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On the origins of giant screw dislocations in polymer lamellae

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Abstract

Giant screw dislocations in chain-folded polymer crystals, having axes necessarily parallel to chain stems, traverse lamellar thickness and, although without hollow cores, have large Burgers vectors, often in excess of 100 Å. From a geometrical standpoint, their mode of formation was recognized four decades ago by Geil and Reneker. On a molecular scale, however, mechanisms by which shear forces, and necessary planes of easy shear oblique to growth faces (effectively tears or slits), arise during crystallization by chain folding have long remained obscure. For some time shear has credibly been associated with lamellar warping under the influence of inhomogeneously distributed congestion in fold surfaces. A study of dendritic crystals in polyethylene has now shown how on occasion impingements inherent in layer spreading by folded chains, combined with kinetic barriers of entropic character, can produce defects that permit shear across nominal fold planes with little or no encumbrance from bridging folds. Evidence for this mechanism is particularly clear for dislocations initiated at reentrant corners and, although not readily amenable to direct observation, similar behavior likely underlies marked increase in dislocation densities observed with transition from Regime I to Regime II in crystallization from the melt. Proposed mechanisms do not rely upon specific characteristics of the experimental system studied. © 2002 Published by Elsevier Science Ltd.

Keywords: Morphology; Lamellae; Dislocations

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1. Introduction

A common feature of lamellar crystals in synthetic polymers, whether crystallized from solution or melt, is that they develop multilayer character by forming spiral or terraced overlayers having chain-folded structures similar to the principal or basal layers. Spiral overlayers originate at giant screw dislocations, stepped terraces are produced by layer-spreading from adjacent pairs of dislocations having opposite hands, and both behaviors are imitative of the Frank mechanisms by which layered growth often occurs on singular surfaces (close-packed low energy facets) of monomeric and small-molecular crystals. In polymer lamellae, however, the screw dislocations have exceptionally long Burgers vectors of order 100 Å or more (equal to total lamellar thickness − crystalline core plus fold surfaces), yet they do not have hollow cores as would be required of such large dislocations in most materials. It is essential in these lamellae that axes of giant screw dislocations be parallel to molecular stems; consequently, large apparent shears near these axes can be accommodated locally, with little elastic strain and relatively small cost in free energy, by a staggering of folds. It follows that appreciable glide (lateral movement) of such primarily topological dislocations would necessarily involve rapid readjustment in folding on a scale approaching catastrophic disruption of local crystalline order; in effect they are immobile. During crystallization, they mostly appear to be formed sporadically at growth fronts, especially at reentrant features, and then to be absorbed in place within resulting lamellae. All of this, together with awareness that giant screw dislocations play a vital role in lamellar branching and in morphological development of radiating polycrystalline aggregates of various kinds, was already appreciated within a few years of the discovery (ca. 1957) of crystallization by chain folding (see, for example, an excellent review in Geil's book [1], also a discussion of permissible dislocation processes in polymer crystals [2]). Nevertheless, understanding of how these relatively sparse but very significant defects arise is still evolving slowly.

Generation of giant screw dislocations can most easily be studied in solution-grown crystals, particularly in dendritic crystals having abundant reentrant corners. An early investigation of such dislocations in lamellae of polyethylene and

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polyoxymethylene was reported in considerable detail by Geil and Reneker [3]. They recognized that these dislocations appeared to imply extensive and cooperative departures from the 'normal' laying down of folded chains on growth faces, but were unable to suggest a credible explanation for how such marked anomalies might arise, either along exposed faces or at reentrant corners. It has since been recognized that chain folding is not so orderly a process as was thought at that time, and molecular packing in lamellae is subject to considerable and irregularly distributed disorder, especially at fold surfaces; even now, however, there is still no clear indication from theory as to how such gross anomalies could arise *directly* as part of the growth process as presently understood. Geil and Reneker then focused attention upon what they believed to be short tears or fractures leading inward from crystal faces to dislocations. They considered these to be produced by hydrodynamic forces caused by convection currents in solution, and suggested that lateral growth on the freshly exposed faces, should they become sheared sufficiently out of the same plane, could initiate overlapping spiral growths that then persist as active topological screw dislocations. In the absence of a better alternative this interpretation has been widely held, despite obvious difficulty in extending it to crystallization in viscous polymer melts.

With passage of time, however, it has become clear that, as originally proposed, Geil and Reneker's interpretation is untenable. To tear a lamella as they envisaged is equivalent to driving a theoretically immobile giant screw into the crystal; to suppose bond-breaking fracture across internal fold planes is just as unlikely. Moreover, the free energy associated with a giant screw dislocation has now been estimated as of order $10^2 kT_c$, where T_c is crystallization temperature [4]; no reasonably quiescent solution is likely to produce such defects in profusion by thermal activation. Nevertheless, we believe that Geil and Reneker were on the right track.

Whereas giant dislocations in solution-grown crystals show little preference for one or other hand, those in banded spherulites grown from melt appear to be predominantly isochiral with one another and with lamellar twisting [5,6]. Attempting to account for this selectivity in a broadened context has recently stimulated renewed interest in the unresolved general problem [4,7]. In essence, the emerging view is that dislocations evolve much as Reneker and Geil proposed, though not at the ends of mechanically induced tears or fractures but around small, almost imperceptible, 'slits' that may develop naturally in the growth process. Initially, this view alone seemed to afford means by which necessary shears, likely driven in favorable circumstances by inhomogeneous congestion at disordered fold surfaces, could occur without conspicuous detriment to crystalline order. Preliminary observations were encouraging (scarcely surprising in view of Geil and Reneker's early work) and a promising explanation for occasional occurrence of the all-important slits was suggested by Frank's discussions of bunched layer spreading and formation of lacunae in crystal growth [8,9]. In this context, the term lacuna very aptly implies a lapse in temporal continuity, or a blank space or missing part or, conceivably, both in combination. Our purpose in this paper is to discuss these mostly unpublished developments, and to provide evidence supporting a revised interpretation of the origin of giant screw dislocations that is based on them.

2. Background and approach

The ubiquitous occurrence of dislocations (in the following we mostly omit the implied adjectives 'giant screw') in polymer lamellae in general assures us that the origins we seek do not involve chemical structure in an essential way (apart from requiring reasonably stereoregular long chain character). Thus, we infer that the sequential process of laying down folded chains on crystal faces, albeit with disorder on a molecular scale (non-adjacent reentry, loose loops, cilia), is subject on occasion to special dislocation-producing quirks having major consequence. Since this seems to be true for most, if not all crystallizable chains, we also infer that recognition of principles underlying occurrence of these peculiarities in one polymer would likely have wide, if not universal, applicability. Proceeding on this basis, we shall in the following avoid specificity when exploring the dynamics of layer spreading in chain-folded crystals and later, as exemplar, we shall correlate deductions with observations made by electron microscopy on dendritic crystals of a linear polyethylene. To some degree we shall depart from the customary order of presenting all data before attempting an interpretation, in the belief that in this instance it will make for condensation of text and ease of comprehension. After all, we are synthesizing a new interpretation by adapting and combining elements which, although not previously considered in association, are scarcely novel in concept.

Common experience suggests that although dislocations occur under almost all conditions of growth, incidence of their formation increases in response to faster growth at increasing supercooling, especially upon entering Regime II conditions where roughened growth faces produce copious reentrants. It also increases to some degree with increasing molecular weight. Nevertheless, densities of dislocations in lamellae are seldom as large as $5\ \mu\mathrm{m}^{-2}$ which, in polyethylene, would correspond roughly to one dislocation line for every 10^6 molecular stems and, depending upon molecular weight, every 10^4–10^5 molecules. Apparently, the quirks we seek *always have finite probability* of occurrence during crystallization by chain folding, yet at best that probability is distinctly small. Our approach will be first to consider how pronounced reentrants are typically produced along serrated growth faces in dendritic crystals (see later, Figs. 1, 2 and 4). We shall then explore what special opportunities these reentrants may provide for

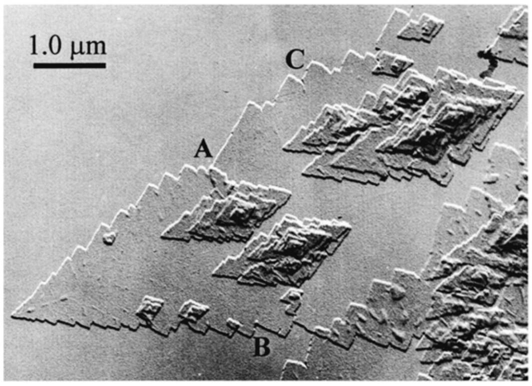

Fig. 1. Tip of a dendritic crystal of linear polyethylene grown in dilute solution; initial growth was rapid but crystallization temperature was maintained until all polymer had deposited. (Letters in this and subsequent micrographs indicate features discussed in text.)

generation of dislocations; in turn, the question will present itself as to whether or not similar opportunities might also arise, albeit with reduced probability, at less prominent surface singularities.

3. Experimental methods

Dendritic crystals suitable for our purposes were prepared using a linear polyethylene of moderate molecular weight (NBS SRM 1483, $M_w = 32,000$, $M_n = 28,900$) and grown from 0.01% solution in *p*-xylene at temperatures close to 67 °C. The simple procedure, using a preheated micropipette with squeeze bulb, was to transfer 1 ml of 0.1% solution held at 100 °C to 9 ml of *p*-xylene already equilibrated at 67 °C by immersion in a temperature-controlled bath. The stronger solution with partly immersed micropipette had been cleared by prior heating above the temperature at which self-seeding nuclei are dispersed. Transfer to pure solvent in a thin-walled test tube was rapid and followed by very brief stirring so that temperature during nucleation and growth would have fallen from no higher than 70.3 to 67 °C. (For some preparations a lower final temperature (65 °C) was used; of micrographs shown later only Fig. 1 refers to corresponding crystals.) Several days were allowed before slow cooling to room temperature. Deposition of crystals on carbon-coated grids for examination by TEM, including shadowing with Pt/C, was by conventional means.

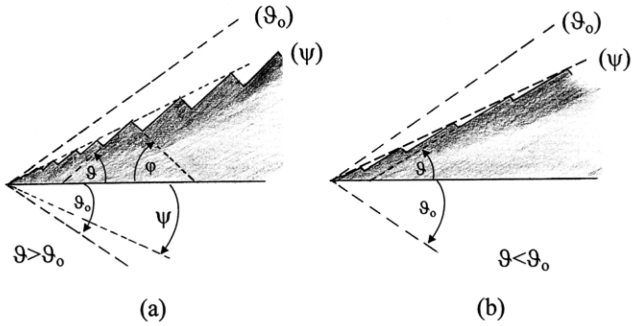

Fig. 2. (a) Schematic representation of Fig. 1 identifying angles for discussion in text. (b) Same crystal tip as it may have appeared during initial period of rapid growth.

4. Dynamics of layer spreading

Experience shows that most of the crystal growth in chain polymers obeys nucleation kinetics ($\ln G \sim -1/T\,\Delta T$) apparently signifying that growth faces, usually close-packed low-energy facets, advance by repeated spreading of freshly nucleated layers presumed to be one molecular width in thickness. Although commonly treated as stochastic, in practice the process is seldom truly sporadic. Nucleation rate is an extremely sensitive function of thermodynamic driving force and, in the case of facetted crystals, can be strongly favored in the vicinity of protuberant corners where active growth faces meet, usually along a major symmetry axis. These are sites where concentration of solute is greatest and where locally enhanced nucleation generates new layers that spread partly toward, *but predominantly backward away from* the corners. Fig. 1, for example, shows the result of fast dendritic growth along the *a*-axis in a polyethylene crystal of rhombic habit where {110} growth faces intersect at an angle close to theoretical (67.4°). It is evident that spreading layers, likely generated at a fairly steady rate, have not progressed uniformly along the growth faces but have bunched together repetitively to form a series of steps each many layers high; these features, which provide reentrants, are examples of lacunae. In simple terms, this behavior is attributable to the fact that, as successive layers move further back from a leading tip, their rates of advance are coupled and progressively retarded because of demands placed upon a common decreasing supply of solute.

The reader will recall that, in polymers crystallizing isothermally from solution or melt, local variations in thermodynamic driving force are generally governed much more by corresponding variations in composition (chemical potential) than by variations in temperature associated with changes in enthalpy. This can easily be overlooked because the profusion of distinct species in a typical polymer renders accurate quantification of supersaturation or chemical potential extremely difficult. The common practice (as in the relation in parenthesis above) of relating a representative driving force, expressed as supercooling from a 'terminal' dissolution or melting temperature, to a measured growth rate (often along an axis rather than normal to a facet) is an unavoidable, though helpful, circumvention of such difficulty.

In Appendix we outline Frank's analysis of unidirectional spreading of layers away from a crystal edge, or other growth-promoting center, in a monomeric crystal. Two key considerations are: continuity, from which follows a relation between variations in *k*, the local density of monomolecular steps, and in q, their flux past a given point; and obvious inference that the function $q(k)$ increases at a rate slower than linear and must eventually saturate. Monomolecular steps inevitably bunch into slower moving giant steps, and in some circumstances these may ultimately halt and create permanent lacunae [9]. (Application to interpretation of complex morphologies in ice crystals on pp. 11–19 of Ref. [9] is highly recommended for reading.) We are here concerned with a somewhat less orderly process, the predominantly unidirectional spreading of layers consisting of adjacent stems of folded molecules during advance of the prominent axis of a dendritic crystal as in Fig. 1 (also see subsequent micrographs). This process differs in several obvious respects from that treated by Frank; nevertheless, the physical bases have much in common and it seems reasonable to attribute closely similar outcomes to similar causes. Our immediate concern is to discern how in the polymer case there is an unmistakable tendency for dislocations to form at prominent reentrants where large steps appear effectively to have come to a halt.

Unfortunately, electron micrographs, such as we show, represent conditions of dendritic crystals after all accessible solute has crystallized, but do not directly reveal transient states during earlier vigorous dendritic growth. Moreover, later stages of prolonged isothermal crystallization doubtlessly involve widespread deposition of shorter molecules at decreasing rates under conditions such that concentration gradients have little influence. Nevertheless, significant aspects of prior transient behavior can be appraised by reasoning as follows.

In Fig. 2(a), a schematic representation of the crystal in Fig. 1, we indicate our notation for identifying important angles. In Fig. 2(b) we shall later suppose to give a closer representation of how the advancing tip of this crystal would have appeared during its period of rapid growth; steps near the tip are shown wider than they would become in later stages of growth. In both cases, heavy dashed lines at $\pm\theta_0$ to the axis ($\theta_0 = 33.7°$) indicate orientations of $\{110\}$ planes as seen in chain axis projection; in the case of Fig. 2(a) we make the supportable assumption (see later) that in Fig. 1 something close to this orientation resulted from drying down the crystal upon a substrate. We note that steps are oriented at angles θ close to θ_0, and that intervening 'risers' at angles denoted by ϕ fall off steeply from them. These risers are not growth faces in the conventional sense but, rather, envelopes at which successive layers upon true growth faces (fold planes) have approached almost orthogonally and then terminated. Not surprisingly, values of ϕ vary from one riser to another; in crystals grown at 65 °C the range is about 40–52°, and in crystals grown at 67 °C from 40 to 50° but more closely bunched near 40°. From their variable orientations, which do not include a low index plane suitable for deposition of folded chains ((320) at $\phi = 45°$ is the first but unrealistic possibility), we must suppose that the faces of the risers involve irregular alternations of very short microfacets of favorable (110) and unfavorable (200) character. Continued advance of established steps is therefore likely to be seriously retarded regardless of whether or not availability of solute is renewed by diffusion. Initiated by local nucleation, steps continue to grow away in echelon from the central axis with their risers trailing lengthening traces (see later) along paths followed by reentrant corners, *and along some of which dislocations have been left behind*. Particularly significant is the manner in which these risers (lacunae) have become increasingly engulfed within the growing crystal. *Clearly, they have been met by crystallization fronts approaching from directions opposed to that of the original layer spreading*. Similar evidence emerges from consideration of the steps. During initial advance of the tip (Fig. 2(b)) we expect steps to be inclined at angles θ somewhat less than θ_0 since layers would then be moving left to right. This, however, is not what we see in Fig. 2(a) where steps are inclined at angles greater than θ_0. In crystals grown at 65 °C values of θ vary from 37 to 44°, tending to increase with distance from the tip; the corresponding range for crystals grown at 67 °C is 35–42°. It is again evident that in these later stages of crystallization molecular layers have nucleated near protuberant step edges and spread predominantly toward the tip of the dendrite, even at positions close to the tip itself.

Despite these somewhat unexpected deductions, however, there is no doubt that layer spreading near the *actively growing* tip was overwhelmingly away from the tip as has been stated. The very existence and geometry of the steps, and the facts (i) that all growth is confined within envelopes at $\psi \approx \pm 25°$—considerably less than θ_0—and (ii) that overall axial ratios (a/b) in these dendrites exceed significantly the value ≈ 1.50 expected of the basic $\{110\}$ rhombic habit, all bear witness to this conclusion. The evolving competition between greatly favored fast nucleation on highly localized surfaces near the tip at early stages, and increasingly significant slow nucleation that gradually becomes widespread over all viable growth faces, involves interplay between kinetics and diffusion on two different scales (see Appendix) and is not a simple process. Including the observation that in many cases the edges of exposed steps eventually initiate dendritic branches that grow orthogonally to the axis, this process would make an interesting topic for further but separate study. The aspects *of immediate relevance* are formation of lacunae through temporary localized exhaustion of solute and reverse growth to meet them as a more uniform distribution of solute is attained by diffusion; are there significant implications when the depositing units are stems of folded chain molecules? Approached in this way, an answer seems almost self-evident.

Processes in which chain molecules condense by folding on the growth face of a polymer lamella remain the subject of intense controversy. Nevertheless, some inferences from phenomenology, if not pushed to unreasonably detailed interpretation, seem persuasive. A point of particular interest is that, regardless of how regularly or adjacently it

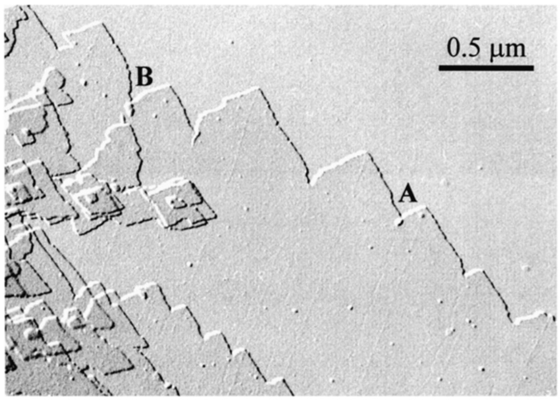

Fig. 3. Area of crystal showing reentrants with possible embryonic dislocations (also striae).

has folded, each molecule has two terminal stems within its own fold plane. Commonly, such a stem is found near an end of the molecule where it constitutes a (transitory) surface step and associated short cilium (the step being a favored site for initial attachment of the next molecule in the plane); it may also occur when the folding molecule encounters another chain already positioned in the same plane, possibly leaving a long cilium that may ultimately form a bridge to another fold plane (as in superfolding) or to another lamella. Another significant point is that, in contradistinction to behavior in monomerics, where reentrant corners promote greatly enhanced nucleation and growth, reentrant corners in polymer lamellae have the opposite effect. Polymer molecules in melt or solution are reluctant to penetrate closely confined spaces, apparently in order not to decrease conformational entropy. Not only does mobility become restricted under confinement but also penetration into extreme corner sites, as needed for enhancement of surface nucleation, would require relatively improbable reptation, whether by a chain end or a molecular loop. Implied behavior of this kind was first evidenced by unexpectedly slow growth at reentrants in twinned crystals [10] and has since been reported in other contexts (see, for example, Refs. [6,11]).

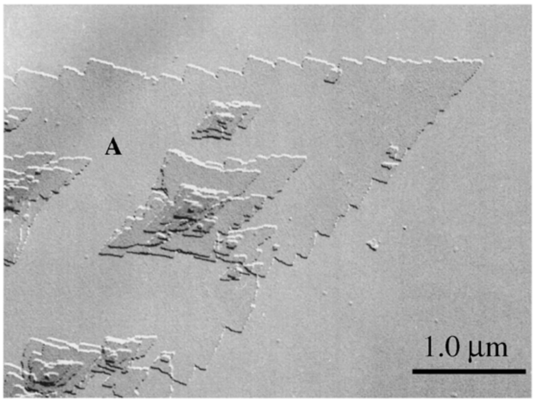

Fig. 4. General view of striae transverse to principal axis. If held facing bright light and viewed toward 11 o'clock these features, though faint, are readily visible.

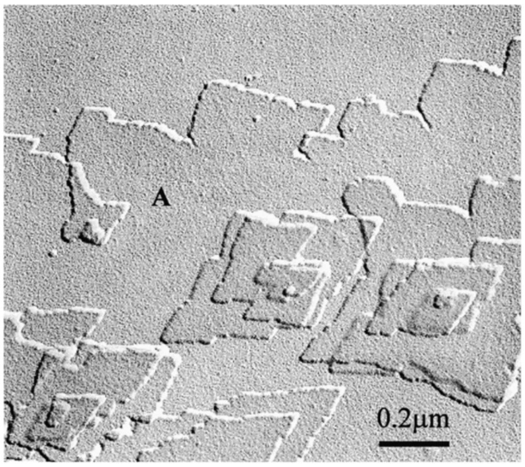

Fig. 5. Detail of features at higher magnification (see text).

From these two points in combination it becomes credible that, as reverse layer spreading begins and approaches the base of a riser, a folding molecule has a fair probability of depositing a terminal stem when still a few spaces short of the riser. That a similar occurrence might also take place on the next layer would have a smaller but still far from negligible probability. Further, since risers are many layers high, probability of such an occurrence *at some position* on the riser would be appreciably enhanced. An event of this kind might well initiate formation of a narrow, deepening and increasingly impenetrable furrow between old and new growth—in effect, give rise to a sheet or a few contiguous sheets of vacant stem sites. However, for such sheets to become a fissure or slit effective for generating a dislocation would require adventitious cooperation from shears accompanying warping likely induced by unbalanced stresses in irregularly congested fold surfaces. It would also depend crucially upon whether, in subsequent layer spreading, those folding molecules that encounter vacant sites when still having considerable uncrystallized contour length would tend to bridge the gap and build onto the riser surface or would turn back upon themselves onto the next upper layer as in superfolding. Speculative arguments can be made either way; probabilities cannot be assessed reliably and we must be guided by empiricism. In this respect, polyethylene is disadvantageous because of the minimal cross-sectional area if its chains; slits comprising a few sheets of vacant stem sites would be difficult to image clearly. Polymers having helical conformations with large diameters pose other problems. In the event, the disadvantage proved not to be crippling.

5. Electron microscopy

Our choice of polymer was based partly upon reliable characterization, and partly upon a modest molecular weight which suggests potential on average for about 15 stems per folded molecule. Despite small polydispersity

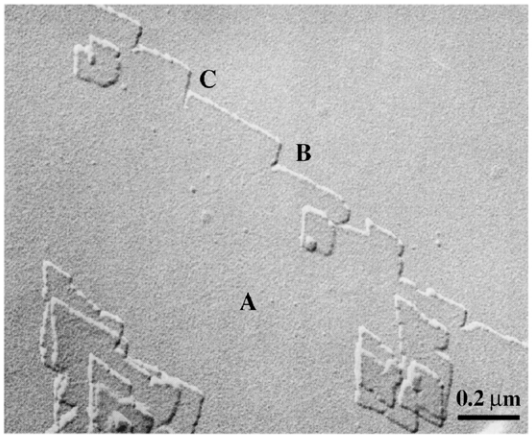

Fig. 6. Detail of features at higher magnification (see text).

(< 1.2) indicating a simple bell-shaped distribution it is not, from its behavior, a sharp fraction; nevertheless, for our purpose it is a favorable representative of a much studied and familiar polymer. In particular, it was anticipated, apparently correctly, that complication from tent-like or ridged morphology [12] would be slight and likely obviated by shear as crystals dried down with stems more or less normal to a substrate. (Such shear, however, could not materially alter the occurrence or appearance of existing dislocations.) Convenience in surveying and photographing many crystals for later examination entailed study of shadowed specimens commonly after appreciable loss of crystallinity by radiation damage. Accordingly, resolution was limited to several nanometers, still adequate for most original features to be readily discernible at a magnification, say, of 30,000 ×. We show in Figs. 3–10 a number of micrographs (with markers identified in text or legends) which, between them, will serve to illustrate various points as they arise in subsequent discussion. First, however, some general remarks are in order.

Crystal growth is not in general an orderly process that follows rigidly the predictions of (inevitably oversimplified) theoretical models. Fluctuations and other vagaries become increasingly apparent in their effects as morphology is studied on finer scales. In our survey, we sought evidence concerning early signs of relatively rare departures from the anticipated norm, departures not necessarily unique in character or mode of formation. For these, relative frequencies of occurrence can be reported, but not faithfully represented, in a few illustrations chosen with other priorities in mind. We trust the reader will keep this in mind. Our attribution of lamellar warping, without which there might be no dislocations, to irregular structure in fold surfaces does not rely upon any of the observations reported here. Existence of such warping is soundly based on the experience from microscopy of lamellae still suspended in mother liquor [1,12], from behavior of twisted lamellae in spherulites [4,13] and, strikingly, from studies by scanning electron microscopy of lamellar clusters prepared by critical point drying to obviate distortion by capillarity [14]. It is on a scale that cannot be explained plausibly by erratic lattice disorder but, in such thin and flexible crystals, could easily result from elastic deformation caused by considerable inhomogeneous congestion in fold surfaces. It will be recalled that, under relevant circumstances, theory predicts a significant limit to adjacent reentry and emphasizes statistical considerations (as in the 'Gambler's Ruin' approach); elastic energy is readily derivable from the circumstance that nucleation and growth occur inevitably at supercoolings generally exceeding 20 °C.

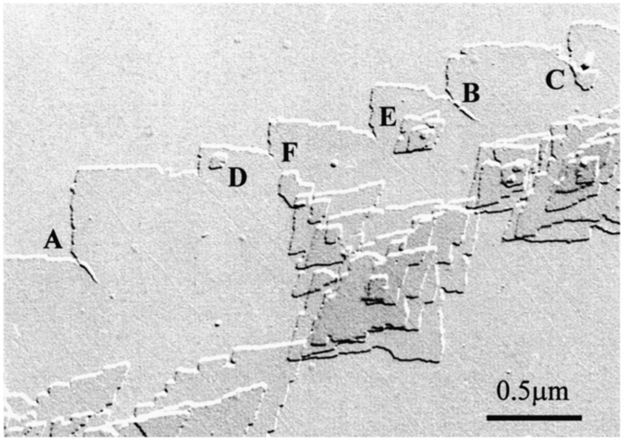

Fig. 8. Detail of features at higher magnification (see text).

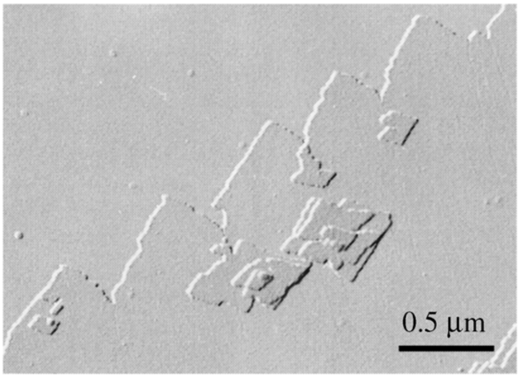

Fig. 7. Detail of features at higher magnification (see text).

6. Observations and implications

As a concise and convenient approach, we shall address relevant points in sequence, choosing illustrations from among our micrographs as needed.

First, lest there be doubt, we emphasize that reentrants are a major source of dislocations and not the reverse. It is found that, on rare occasions, especially in crystals grown slowly (for polyethylene, at higher temperatures than employed here) one encounters small overlayers at dislocations which have just been formed at growth faces without visible evidence of initiating reentrants. Much more common, however, are situations as we describe in which,

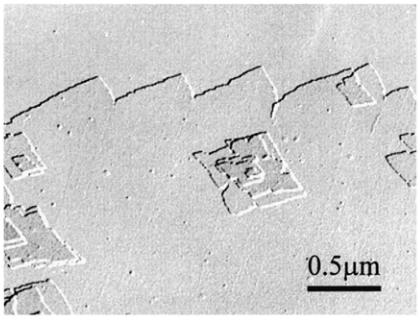

Fig. 9. Detail of features at higher magnification (see text).

once a dislocation becomes established at a significant reentrant, it tends to deepen that reentrant by providing additional growth faces to consume locally available solute. This effect is evident at Fig. 1(A) (by this notation we refer to marker A in Fig. 1); distinction between cause and effect should be clear from general perusal of many of our figures. In several instances (for example, Figs. 1(B) and 3(A) there are small blob-like features deep in reentrant corners. It is unclear whether these are embryonic dislocations—a very small one at Fig. 3(B) seems to be so—or indicate sites where coiled molecules have become trapped, perhaps by adsorption within a 'V'. Occasional small blobs embedded in crystals may have such origins.

Secondly, when shadowing has been directed more or less along a central (*a*) axis and there is sharp focus, faint striae that terminate either at protuberant step edges or at reentrant corners are seen extending in transverse directions. Near leading growth tips these are orthogonal to the axis (Figs. 4(A) and 6); however, in regions of more mature growth that reach further from the axis some striae are oriented slightly differently (see later). At first, we missed the significance of these important features, thinking them a possible legacy of ridged structures prior to collapse on substrates. (Transverse ridges along *b*-axes are known in elongated polyethylene lamellae grown slowly in melt; in crystals of rhombic habit these are unknown although tent-like distortions often leave traces of ridges along ⟨130⟩ directions at 63.5° to *a*-axes [12].) Closer examination of the faint striae, however, revealed clearly that *in all cases* those leading inward from reentrants appear to be shallow furrows and those leading from step edges appear to be slight ridges (see, for example, Figs. 3, 5–7). This conclusively rules out ridged precursors with serrated edges since all ridged crystals would then have had to deposit the same way up (all with longer ridges on top). As it is, furrows leading from lacunae suggest local thinning or density defects, and ridges suggest local thickening (possibly attributable to chains at protuberant corners offsetting reduced stability by increased stem length). Further examination of the striae showed that, whereas ridges remain orthogonal to *a*-axes in mature growth, furrows tend to lean from this orientation in directions away from axial growth tips by angles up to about 5° (Figs. 5(A), 6(A), 8(A) and (B)). Evidently, there is slow later growth on the risers so that furrows traced out by reentrant corners diverge slightly from their associated ridges. In later growth it is also noticeable that steps often curve downward into reentrant corners (Fig. 6(B) and (C)), thus giving additional support for views expressed earlier about reversal of growth directions and kinetic retardation in confined spaces.

Thirdly, to illustrate that dislocations are generally produced at sites along furrows we refer especially to Figs. 5–9, *which speak for themselves*. In other situations, when dislocations have developed several overlapping layers at some distance into a crystal, the correlation is less distinct but, nevertheless, often apparent. Unquestionably, there are also instances in which, for reasons yet obscure and discussed later, dislocations grow at locations not related to reentrants or furrows and even lie on or close to ridges.

As for defect structures along furrows, and associated freedom for shear to develop, we direct attention first to Fig. 8 where at (A) and (B) there are clear instances of modest shear at reentrants that is still insufficient to have produced viable dislocations. However, shearing over a short distance has initiated a dislocation at (C); and at (D) and (E), as a rarity, there are neighboring examples of unusual formation along ridges. In the same field at (F) there is a string of dislocations (with opposing hands fully compensating) along a furrow; such observations are both striking and meaningful. Further, it will be noted that at (A), (B), (C) and near (E) reentrants penetrate some distance into furrows. Other examples of such indentations are evident from Figs. 1(C), 4, 5 and 9 in circumstances more convincingly consistent with their being growth features rather than products of mechanical intervention. We referred earlier to such features as slits but at readily discernible width they may merely mark inner presence of extensive narrow fissures, much as estuaries lead inland to rivers. On a scale coarser than molecular, the common mode of formation of dislocations at reentrants is now evident and well exemplified, and we may now speculate more confidently about structure along paths delineated by furrows.

7. Discussion and extensions

There seems little doubt that density is subnormal along observed furrows, that vacant stem sites are largely responsible or, moreover, that irregular sheets of stem sites would be unlikely to heal. More in question is the extent of molecular bridging across such fissures. By conventional theory, the critical step in nucleating a new layer of folded molecules on a plane crystal surface is attachment of the first stem, which is but a short segment of one of the many molecules ultimately involved. One might therefore expect that, as reverse growth meets a riser, there could be considerable molecular bridging as longer cilia cross-over and make nucleating contacts, thus tending to thwart shearing or, at the least, to cause detectable disorder when dislocations do eventuate (something we have not observed here or seen in other published micrographs). Before venturing a judgment, however, the following should also be considered. Whereas the giant dislocations we have been considering have great morphological significance, conventional dislocations play no part whatever in *lateral* growth of an individual lamella (a marked difference from common behavior in monomeric crystals). Such dislocations would have modest Burgers vectors (~5 Å) and lie in the lamellar plane; apart from being mobile and unstable against annihilation under the influence of image forces, they would produce surface ramps much too short to assist in establishing stable single-stem nuclei. Now considering a furrow in one of our crystals when shear forces operate, we see that a ramp on its way to initiate a dislocation must pass through stages in which shallow surface steps are created (again see Fig. 8(A) and (B)). These would not only prevent lateral spreading but also, for some distance along the furrow, discourage all molecular deposition and bridging; shear forces could then be relatively unopposed in achieving strains adequate for lateral growth to resume, overlap and lock in a dislocation. This must have some bearing but, on the whole, we interpret our observations as indicating that molecular bridging in general is quite limited along fissures associated with furrows. Lest this should seem a questionable deduction given the modest chain lengths in our polymer, we remind the reader of reinforcing common experience that, other circumstances being comparable, formation of dislocations is more profuse with longer chains in polymers of higher molecular weight. We recognize that as a general conclusion our interpretation is somewhat at odds with conventional theory; this aspect deserves brief commentary, particularly because of relevance to generation of dislocations in circumstances other than those considered thus far.

There are sound reasons for considering the critical step in nucleating a folded chain on the surface of a polymer crystal to be addition of the first stem which, we recall, is only a small part of a single molecule. Processes leading up to and following such an event, however, are uncertain and controversial, largely owing to difficulty in assessing some likely important entropic contributions to free energies of activation in kinetic barriers, and to their consequent neglect. Our observations suggest that crystallizing molecules may accommodate themselves appreciably more compactly on growth faces than is generally presumed on an idealized basis of unimolecular layer spreading. While differing considerably in their interpretations, others investigating crystallization from different standpoints in recent years have nevertheless expressed similar views [15–17]. We envisage a behavior something like the following. Nucleation likely involves rearrangement of a convoluted molecule already attached by local adsorptive contact; we imagine that, once a straightened and oriented segment becomes established as a new stem on the crystal surface, chain length feeds by reptation to support lateral migration of loops that settle progressively into neighboring stem sites. These sites are increasingly removed from as yet uncrystallized chain near the nucleating site and in time contiguity, perhaps aided by drag, induces superfolding back onto an upper layer, a process perhaps repeated several times depending upon molecular length. Conventional theory would demand an activation energy for each such superfolding event equal to that for initial nucleation; we suspect that this apparent penalty can be much reduced by paying attention to commonly overlooked entropic factors [18]. (It is to be remembered that conventional theory is largely concerned with accounting for rapidly varying nucleation kinetics at small or modest supercooling and is not quantitatively absolute: in addition, however, some activation free energy barriers of entropic character would exert a much less temperature-sensitive effect upon absolute rates; there is still considerable latitude for divergence.) Our proposal complicates matters (pays closer attention to real complications would perhaps be more accurate), but we see no reason why it would necessarily be inconsistent with concepts of layer spreading as we have employed them here, or with observed nucleation kinetics, including those aspects dealt within Regime theory; compliance with phenomenology is always a paramount concern.

Whatever the merit of these derivative speculations, deductions based on our observations on one system lead with little further consideration to a broad appreciation of how giant screw dislocations are formed in polymer crystals in general. To a coarser level of detail, similar observations, beginning with those of Geil and Reneker, are common in the literature; Figs. 27 and 41 in Ref. [19] show examples of dislocations developing with appropriately different geometries in crystals of hexagonal or tetragonal symmetry. Most significant among newly appreciated factors, we believe, are (a) layer spreading, specifically of folded molecules (which is subject to lacunae, in part because added units are much larger than unit cell repeats), and (b) ease with which chance congruence of vacancies between such molecules on successive fold planes can develop into fissures (specifically because of conformational entropy inherently associated with jointed chains). Large reentrants are not necessary, although they have aided in interpretation and doubtless do enhance probability of dislocation formation. In slow Regime I crystallization in solution or melt this probability is indeed likely to be very small. However, it is greatly increased upon entry into Regime II conditions when faster growing, multiply nucleated surfaces are roughened and many spreading molecules abut their advancing neighbors, though not infrequently some will leave small vacancies. Moreover, in this faster growth more disordered folding will tend to intrude upon and seal off the ends of vacant stem sites and promote deeper fissures. Dislocations formed in this way would not rely on preexisting reentrants, but may subsequently initiate small ones. These considerations seem to be borne out by a well-known

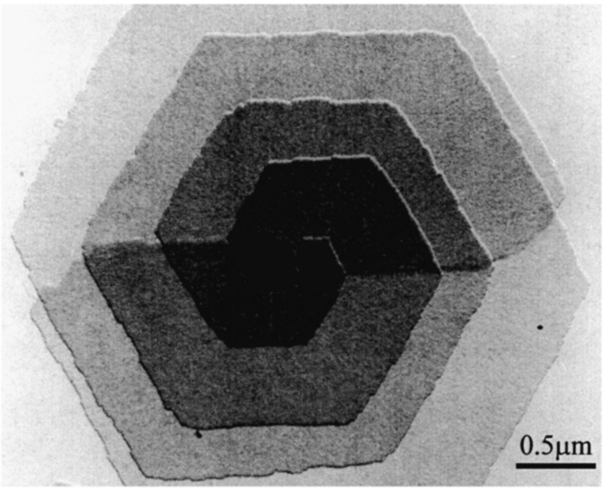

Fig. 10. Generation of double dislocation spirals by heterogeneous primary nucleation in a crystal of isotactic polystyrene. (Reproduced from Ref. [20] with permission from John Wiley & Sons, Inc.)

onset around the Regime transition of increasingly profuse branching that marks gradual morphological conversion from axialites or hedrites to spherulites.

Translating these ideas into the context of spherulitic crystallization from melt requires attention to two qualifying considerations. Diffusion ranges are greatly reduced in response to melt viscosity and behavior, being much compressed in scale, becomes less accessible to detailed observation; at the same time, congested layers of more highly disordered polymer at 'fold surfaces' become increasingly capable of causing distortions favoring formation of dislocations. (The dominant role of such dislocations in morphological development within crystalline polymers has already been emphasized and referenced.) With respect to two papers cited earlier, the following points deserve mention. In an appendix to Ref. [4], purely as a speculative guess working from the answer (observed outcome) backward, an explanation was offered for the generation of isochiral dislocations in twisted lamellae that now seems well supported. In relation to Ref. [7] it is now clear why, in spherulites, dislocations almost always appear down the sides of radial lamellae or, at the least, perceptibly off-axis; such lamellae are in effect dendrites in which branching can develop significantly only in forward (radial) directions. An approximate correlation between scale of transverse organization of lamellae and diffusion range, first proposed four decades ago, and borne out when estimates of diffusivity are based on direct measurement and not upon viscosity using the Stokes–Einstein relation (conceived specifically for entities of roughly spherical shape), derives ultimately from this circumstance.

It is evident from mode of formation that molecular packing at the core of a giant screw dislocation is not at first uniaxial but involves a plane across which there is slight misalignment of axes. It seems likely that, to some degree, there would be subsequent relaxation to a structure closer to that originally envisaged by Geil and Reneker. To the extent this may not be the case our descriptive Section 1 involved a slight error; this was difficult to avoid and has no significant consequence.

As a final topic, we note that some polymer crystals exhibit dislocations at or very close to their geometric centers, defects which appear to have origins different from any discussed above. Primary nucleation is often heterogeneous and much then depends upon the characters of the heterogeneities involved. Fig. 10 shows a pair of dislocations at the center of a single crystal of isotactic polystyrene grown in a thin film of melt; an associated foreign particle is clearly evident. Crystallization had begun at two different locations on this particle and encircling lamellae had come together in slightly different planes, necessarily producing two ramps that were fortuitously aligned. The proximity of the supporting substrate has suppressed growth on lower surfaces, in this case leaving unusually clear delineation of the growth spirals. Heterogeneities, however, are seldom so easily detected nor their intervention so clearly evidenced.

8. Conclusions

Giant screw dislocations without hollow cores are exclusively a polymeric phenomenon. Our experiments have suggested two exclusively polymeric factors that appear to account for their formation in most cases. One is related to irregularities in layer spreading of folded molecules and the other is an important role played by conformational entropy. There is a small, yet finite, probability that these combine in certain circumstances to produce fissures across fold planes that permit axial shear. When driven sufficiently by warping induced by irregularly congested fold 'surfaces', such shear encourages overlapping growth that develops the spiral character recognized as a topological giant screw dislocation. Deductions blend well with morphological experience on a wide basis. Follow-up could make an interesting but demanding challenge for an expert in atomic force microscopy.

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Appendix. Frank's analysis of layer spreading

Unidirectional spreading of monomolecular layers across a crystal face from a source of rapid nucleation (large supersaturation) to a region where nucleation is negligible (significantly smaller supersaturation) can conveniently be characterized by step frequency q (the number passing per unit time) and step density k (the number per unit length), these parameters being related by a function $q(k)$. Both vary with distance traveled (x) and with time (t), and continuity requires $\partial k/\partial t + \partial q/\partial x = 0$. If b is the thickness of a monomolecular layer, $qb = G$ is the rate of normal growth of a step surface and kb is its vicinal slope from the associated close-packed plane.

The velocity of an isolated step, $g = q/k$, is governed by local supersaturation, but at each point in its 'wake' it leaves behind a supersaturation that is slightly reduced until restored by relatively slow diffusion. Under similar conditions, the movement of a succession of steps would become retarded progressively as step density increases. Thus, we infer that, at given supersaturation, $q(k)$ will first increase linearly with k but then at steadily decreasing rate until reaching a limiting value at large k. In the situation under consideration, however, q is determined by the nucleating source and, as steps travel and slow down, the value of q can be maintained only by increasing k. This bunching further enhances retardation and a steep-fronted multilayer step is soon formed. It can shown from the continuity conditions that a state of constant k moves across the crystal with velocity $\mathrm{d}q/\mathrm{d}k$ which, from the form of $q(k)$, is less than q/k, the velocity of individual steps that inevitably overtake it (see later); this adds further weight to the argument for bunching into a giant step. A moving source such as the growing tip of a dendrite will in any event leave behind it a series of multilayer steps, and in polymers, as we have shown in Section 4, there are special reasons specific to crystallization by chain folding for steps being brought virtually to a halt.

Although not addressed by Frank, a related point of relevance is that processes involving interaction between moving solid boundaries and diffusion in fluid phases generate concentration gradients that scale in direct proportion to velocity of movement and in inverse proportion to diffusivity. Local gradients near crystal faces induced by movement of steps with velocity g and by normal growth of faces, velocity G, can be of quite different magnitudes depending upon step density. Because of polydispersity or stereoirregularity, behavior in crystallization from polymer melts is similar in all of these respects but *on much smaller scales of distance because of greatly reduced diffusivity*.

Finally, we note that the above continuity condition can be presented in the form $\mathrm{D}k/\mathrm{D}t = \partial k/\partial t + \mathrm{d}q/\mathrm{d}k \partial k/\partial x = 0$ which admits of simple physical interpretation. From an obvious hydrodynamic analogue it implies that the *convective* derivative of k with respect to time is zero at a point moving with velocity $\mathrm{d}q/\mathrm{d}k$. A further suggestive, but in this case inexact, analogy is with wave motion for which, expressed in terms of frequency ν and wavenumber k, phase velocity is ν/k and group velocity is $\mathrm{d}\nu/\mathrm{d}k$. In the context of layer spreading Frank referred to $\mathrm{d}q/\mathrm{d}k$ as 'group velocity' but was (characteristically) careful to include quotation marks.

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