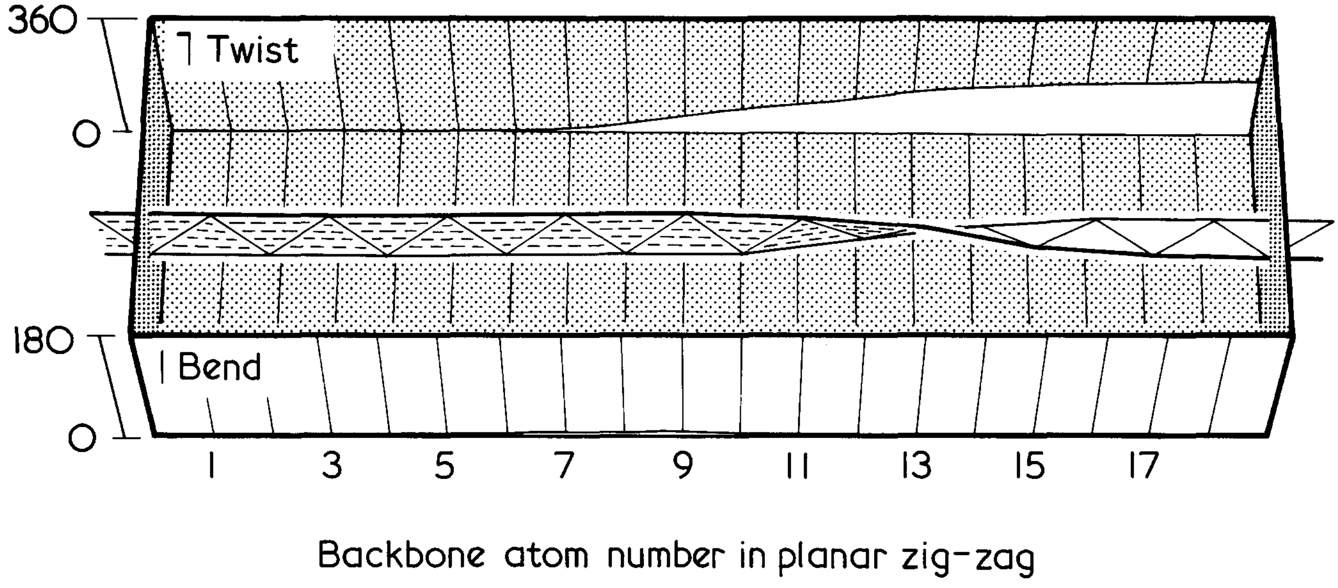

Figure 10 Minimum energy conformation of a polyethylene chain with 180° of twist in a lattice composed of identically twisted chains which pass through a twist boundary

Table 1 Total and excess energies of partial defects

			Energy of central chain		Excess energy over twist boundary		Excess energy over planar zig-zag	
	Surrounding chains[1]	Central chain[1]	Total	Intra	Total	Intra	Total	Intra
1	180° Twist	180° Twist	–38.81	15.69	–	–	15.42	8.74
2	180° Twist	180° Twist + dispiration	–35.09	17.20	3.72	1.51	19.14	10.25
3	90° Twist	90° Twist	–46.02	9.42	–	–	8.91	3.90
4	90° Twist	90° Twist + dispiration	–35.45	17.05	10.57	7.63	18.78	10.10

[1] All chains, central and surrounding, contain 21 C-atoms. For the central chains that contain a twist dispiration loop a surface vacancy is created. The 1.44 kcal mol^{-1} associated with the surface vacancy should be subtracted from the excess energy of the defect in the central chain. Line one describes the 180° twist boundary. The total energy is that calculated for the central chain of the 21 chain assembly. The intramolecular part of the energy for the central chain is given in the columns headed Intra. The excess energy over planar zig-zag is obtained by subtracting the total energy of a planar zig-zag chain (54.93 kcal mol^{-1}, see *Table 2*) from that of a twisted chain of equal length.
In line two a twist dispiration loop with a sense of twist opposite to that of the twist boundary is located at and incorporated into the twist boundary. The dispiration and the twist boundary combine and reduce the sum of their separated energy by about one-half.
Lines three and four provide similar information about a 90° twist boundary and the interaction of a twist dispiration loop with a 90° twist boundary

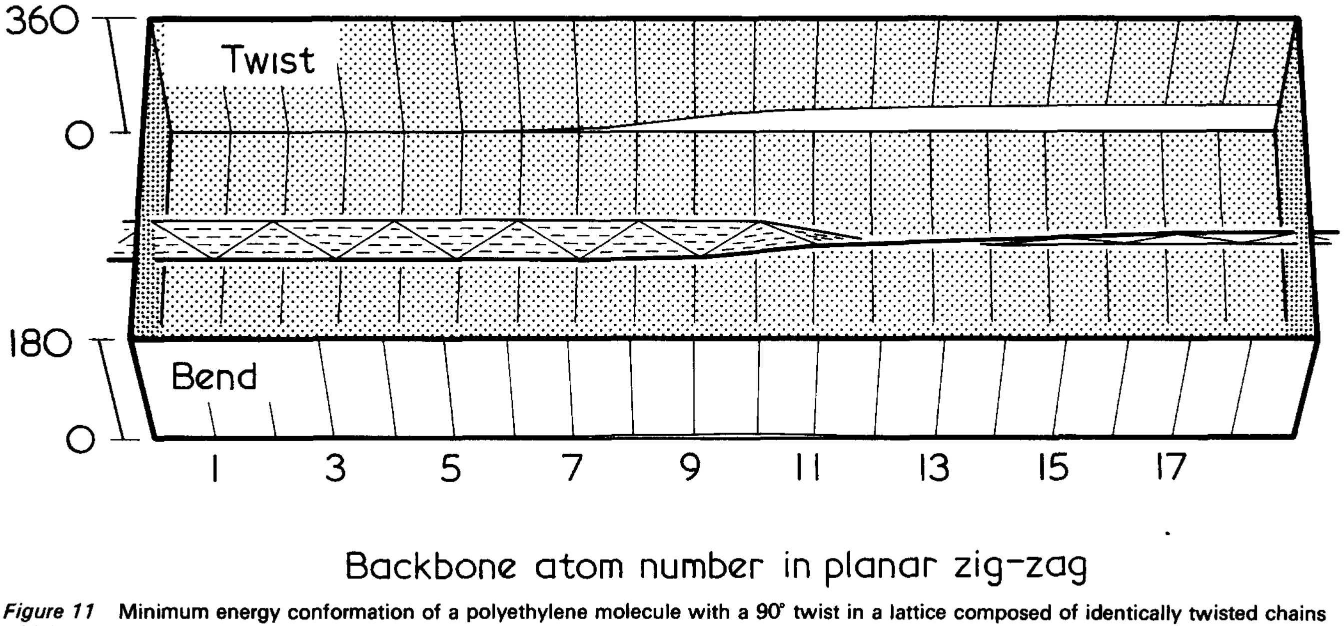

Figure 11 Minimum energy conformation of a polyethylene molecule with a 90° twist in a lattice composed of identically twisted chains which pass through a twist boundary

dispiration must move through twist boundaries.

This process for converting a simple twist boundary to a region of lower density can be described generally as proceeding in the following somewhat artificial sequence of steps. First, a series of dispirations diffuses along the molecules in a way that moves the chain ends or folds originally trapped at arbitrary positions in the lattice to the twist boundary. Second, dispirations move the ends or folds slightly away from the boundary leaving vacancies behind. Third, the conformation of the neighbouring chains relaxes to distribute the free volume of the vacancies and create a layer or more or less disordered chain segments that is often referred to as amorphous material. The artificiality of this description lies in its step-like nature. In fact, all the processes in the three steps proceed simultaneously. All require a mechanism for transporting chains along their axis through both the crystal and the twist boundary. Fischer[20] has recently put forward a model for segregation of defects at boundaries based on spinodal decomposition which does not display the special roles of particular kinds of defects. Dispirations were already shown[3] to be capable of transporting the chains through crystals. Here we calculate the interaction of dispirations with twist boundaries and show that dispirations can move into a twist boundary and lower the energy of the crystal. The twist boundary acts as a weak trap for a dispiration. Thermal activation of a twist boundary containing a dispiration can cause the dispiration to be emitted from the boundary.

(*a*) *Interaction of dispiration and 180° twist boundary.* This was investigated by placing a twist dispiration loop in a $C_{21}H_{44}$ oligomer that also contained a 180° twist boundary. The 'bond driving' method described earlier[3] was used to drive the dispiration toward the twist boundary. The sense of the 180° twist associated with the dispiration was chosen to be opposite that of the twist boundary. *Figure 12a* shows a dispiration and a 180° twist boundary in a polyethylene chain. At the separation of four bonds shown, the defects interact only slightly and each retains its own identity. An intermediate stage of the calculation at which the dispiration has approximately 127° of twist and the twist boundary contains only $-105°$ of twist is shown in *Figure 12b.* In *Figure 12c* the dispiration has moved to the twist boundary. The opposite twists are cancelled but the extra CH_2 carried by the dispiration remains. The resulting conformation can be thought of as a partial dislocation trapped at the twist boundary. The partial dislocation serves the same role of adjusting the spatial phase of the zig-zag of the chain it is in, as the 180° twist boundaries serve in the surrounding chains. Just as the 180° twists cannot diffuse away, because they would rotate the chain to a higher energy setting angle, the partial dislocation is also trapped since it would transport the chain by $c/2$ to a similar high energy position.

The total excess energy of the dispiration and twist boundary shown in *Figure 12a* is 29.17 kcal mol^{-1}. This value, from which an amount of 1.44 kcal mol^{-1} which is needed to fill a vacancy in the central chain must be subtracted, is close to the sum of the energies required to put a dispiration loop and a twist boundary in the crystal, i.e. 27.96 kcal mol^{-1} (see *Tables 1* and *2*). As the dispiration approaches the twist boundary and begins to interact with it as shown in *Figure 12b*, the excess energy drops to 25.40 kcal mol^{-1}. Finally, when the dispiration is incorporated into the boundary as shown in *Figure 12c*, the excess energy drops to 19.14 kcal mol^{-1} as shown in *Table 1*. This is about two-thirds the combined energy of the separated defects. The 10 kcal mol^{-1} drop in energy is only about 2.5 kcal mol^{-1} less than the excess energy of the dispiration.

This calculation shows that a dispiration can move into a twist boundary, and with the addition of a modest activation energy a dispiration in a boundary can move away to either side of the boundary. This provides an important mechanism for the chain transport described earlier that is needed to adjust the density (or free volume) of the fibre in the vicinity of the twist boundaries, the distance between twist boundaries and the amount of twist per unit length of chain.

The interaction of a dispiration and a twist boundary which have the same sense of twist was not modelled in detail. Intuition suggests that this pair of defects would tend to repel each other. However, if a dispiration and a twist boundary of the same sense are forced together the resulting conformation could be described as a disclination (with a twist of 360°) combined with a partial dislocation (with an extra CH_2). The presence of extra free volume as described above would tend to provide the geometric freedom that would allow the 360° twist to accumulate in a single bond dihedral angle and thereby disappear. If the twist disappeared in this way, a partial

Table 2 Energies of crystallographic defects

Surrounding chains		Central chain		Energy of central chain		Excess energy of defect in central chain over planar zig-zag		Energy of surface vacancy[5]
Number of C-atoms	Conformation	Number of C-atoms	Conformation	Total[1]	Intra[2]	Total[3]	Intra[4]	
21	Planar zig-zag	21	Planar zig-zag	–54.23	6.90	–	–	–
21	Planar zig-zag	22	Dispiration	–41.69	16.42	12.54	9.52	1.44
21	Planar zig-zag	21	Disclination	–36.26	18.34	17.97	11.44	–
21	Planar zig-zag	23	Dislocation	–26.54	21.12	27.69	14.22	4.37

[1] The total energy is that calculated for all the interactions of the central chain with itself and the surrounding 18 chains

[2] The intramolecular energy 'Intra' is the sum of the interactions between atoms on the central chain

[3] The excess energy of the defect in the central chain is the difference between the total energy of the 19 chain assembly minus the total energy of the 19 chain assembly with the central chain in the planar zig-zag conformation

[4] The excess intramolecular energy associated with a defect is the difference between the intramolecular energy of the central chain containing the defect and a planar zig-zag central chain

[5] If the dispiration were formed in a 21 carbon atom chain the end of the chain would be pulled into the crystal, leaving a surface vacancy. This is avoided by adding an extra CH_2 group. If the group were not added the energy associated with the surface vacancy would be 1.44 kcal mol^{-1}. Similarly, the energy associated with the vacancy (two CH_2 groups in size) resulting from the dislocation is 4.37 kcal mol^{-1}. These energies not related by a factor of two because the CH_2 near the surface has fewer opportunities to form attractive interactions

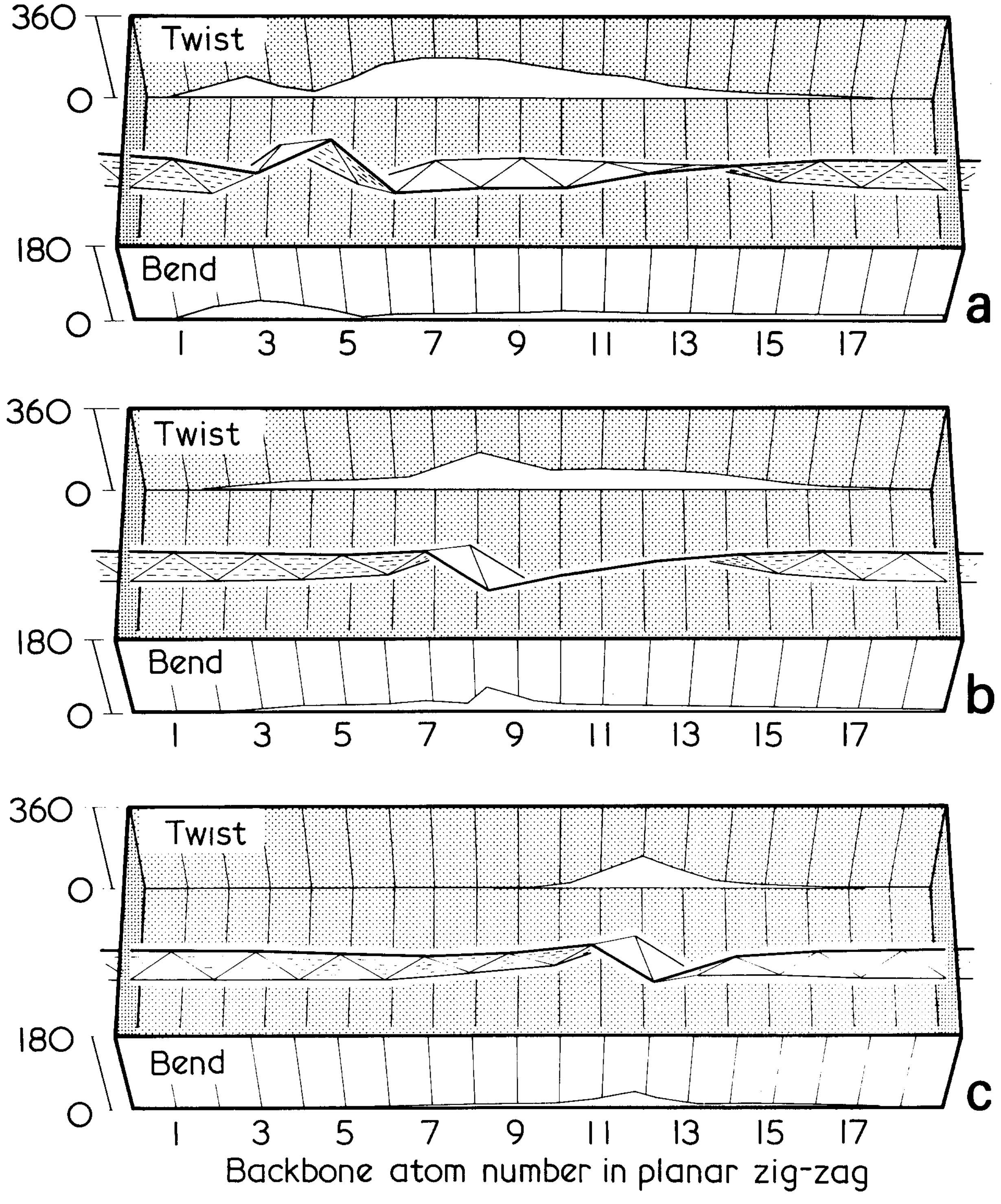

Figure 12 (a) A dispiration and a 180° twist (part of a twist boundary) in a single chain. The two defects are separated by about four bonds. The defects contain twist of opposite sense at this stage, prior to 'bond driving' the dispiration toward the twist boundary, the defects retain their individual identity and interact only slightly. (b) Intermediate stage of the process of driving a dispiration toward a twist boundary. Both defects retain only a part of their twist and the total energy is lowered. (c) End stage of the process. The dispiration is incorporated into the twist boundary, cancelling the twist originally there, lowering the energy and leaving an extra CH_2 group at the boundary. This situation can be described as a partial dislocation at a twist boundary

dislocation would remain at the twist boundary, as for the case in which the defects had opposite signs, although the sequence of conformations and the energy barriers surmounted to reach that case are somewhat different. As more free volume accumulates in the vicinity of the twist boundary the resulting conformational freedom increases the probability that the twist could disappear by a 360° rotation around one bond.

(*b*) *Interaction of dispiration and 90° twist boundary. Figure 13a* shows a dispiration and a 90° twist boundary. The total excess energy of the combination is 22.22 kcal mol^{-1}. This number from which 1.44 kcal mol^{-1} energy vacancy should be subtracted, is in good agreement with the sum of the separate excess energies of a dispiration loop and a 90° twist boundary, i.e. 21.45 kcal mol^{-1} (see *Tables 1* and *2*). *Figure 13b* shows

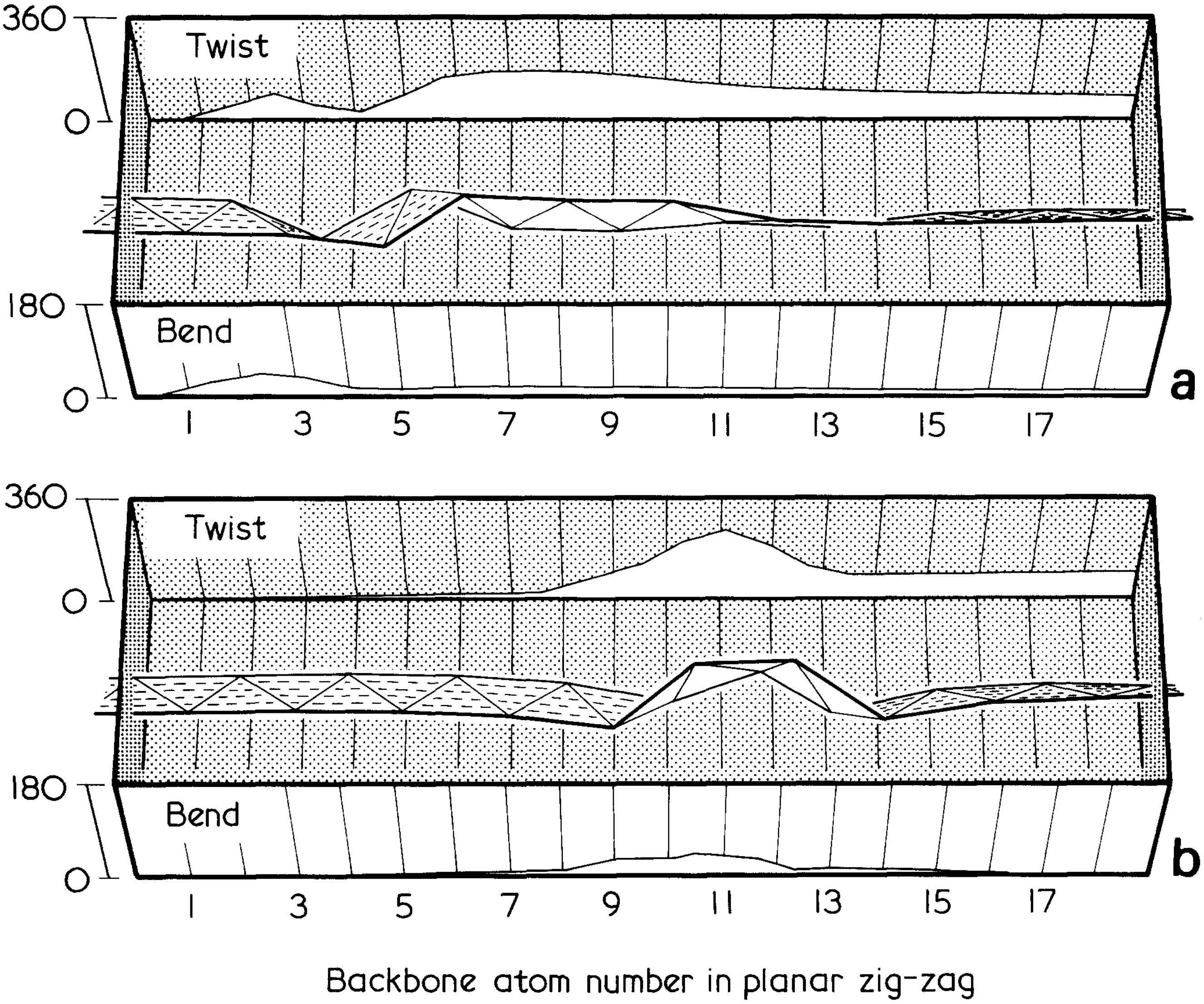

Figure 13 (a) A dispiration loop in a chain that passes through a 90° twist boundary with the opposite sense of twist. (b) End stage of driving the dispiration into the 90° twist boundary. This minimum energy conformation shows a reversal of the initial 90° twist and it contains an extra CH_2 group

the minimum energy conformation of the dispiration in the 90° twist boundary. Since the dispiration contains 180° of twist with a sense opposite to the 90° twist of the boundary, the resulting conformation contains an extra CH_2 and a twist of 90° of opposite sense from the starting twist boundary. The excess energy of the dispiration in a 90° twist boundary is 18.78 kcal mol^{-1} a drop by about 3.5 kcal mol^{-1}. This smaller energy drop which accompanies the mutual dispiration-90° twist interaction as compared to the energy drop for the dispiration-180° twist interaction is associated with the fact that a 90° twist requires much less energy than a 180° twist. The energy of a dispiration at a 90° twist boundary is almost the same as that of a dispiration at a 180° twist boundary. A similar conformation can result from the interaction of a dispiration and a 90° twist boundary having the same sense of twist by a 360° twist around one dihedral angle, but this is a more difficult path to model and the energy barriers may be somewhat higher.

Conformation and energy of disclination

A model of a twist disclination loop was created by placing two partial disclinations with 180° of twist in a polyethylene molecule. The conformation was then allowed to adjust to minimize the energy of the defect. The pseudo-stable conformation with an excess energy of 19 kcal mol^{-1} shown in *Figure 14a* was found. The uniformly distributed twist was concentrated into two localized regions that each contained 180° twist of the same sense and were separated by four bonds in the *trans* conformation. This four-bond segment can be regarded as a stacking fault. Further adjustments of the conformation to lower the energy of the disclination resulted in the conformation shown in *Figure 14b* which had an excess energy of 17.97 kcal mol^{-1} as shown in *Table 2*. *Figure 14b* shows that approximately 240° of the twist occurs in large departures from planar zig-zag of four adjacent bond dihedral angles, two of which are near the *gauche* minimum. The remaining 120° of twist required to complete the 360° rotation is distributed in much smaller rotations around a larger number of adjacent bonds in an asymmetrical way. Starting with a gently twisted conformation which contained 360° of twist equally distributed over 15 bonds led to the same final conformation after energy minimization.

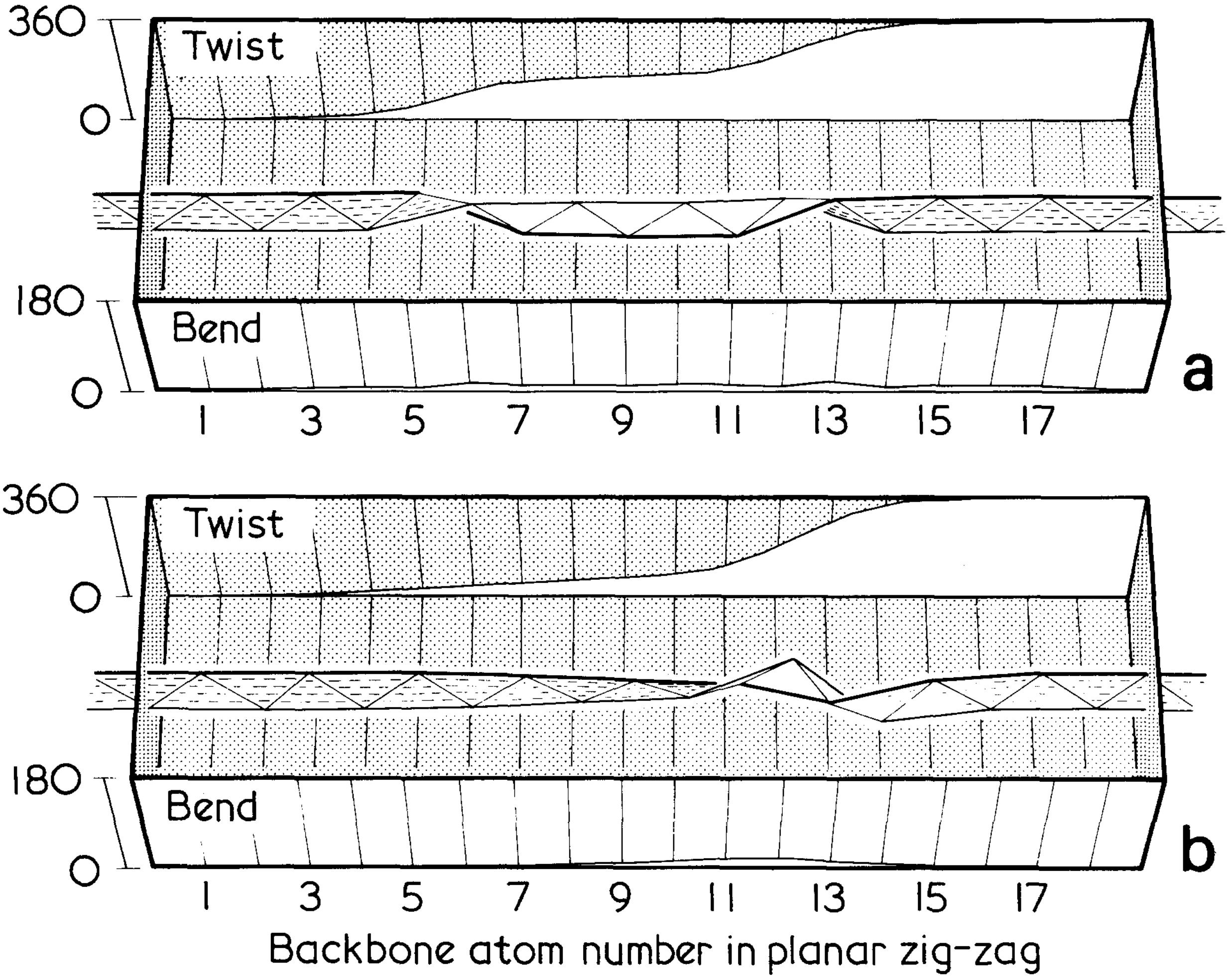

Figure 14 (a) Symmetrical but pseudostable conformation of a disclination created by placing two partial disclinations in a chain. (b) Minimum energy conformation of a disclination. The total twist of 360° is distributed between a compact, distorted region involving about four bonds and a gentle twist spread over a longer segment

Conformation and energy of dislocation

A dislocation loop in an arbitrary conformation was placed near the centre of a $C_{21}H_{44}$ alkane model chain in the crystal model. Adjustment of the conformation to minimize the energy resulted in a conformation which had an excess energy of 27.69 kcal mol^{-1} as shown in *Figure 15* and *Table 2*. Approximately eight adjacent bond dihedral angles underwent large rotations from the planar zig-zag conformation to accommodate the two extra CH_2 groups included in this defect. It is also interesting to note that the molecule twists almost 180° as it enters the defect and then twists back by the same amount so that it emerges from the defect with the initial setting angle, which, of course, fits into the surrounding crystal. The vacancy of two CH_2 groups that would be left at the end surface of the crystal if the central chain were not made 23 CH_2 groups long has an energy of 4.37 kcal mol^{-1}.

Conformation and energy of dispirations

Although the conformation of twist dispiration loops and their energy have been described previously[3], *Figure 16* is included for comparison with the other defects described in this paper and to show the characteristic way that twist and bend are distributed in a low energy conformation of the dispiration. Note that the dispiration increases the twist by 180° and the net bend is zero which shows that the defect is accommodated in an otherwise straight chain. The energy associated with the one CH_2 vacancy at the surface is 1.44 kcal mol^{-1}.

Table 1 summarizes the computed energies for twist boundaries and twist boundaries containing a dispiration. *Table 2* provides similar information for the three crystallographic defects and includes energy values of a planar zig-zag chain for reference. In both Tables the part of the calculated energy that results from intramolecular interactions, including Van der Waals interactions, rotational potentials, bond stretching, and bond deformation energies is listed in columns headed Intra. The remaining energy comes from interactions between the central chain and its neighbours. It is worth noting that the intramolecular energies of the crystallographic defects cover a rather narrow range of values from 9.5 to 14.2 kcal mol^{-1}. This results from the fact that all three defects involve a contiguous sequence of five to seven dihedral angles not at the *trans* energy minimum.

The Appendix Table lists the coordinates that describe the conformation of the various defects described in this paper.

SUMMARY

Analysis of the packing energy of polyethylene chains leads to the proposal that twist boundaries at which each chain is twisted by 90° or 180° about its axis as it passes through the boundary are an underlying cause of the long period commonly observed in polyethylene fibres. The twist may both originate and change during crystallization and drawing. Free volume and non-

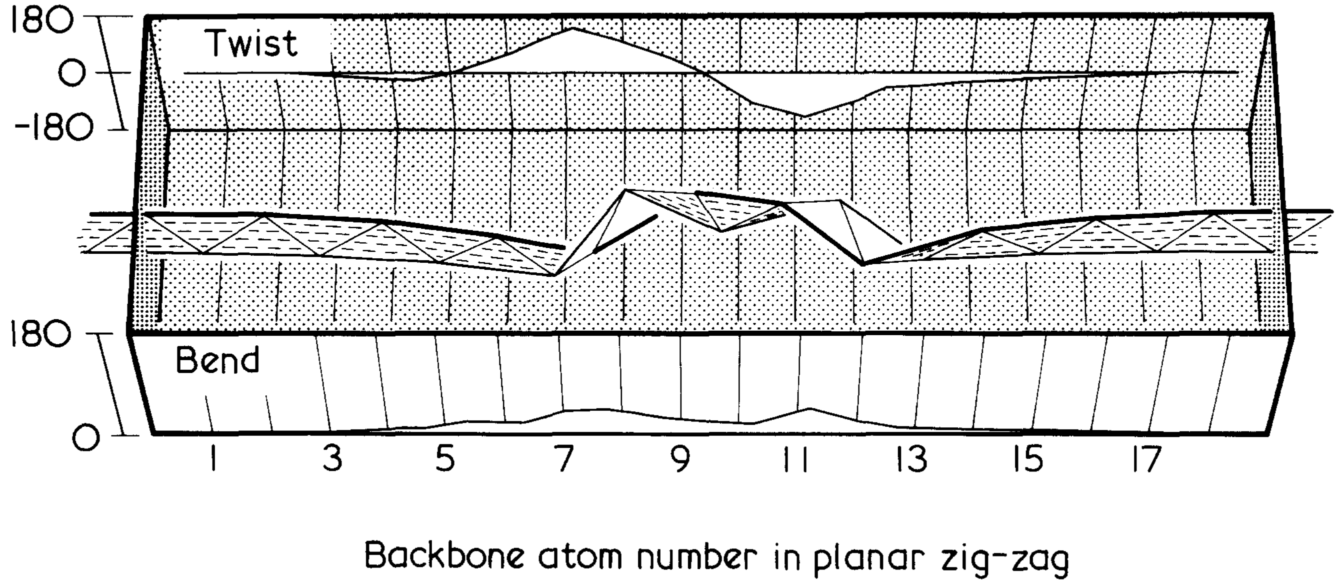

Figure 15 A dislocation in its minimum energy conformation. Local twist at the ends of the defect is of opposite sense and cancels, leaving no twist outside the defect. The dislocation contains two CH_2 groups, that is, one unit cell repeat along the chain axis

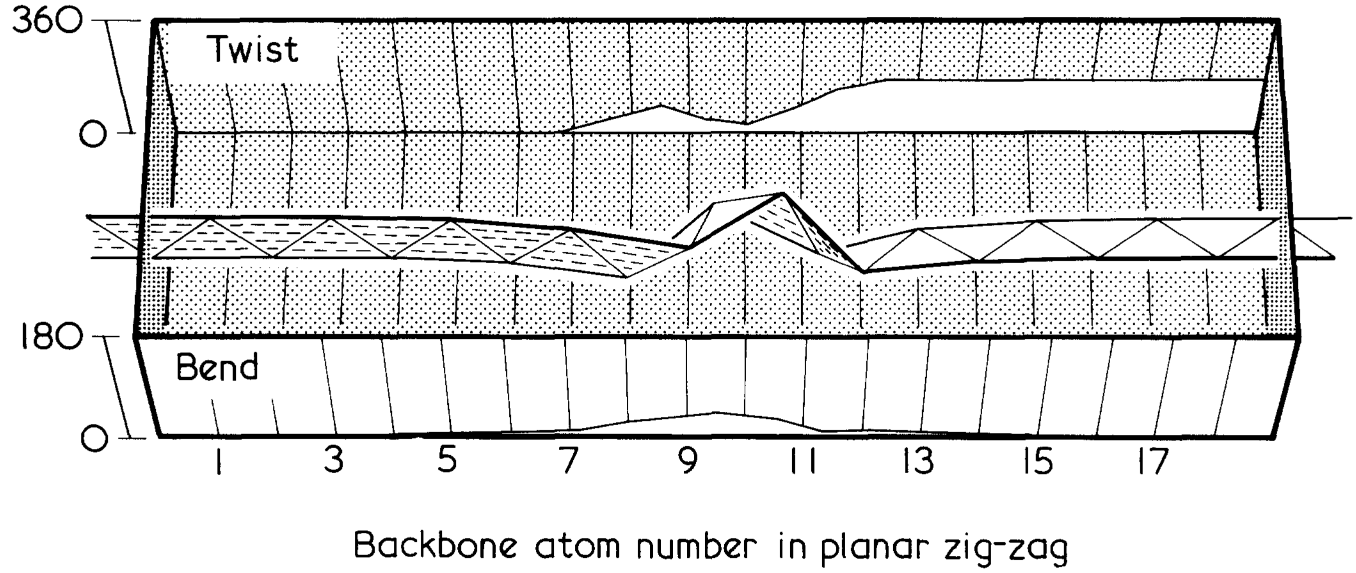

Figure 16 A dispiration in its minimum energy conformation. The chain on either side of the loop is in proper crystallographic register. The dispiration contains 180° of twist (a partial disclination) and one extra CH_2 group (a partial dislocation)

crystallographic chain conformations tend to accumulate at the twist boundaries.

Descriptions of the conformations of the chains are facilitated by parameters called twist and bend which are defined in terms of the Eulerian angles that relate the orientation of chain segments in space. This description is expected to be useful in describing the conformation of molecules with helical structures more complicated than the two residues per turn encountered in polyethylene.

Adjustment of the density near the twist boundary requires the transport of chain ends, folds, and associated vacancies which carry free volume to the vicinity of the twist boundaries. This transport can be accomplished by defects which can diffuse through the crystal. The twist dispiration loop is the lowest energy conformational defect in a single molecule inside a polyethylene crystal. Two other higher energy defects in a chain can also fit into a polyethylene crystal. These are the single chain dislocation loop and the single chain disclination loop, which are described here for the first time for polyethylene. Two partial defects, the partial dislocation and the partial disclination are also described. Partial defects are rejected from crystals because they result in lattice misfits that extend over great distances. Partial defects are a useful concept because they combine in various ways to produce low energy defects. For example, in polyethylene two partial dislocations form a dislocation loop; two 180° partial disclinations form a disclination loop, and a partial dislocation plus a 180° partial disclination form a twist dispiration loop which has a lower energy than either the dislocation or the disclination. The relationships between the three crystallographic defects and the two partial defects are shown schematically in *Figure 1*. Diffusion of a dislocation along the chain transports the chain along its axis. Diffusion of a disclination rotates the chain about its axis. Diffusion of a dispiration both transports and rotates the chain. Partial defects tend to be rejected to the boundaries of crystals or to aggregate in a region of disorder. Partial disclinations can aggregate into twist boundaries. Partial dislocations would tend to straighten out and disappear if they aggregated in boundaries, but a twist boundary can stabilize partial dislocations in a fraction of the chains.

The defects discussed here are characterized by different patterns of bend and twist. For a dislocation, the twist is first in one sense and then the other for a net value of zero. For a disclination, the twist accumulates to 360° which in the lowest energy conformation found is composed of about 180° of gentle twist and equal amount of twist associated with larger dihedral angles at a few bonds. For a dispiration, the twist accumulates to 180° in an irregular way. For all three defects the bend starts at zero and returns to zero as the chain returns to the planar zig-zag conformation of the perfect crystal. The maximal amount of bend is the smallest for a disclination and largest for a dislocation.

The family of defects described here, along with folds, chain ends, and the ordinary edge and screw dislocations that can occur in polyethylene crystals provides a basis for understanding many properties of solid polyethylene. Similar defects appropriate to other crystalline polymers can also be described[21].

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Part of the calculations were based on the 'Molecular Builder' programs provided by R. H. Boyd and is referred to in ref. 3. The algorithm for driving a defect via dihedral angle rotations was particularly useful for investigating defect interactions.

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APPENDIX

To facilitate reproduction of the various defect conformations by readers a Table of the values of the internal coordinates is presented. It is a good approximation to consider that the bond lengths are constant at the value of 1.54 Å. All conformations given here are the minimum energy conformations of the defect in a lattice in which the conformations of the six chains nearest to the defect bearing chain were also adjusted to minimize the energy. The dimensions of the unit cell used are $a = 7.40$ Å, $b = 4.95$ Å with a setting angle of 48°. Bond angle i is centred on atom i and dihedral angle i corresponds to a rotation about the bond connecting atom i with atom $i+1$. The dihedral angle sequence for the 180° twist boundary was 173, 159, 143, 157, 167, 154, 151, 160, 170, 173 and for the 90° twist boundary 173, 162, 143, 158, 173, 174. A constant value of 112° can be assumed for the bond angles.

Bond angles χ and dihedral angles τ for various defects

	Dispiration		Disclination		Dislocation		Dispiration + 180° twist		Dispiration + 90° twist	
Atom	χ	τ	χ	τ	χ	τ	χ	τ	χ	τ
1	112	180	113	178	112	180	112	180	112	179
2	112	180	113	175	112	185	110	179	112	181
3	112	181	113	174	111	186	111.5	183	111	180
4	110	177	113	172	111.5	196	111	179	113	179
5	113	184	113	169	112	183	112	185	110	180
6	110	173	113	165	112	89	109	182	114	175
7	113	185	114	166	111	71	112	186	109	180
8	113	289	112	165	113	115	110	226	115	169
9	111	201	115.5	170	112	294	113	302	114	63
10	111	71	111	168	112	218	111.5	189	112	141
11	112	225	116	141	115	298	111	63	113	57
12	113	289	115	74	112	290	112	143	112	232
13	110	240	115.5	106	111.5	196	109	172	111	287
14	112	186	116	82	113	62	112	172	112	186
15	110.5	176	111	164	109	153	108.5	168	111	170
16	111.5	184	115	184	114	168	111	181	112	183
17	111	179	111	174	109	173	110	179	112	174
18	112	180	112	180	112	171	110	180	112	181
19	112		112		110		112		112	