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Twisting orientation and the role of transient states in polymer crystallization

H. D. Keith and F. J. Padden, Jr.
Bell Laboratories, Murray Hill, New Jersey 07974, USA
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A possible connection is suggested and explored between non-planar crystal habits in banded polymer spherulites and disordered chain folding in polymers crystallized relatively rapidly from the melt. It is proposed that, when lateral growth faces and fold surfaces are not orthogonal (because chain stems are tilted with respect to the lamellar normal), different degrees of disorder develop at opposite fold surfaces. Resulting differences in surface stress give rise to bending moments, but these are likely to be of transient existence. It is shown that, on this basis, an appealingly simple rationale can be developed to account for the complex and hitherto puzzling observations of Bassett and Hodge on polyethylene spherulites, including S-bending and non-uniform axial twisting in lamellae, and also an empirical correlation between these deformations. Much depends, however, upon interactions between interleaved crystals and upon relaxation of bending moments. Existing evidence in support of the rationale is outlined. Implications with respect to polymers other than polyethylene, and to kinetics of crystallization in general, are discussed briefly. Calculations concerning axial twisting under the influence of surface stresses suggest that the twisted crystals incorporate twist boundaries, possibly formed by aggregation of dislocations generated during the growth of what must initially be relatively disordered crystals. The 'chiral' factor determining handedness of twisting in a given crystal is the direction in which chain stems tilt with respect to the lamellar normal.

Keywords Polyethylene; morphology; crystallization; crystal habits; chain folding; surface stress

INTRODUCTION

The aim of this paper is to suggest and explore a possible connection between non-planar habits of lamellar crystals in polymer spherulites and the substantial disorder that accompanies chain folding during relatively rapid crystallization from the melt. The bending, and particularly the twisting, of crystals is considered in the specific case of polyethylene spherulites. However, these considerations have relevant implications both with respect to morphological detail in other polymers and, ultimately, with respect to formation during crystallization of transient states that may complicate interpretation of solidification processes by relaxing before morphological examinations can be carried out.

New aspects of spherulitic morphology in polyethylene

Largely as a result of systematic studies by Bassett and Hodge[1–6] (referred to hereafter as B. & H.), there has developed in recent years a much more detailed appreciation of the variety of morphological forms exhibited by lamellar crystals in melt-grown spherulites of polyethylene. A pattern of considerable complexity has emerged. Except under conditions of extremely slow growth at temperatures $> \approx 127^\circ$–130°C (depending upon molecular weight) the lamellae that first grow radially outward during primary crystallization (called dominant lamellae by B. & H.) show curved cross-sectional profiles, commonly in the form of S-bends as depicted schematically in *Figure 1a*. These lamellae have two remarkable characteristics. (1) Molecular orientation in a lamella appears to be more or less uniform across most of its cross-section and to rotate slightly with the bending of the lamella only near its lateral edges. The 'common' chain axis, *c*, is canted by some $30 \pm 5^\circ$ with respect to the normal to the midsection of the lamella (*Figure 1a*). Moving outward toward either edge, chain orientation approaches parallelism with the local lamellar normal and then begins to cant in the opposite direction; significantly, there are two positions at which the chains are perpendicular to the plane of the lamella. (2) The sense of the S-bend is not only the same for adjacent lamellae in a given region but is related to the sense (handedness) in that region of the twisting of molecular orientation about the radius. (Such twisting underlies the appearance of extinction rings (banding) in polarized-light optical microscopy of polyethylene spherulites.) As B. & H. have expressed it, 'travelling outward, an S rotates so as to scoop up the melt.' In a related study of lath-shaped crystals of polyethylene grown from solution in poor solvents (to simulate habits obtained in crystallization from the melt), Khoury[7] has observed variations in molecular orientation that may be consequences of similar, though seemingly less pronounced, S-bending; he has also recognized a possible connection with twisted habits in melt-grown crystals. However, explanations for S-bending in polyethylene crystals and, in particular, for the observed correlation between such bending and the handedness of twisting orientation in polyethylene spherulites, have not yet been proposed.

Disordered chain folding: theoretical assessments

Recent neutron-scattering studies (for a review, see Sadler[8]) and revisions of relevant theories[9] have led to a

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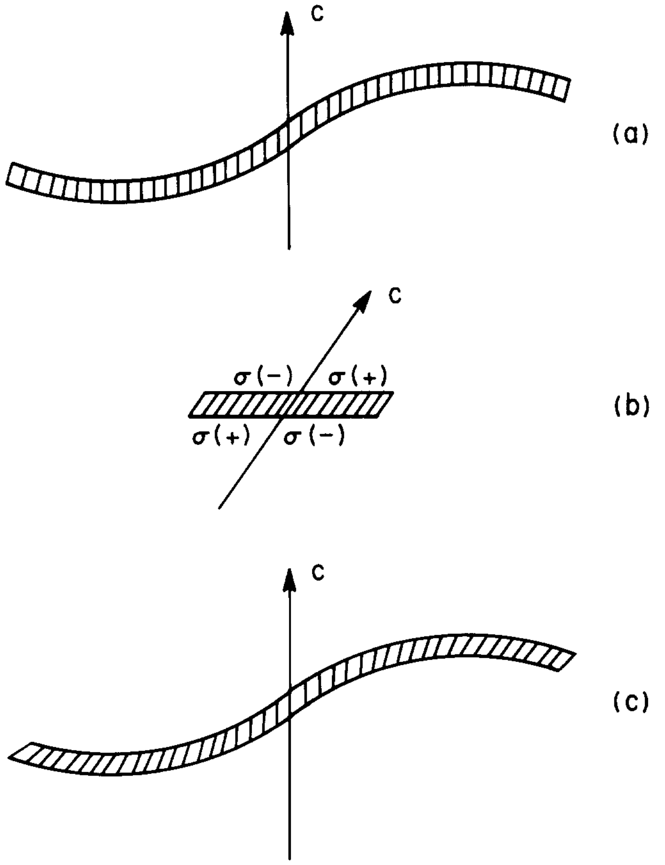

Figure 1 Cross sections of lamellar crystals of polyethylene (schematic). In each case the arrow c denotes the molecular orientation at the central axis and the short lines indicate molecular orientation at various positions off-axis. (a) The situation as described by Bassett and Hodge on the basis of experimental observation; (b) a flat lamella with canted chains; and (c) a crystal elastically bent before molecular shearing (see text)

re-evaluation of factors thought to cause chains to fold, and to govern the regularity with which they fold, during crystallization from the melt. It is now generally believed that such folding is not nearly so regular, with respect either to adjacency of re-entry of chains into crystals or to tightness of molecular loops at fold surfaces, as was once supposed by many workers.

A significant change of emphasis is that, under conditions such that banded spherulites are formed in polyethylene (i.e., mostly Regime III crystallization[9]), growth fronts are now considered to be relatively rough on a molecular scale. The average separation between 'niches' (the polymer analogue of kink sites in more conventional crystal growth) is estimated to have shrunk to a length only a few times the width of a molecular stem. Temperature dependence of growth rate would still be governed as before by primary nucleation of chain stems on flat surfaces, that is, by events not involving niches. It is energetically favourable, however, for most chain stems to deposit at niches, as this minimizes creation of new surface. The abundance of these niches, in combination with a large driving force provided by substantial supercooling, invites deposition with loosely looped folds and non-adjacent re-entry on a large scale. That there would still be a predominant tendency for adjacency of re-entry (the probability is estimated to be approximately two-thirds) now arises through consideration of 'gambler's ruin' statistics as applied to chains emerging from crystal surfaces[43]. This is, in effect, a mechanistic expression of two fundamental ideas first advanced by Frank[10] in 1958, and further elaborated by him more recently[11]. These are (1) that emergence of chains from the surface of a 'fringed micelle' crystal of polyethylene would create impossibly congested molecular packing on the 'amorphous' side of the phase boundary, and (2) that there is significance to the fact that fold periods are commensurate with root-mean-square end-to-end lengths of coiled chains in the melt. Currently, it is generally believed that, during relatively rapid crystallization from the melt, coiled and interpenetrating molecules condense on growth fronts predominantly in folded conformations, and that a key factor promoting chain folding and governing its regularity is congestion at fold surfaces.

Such overcrowding at fold surfaces is likely to be severe, not least because of considerations which appear to have been generally overlooked. Permitted degrees of disorder in chain folding are limited more stringently in already-grown regions of a lamellar crystal than at, or very close to, an edge where it is still growing. The reason is that, whereas chains emerging from the middle of a fold surface are surrounded *on all sides* by other emergent chains competing with them for space, chains emerging from stems in or very close to a growing edge are subject to severe competition for space *only on the crystal side of the edge*. With rapid growth, initial attachment of chains at the edge is likely to involve substantial disorder in terms of contour lengths and disposition of folds. It might even involve a degree of disorder greater than could be tolerated in the body of the crystal after further growth. In such a case, growth in a steady state would then involve a dynamic balance between processes of molecular attachment and molecular rearrangement behind the growth front, the latter being needed to adjust fold surfaces to attain tolerable packing densities. (This point and its possible relevance in terms of crystallization kinetics is considered later). For present purposes it is sufficient to note that, in crystals formed during crystallization which is rapid in relation to molecular transport in the melt, fold surfaces may well be overcrowded to a degree close to the tolerable limit; they must, in any event, be under considerable compression in their own planes. However, the experimentally well-established process of isothermal thickening after crystals are formed[12,13], a process which involves longitudinal motion of chain stems and readjustment of folds, implies that initially severe congestion at fold surfaces is likely to be relieved considerably by subsequent relatively slow molecular rearrangement.

As already indicated, the aim here is to explore a possible relation between bent and twisted crystal habits in polyethylene spherulites and surface stresses attributable to disordered chain folding. A rationale is presented that leads to appealingly simple explanations for several prominent but hitherto puzzling morphological observations, some of them pre-dating the work of B. & H. by many years. Some of the experimental results that appear to support this rationale are presented but more detailed discussions of experimental evidence will be published later. It is emphasized that this rationale is based upon a *novel postulate* which has not yet been tested directly; indeed, it is not obvious how it could easily be tested by *direct* experiment. Although polyethylene specifically is considered, this being the polymer for which available experimental evidence is presently most detailed, a brief indication is given of how the ideas developed might be relevant to interpretation of crystalline morphology in other polymers crystallized from the melt.

STRESSES AT FOLD SURFACES IN LAMELLAR CRYSTALS

That appreciable compressive stresses probably occur within disordered fold surfaces of polymer crystals has long been recognized, but hitherto it has been assumed implicitly that opposite fold surfaces of a lamella are stressed equally. Stresses of this type have been invoked, indeed, in earlier attempts to explain twisting orientation on the ground that a lath-like lamella so stressed, as with a heated trimetallic strip of symmetrical design, could become mechanically unstable and might buckle or twist[14]. Similar models have also been discussed in terms of stresses arising in other ways but still with symmetry with respect to opposite faces[15]. However, calculations carried out recently by the authors in collaboration with Dr T. T. Wang show conclusively that, with any reasonable choice of relevant parameters, it is impossible to account in these ways for the very rapid rotation of orientation commonly observed along radii in polyethylene spherulites. It is noteworthy also that the bending of a lamella would do nothing overall to relieve compressive stresses at fold surfaces if these are equal in magnitude on opposite sides of the crystal. The point of view developed in this paper is that stresses at opposite fold surfaces may initially be different.

Consider a lath-like polyethylene crystal for which the long axis is [010] and the chains are canted in the *(hOl)* plane by ≈35° with respect to the lamellar normal so that the fold surfaces are close to (201) in orientation. This is then a close approximation both to the crystals reported by Khoury and to axial regions of dominant lamellae as described by B. & H. The reason for the canting of chains is that folds are staggered, a feature that in one form or another is general in polyethylene crystals. Staggered folding occurs even in crystals grown very slowly from dilute solution, irrespective of the nature of the solvent, and appears to reflect an influence of repulsive interaction between folds that is felt even with optimally ordered folding. The orientations of fold surfaces vary but in elongated crystals something close to (201), though not unique, is relatively common.

Continuing growth in a spherulite of such a crystal would occur primarily at the end, and all indications are that this growing end would narrow down in some way to a leading tip. The crystal would certainly not be square-ended because that would imply molecular folding on (020) planes, a situation which is unknown in polyethylene crystals whatever the conditions of their growth or their habit. It is known that the crystals grown from dilute solution in a poor solvent (dodecanol) by Khoury terminate fairly abruptly in {110} planes which meet at growth tips at angles of ≈120°; also that crystals grown from more concentrated solution in paraffinic solvents narrow more gently to tips, either by curving smoothly under some conditions of growth or by becoming microfaceted (alternating (110) and (200) growth faces) under other conditions of growth[16,17]. Regardless, then, of whether the growing end of the crystal curves to a tip as represented later in *Figure 5*, is microfaceted, or simply bounded by {110} planes, a transverse cross-section through this tapered end can be represented schematically as in *Figure 1b*. The inclined narrow edges of the section are traces of the growth faces which, unless they happen to be (200) facets, have been cut obliquely.

The significant point to be made is that the two edges of each growth face, which lie in opposite fold surfaces, are *not equivalent*, one lying at the apex of an acute and the other at the apex of an obtuse angle. This indicates unequivocally that, as the growth face advances, the conditions under which folds are formed at the two fold surfaces are different. It is evident, therefore, that when molecular stems are inclined to the lamellar normal, the conditions under which folds are formed at a growth face in a polymer crystal are *necessarily* different at opposite fold surfaces unless the plane of the growth face and the plane of the lamella are orthogonal.

To introduce the novel postulate it is assumed that the different conditions obtaining during the formation of opposite fold surfaces lead to a difference in degree of congestion and, hence, in the magnitude of compressive stress, initially incorporated in these fold surfaces during rapid crystallization. The ways in which such a difference in congestion might arise are discussed in Appendix 1. From these considerations, greater congestion is expected to occur in a fold surface that meets a growth face at a protuberant acute angle. Such an assessment, indeed, appears to be confirmed by the two cases, polyethylene[4] and α-polypropylene[18], for which there is evidence for a correlation between canting of chains and curvature of crystal. On this basis, the fold surfaces in the crystal represented in *Figure 1b*, would have developed greater compression at the surfaces marked σ (+) and less compression at those marked σ (−). The difference between the associated stresses would give rise to bending moments about axes lying in the plane of the crystal. (Note that the sense of these bending moments is reversed on opposite sides of the central axis). For simplicity in the discussion that follows the ordered cores of lamellar crystals are initially considered to be otherwise unstressed and to have relatively perfect lattices. Questions relating to fine detail, such as internal stresses due to small mismatch in lattice spacing between fold and non-fold planes of the same {*hkO*} set, and mosaic block substructure, are considered later.

BENDING MODES RESULTING FROM SURFACE STRESSES

If bending moments are produced as suggested, the lath-like crystal the cross-section of which near its growth tip is as represented in *Figure 1b* will develop S-bending as shown in *Figure 1c*. Radii of curvature in the S-bent lamellae of B. & H. are ≈1–2.5 μm and it is simple to calculate how large a stress differential at fold surfaces, $\Delta\sigma = \sigma(+) - \sigma(-)$, would be required to produce curvature of this magnitude. This is given by $\Delta\sigma \approx Et^2/6\rho\Delta t$, where E is Young's modulus of the crystalline core of thickness t, ρ is the radius of curvature and Δt the thickness of each fold 'surface'. Taking $t = 200$ Å, $\rho = 1.5$ μm, $\Delta t = 15$ Å, then $\Delta\sigma/E = 0.03$. Expressed in terms of the modulus of the core, this means a difference between compressive strains in the two surfaces of ≈3%, a substantial but not unreasonable value if the more congested fold surface is overcrowded to something close to the tolerable limit. The corresponding elastic strains in the crystalline core at the interfaces with the fold surfaces would be approximately $\pm 0.7\%$.

In terms of molecular orientation, the elastically bent crystal described is different from those observed by B. & H. It is now necessary to consider what is likely to happen if, subsequent to its growth, there are molecular rearrangements within the crystal.

Even before appreciable thickening has occurred, surface stress will probably relax, principally at the more highly stressed surface, so that stresses at the two fold surfaces will tend to equalize. As the bending moment is reduced, the bent crystal core will also endeavour to relax i.e. spring back to bring slightly divergent chain stems into parallelism. This could be accomplished most easily by the crystal flattening out as it would be free to do if, for example, it had been grown from dilute solution and were still suspended in solvent. However, if it is embedded in viscous melt, and possibly constrained also by neighbouring crystals in a spherulite, it is more likely to adopt a different mode of deformation. Diverging chain stems in the bent lattice could approach parallelism, but without significant change in the overall S profile if, as a consequence of their longitudinal mobility, they were to shear past one another and folds were to readjust accordingly. Assuming such shearing to progress outward from the axis of symmetry, the situation would be close, in essential detail, to that found by B. & H. This, however, is a much oversimplified description of what would have to be a complicated process, but it does highlight the essential elements of the viewpoint developed here.

In the present context, this viewpoint does not necessarily differ as markedly from that of B. & H. as at first may appear. They have discussed the growth of their S-bent crystals as combining shear through staggered folding with some elastic bending imposed near the outer edges by unspecified external forces[4]. The latter contribution is regarded as minor as its effects are often imperceptible until the crystal has curved beyond the point at which molecules are oriented parallel to the local normal to the lamella. The forces would be identified here as arising at fold surfaces, emphasizing that there is elastic bending followed by shearing rather than growth of a crystal that is sheared *ab initio* by staggered folding. Shearing as B. & H. have proposed would require an occasional irregular staggering of folds but, to cause curving of profile, one that would have to become more frequent at points further and further removed from the axis of the crystal. Although such staggering, which can be regarded as a shearing from the (201) habit, might be induced by the same considerations that lead to the expectation of different stresses at opposite fold surfaces (see Appendix 1), it would tend to aggravate surface congestion and, if anything, become self-limiting.

However, there are also other considerations. Curvature beyond the point of zero canting angle is shown in the micrographs of B. & H. only for S-lamellae 2.5–3.5 μm wide and grown at 128.1°C. It appears that their detailed assessments of molecular orientation have been made mostly with these wider lamellae. Lamellae in banded spherulites are shown as being ≈ 1 μm wide and as not curving far enough to reach, or at least to pass appreciably, such a point of zero canting. The two situations are distinguished, therefore, by differences in range of angles covered in S-profiles and in rate of isothermal thickening. At 128.1°C, rates of crystal growth ($\approx 10^{-6}$ cm sec^{-1}) are slow enough for appreciable isothermal thickening to occur close to the axis near a growing tip (such as in *Figure 1b*) even while the edge of the crystal at that position is still growing. However, in banded spherulites, inevitably grown at temperatures $< \approx 123$°C where growth rates are much faster and thickening much slower, this is certainly not the case, although some relaxation of surface stress might take place in the interval between growth occurring and morphology being studied. With S-bent crystals grown at 128.1°C, therefore, thickening is a factor which must also be considered on either interpretation (by B. & H. or here).

When such thickening occurs, there must either be an overall lateral contraction of the crystal, an introduction of new material from the surrounding melt or the formation of vacancies. The first seems unlikely, particularly as there is strong evidence that the second and third processes can occur with facility. The diffusion of new chains into one crystal from disordered material at the fold surface of a neighbouring crystal during annealing is known[19]. Further, thickening must involve fairly frequent events in which chain ends pull through and out of the crystal so that neighbouring stems can lengthen appreciably, thus creating line vacancies, i.e. vacant stem sites. (With crystals supported on substrates sizable voids even develop during thickening[20]). Vacant stem sites would afford an efficient means for relieving the very considerable surface stress that would otherwise make a crystal the chain stems of which are orthogonal to fold surfaces appear energetically most unfavourable. On this basis, the *post facto* shearing of a thickening crystal into a zero canting situation need not involve an increase in surface congestion at all. Formation of such vacancies, in large and increasing numbers at the growth face itself during its advance would, however, seem unlikely.

The principal objection to the interpretation of B. & H. is that, without some such creation of vacancies at growth faces, it is difficult to see how a crystal would grow smoothly and spontaneously into what seems an energetically most unfavourable situation and then continue to grow out of it again. Using the interpretation proposed here, the problem is less significant because, at worst, chains would be considered at some points to be forced into energetically unfavourable situations when even less favourable situations relax. Some elements of both interpretations may contribute but, for reasons that are clarified later the dominance is emphasized of the role of substantial bending moments which may subsequently relax, these bending moments arising because of disparity between stresses at opposite fold surfaces.

Speculative discussion of how the extensive shearing between conditions as represented in *Figures 1c* and *1a* might take place when bending moments relax is not directly relevant here; therefore, only the major points are described briefly. The driving force is the relief of elastic strain in the crystalline core which permits neighbouring chains to align themselves, for the most part, in parallel orientation. Elastic energy is not involved alone as thickening (a thermally activated process) contributes also. The relaxed crystal might be expected to break up into misaligned mosaic blocks but, because of highly disordered folding, there are no well-defined fold planes for 'cracks' to form between blocks without them being copiously stitched together top and bottom by molecular loops. Considering the large molecular mobility and extensive molecular re-folding implied by the very existence of the thickening process, it is believed that there are repeating series of coupled small realignments, probably not well co-ordinated except in the statistical sense that there is a drive toward overall alignment of chains. The anchor point defining the orientation toward which all chains tend to align would be near the central axis. The rotation required, and the amount of shearing needed to maintain relatively smooth (at least not grossly stepped) fold surfaces, both increase away from the axis. This would be a decelerating process and may account for residual bending at the edges of partly relaxed crystals.

TWISTING AND ITS RELATION TO BENDING MODES

In addition to the transverse components of surface stress which, it is suggested, are the primary cause of S-bending in a polyethylene crystal of the type considered here, there would also be substantial longitudinal components. In general, these would be different in magnitude from corresponding transverse components, but it is assumed that they are also different at opposite fold surfaces, the inequality being in the same direction as for transverse components. If the crystal is 'symmetrical'*, these axial components of surface stress would tend to bend the two halves of the lamella into arcs around transverse axes, convex upward in one half and concave upward in the other (see Appendix 2, *Figure 8*). Such latent bending is, of course, frustrated by the two equal halves being joined along a (straight) central axis where opposed bending moments cancel. Even in the absence of transverse stress components, the influence of which are presently disregarded, likely response to opposed bending moments about transverse axes is not so immediately obvious as was S-bending under the influence of bending moments about longitudinal axes. Provided there is no instability with respect to buckling, it is evident that the middle section (i.e. remote from either end) of an isolated lath-like crystal would remain flat but, as shown in Appendix 2, its ends are likely to twist. When there are bending moments acting *simultaneously* about longitudinal and transverse axes, S-bending of transverse profile throughout the length of the crystal and super-imposed twisting near its free ends would be expected.

That this is an accurate assessment can be shown by model experiments carried out as follows. Strips (usually 1.5–3.5 cm in width) of thin (0.8 mm) neoprene rubber are coated equally about their long axes (one half on one side, the other half on the opposite side) with a thin film of poly(acrylic acid) from a 3% solution in methanol, and then immersed to various depths in a swelling solvent (commonly 1 part trichloroethylene and 2 parts toluene). The coating acts as a barrier to diffusion and solvent, therefore, enters and swells uncoated surfaces preferentially, thereby creating surface stresses (isotropic in this case) and bending moments that simulate closely the situation assumed to exist in 'symmetrical' lath-like crystals of polyethylene.

Figure 2 shows different views of a 2.5 cm strip after having been immersed to a depth of 5 cm for 75 s. The stressed portion shows both S-bending and torsion about the long axis. In transverse cross-section, it gives a reasonable representation, on a scale of approximately 1 cm:1 μm, of corresponding cross-sections of polyethylene crystals as shown by B. & H. (see, for example, Figure 5 of ref.4). In addition to the S-bending there is in this case axial twisting by ≈45° with respect to the plane section which had not been immersed. (As shown later, this rotation is in relatively good agreement with calculated values for this case.) Similar strips, when coated in the same way and then totally immersed, show only S-bending in their midsections, as expected; superimposed axial twisting is confined to regions near their ends and, predictably, is oppositely handed at opposite ends. When such strips are withdrawn from the solvent before S-bending is extreme and cut across midsections, the newly formed ends then twist with opposite handedness, a response again emphasizing that with symmetrical lamellae twisting is confined to regions near free ends.

The bending and twisting of rubber strips has been examined in detail but remarks here are confined strictly to what is needed in the present context.* First, it is emphasized that the ends of these S-bent strips twist as does a drill bit i.e. in the same sense as B. & H. have observed in polyethylene crystals. Secondly, it does not make much difference whether the end of a strip is cut squarely or cut to a V-point; only when the angle subtended at the V is less than a right angle does the pitch of the twisting begin to diminish appreciably. Curved spearheads also twist significantly provided they do not come too sharply to a point. The ends of these 'symmetrical' twisted strips of various shape obviously have the character of right helicoids, though not necessarily of constant pitch.

It is clearly apparent in these cases how the handedness of twisting is decided. Translated in terms of polyethylene crystals for which the strips are models, this handedness is governed by the directions in which chain stems are canted with respect to lamellar normals. Most significantly, it follows that, if growing lamellae proliferate (branch) in spherulites through the agency of screw dislocations, continuity of crystal lattice demands that daughter lamallae must inherit from their parents, without change, their orientation, their direction of chain canting, and the handedness of their twisting. It is believed that this may provide an important insight into the co-operative nature of twisting in polyethylene spherulites. It is known that right- and left-handed twisting occur equally on average, but that there are distinct sectors in which twisting with one or other hand dominates; this particular hand, moreover, is preserved indefinitely along a given radius[21].

Thus far, only the behaviour of crystals which have grown 'symmetrically' has been considered. In practice, a lamella in a spherulite might well develop a lopsided shape by growing more rapidly at one side than the other in response, for example, to diffusive processes in the melt or to impingement upon neighbouring crystals. In such an 'asymmetrical' lamella it would be anticipated, from an

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* The term 'symmetrical' is used here, and frequently in what follows, to describe a crystal that, except for the canting of chain stems and growth faces, has grown equally on the two sides of a central axis

* Reproducible behaviour, which includes the twisting described, requires that these experiments be carried out within a few hours of coatings being applied. The coatings then retain some plasticity, which protects against cracking or weakened adhesion when later immersed in solvent. Without these precautions another mode of deformation is observed at times, particularly with deeper immersion, in which S-beinding only is found throughout the length of the strips. It appears that this occurs when S-bending is initially faster in some regions than others, presumably because the coating has cracked under stress or lost adhesion to the rubber. Pronounced S-bending increases torsional stiffness and it appears that this can in some cases frustrate twisting

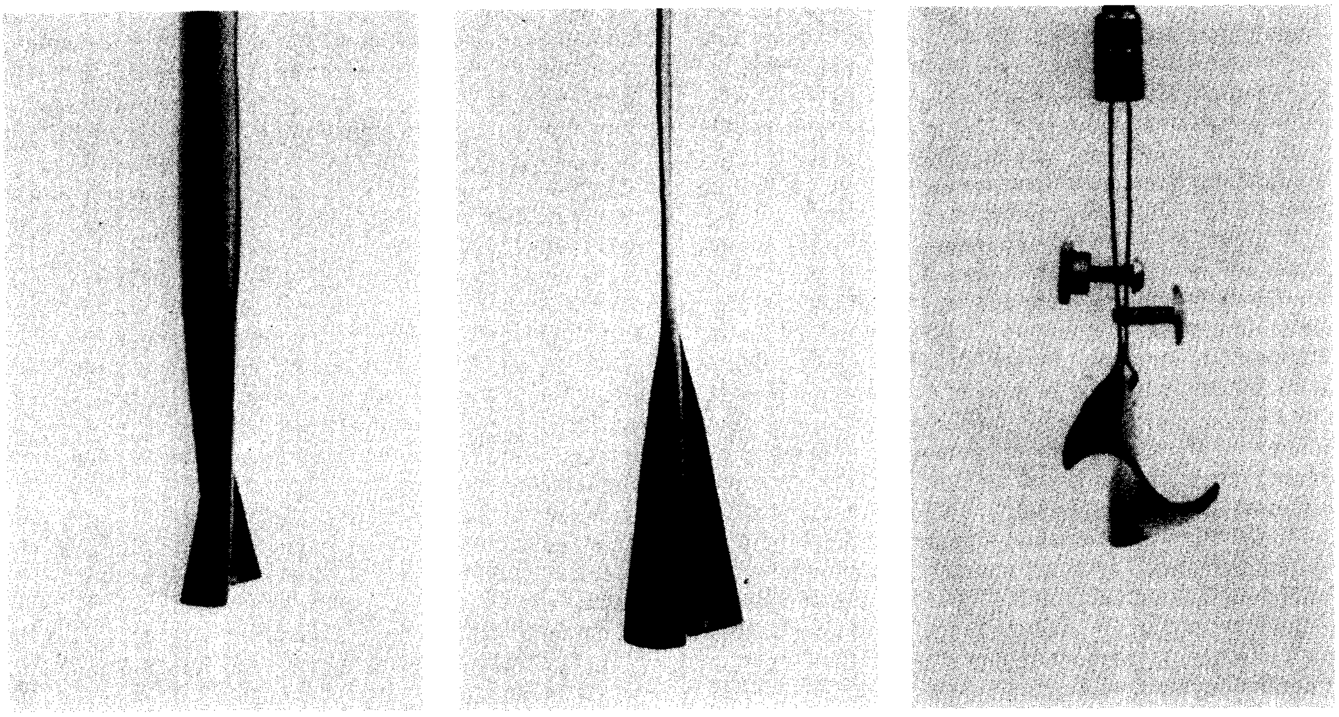

Figure 2 Three views of a rubber strip after partial immersion in a swelling solvent. The strip was coated so that surface stresses developed in a manner simulating those postulated in a 'symmetrical' lath-like crystal (see text). The strip is suspended vertically in two views and held horizontally, with the undeformed section in a vertical plane, in the third. S-bending and helicoidal axial twist at the end are both clearly evident

extension of earlier arguments, that it would bend into an asymmetrical S-profile i.e. one reaching out further from the point of inflection in one direction than the other. (Many examples of such a profile are evident in electron micrographs published by B. & H.). The imbalance between bending moments about transverse axes in the two unequal 'halves' of such a lath would then be expected to twist it into a helix, rather like a tape wrapped as a lazy spiral around a cylindrical mandrel. Experiments with rubber strips coated asymmetrically to simulate such a case confirm this assessment (*Figure 3*). The handedness of twisting, as previously, would be pre-determined in the crystal by the canting of chain stems.

However, there are two important differences between helicoidal twisting near the tip of a 'symmetrical' lamella and helical twisting of an 'asymmetrical' lamella. First, helical twisting will occur *throughout* the length of an 'asymmetrical' lamellar lath, whereas helicoidal twisting in a 'symmetrical' lath appears, in the first instance at least, to be confined to the region near a free end. Secondly, helical twisting can easily achieve a much smaller pitch than helicoidal twisting. This is not only evident from the model experiments, but easily confirmed by manually twisting a strip of rubber or thin metal while, in one case, permitting axial contraction and, in the other, preventing it. Indeed, a helicoid under torsional stress, given the opportunity, will readily relax into a helix. Twisted lamellae in polyethylene spherulites often do appear wavy, i.e. to have slight helical rather than strictly helicoidal character (see, for example, Figure 7 of ref. 6 and Figure 6 of ref. 16), but there should be caution in making inferences from this observation.* Volume contraction accompanying secondary crystallization will tend to cause axial contraction in twisted dominant lamellae; consequently, it is not possible to establish *ab initio* whether they first grew 'asymmetrically' as helices, or 'symmetrically' as helicoids. In later discussions 'symmetrical' lamellae are examined in detail as these represent the most difficult case to consider, both in terms of accounting for progressive twisting throughout a spherulite (see later) and in terms of their resistance to torsion.

It is relevant in a broader context to consider the behaviour of rubber strips coated completely on one

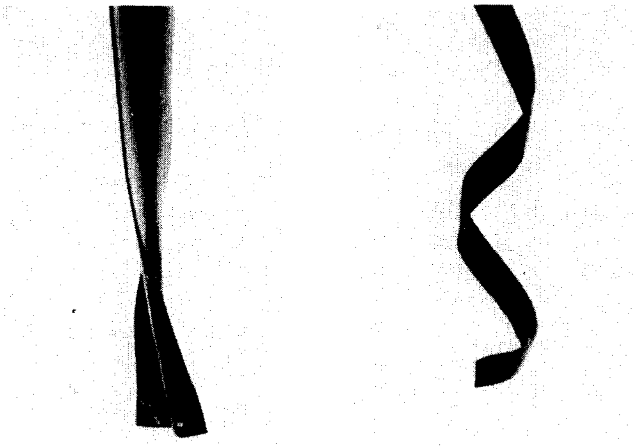

Figure 3 End sections of rubber strips after deeper immersion than in *Figure 2*. The strip on the left was coated so as to simulate an 'asymmetrical' lamella and shows both asymmetrical S-bending and extended helical twisting. That on the right was coated on one side only and shows marked helical twisting (see text)

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* To some extent, irradiation damage can influence such observations. That the waviness is real, however, is evident from its appearance also in surface replicas of unirradiated specimens

surface only. When immersed in a swelling solvent, these simulate stressed lamellae in which chain stems are canted, not in the plane transverse to the growth direction, but toward the growth direction. At least two well-documented cases of this type arise in banded spherulites of aliphatic polyesters, and with the attendant complication that lamellae with opposite directions of canting appear to be interspersed approximately randomly[22]. In a swelling solvent that provides neutral buoyancy, strips coated on one side would obviously tend to roll up lengthwise. When suspended in less dense solvent, however, they rapidly wind into helices which can be of relatively short pitch (*Figure 3*); the handedness of twisting appears to be a matter of chance although, doubtless, it does respond to hidden geometrical imperfections or fluctuations in uniformity of swelling. For present purposes it is noted only that a lath subjected uniformly to a bending moment about a transverse axis, and under slight axial tension, is prone to helical twisting with a handedness that can go either way depending upon the chance factors that start it off. (As the specific volume of the melt is usually larger than that of the crystalline phase, dominant lamellae as they advance in a growing spherulite must experience some axial tension.) It should also be noted that lamellae of the type described would be likely to have C-shaped cross-sectional profiles. C-bent lamellae have been seen by B. & H. in polyethylene along with more common S-bent crystals. A possible explanation for these could be a growth habit (without precedent in solution-grown crystals of this polymer) in which there is but one (110) growth plane slanted across a growing end.

It is noteworthy that although long lath-like crystals are referred to throughout this paper, this does not imply that individual dominant lamellae in a spherulite extend continuously as discrete entities from their points of origin (the nucleus or, more generally, branch points at which they multiply) to the outer boundary. In a competitive growth regime some dominant lamellae may encounter barriers to further growth, for example through impingement upon other lamellae in a somewhat disordered array, while their neighbours continue to advance[6]. Provided that restrictions of this kind do not intrude very frequently, and that crystals grow to lengths appreciably larger than their widths, this does not interfere significantly with any of the inferences here.

INTERACTIONS BETWEEN DOMINANT LAMELLAE

So far, the bending and twisting of crystals have been considered in isolation from other crystals. Interactions between crystals growing more or less parallel to one another in close adjacency are now considered. It is clear that dominant lamellae in banded spherulites, i.e. the lamellae which participate at the leading front during radial growth, interleave long before they have attained their final width (usually 1–2 μm). This is implied by co-operative phasing of twisting, and is evident in electron micrographs of tangential sections as shown by B. & H.

As a first simple case, consider a number of identical crystals growing towards the observer along parallel axes which are disposed on a two-dimensional hexagonal lattice as shown in *Figure 4*. It is assumed that near their tips the crystals twist helicoidally with the same phase. It is assumed also for the moment that the rotations involved in the twisting are relatively large, at least large enough for the purposes of the following discussion (twisting in quantitative terms is discussed later). The cross-section in *Figure 4a* represents an instantaneous snapshot at a position just behind the plane of furthest advance of the tips where narrow sections of lamellae happen to be aligned horizontally. A similar and simultaneous snapshot taken further back from the tips would have shown wider sections rotated as in *Figure 4b*, and another section further back still would show yet wider sections interleaved as in *Figure 4d*. (As the width of the lamellae increases, interleaving forces their planes more toward parallelism.) Between the sections shown in *Figure 4b* and *d*, however, there must arise at some instant close to the timing of these simultaneous snapshots, a situation as depicted in *Figure 4c* where the shoulders of neighbouring lamellae have just touched.

However, these touching edges are not precisely parallel; because of the twisting they follow helical paths and are, therefore, inclined slightly in opposite senses with respect to the common growth direction. The initial point of contact between two crystals then becomes a locking site that locks them firmly together for as the crystals continue to grow wider both behind and ahead of the locking site, they become, in effect, an interpenetrating pair (see *Figure 5*). Moreover, such a locking site is on the axis of what is now topologically a screw dislocation, and this has obvious implications with respect to further crystallization. (It is noteworthy that spiral growths generated at contacts between almost parallel lamellar crystals are known both in polymers[23] and in simpler crystals such as cadmium iodide[24]. It is noteworthy also that, in the present case, right-handed twisting would give rise to right-handed dislocations, and conversely.) Considering the entire ensemble of lamellae represented in *Figure 4*, it is now evident that nearest neighbours would develop mutually locking sites repeatedly during their advance. The orientation of each lamella becomes locked by interpenetration with two parallel neighbours at positions that are separated along the growth axis by a distance corresponding to a rotation of twisting tips by

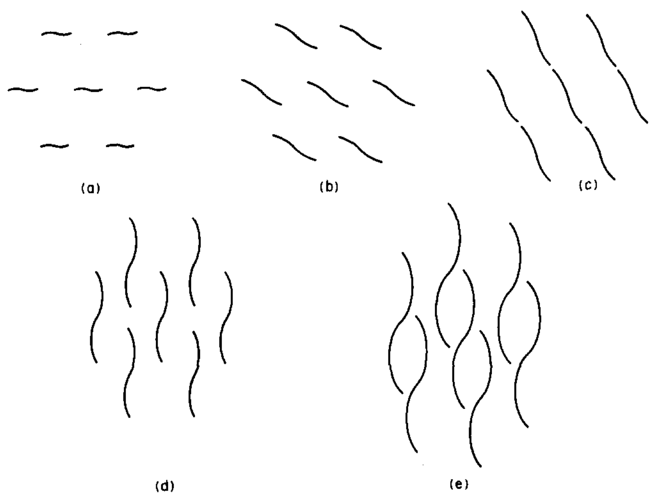

Figure 4 Representations of instantaneous sections through advancing S-bent, helicoidally twisted, lamellae whose axes lie on a hexagonal lattice; (a) close to the advancing tips; (b) further back; (c) at a position where neighbouring lamellae first 'touch' (small gaps still shown for clarity); (d) further back still where the lamellae interleave; (e) shows the condition at position (d) after further lateral growth has widened the lamellae

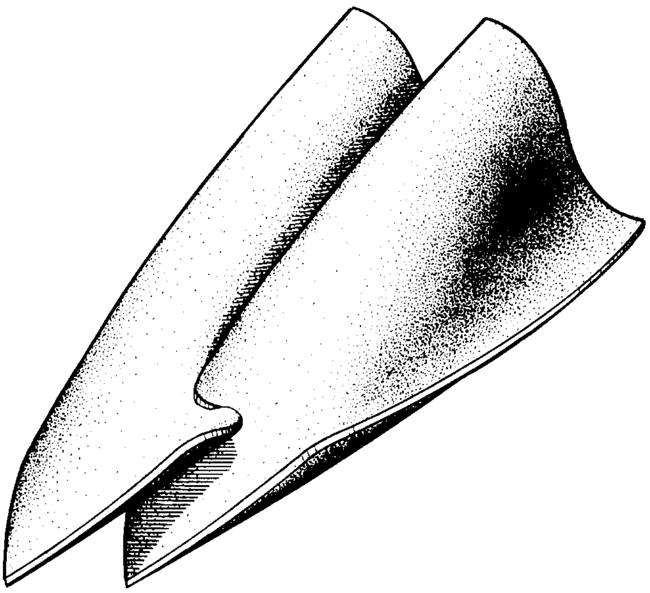

Figure 5 Illustration of a 'locking' site where two twisting lamellae have touched and begun interpenetrating growth. Note that the first point of contact lies on what, topologically, is a screw dislocation where spiral growths on both sides of the common 'plane' are initiated

60°. Thus, although an *isolated* lath may not twist over most of its length but only near free ends, interpenetrating growth of an array of such lamellae may have the effect of rigidly locking in a progressive twisting that, in the first instance, developed as a potentially transient condition localized at advancing growth fronts.

Had the axes of lamellae in *Figure 4* been placed on a square lattice the rotation between successive locking sites would have been 90° and this is the largest angle possible with a regular space filling arrangement. However, once the strict geometrical regularity represented in *Figure 4* is relaxed, and a more realistic representation of conditions within a growing spherulite is approached, it is evident that the situation at once assumes considerable complexity. It is clear, nevertheless, that closely packed interleaving lamellae growing with twisted tips must still develop mutually locking sites; and that the radial separation between these sites must correspond to rotations of averaged molecular orientation that are variable but mostly fall in the first quadrant. An average rotation of about 60° seems reasonable. B. & H. have clearly recognized the interpenetrating growth that is implied by a locking mechanism of the type described here in their words, the lamellae they have seen in banded spherulites of polyethylene are 'multiply connected'.

Interpenetration of 'asymmetrical' lamellae twisting helically is more difficult to visualize. Interleaving would again imply frequent formation of locking sites although, in this case, these would *not* be essential for twisting orientation to be manifested throughout a spherulite. As noted previously, many of the lamellae shown by B. & H. have asymmetrical profiles. However, there is ambiguity as to whether these lamellae grew asymmetrically or developed asymmetry at later stages of crystallization (after twisting was locked in) because of irregular packing that restricts continuing lateral growth of lamellae more at one side than the other.

THE DETAILED SITUATION AS DESCRIBED BY BASSETT AND HODGE

Although twisting of molecular orientation about the radius in banded spherulites is smooth and uniform *when averaged over volume elements of order* 10 μm^3[21], it does not follow that individual crystals are themselves twisted uniformly. The careful and detailed observations of B. & H. on polyethylene show much more complex behaviour that, at first sight, seems at odds with the viewpoint just developed (reconciliation of this apparent divergence is attempted later).

B. & H. have found no evidence for uniformly twisted helicoids but have observed lengths of S-bent crystal that are only slightly twisted and extend along the radius for approximately one-third of the spacing between extinction bands. Between one such section of crystal and the next (in a radial direction) there are 'sudden quasidiscontinuous rotations and splittings'[6]. Bassett, in a personal communication, has confirmed that, by this, B. & H. do not imply that there are separate crystals involved, or that there are twist boundaries which are abrupt and discontinuous on an observable scale. Rather, the twisting is smooth and continuous, but the rate of rotation of molecular orientation about the radius, $d\Theta/dr$, while of constant sign, oscillates in magnitude. It is relatively small over a length approaching $s/3$ on average (s being the spacing between extinction bands, a distance over which orietnation rotates by π) and then peaks sharply. (These lamellae are referred to here as being non-uniformly twisted, as distinct from those which are uniformly twisted with constant $d\Theta/dr$.) Others have also remarked upon the fact that lamellae seen at surfaces by scanning electron microscopy do not show uniform twisting[25]. B. & H. have made the additional observation, however, that, where rapid rotations occur, there is a marked growth of new lamellae the chain axes of which are approximately parallel to those of adjacent dominant lamellae[6].

RECONCILIATION OF THE MODEL WITH OBSERVATIONS BY BASSETT AND HODGE

It is proposed here that twisting of orientation in polyethylene spherulites is determined by what happens near the tips of growing dominant lamellae. It is suggested that these tips twist smoothly and reasonably uniformly, possibly as helicoids, and that the progressive rotation becomes fixed irretrievably as soon as the crystals are wide enough to interleave and form locking sites as described previously. For neighbouring lamellae the locking sites are separated on average by radial intervals corresponding to rotations by $\approx 60°$, i.e. by intervals approximately equal to $s/3$. The twisting in a given region is locked in, therefore, at an early stage after passage of the advancing boundary of a growing spherulite. However, on a local scale the volume fraction of crystalline material is then still relatively small. It is now necessary to establish what is likely to happen in this region as further crystallization occurs.

Sections of dominant lamellae, approximately $s/3$ in length and pinned at both ends by successive locking sites, will grow wider. Further, they will do so most rapidly in middle regions away from the locking sites at which continuing growth must take on the character of embryonic growth spirals (see *Figure 5*). Continuing lateral growth would do little to increase or even maintain axial torques on the widening crystals but may, nevertheless, persist in impressing S-bends upon them. As widening continues it would not be surprising for the increasingly stiff S-bent middle regions to flatten, and for torsion to become concentrated near the narrower locked ends of these regions where torsional rigidity is least. It is shown later that relaxation of surface stresses may also contribute to development of markedly non-uniform, as distinct from uniform, twisting. As the lamellae widen, continuing to S-bend as they do so, a common juxtaposition of neighbouring lamellae would be expected as shown in *Figure 4e*. B. & H. have, indeed, noted a marked tendency for the edge of one dominant S to approach the centre of its neighbour. Resulting curtailment of lateral growth in such cases may contribute to the incidence in their micrographs of asymmetrical S-bends.

The presence of screw dislocations at locking sites would provide preferred centres for continuing growth, extending into the secondary crystallization regime, that would be capable of generating new lamellae to the extent allowed by available space. These are also the locales in which, following a previous argument, more rapid twisting might occur. Taken in conjunction, the two effects may offer an explanation for the quasidiscontinuous rotations and splittings reported by B. & H.

It would be difficult to account for markedly non-uniform twisting as observed by B. & H. in terms of its being a feature that developed directly during the initial growth of dominant lamellae. It would be necessary to invoke an influence that is not only periodic but is co-ordinated between neighbouring lamellae both in the sense of handedness and of phasing.

RELAXATION OF SURFACE STRESSES AFTER CRYSTALLIZATION

If, as suggested here, crystalline morphology on a fine scale may reflect significant modifications of structure resulting from relaxation of surface stress after solidification, much will depend upon relative time scales involved. It has been shown previously that relaxation can occur at relatively short distances behind a growth front during crystallization at temperatures in the region of 128°C. With banded spherulites the situation is more difficult to judge. Intervals required for isothermal growth to increase the radius of a polyethylene spherulite by one band spacing vary from $\approx 7 \times 10^{-3}$ s at 110°C to ≈ 3 s at 120°C. Isothermal thickening is imperceptible after 1 day at 122°C but its rate increases rapidly with temperature above this value[13]. Banding usually becomes less distinct at crystallization temperatures $> \approx 120$°C and is generally no longer discernible at >123°C; in this range the bands are spaced 5–7 μm apart and become ragged in appearance, suggesting not only that the pitch of twisting is increasing rapidly but also that co-ordination of orientation is breaking down, possibly because dominant lamellae are now spaced wider apart during growth. It is clear, then, that thickening as such has little influence on banded spherulites in polyethylene *unless they are annealed above crystallization temperature.* (Even this has little observable effect on the optical microscopic scale[26], which is understandable as twisting molecular orientation is already locked in and cannot unwind.)

It does not follow, however, that stress relaxation cannot occur at disordered fold surfaces in banded spherulites at crystallization temperature, although this would presumably be considerably slower and less effective than at higher temperatures. Such relaxation may reduce bending moments and play a part in development of non-uniform twisting near locking sites. As shown in Appendix 2, melt viscosity would not necessarily prevent the rotations required. However, little change would be expected across S-profiles in terms of shearing of the type discussed previously (*Figure 1*). The small elastic energy available from bending in the core (which is considerably less than that associated with twisting) is insufficient on its own to cause shearing; and thickening, which would otherwise facilitate shearing and create line vacancies, is essentially inoperative. Therefore, S-bending in unannealed banded spherulites is expected to remain elastic i.e. with fanning chain orientation, except insofar as polygonization might develop (formation of progressively misaligned mosaic blocks). B. & H. are not explicit on this point; orientation may be more difficult to judge from surface features in sections of thinner lamellae, but resolution of the question is obviously of interest.

THE ROLE OF TRANSIENT STATES

In several ways, major significance has been attributed to transient states produced during crystallization from the melt, states that are capable of relaxing to varying degrees depending upon temperature and time. If the proposals here are correct there is an implied warning that interpretation of morphological detail should not be attempted in terms of growth processes alone; such details could be misleading if later relaxations are not taken into account. Wide variations in growth rate between different polymers at comparable supercooling would not, of themselves, mean that there are significant differences with regard to the existence or role of transient states. In particular, they would not imply that the magnitudes of surfaces stresses caused by disordered folding would differ greatly. Variation of growth rate with temperature in a given polymer, however, would be expected to have considerable effect.

It is to be emphasized that the transient states discussed are *not* readily amenable to study by direct experiment. They represent somewhat elusive departures from final states and, should they be of short duration, only a small fraction of a crystallizing specimen could at any instant show incontravertible evidence of their existence. At present no observations that relate *directly* to the transient states postulated here, are known.

There are possibly important implications with respect to crystallization kinetics which are only mentioned briefly here. If initial attachment of chains at a growth face involves folding that is disordered to a greater degree than can be tolerated ultimately in the body of the crystal, continuing growth in a steady state would require a dynamic equilibrium between molecular attachment at the face and rearrangement in molecular layers immediately behind it. (The work of Rault[27] is of particular relevance.) In extreme cases (for example, in polymers which at large supercooling exhibit a positive temperature coefficient of growth rate), relaxation processes could become rate-determining. It may prove informative to re-examine growth rates of crystals of different polymers at relatively large, but comparable, supercoolings, and taking a possible influence of relaxation processes into account. The apparent free energy of fold surfaces in polyethylene crystals, σ_e, as determined from kinetic data, increases with supercooling approximately as $\sigma_e = \sigma_{eo}(1 + y\Delta T)$, y being $\approx 0.014\ K^{-1}$ [28]. This may in part reflect an influence of relaxation which becomes slower at lower temperatures.

BROADER IMPLICATIONS: OTHER POLYMERS

As a desirable simplification it has been assumed thus far that stresses in fold surfaces, although anisotropic, are homogeneous throughout these surfaces. Sectorization due to faceting at growth fronts, and fluctuations of other kinds, are likely in practice to cause these stresses to be inhomogeneous. It is not surprising therefore that, with the exception of some lamellae of simple polyhedral shape precipitated slowly from dilute solution, polymer crystals as grown are usually warped and buckled in complex ways. This is particularly well exemplified by a recent study of multilayer crystalline aggregates and spherulites of polyethylene grown from concentrated ($\approx 5\%$) solution and preserved essentially in an as-grown condition for scanning electron microscopy by critical point drying[29]. S-bending and twisting in crystals grown from the melt are presumably superimposed upon vagaries of this kind; however, it is probable that they predominate overwhelmingly because their origin lies in a co-ordinated influence, the canting of molecules, that persists consistently regardless of superimposed fluctuations. Consistent curvature in all sectors of bowl-shaped polyhedral crystals as described by Khoury and Barnes[30-32] appears, however, to have a different origin. Small differences ($\approx 0.1\%$) in lattice spacing between fold planes and otherwise equivalent non-fold planes as discussed by them, and earlier by Bassett[33], may contribute to non-planar habits in melt-grown crystals, but when folding is highly disordered they are not likely to have much overall effect.

There would appear to be no reason why the arguments proposed here should not also be applicable to spherulites in polymers other than polyethylene, provided that molecules cant appreciably in lamellae of comparably simple habit. However, no close analogues can be cited with certainty because of presently limited information, mostly concerning canting. Banding and molecular canting (by $\approx 25°$ with respect to lamellar normals) are known to occur simultaneously in spherulites of two aliphatic polyesters[22], but these are cases of canting toward the radius (rather than in the tangential plane) so that helical, not helicoidal, twisting would be expected. Banded spherulites of α-poly(vinylidene fluoride) may provide a close analogue but no information is yet available about molecular canting (canting by $\approx 30°$ is established in the γ-polymorph[34] but the accompanying lamellar habits are then more complicated).

The absence of banding in many polymers requires explanation by establishing whether the lamellae in these spherulites do not twist at all, or twist but without co-operative phasing. Calculations, confirmed by experiments with coated rubber strips, suggest that little is possible in the way of helicoidal twisting unless lamellae are significantly wider than they are thick. Two polymers are known, poly(ethylene oxide) and β-polypropylene, in which lamellae in unbanded spherulites are indeed narrow ($\approx 0.1\ \mu m$) and not perceptibly twisted, whereas lamellae in banded spherulites (grown under different conditions) are substantially wider and now twisted[35]. The growth of lamellae that are inherently very narrow is known in many polymers, an outstanding example being poly(phenylene sulphide)[36], and generally the corresponding spherulites are not banded.

There are also polymers in which single crystals grown from solution, or grown very slowly as hedrites from the melt, exhibit no perceptible molecular canting. It does not follow, however, that their spherulites are necessarily unbanded. Examples of banding in such circumstances are found in poly(methylene oxide) and isotactic polystyrene (poorly co-ordinated banding in this latter case has been seen only after addition of low molecular weight diluents to the melt[35]). It is proposed here that despite their ability to crystallize very slowly without canting, molecules in these polymers may nevertheless cant during rapid growth from the melt; such canting would certainly assist the accommodation of disordered folds (see Frank[11]) and, more significantly, would introduce an asymmetry of the type needed for the arguments proposed previously to apply. These various themes will be expanded in later papers. Generally, there is a need for further experimental work directed at specific questions raised by the considerations here.

Lastly, it is noteworthy that these considerations would obviously have little direct relevance to twisting orientation found in spherulites of non-polymeric and of inorganic compounds (mostly in natural minerals). Twisting in these cases appears to be linked mostly to chirality of structure, whether in crystalline packing or, at a deeper level, in the molecules themselves. This view, which is by no means new, has recently received strong, if indirect, support from the work of Lotz *et al.*[37] on the growth of twisted crystals in chiral polymers of biological interest (silk fibroin and poly-α-amino acids).

OUTLINE OF SUPPORTING EXPERIMENTAL EVIDENCE

Considerably more evidence would be needed to provide compelling experimental support for the views developed here. Nothing appears to be known about S-bending in polymers other than polyethylene; however, if the case of polyethylene is representative, experiments of a novel kind are necessary, and the absence of evidence for such bending in previous investigations is not a significant indicator. Current evidence suggesting that bending moments due to congested fold surfaces are significant in determining crystal habits comes from studies of banding in spherulites of various polymers.

In comparing band spacings observed in different polymers (thirteen cases are documented) no correlation is observed with relative rates of crystallization (as expected – see previously), with chain stiffness or, with one exception, any of the other parameters that logically may be appropriate. The exception, which has been known for some time but not understood[38], is that there is a strong correlation between band spacing, s, which ranges from $< 1\ \mu m$ to $\approx 100\ \mu m$ depending upon the polymer, and the relative change in specific volume during solidification. This takes approximately the form $\ln s \sim \{A - B(\Delta v/v)\}$, and at once focuses attention on mismatch at phase boundaries, and upon fold surfaces in particular. Changes in melt viscosity exert an influence upon s in a given polymer in a consistent way; the larger the viscosity the smaller is s for crystallization at a given supercooling, but the effect is usually not large. A larger volume disparity $\Delta v/v$ would clearly tend to increase stresses at fold surfaces, and reduced molecular mobility in the melt would impede regularity of folding, so that both should promote larger crystalline curvature and more rapid twisting, i.e. a smaller s, as is found.

Commonly, but not universally, it is the case that the dominant factor controlling variations of s in a given polymer (these are much smaller than variations between different polymers) is temperature or, more accurately, supercooling during crystallization. It is believed that this influence is exerted principally through changes in lamellar thickness (and hence lamellar rigidity) which varies approximately as $t \approx \Delta T^{-1}$. As the radii of curvature discussed here would depend upon t^2, other factors remaining constant, and s probably varies in the same way, a dependence $s \approx \Delta T^{-2}$ would be expected initially. However, as crystallization temperature increases, and growth becomes slower while relaxation processes accelerate, the difference in stress between opposite fold surfaces should decrease. A simple power-law dependence would imply $s \approx \Delta T^{-n}$, where $n > 22 < n \lesssim 4$. Results of measurements made recently with various linear polyethylenes (fractions and whole polymer) conform closely to such a dependence, with n in the range 2.65–3.4 depending upon molecular weight.

In an attempt to focus attention on disordered fold surfaces, spherulitic crystallization has been studied in heavily ethyl-branched polyethylenes (hydrogenated polybutadienes with $\approx 18C_2H_5/1000C$ and molecular weights in the range $5\text{–}10 \times 10^4$). Ethyl branches occur on average every 70 Å along the backbone chains, and are apparently spaced statistically. Such branches are generally considered to be reasonably rigidly excluded from the crystalline phase, so that segments of unbranched chain long enough to crystallize are presumably separated frequently by long intervening segments that are unable to crystallize. In these circumstances extremely congested fold surfaces would be expected. (Strong evidence that fold surfaces in these materials are not only highly strained but also unusually thick has recently been provided by the work of Marks and Carr[39].) Also, severe restrictions upon longitudinal motion of crystallized segments would be expected to impede greatly relaxation of this congestion. These polymers do in fact have the remarkable property of forming banded spherulites at small supercoolings (4°C relative to their own melting points – which are, of course, significantly depressed below that of linear polyethylene). Moreover, despite their very slow growth (≈ 6 Å min^{-1}), the well-defined banding has a relatively small spacing ≈ 2 μm. In linear polyethylene, a supercooling of ≈ 20°C is required to get banding at all, and a supercooling of ≈ 35°C (at which the growth rate is ≈ 3 cm min^{-1}) is needed to obtain a comparably small band spacing.

These, and other, experiments are continuing. As yet no results, from this or from previous work, appear to conflict irresolvably with the proposal here. Many open questions remain, but the evidence outlined seems to be encouraging.

QUANTITATIVE CONSIDERATIONS: THE ORIGIN OF TWISTING ORIENTATION

Quantitative consideration of twisting orientation has been deferred to develop a new rationale and to indicate the extent to which available evidence appears to support it. These quantitative aspects which yield insights concerning molecular mechanisms, are now considered.

Appendix 2 shows that, for small linearly elastic deformations at least, the angle of helicoidal twisting developed at the tip of a flat lath of width w is $\Theta = 9w/32\rho_t$. ρ_t is the radius of curvature which either half of the lath would assume on its own if completely relaxed and is, therefore, a measure of the bending moments about transverse axes which caused the twisting. It is noteworthy that, by considering helicoidal rather than helical twisting, the case in which twist is energetically more costly is being considered. If $w/\rho_t = 1$, then $\Theta \approx 16°$. With lamellar crystals in banded polyethylene spherulites, for which observed values are $w \approx 1$ μm, $\rho_1 \approx 0.5$ μm, then $\Theta \approx 30°$ on the assumptuon that $\rho_t = \rho_1$ i.e. that stresses in fold surfaces are isotropic. In the rubber strip shown in *Figure 2* (for which ρ_t and ρ_1 are certainly comparable) $w/\rho_t \approx 4.3$ and the above expression would give $\Theta \approx 70°$. With such a large deformation, however, the model upon which the calculation is based is no longer valid; nevertheless, the observed axial twist in the strip is $\Theta \approx 45°$, suggesting that the calculation probably gives reasonably accurate predictions for small twists. On this basis, then, predicted helicoidal twisting appears to fall short, by a factor 2–3, of being sufficient to support the previous argument that progressive twisting in spherulites could result from repeated locking-in of torsions which develop at growth tips to extent of at least 60° on average. In reaching this conclusion, however, a 'worst case' has been chosen deliberately and, more importantly, linear elasticity has been assumed throughout.

In an attempt to avoid this difficulty it is not reasonable to suggest that longitudinal components of stress in fold surfaces may be substantially larger than transverse components; the longitudinal surface strains required would be inordinate. Helical growth, as suggested (though not unambiguously) by the wavy appearance of lamellae mentioned previously, would reduce torsional rigidity and make twisting easier, but this is not convincing either. There will presumably be some torque on twisted tips during their growth due to flow of melt into the spherulite to compensate for volume contraction due to secondary crystallization; such a 'windmill' action would enhance existing twists but might not add significantly to the considerable torques already operative. The most promising line of inquiry is the following.

Bending strains in the crystalline core of a twisted polyethylene lamella are of the order of 1% but shear strains appear to be very much larger. For example, in a helicoid of width w twisted uniformly so as to turn by 180° in a length $3w$, the angle of shear at the edges is approximately 27.6° (*Figure 6*). Fold surfaces near the edge would, therefore, be very close to (211) in orientation; i.e., at this edge the shear displacements in the chain direction of one (010) molecular plane relative to the next would correspond to one chain repeat. It is as though in this region folds are staggered by one chain repeat per unit cell along *both* [200] and [010] axes. Energetically, this is not at all an unfavourable situation. Across the width of the twisted lamella shear in the chain direction is, of course, variable. This could be accommodated by fold staggering which varies in frequency from one chain repeat between successive (010) planes at the edge, through one chain repeat occurring on average every second (010) plane at $w/4$ from the axis, to no staggering at the axis. This implies irregularly stepped boundaries between ordered crystalline cores and fold 'surfaces', but the steps need only be 2–3 Å in height and the fold surfaces

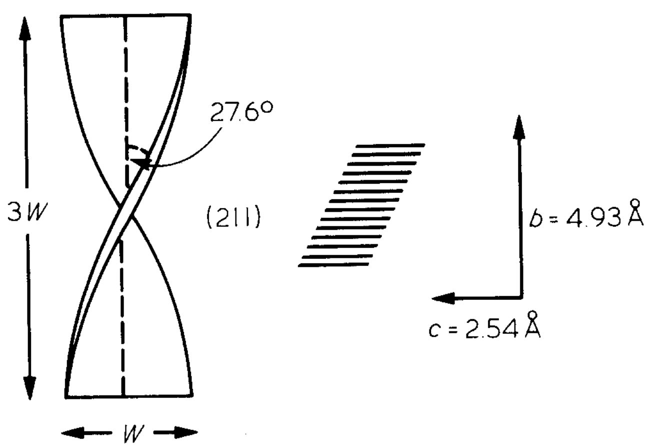

Figure 6 Uniformly twisted helicoid showing large shear at edges, corresponding to possible fold staggering

are, in any event, already highly disordered. Apparent shear displacements along chain axes in a twisted crystal can arise, therefore, through appropriately controlled fold staggering and need not necessarily involve deformations that are costly in terms of strain energy.

However, there are other shear strains to be considered. In a polyethylene crystal that twists by 180° in a length 1 μm (approximately corresponding to the smallest band spacing observed in linear polyethylene), successive (010) planes would rotate by $\approx 0.09°$, provided the twisting is uniform on a molecular scale. It is unlikely that twisting could be uniform to this degree. Previous remarks about fold staggering notwithstanding, the strain energy associated with uniform twisting would still be a substantial fraction (≈ 0.5) of that estimated in Appendix 2. The difficulty in accounting for observed twisting in spherulites could therefore remain. In larger non-polymeric crystals, appreciable rotational deformations usually involve twist boundaries which consist of cross-grids of screw dislocations the strain energy of which in aggregate is relatively small because there are no extended stress fields[40]. In the present case, a twist boundary would have to be thought of in terms of a cross-section of a highly anisotropic crystal and measuring ≈ 1 μm by 200 Å. Estimation of likely behaviour and of strain energies is, therefore, unusually difficult. Nevertheless, it appears likely that twist boundaries would be formed at intervals of perhaps 100–200 Å along the axis (rotations of 2.25°–3.5°) and that, despite the large dislocation densities implied, the strain energy would be significantly less than in a perfect crystal twisted uniformly to the same overall extent. In terms of the mechanical model discussed in Appendix 2, this is equivalent to assuming torsional yielding so that angles of twist can be considerably larger than are calculated using strain energies based upon linear elasticity. Useful as this model has been, however, it can now become misleading unless it is remembered that the crystals being considered have not been deformed by external forces but have grown in twisted form. If twist boundaries are present, as now seems likely, they form during growth. Perhaps Regime III crystallization from the melt should be thought to give rise initially to a disordered packing in which molecules still have appreciable mobility. Even more disordered fold surfaces impose twisting deformations which are accommodated partly by fold staggering and partly by defects. The crystals probably settle down with twist boundaries of some type, though whether these would be better described in terms of dislocation arrays or of mosaic substructure remains to be seen.

Referring to *Figure 8* (Appendix 2), it is shown that the torque which causes axial twisting in a lamella also implies the existence at growth fronts of shear stresses directed along the normal to the crystal. Being of considerable magnitude, these stresses might generate screw dislocations with Burgers vector *c* [001]. Dislocations of this type represent the defects needed in greatest number to form twist boundaries. They would also be relatively mobile[41]. It is possible that, acting under the influence of the considerable torques generated by stressed fold surfaces, they then aggregate to form twist boundaries. Thus, large axial torsions might be produced with relatively little cost in strain energy. Details of such a mechanism require further study but, without the participation of twist boundaries in some way, the growth of crystals having rapidly twisting orientation would seem impossible.

APPENDIX 1

Chain folding at oblique growth fronts

Consider how different degrees of disorder might arise at opposite fold surfaces of a lamellar crystal during rapid advance of a growth front which is oblique to the plane of the crystal. The principal factors contributing to such disorder are non-adjacent re-entry of chains to the crystal and looseness of fold loops, both of which introduce overcrowding and inefficient packing. However, chain ends that lie within the crystal close to a surface afford considerable relief to the overcrowding of folds in their immediate surroundings, but unless the molecular weight is low these will be sparsely distributed. The relatively small proportion of emergent chains that do not re-enter the crystal probably have an influence intermediate between these extremes. It is necessary, therefore, to establish how obliquity of a growth face to its growth direction might influence the packing of chains as they deposit from the melt.

The situation to be considered as representing average behaviour is shown schematically in *Figure 7a*. The growth front has just encountered a molecule in the melt the centre of mass of which is along the midplane of the lamella in the direction of growth *G*. This is depicted approximately to scale for a random coil (polyethylene) of molecular weight 100000 and a lamella which is 200 Å thick. Chains are shown as being canted at 25° to the lamellar normal, this being an angle intermediate between values appropriate for (110) and for (200) growth faces in a lamella with (201) fold planes. If the molecule now deposits on the crystal in a folded conformation, there would probably be a tendency for tighter folds to form at the lower fold surface. In reaching this surface the attaching segments would more frequently have to 'drag their loops' with them as represented in *Figure 7b*. The upper fold surface would appear to be more accessible to lengths of the molecule that could more easily form loose loops. Further, the tighter fold formed by a 'dragged' loop would be more likely to involve adjacent re-entry to the crystal than a fold between stems that have attached more or less independently to niches in the vicinity of the upper fold surface. The distinction between the two situations

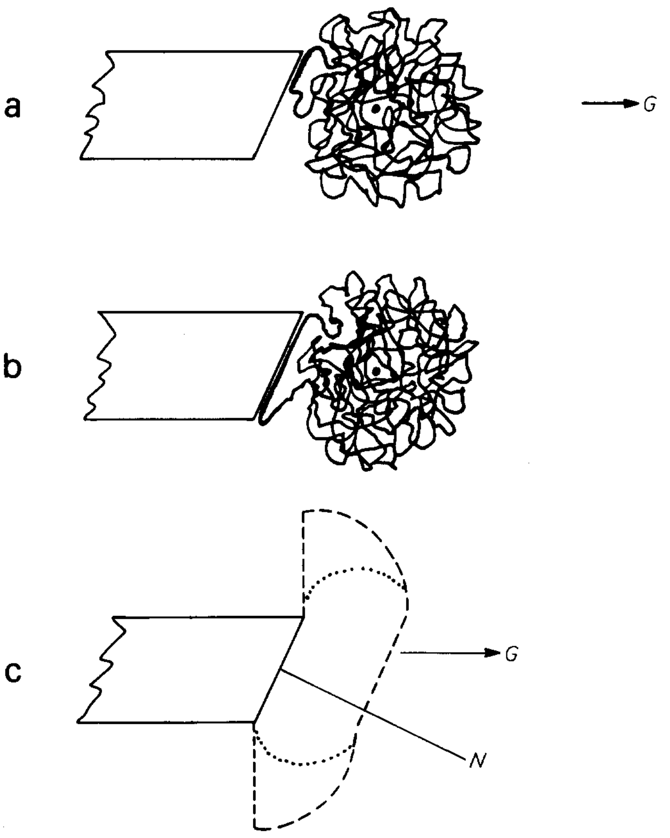

Figure 7 Representation of an oblique growth face encountering a coiled molecule in the melt; (a) shows attachment beginning. This leads, in (b), to formation at the lower fold surface of relatively tight folding (see text). In (c), the dashed curve defines the region within which the centre of mass of a molecule must lie in order that it may begin to crystallize

would not be absolute but one of bias in a spectrum of events. Nevertheless, the incidence of tight adjacent folding and of loosely-looped and/or non-adjacent re-entry folding need not be greatly different at the two surfaces to produce significantly disparate overcrowding and associated surface stress when the newly-added molecular layer is engulfed as growth continues.

It can now be argued that the same considerations would have led to precisely the opposite result had the centre of mass of the encountered molecule been well below the midplane of the lamella. This is so. Each molecule adds only a limited number of molecular stems to the crystal and there is a possible bias in behaviour averaged over many molecules. For another coil of the same effective 'radius' to be encountered by a similar growing crystal at the instant depicted in *Figure 7c*, its centre of mass would have to be within the region bounded by the dashed curve. If it is on N, the normal to the growth face at its midplane, the molecule would be expected to contribute nothing to development of a difference between fold surfaces. If it is above N it would contribute to a difference in one sense and, if below it, in the other sense. Averaged over many molecules the centres of mass of which are disposed at random, there would appear to be a clear bias in favour of less ordered folding developing at the upper fold surface which meets the growth face at an acute angle.

Clearly, the molecules likely to contribute most to the growth of the crystal, particularly if that growth is fast, would be those the centre of mass of which are in the main path of the advancing front, perhaps within the dotted curve in *Figure 7c*. The bias indicated would then be significantly more pronounced than is first suggested when the entire area of the region inside the dashed curve is divided by the normal N. The faster the growth of the crystal and, to some degree, the less the mobility of chains in the melt (to the extent that these are compatible), the greater would be the dissimilarity between resulting fold surfaces.

This dissimilarity could have either of two effects, or a combination of both. The first is the imposition of elastic bending as already noted. The second is that there could be a tendency for an occasional downward stagger of succeeding molecular layers on the growth face in *Figure 7a*. This could also introduce a component of curvature in the crystal, but only at the expense of aggravating overcrowding at both fold surfaces because it would reduce the obliquity of chain stems with respect to those surfaces. It is unlikely, therefore, to make a major contribution in the growth process.

It is recognized that these arguments are based upon largely unsupported, though commonly voiced, views about the conformations of chains near a growth front and how these chains move as they attach themselves to that front. While these views seem persuasive in the case of crystallization from solution, they may be of questionable value in the context of solidification from a melt. In this latter case, molecular motion is now thought to occur by reptation, stimulated to some degree in crystallizing molecules by a 'force of crystallization'[42]. It is difficult, however, to see how perturbations of molecular conformation induced by vigorous motion of crystallizing chains could invalidate the reasoning followed here. There is as yet little or no reliable knowledge of just how in these circumstances molecules approach growth fronts and adjust their conformations during crystallization. The argument proposed here probably has validity but this cannot be claimed with confidence. There may be other molecular mechanisms that would lead to similar consequences and seem no less plausible. It is for this reason that in the main text the suggested difference in degrees of overcrowding at opposite fold surfaces is advanced as a postulate rather than a demonstrable premise. It is believed that this postulate commands attention because deductions based upon it appear to represent a significant advance in interpretation of diverse and hitherto unexplained morphological observations in a reasonably coherent way.

APPENDIX 2

Approximate analysis of helicoidal twisting

As model for a lath-like crystal subjected to equal but opposed bending moments on opposite sides of a central axis, consider the following hypothetical situation (*Figure 8*). Two strips of width w and thickness t which, in a relaxed state, are in the form of cylindrical arcs with radius of curvature ρ_0, are flattened and joined along their edges to form a strained flat lath of width $2w$. It is now necessary to establish whether the elastic strain energy of the system can be reduced by mechanical relaxation. It would appear that it can. For example, suppose that a twist develops over a length s from the end (see *Figure 8*) and take axes with origin on the axis of the lath at the position where

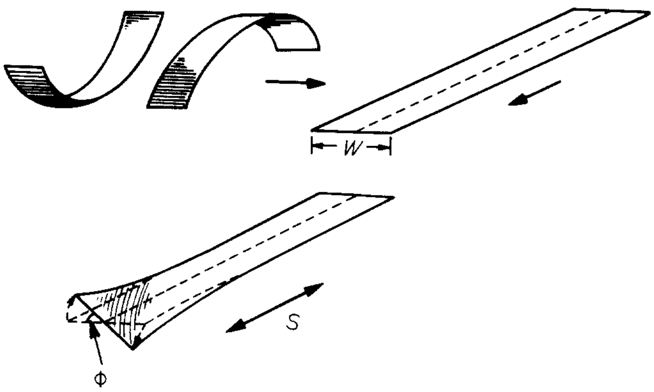

Figure 8 Illustrating the relaxation by twisting of a lath subjected to oppositely directed bending moments in opposite halves

twisting begins, x along the axis towards the end, and y transverse in the plane of the flat section. For simplicity, suppose further that, over the length s, narrow strips dy in width and running parallel to the long axis are relaxed into circular arcs, varying in curvature from zero at the axis to a maximum at the edge where the radius is $\rho(w)$. Transverse cross-sections in the twisted region are still flat but rotated, and twisting, which attains a maximum angle Θ, is non-uniform, the angle of twist varying as $\phi(x)=(x/s)^2\Theta$. It is now shown that as Θ increases from zero, strain energy due to bending decreases faster than strain energy due to torsion increases and that a position of equilibrium is attained with finite twisting. It is assumed that Θ is small so that $\sin\Theta\approx\tan\Theta\approx\Theta$.

The strain energy of a strip bent to radius ρ can easily be shown to be:

$$\frac{Et^3}{24}\left(\frac{1}{\rho}-\frac{1}{\rho_0}\right)^2$$

per unit area, where E is the Young modulus and ρ_0 is the radius in the relaxed state. The radius of curvature of a line element at y from the axis if $\rho(y)$ where:

$$\rho(y)=s^2/2y\Theta$$

and hence the bending component of strain energy in each half of the twisted end, $0\leqslant x\leqslant s$, is:

$$W_\mathrm{B}=\int_0^w\frac{Est^3}{24}\left(\frac{2y\Theta}{s^2}-\frac{1}{\rho_0}\right)^2\mathrm{d}y$$

$$=\frac{Ewst^3}{24}\left[\frac{1}{\rho_0^2}-\frac{2w\Theta}{\rho_0S^2}+\frac{4w^2\Theta^2}{3s^4}\right]$$

Provided $w\gg t$, the twisting energy in each half of the twisted end is:

$$W_\mathrm{T}=\int_0^s\frac{Gwt^3}{6}\left(\frac{\mathrm{d}\phi}{\mathrm{d}x}\right)^2\mathrm{d}x=\frac{2Gwt^3\Theta^2}{9\quad s}$$

where G is the rigidity modulus. The equilibrium value of Θ is determined from the equation $\partial(W_\mathrm{B}+W_\mathrm{T})/\partial\Theta=0$ and, when simplified, is:

$$\Theta=\frac{3w}{4\rho_0\left\{\left(\frac{w}{s}\right)^2+\frac{4G}{E}\right\}}$$

Taking $G/E=1/3$, and noting that $(w/s)^2\ll 1$, then $\Theta=9w/16\rho_0$. Expressed in terms of $W(=2w)$, the full width of the lath, this becomes $\Theta=9W/32\rho_0$. In applying this to polyethylene crystals ρ_0 must identify with ρ_t, a measure of bending moments about transverse axes. Only if stresses in fold surfaces are isotropic will $\rho_t=\rho_l$, ρ_l being a measure of bending moments about longitudinal axes and approximately the radius of curvature seen in S-bending.

Two additional points should be made. First, S-bending tends to increase torsional stiffness so that an S-bent crystal would be slightly less twisted than a flat crystal. Secondly, it will be apparent that twisting would be reduced if the crystal is not square-ended but tapers as a V to a point. However, provided the angle subtended at the V is not less than a right angle, the effect would be slight, as has been confirmed by the experiments with rubber strips discussed in the main text.

It is instructive to consider the relative magnitudes of energies involved in deformed polyethylene lamellae. The following estimates refer to a crystal the ordered core of which measures $s=1\ \mu$m in length, $w=0.5\ \mu$m in width, and $t=200$ Å in thickness; elastic moduli are taken to be $E=3\times10^{10}$ dyne cm^{-2} (3 GPa), $G=10^{10}$ dyne cm^{-2} (1 GPa). Assuming the crystal grew at a supercooling of 30°C, free energy of order 10^{-7} erg (1 erg$\equiv10^{-7}$ J) is liberated during solidification and is available to generate non-equilibrium conditions including mechanical deformation of this crystalline core. Much of the strain energy associated with fold surfaces would already have been accounted for in σ_e, the free energy per unit area of fold surface, to which it would contribute ≈ 10 ergs cm^{-2}, or $\approx 10\%$ of the measured value. S-bending to a radius of 1 μm involves a strain energy $W_\mathrm{B}=Ewst^3/24\rho^2\sim5\times10^{-9}$ erg. Helicoidal twisting such that the torsion is π over the length s would involve an energy $W_\mathrm{T}=\pi^2Gwt^3/6s=6.6\times10^{-8}$ erg, assuming linear elasticity to apply. While energy of this magnitude is available in principle it seems unlikely that elastic energy would be partitioned so inequitably between the two modes of deformation; this reinforces conclusions reached at the end of the paper concerning twist boundaries which would allow large torsions to develop without large strain energy.

Lastly, it is possible to estimate the energy required to rotate the crystal about its central axis in the long dimension in a medium of viscosity η. By considering the crystal to carry with it a cylinder of melt of radius $w/2$ within a fixed boundary of radius w (Couette flow), the energy required for a rotation of 30° is $W_\eta=(2\pi^2/9)ws\eta$. Taking $\eta=10^4$ poise (10^3 kg m^{-1} s^{-1}), a value representative of linear polyethylene of molecular weight 45000 at ≈115°C, then $W_\eta\approx6\times10^{-9}$ erg. Slight flattening of S-profiles, or rotations to produce non-uniform twisting from more uniform twisting, are not necessarily prohibited by melt viscosity, therefore, if bending moments are relaxed subsequent to crystallization.

Note added in proof

Sir Charles Frank has pointed out a very simple way of approximating the above result. Take lines joining the midpoint of the free end of the lath to points on the sides at distance s from the end (these could be locking sites). Consider the lath to remain flat within these lines but to curl up and down at opposite corners. If stresses are isotropic in the surfaces these cylindrically curved corners acquire a radius of curvature ρ_0 about axes parallel to the lines. On this basis the angle Θ would be approximately $W/4\rho_0$, a value only $\approx 10\%$ different from that calculated above.

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REFERENCES

1 Bassett, D. C. and Hodge, A. M. *Polymer* 1978, **19**, 469
2 Bassett, D. C. and Hodge, A. M. *Proc. Roy. Soc.* 1978, **A359**, 121
3 Bassett, D. C. and Hodge, A. M. and Olley, R. H. *Discussions Faraday Soc.* 1979, **68**, 218
4 Bassett, D. C. and Hodge, A. M. *Proc. Roy. Soc.* 1981, **A377**, 25
5 Bassett, D. C. and Hodge, A. M. *Proc. Roy. Soc.* 1981, **A377**, 39
6 Bassett, D. C. and Hodge, A. M. *Proc. Roy. Soc.* 1981, **A377**, 61
7 Khoury, F. *Discussions Faraday Soc.* 1979, **68**, 404
8 Sadler, D. M. in 'Static and Dynamic Properties of the Polymeric Solid State' (Eds. R. A. Pethrick and R. W. Richards) Reidel, 1982, pp. 81–108
9 Hoffman, J. D. *Polymer* 1983, **24**, 3
10 Frank, F. C. in 'Growth and Perfection of Crystals' (Eds. R. H. Doremus, B. W. Roberts and D. Turnbull), Wiley, 1958, pp. 529–30
11 Frank, F. C. *Discussions Faraday Soc.* 1979, **68**, 7
12 Hoffman, J. D. and Weeks, J. J. *J. Chem. Phys.* 1965, **42**, 4301
13 Dlugosz, J., Fraser, G. V., Grubb, D., Keller, A., Odell, J. A. and Goggin, P. L. *Polymer* 1976, **17**, 471
14 Hoffman, J. D. and Lauritzen, J. I., Jr. *J. Res. Natl. Bur. Std.* (*US*) 1961, **65A**, 297
15 Keith, H. D. and Padden, F. J., Jr. *J. Polym. Sci.* 1961, **51**, S4
16 Keith, H. D. *J. Appl. Phys.* 1964, **35**, 3115
17 Keith, H. D. *J. Polymer Sci., Phys. Ed.* 1964, **2**, 4339
18 Lovinger, A. J. *J. Polym. Sci., Phys. Ed.* 1983, **21**, 97
19 Statton, W. O. *J. Appl. Phys.* 1967, **38**, 4149
20 Statton, W. O. and Geil, P. H. *J. Appl. Polymer Sci.* 1960, **3**, 357
21 Keith, H. D. and Padden, F. J., Jr. *J. Polym. Sci.* 1959, **39**, 101, 123
22 Keith, H. D. *Macromolecules* 1982, **15**, 114, 122
23 Lotz, B. Personal communication
24 Forty, A. J. *Phil. Mag.* 1952, **43**, 377
25 Breedon, J. E., Jackson, J. F., Marcinkowski, M. J. and Taylor, M. E., Jr. *J. Mat. Sci.* 1973, **8**, 1071
26 Chivers, R. A., Barham, P. J., Martinez-Salazar, J. and Keller, A. *J. Polymer, Sci., Phys. Ed.* 1982, **20**, 1717
27 Rault, J. *J. Physique Lett.* 1978, **39**, L-411
28 Hoffman, J. D., Davis, G. T. and Lauritzen, J. I. in 'Treatise on Solid State Chemistry' (Ed. N. B. Hannay) Plenum Press, 1976, Vol. 3, Chap. 7
29 Padden, F. J., Jr. to be published
30 Khoury, F. and Barnes, J. D. *J. Res. Natl. Bur. Std.* (*US*) 1972, **76A**, 225
31 Khoury, F. and Barnes, J. D. *J. Res. Natl. Bur. Std.* (*US*) 1974, **78A**, 95
32 Khoury, F. and Barnes, J. D. *J. Res. Natl. Bur. Std.* (*US*) 1974, **78A**, 363
33 Bassett, D. C. *Phil. Mag., Ser. VIII* 1964, **10**, 595
34 Lovinger, A. J. and Keith, H. D. *Macromolecules* 1979, **12**, 919
35 Keith, H. D. and Padden, F. J., Jr. to be published
36 Lovinger, A. J. and Padden, F. J., Jr. *Bull. Phys. Soc.* 1982, **27**, 259
37 Lotz, B., Gonthier-Vassal, A., Brack, A. and Magoshi, J. *J. Mol. Biol.* 1982, **156**, 345
38 Keith, H. D., Padden, F. J., Jr. and Lovinger, A. J. *Bull. Amer. Phys. Soc.* 1980, **25**, 251
39 Marks, B. S. and Carr, S. H. *J. Appl. Phys.* 1982, **53**, 6526
40 Cottrell, A. H. 'Dislocations and Plastic Flow in Crystals' Oxford U. Press, 1953
41 Keith, H. D. and Passaglia, E. *J. Res. Natl. Bur. Std.* (*US*) 1964, **68A**, 513
42 DiMarzio, E. A., Guttman, C. M. and Hoffman, J. D. *Discussions Faraday Soc.* 1979, **68**, 210
43 Guttman, C. M., Di Marzio, E. A. and Hoffman, J. D. *Polymer* 1981, **22**, 1466