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Self-induced field model for crystal twisting in spherulites

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Abstract

The observed twisting of crystals about the growth direction in spherulites is modeled as a response to fields generated during the crystal growth process. These fields can be compositional or mechanical. In either case, the high local field value in the melt near the interface acts to reduce the growth velocity. Twisting of the crystal about the growth direction places all portions of the growth surface in contact with melt of lower field value than would be the case for untwisted growth, thereby increasing the growth velocity. The effect of a compositional field is analyzed here, using an extension of the moving point source to compute the composition in the melt ahead of a twisting crystal. The retarding effect of the elastic twisting of the crystal is included in the analysis. Simulations using parameters for a crystallizable/uncrystallizable polyethylene blend are carried out for a crystal with thin, rectangular cross-section. The results are quantitatively and qualitatively consistent with observation. Comments on simplifications within and implications of the model are given.

Keywords: Crystallization; Banding; Crystal twisting

1. Introduction

1.1. Background on twisted crystals

The twisting of fibrillar crystals about their growth directions is a relatively common feature, for both organic and inorganic materials grown from the melt [1,2]. Bernauer lists 136 organic compounds in which twisted crystals were known to him in 1929 [1]. All crystal systems, except cubic, are represented in this list. In spherulitic polymeric systems, crystal twisting manifests itself, under crossed polarizers, as regular radial banding within the spherulite [3–6]. Radial banding and crystal twisting are pervasive in polymer systems.

In the present work, we examine the premise that fields which are self-induced during crystallization may play a role in inducing crystals to twist during crystallization. The model is made quantitative and the absolute magnitude of the induced twist is predicted. The self-induced field effect may operate in conjunction with other effects which are known empirically to play a role in crystal twisting.

We begin by examining extant models of crystal twisting and contrast these against the self-induced field model. The following is a summary of some of the models put forward to explain twisting.

(1) *Surface stresses within the crystals*. Lehmann had suggested in 1888 [7] that the twisting of ribbonlike crystals is associated with surface stresses. Noting that lattice parameters at the surfaces of a crystal are generally dilated with respect to the core, Yoffe in 1944 [8] suggested that the stresses associated with such a gradient in lattice parameter could be reduced by twisting of thin, lathlike crystals. Since such twisting is not universally observed in lathlike crystallization, the dilatation near the surface would need to exceed some critical value in order to force the crystal to twist. Hoffman and Lauritzen later suggested that bulky chain-folds at the surfaces of lathlike polymer crystals would provide the stresses needed to force twisting [9]. Bassett and coworkers have extended this concept. They have found that in polyethylene, twisting is associated with an S-shaped cross-section of the crystals [10,11]. They suggest that the S shape arises from surface stresses and that these stresses develop after crystallization, as internal rearrangements occur, to regularize initially irregular folding [12,13]. Lotz et al. [14] have recently demonstrated that differences in fold structure on opposite faces of crystals of the γ form of poly(vinylidene fluoride) produce sufficient stress to induce the crystals to scroll about the growth axis (the *b*-axis) (2) *Surface stresses induced by the surrounding melt or intervening amorphous layer*. Keith

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and Padden [15–17] propose that the melt immediately ahead of growing lamella produces compressive and dilatational stresses on opposite faces of the lamella, provided that the growth face is not normal to the growth direction (nonorthogonality of growth plane and growth direction is known to apply to polyethylene and many other polymers). These asymmetrical stresses derive from a geometrical condition: that on average, chain segments in a coiled molecule lie farther from the obtuse edge of the growing crystal than from the acute edge. Bassett and coworkers, on the other hand, suggest that pressure from cilia trapped between the faces of adjacent lamellae, near giant screw dislocations, plays a major role [18–20]. Keith et al. [21] have demonstrated that the sense of twisting in polyethylene crystals grown from a thin film melt correlate to the direction of chain tilt, qualitatively as predicted by Keith and Padden [15–17].

(3) *Queues of giant screw dislocations*. A screw dislocation has associated with it a lattice twist about the axis of the dislocation [22]. From this, it can be seen that associated with a queue of isochiral dislocations is a twist about the axis of the queue. Kinloch and Schultz [23] and Bassett [12,13,18–20] have proposed the creation of queues of giant screw dislocations (dislocations whose Burgers' vector has the magnitude of the crystal thickness) as the source of twist in lathlike polymer crystals. Kinloch and Schultz showed that thermal energy should be sufficient for the creation of the dislocations, whereas Bassett proposed causation via stresses from the amorphous layers intervening between crystallites.

(4) *Surface stresses promoted by 'impurities'*. Noting that in polymer systems, the 'impurity' can refer to differences in molecular weight or in the defect level of the chains, one of the oldest proposals for the source of lamellar twist considers a microscopic picture of crystallization in systems with crystallizable and noncrystallizable moieties [2]. The kinetics of such crystallization require redistribution of species on a micro- or nano-scale [24], a process which promotes cellular or dendritic growth. Here cellulation refers to the very local partitioning of the impurity lateral to the growth direction, such that the cells of relatively pure crystallized material are separated from each other by regions of lower purity. Growing fibrillar polymer crystals or bundles of crystals could also experience such cellulation (driven, as in all systems, by the more rapid crystallization of the relatively pure material at the core of the cell). Keith and Padden suggested that the surfaces of a lathlike crystal (or perhaps a bundle of crystals) could contain high concentrations of defective molecules. The accompanying dilatation of those surfaces could then be high enough to cause twisting to ensue, thereby reducing the level of strain energy [2]. (Their later work has not continued this suggestion.)

(5) *Escape from impurity concentrations*. In general, uncrystallizable material rejected by a growing lath exists in high concentrations near the growing interface and slows the growth. Any means by which the growth surface may reposition itself so as to encounter lower concentrations would increase the growth and would be adopted (providing the means of doing so is not too energetically expensive). In a recent paper, Abo el Maaty and Bassett comment that "a change in azimuth around the radial growth direction would enable growth to move into regions of lower segregant concentration than would otherwise be the case" [25]. Since they see little evidence for twisting of individual crystals in the polyethylene they have studied, they suggest that the effective twisting into lower concentrations occurs via branching into or creation of crystals with new azimuths.

Each of the above models is grounded in either solid morphological evidence or in scientific reasonableness. Further, it appears very likely that mechanisms based on surface tractions due to anisotropic surface stresses contribute to or control crystal twisting in polymers. Nevertheless, the models should be reconsidered for the following reasons:

1. None of the models is quantitative. It is not obvious whether or not the magnitude of the proposed effects is sufficient to overcome elastic constraints and to cause twisting at the levels observed.
2. Most models relate to features specific to polymers or even to specific polymers. It is possible that there is a more generic basis for twisting in the many, diverse systems in which it is observed.
3. None of the models account for the resistive effect of stored elastic energy in the twisted crystals.
4. The extant models are all based on equilibrium. However, crystal morphologies and supermolecular organization develop more often in response to kinetic conditions. The present model represents crystal twisting as a kinetic response.

To set the context of the present work, Keith and Padden pointed out, over 40 years ago, that crystal twisting occurs only in systems of high viscosity, and that the level of impurity of the system may be important [2]. In this manuscript, we explore the possibility that escape from fields self-generated during crystallization (aligned with explanation 5, above) could provide such a basis. We present a quantitative model, and show that the effect is sufficient to produce crystal twisting at the observed level in polyethylene. The model is more general than the existing ones and includes the important elastic resistance. The results demonstrate that fields induced during dynamic crystallization can be of sufficient magnitude to induce twisting, but not necessarily that this will be the sole or controlling effect in each system. In fact, as will be seen in Section 4, some other mechanism-such as plastic shearing or dislocation generation-is necessary to cause retention of the twist and to direct the handedness of the twist.

1.2. Background on self-generated fields

As materials crystallize, they can, and normally do, generate fields in the melt near the growing surface [26]. The fields can be thermal (resulting from the heat of fusion), mechanical (resulting from different densities in crystal and melt, coupled to the difficulty of relaxation of the melt), and compositional (resulting from the exclusion of poorly crystallizable or noncrystallizable moieties (impurities) from the crystal). Each of these types of fields normally acts to reduce the velocity of growth. Sometimes rearrangement of its growth pattern allows the growth surface to contact lower values of temperature, stress or impurity concentration. For, instance, a sharp protuberance of the growth front into the melt will encounter a lower magnitude of whichever field is inhibiting its growth. In this case, the surface can become unstable to such protuberances and the breakdown of the growth front into dendrites or fibrils will ensue. Such physics has long been understood to be important in the crystallization of small molecule systems ([24] for an overview). Keith and Padden [27–29] were the first to recognize that when the magnitude and gradient of the field are large and localized near the growth front, the field can be decisive in defining the morphology of a spherulitic polymer system. Subsequent work by Keith and Padden [30–32], as well as by Calvert [33], Goldenfeld [34, 35] and Schultz [36] has further developed this concept for explaining the size and spacing of growth arms (bundles) within polymer spherulites. Rather recent work has sought to quantitatively model the effects of compositional fields on the dimensions of growth arms [37], the breakdown of spherulitic fronts [38], the apportionment of impurities between crystallites or between growth arms [39], and the kinetics of spherulitic crystallization in polymer systems [40–42].

The present work explores the possibility that crystal twisting may occur as a response to fields ahead of the growing surface. Of the three possible types of fields which can, in principle, foster such a response, thermal fields can be ruled out immediately, since their diffusion distance is very large; i.e. in the time-frame for crystallization, the liberated heat of fusion has diffused away so rapidly that the temperature at the interface is little different from that of the far-field melt [36]. Schematically, the concept is illustrated in Fig. 1. Here, viewing a lathlike crystal (or bundle of laths) along the growth axis, the field is represented by the thin contour lines (Fig. 1(a)). If the crystal were to grow at steady state without twisting, it would always encounter the field exactly as shown. By twisting, the crystal (or bundle of crystals) moves the growth face into regions of lower field values (Fig. 1(b)). By doing so, its growth velocity is increased and the process will occur spontaneously, provided that the elastic energy stored in the twisted crystal is not too great. That elastic energy increases the free energy of the crystal, thereby lowering the undercooling and decreasing the driving force. In order for twisting to occur, this decrease in undercooling must affect the growth velocity less than does the concentration effect.

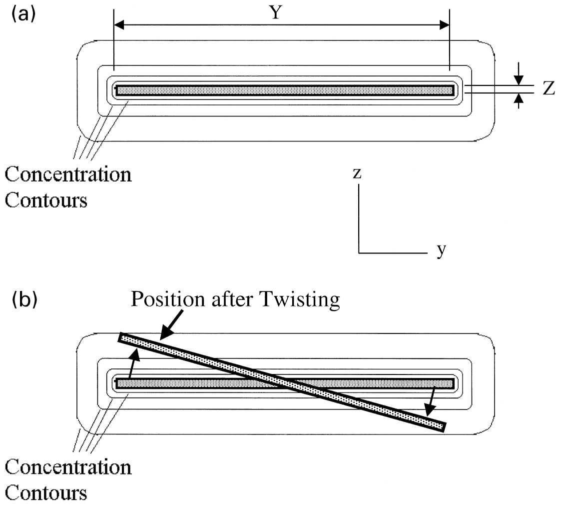

Fig. 1. Schematic of field contours about the growth surface of a lathlike crystal: (a) crystal before twisting, (b) crystal growth surface before and after twisting about the growth axis.

The scope of the present work is to examine quantitatively the possibility that a field in the melt can exert sufficient influence to overcome the elastic resistance and can induce continuous twisting into the growing crystal. For the sake of convenience, we shall deal in the analysis only with compositional fields, acknowledging, however, that it is only through a stress field that field-driven twisting may occur in relatively pure material. Furthermore, only continuous twisting of long, lathlike crystals is considered.

Before proceeding, a comment on discontinuous twist is in order. Bassett and coworkers have shown that in at least some polymer systems, the macroscopically observable twisting occurs through the relaying of changes in the orientation of the growth face about the growth direction from one short crystal to another along the spherulite radius, each individual short crystal having itself little or no internal twist [11,13]. (There are other observations of large twist in otherwise similar crystals [43–45]. While these observations show that Bassett's observations are not completely general, they do not obviate the correctness of those observations.) The present work thus examines a worst-case scenario, in which the crystals contain the maximum degree of elastic strain. For the discontinuous twist case, there would be no or little elastic hindrance to twisting. As the worst-case model, the present analysis should adequately assess the appropriateness of the solute-field model.

2. Analytical method

2.1. Scheme of the analysis

The overall concept, again, is that by twisting as it grows, the growth surface of a lathlike crystal (or a stack of laths) encounters a lower concentration of poorly crystallizable species than it would if no twist were in effect. Because of the higher concentration of crystallizable species at the growing interface, the growth velocity will be higher than were there no twist. Countering this effect is the elastic energy associated with the twist, stored in the crystal. This elastic energy raises the free energy of the crystal and thereby depresses the melting point, by an amount $\delta T_m(\theta)$, where θ is the twist, in rad/cm. The melting temperature depression, in turn, lowers the undercooling for isothermal crystallization at a given temperature T. In general, the crystallization velocity is given by Ref. [26]

$$V(T,\theta) = A(T)[1 - X_\infty - X(T,\theta)] \exp\left\{-\left[\frac{B(T)}{T(T_m - T)}\right]\right\} \tag{1}$$

where $A(T)$ contains a mobility term; X_∞ is the far-field mole fraction of poorly crystallizing material; $X(T,\theta)$ is the additional mole fraction of those species at the interface, due to rejection by the growing crystal; T_m is the actual melting point for the crystal near the growth surface; and $B(T)$ is a Hoffman–Lauritzen term [46] of the form

$$B(T) = \frac{\lambda b_1 T_m \sigma_s \sigma_e}{k_B T \Delta h_f} \tag{2}$$

where λ is a constant of order unity, b_1 is the interchain spacing in the growth direction, T_m is the melting point of the twisted crystal, σ_s is the surface energy of the growth face, σ_e is the surface energy of the broad surfaces of the lathlike crystal, k_B is Boltzmann's constant, and Δh_f is the enthalpy of fusion.

Changes in concentration near the growth surface can affect several of the parameters above, most importantly, $A(T)$, T_m, and Δh_f. However, we wish to keep this problem as simple as possible. For very similar crystallizable and poorly crystallizable species (e.g. chains of similar chemistry but different tacticity, defect concentration, or molecular mass) there will be little change in T_m and Δh_f and only molecular mass would markedly affect $A(T)$. In the following, we shall assume such a blend: one in which the concentration of poorly crystallizable species at the front affects the growth velocity only through the $[1 - X_\infty - X(T,\theta)]$ term, which represents the dilution of crystallizable species in the melt near the growth front.

The stored elastic energy of twisting affects the crystallization velocity by depression of the melting point below that of an untwisted crystal. We can write for T_m then

$$T_m = T_m^* - \delta T_e \tag{3}$$

where T_m^* is the melting temperature of an untwisted crystal and δT_e is the melting point depression due to twisting.

What is needed now, is to obtain a Fickian solution for the concentration $c(T,\theta)$ of poorly crystallizable species and an elastic energy expression for δT_e. Once these are found, we may seek the value of θ which maximizes the growth velocity.

2.2. Concentration field about a crystallizing front of a lathlike crystal

The inspiration for the method used here was provided by earlier work by Keith and Padden [32], wherein they utilized the point source of diffusion analysis to study the compositional field near a growing thin lath. The present analysis extends the moving point source and moving line source analyses given by Carslaw and Jaeger [47] to a crystal which twists about its growth axis during growth. While their analysis is for diffusive heat dissipation, it is transposed here for the solute case. Consider a point source of solute moving at velocity V parallel to the x-axis. This source emits q grams of solute per second. In the usual moving point source problem, the source is actually maintained fixed at $x, y, z = 0$ and a volume element which is at x, y, z at time t has moved to that point from elsewhere along the x-axis, i.e. the point which is at x, y, z at t has moved there from $[x - V(t - t')], y, z$, where it was at time t'. In the time interval dt', $q\,dt'$ grams of solute are deposited at the origin. The increment of solute concentration (g/cm^3) at x, y, z at time t for solute which accumulated in the time interval dt' at the volume element which initially was at $[x - V(t - t')], y, z$ is

$$dc = \frac{q\,dt'}{8[\pi D(T)(t - t')]^{3/2}} \exp\left\{-\frac{[x - V(t - t')]^2 + y^2 + z^2}{4D(T)(t - t')}\right\} \tag{4}$$

where $D(T)$ is the diffusivity of the solute in the host polymer. And the total solute buildup at x, y, z from 0 to t is

$$c(t) = \frac{q}{8[\pi D(T)]^{3/2}} \int_0^t \frac{\exp\left\{-\frac{[x - V(t - t')]^2 + y^2 + z^2}{4D(T)(t - t')}\right\}}{(t - t')^{3/2}} dt' \tag{5}$$

Since we are ultimately dealing with a crystal which twists about x as it grows, and since we are analytically holding the growth surface fixed and moving the medium past it, we need to move each point of the medium in a helical path. Thus a volume element which is at x, y, z at time t was at

$$x - V(t - t'), y\cos[2\pi V\theta(t - t')] + z\sin[2\pi V\theta(t - t')], y$$

$$\sin[2\pi V\theta(t - t')] + z\cos[2\pi V\theta(t - t')]$$

at time t'. Defining

$$y'(\theta, t - t') = y\cos[2\pi V\theta(t - t')] + z\sin[2\pi V\theta(t - t')];$$
$$z'(\theta, t - t') = y\sin[2\pi V\theta(t - t')] + z\cos[2\pi V\theta(t - t')] \tag{6}$$

c(t) becomes

$$c(t) = \frac{q}{8[\pi D(T)]^{3/2}} \int_0^t \frac{\exp\left\{-\dfrac{[x - V(t-t')]^2 + y'^2 + z'^2}{4D(T)(t-t')}\right\}}{(t-t')^{3/2}} \mathrm{d}t' \tag{7}$$

Now let the moving source be the entire rectangular face of a lathlike crystal, with width $2Y$ and thickness $2Z$, these dimensions parallel to the y- and z-directions, respectively. Here y and z are along the width and thickness, respectively, of the growth face. Now each point within that surface acts as a point source, each emitting solute at the same rate. Integrating the effects of the continuous point sources of strength q' g/cm^2 s over the growth surface, we now have

$$\begin{aligned} c'(t) &= \frac{q'}{8[\pi D(T)]^{3/2}} \int_{-Z}^{Z} \int_{-Y}^{Y} \int_0^t \frac{\exp\left\{-\dfrac{[x - V(t-t')]^2 + (y'-Y)^2 + (z'-Z)^2}{4D(T)(t-t')}\right\}}{(t-t')^{3/2}} \mathrm{d}t'\,\mathrm{d}y\,\mathrm{d}z \\ &= \frac{q'}{8[\pi D(T)]^{3/2}} \int_{-Z}^{Z} \int_{-Y}^{Y} \int_t^0 \frac{\exp\left\{-\dfrac{[x - V(u)]^2 + (y'-Y)^2 + (z'-Z)^2}{4D(T)(u)}\right\}}{u^{3/2}} \mathrm{d}u\,\mathrm{d}y\,\mathrm{d}z \end{aligned} \tag{8}$$

where $u = t - t'$

Steady state is represented by $t \to \infty$. The concentration $C(x, y, z)$ (in g/cm^3) at position x, y, z at steady state is then

$$C(x,y,z) = \frac{q'}{8[\pi D(T)]^{3/2}} \int_{-Z}^{Z} \int_{-Y}^{Y} \int_\infty^0 \frac{\exp\left\{-\dfrac{[x - V(u)]^2 + (y'-Y)^2 + (z'-Z)^2}{4D(T)(u)}\right\}}{u^{3/2}} \mathrm{d}u\,\mathrm{d}y\,\mathrm{d}z \tag{9}$$

and the mole fraction at that position is

$$X(T, \theta) = \frac{M_\mathrm{b}}{\rho_\mathrm{b} M_\mathrm{s}} C(x, y, z) \tag{10}$$

where ρ_b is the density of the blend, M_b the mean molecular mass of the blend and M_s the molecular mass of the ‘solute’. For a system in which the concentrations of components which are difficult to crystallize are given as c_s in the crystallizing body and c_∞ in the far-field melt, q' is

$$q' = (c_\infty - c_\mathrm{s})V \tag{11}$$

Thus the point-by-point concentration of poorly crystallizable species in the melt is given by Eq. (9), where the effect of crystal twisting is contained in the expressions for y' and z' Eq. (6) and q' is given by Eq. (11). In the analysis, c_s is taken as 0, a reasonable situation for polymers.

2.3. Stored elastic energy for a twisting lathlike crystal

We expect that the concentration of poorly crystallizable species in front of a growing lathlike crystal will decrease continuously with the degree of twist. Were there no inhibition to such twisting, we would expect then that a growing crystal would twist to the maximum possible extent, in order to maintain the greatest concentration of crystallizable species at its growth front. In reality, however, twisting results in elastic energy being stored in the crystal. This elastic energy per unit volume ΔW_e must depress the melting point of the material by an amount

$$\delta T_\mathrm{m} = \frac{\Delta W_\mathrm{e}}{\Delta H_\mathrm{f}} T_\mathrm{m}^0 \tag{12}$$

where ΔH_f is the heat of fusion and T_m^0 is the melting point of an infinitely large, perfect crystal.

An expression for ΔW_e is found as follows. In general, the torque $\mathbf{T}$ necessary to maintain a twist of θ rad/cm is given by Ref. [48]

$$\mathbf{T} = GJ\theta \tag{13}$$

where G is the shear modulus and J is the torsional constant. For a thin lath of rectangular cross-section [48],

$$J = 16YZ^3\left(\tfrac{1}{3} - \frac{64}{\pi^5}\frac{Z}{Y}\tan\mathrm{h}\frac{\pi Y}{2Z}\right) \tag{14}$$

where $2Y$ and $2Z$ are, respectively, the width and thickness of the growing lath. If $Y \gg Z$, then

$$J \cong \frac{16YZ^3}{3} \tag{15}$$

The torque is the product of a force couple and the radial distance r at which it acts. Thus the force F acting to twist the bar is given by $F = \mathbf{T}/r$. Likewise, the work $\Delta W'_\mathrm{e}$ necessary to twist the lath is given by the force acting multiplied by the distance twisted. For the force F acting at r, then,

$$\Delta W'_\mathrm{e} = F(r\theta) = \frac{T}{r} r\theta = GJ\theta^2 L \tag{16}$$

where L is the length of the crystal along the growth direction (along x). Per unit volume,

$$\Delta W_{\mathrm{e}} = \frac{\Delta W'_{\mathrm{e}}}{V} = \frac{GJ\theta^2 L}{4abL} = \frac{GJ\theta^2}{4ab} = \frac{4a^2 G\theta^2}{3} \tag{17}$$

where V is the volume of the crystal.

Finally, the melting point depression due to crystal twisting is

$$\delta T_{\mathrm{m}} = \frac{4a^2 G\theta^2 T_{\mathrm{m}}^0}{3\Delta H_{\mathrm{f}}} \tag{18}$$

2.4. Implementation

We seek to find the dependence of the growth velocity $V(T,\theta)$ on the twist θ at some crystallization temperature T. We then seek the value of θ which will maximize $V(T,\theta)$, and take this as the operating condition. The problem then amounts to solving Eq. (1), using reasonable values of the parameters contained.

We take moderately branched polyethylene as a model, in order to use a material whose thermodynamic parameters are well known and whose growth velocities are accessible. The following values are used:

$$\left.\begin{aligned} &\lambda = 2 \\ &b_1 = 4.15 \times 10^{-8}\ \mathrm{cm} \\ &T_{\mathrm{m}}^0 = 418\ \mathrm{K} \\ &\sigma_{\mathrm{s}}\sigma_{\mathrm{e}} = 1.280 \times 10^3\ \mathrm{erg}^2/\mathrm{cm}^2 \end{aligned}\right\} \quad \text{(from Ref. [46])}$$

$$G = 1.98 \times 10^{10}\mathrm{dyne/cm}^2 \qquad \text{(from Ref. [49])}$$

Additionally, a temperature of 393 K has been chosen and we work with a single lathlike crystal with $Y = 1.0 \times 10^{-4}$ and $Z = 1.25 \times 10^{-6}$ cm.

We monitor the melt at a position a few chain stems from the growth surface, $x = 1.0$ nm, and at y- and z-positions 500 and 10 nm, respectively,—a position laterally halfway from the centerline to the edge of the lath and heightwise somewhat below the top surface, as sketched in Fig. 2.

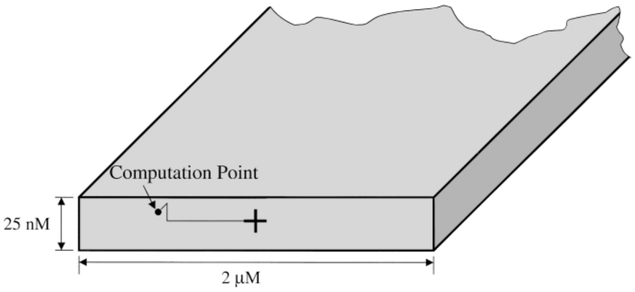

Fig. 2. Sketch of the position of the point at which computations are carried out.

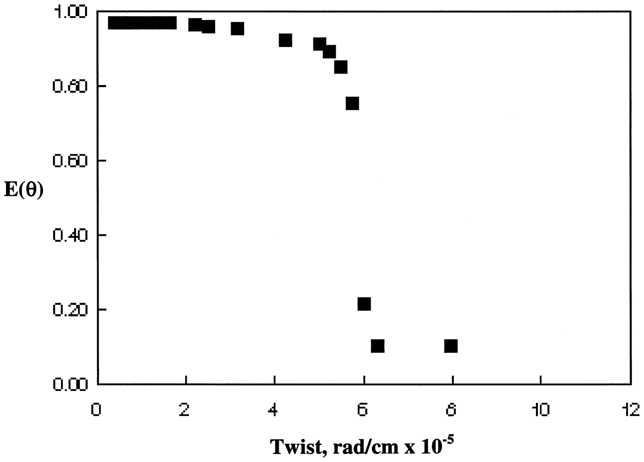

Fig. 3. The elastic factor, $E(\theta)$, of the growth velocity plotted against the twist θ.

3. Results

The growth velocity Eq. (1) can be rewritten as

$$V(T,\theta) = A(T)\{1 - X_\infty - X[V(T),\theta]\}E(\theta) \tag{19}$$

where

$$\begin{aligned} E(\theta) &= \exp\left\{-\left[\frac{B(T)}{T(T_{\mathrm{m}}^* - \delta T_{\mathrm{m}} - T)}\right]\right\} \\ &= \exp\left\{-\left[\frac{B(T)}{T\left(T_{\mathrm{m}}^* - \dfrac{4a^2 G\theta^2 T_{\mathrm{m}}^0}{3\Delta H_{\mathrm{f}}} - T\right)}\right]\right\} \end{aligned} \tag{20}$$

We note that $E(\theta)$, which contains the elastic, retarding term δT_{m} is independent of the velocity of the crystallization front, whereas the concentration term is dependent on both the velocity $V(T)$ and the twist θ.

Let us first examine the behavior of $E(\theta)$. Using the values given above for the several parameters, the behavior shown in Fig. 3 is found. What is observed is that there is little effect until a twist of nearly 5×10^5 rad/cm, after which this factor rapidly decreases to a very small value by $\theta = 6.5 \times 10^5$. Before $\theta = 5 \times 10^5$, $E(\theta)$ shows a very small downward slope.

We now examine the behavior of the composition term, $A(T)\{1 - X_\infty - X[V(T),\theta]\}$, for diffusivity values of 1×10^{-11} and 1×10^{-10} cm^2/s, corresponding to molecular masses of some 200,000 and 80,000–100,000, respectively ([50; Fig. 2]). We solve here for θ at each value of V, using Eqs. (6), and (9–11). The results are shown in Fig. 4. Plotted here is the composition-dependent factor $(1/E(\theta))V/V_0$ of the normalized velocity, V/V_0, versus twist angle, where V_0 is the value of the velocity if there were no solute buildup at the crystallization front. In both cases, the velocity increases gradually toward an asymptote, as one would qualitatively expect. For a diffusivity of 1×10^{-11}, the asymptote is near $V/V_0 = 0.63$ and is approached closely at a twist of some

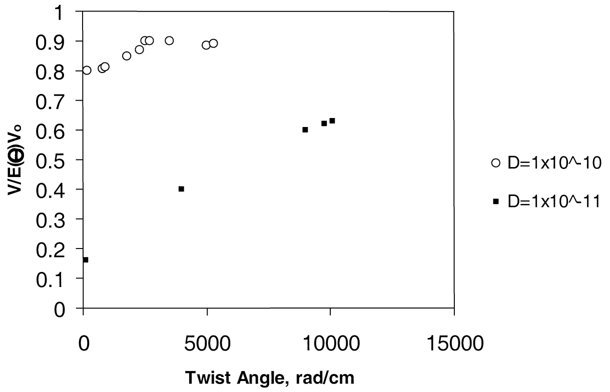

Fig. 4. The composition-dependent factor, $1/[E(\theta)V(T)/V_0]$, of the normalized growth velocity plotted against the twist θ, for $D = 1 \times 10^{-11}$ and 1×10^{-10} cm^2/s.

12,000 rad/cm, while for $D = 1 \times 10^{-10}$, the asymptotic value is near 0.90 and is closely approached at a twist of 2500 rad/cm. For the higher diffusivity, the normalized velocity is high even at $\theta = 0$, because the high diffusivity has already reduced the solute concentration near the interface. On the other hand, the growth velocity at the lower diffusivity is quite low at $\theta = 0$, because a substantial solute concentration is trapped near the interface. More quantitatively, we examine the diffusion length, $\delta = D/V$, a measure of the extent of the compositional field. At $D = 1 \times 10^{-11}$ cm^2/s, δ is approximately 1 nm, while at $D = 1 \times 10^{-10}$ cm^2/s, δ is approximately 10 nm. For the lower diffusivity, the measurement point lies well within the field in which the concentration is rapidly changing, while at the higher diffusivity, the measurement point is much nearer to the interface than to the diffusion length, and the concentration has dropped little from the value at the interface. Note that for $D = 1 \times 10^{-12}$ cm^2/s, the diffusion length would be subatomic, some 0.1 nm, and the measurement point would lie beyond the concentration field. Thus twisting would have no effect on growth velocity and our computations (not shown) demonstrate this to be the case.

When concentration and elastic effects are combined, the results are as shown in Fig. 5 for the two diffusivities given above. We see that for both cases the normalized velocity rises rapidly to a critical point, beyond which the value decreases slowly to the twist range at which elastic energy dictates a rapid drop. The operating point of maximum velocity occurs near $\theta = 12{,}000$ rad/cm for $D = 1 \times 10^{-11}$ cm^2/s and near $\theta = 2500$ rad/cm for $D = 1 \times 10^{-10}$ cm^2/s. These twists correspond to spherulite band spacings of 2.6 and 12.6 μm, respectively.

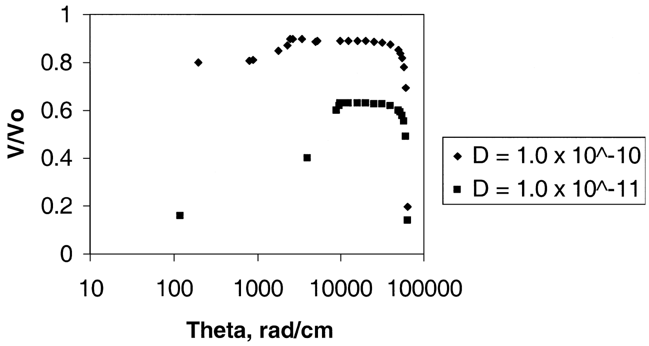

Fig. 5. The growth velocity $V(T, \theta)/V_0$ versus θ, for $D = 1 \times 10^{-11}$ and 1×10^{-10} cm^2/s.

Algebraically (and physically) one expects that the effect of increasing the intrinsic growth velocity (A) should be inverse to the effect of decreasing the diffusivity, but the dependences of the growth velocity on A and D are actually somewhat different. Thus it is useful to also explore the effect of the intrinsic growth velocity V_0 on the computed normalized velocity V/V_0 Fig. 6 shows the effect of two different values of V_0 on the composition-dependent term, $V/(E(\theta)V_0)$ of the normalized growth velocity. We see that increasing the intrinsic growth velocity has the effects of (a) lowering the level of the asymptotic growth velocity and (b) moving the approach to the asymptote to a higher twist level. Increasing the intrinsic growth velocity much above 1×10^{-4} places the diffusion length below atomic dimension and gives no formal solution to the velocity expression.

4. Discussion

The simulations above, as rough as they are, show the correct quantitative and qualitative trends. Quantitatively, the results in Figs. 5 and 6 are in line with experimental results for blends of high- and low-density polyethylenes. For 50/50 blends of high-density polyethylene with $M_w = 41{,}000$ (comparable to the present results for $D = 1 \times 10^{-11}$ cm^2/s) and linear low density polyethylene (which crystallizes very slowly and here acts as the solute), the intrinsic velocity chosen for the computations corresponds to a crystallization temperature of approximately 115 °C. For this blend, band spacings for the blend are significantly smaller than for the homopolymer (which is already polydisperse) and band spacings are near 1.7 μm for the homopolymer and 1.3 μm for the blend after

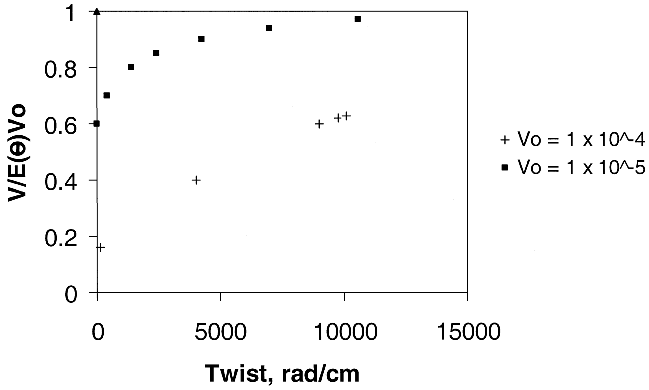

Fig. 6. The composition-dependent factor, $1/[E(\theta)V(T)/V_0]$, of the normalized growth velocity plotted against the twist θ, for $V_0 = 1 \times 10^{-5}$ and 1×10^{-4} cm/s.

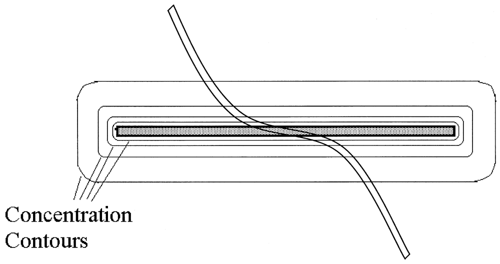

Fig. 7. Sketch of S, shaped growth surface in a twisting crystal. Shown also are the original shape and position of the growth surface and its field contours in the melt.

crystallization at 110 °C [44]. The predicted band spacing for a somewhat higher molecular mass is 2.6 μm and would be smaller for the lower molecular weight material of the experiment. The computation appears to give the right magnitude for the band spacing. In general, one experimentally finds band spacings qualitatively to increase with crystallization temperature and to decrease with molecular mass. These qualitative results are also shown in the simulation. In Fig. 5, it is seen that the twist increases as the diffusivity is increased. Since diffusivity decreases with molecular mass, this result correctly predicts the band spacing to decrease with molecular mass. In Fig. 6, the twist increases with increasing intrinsic growth velocity. Since growth velocity increases strongly with undercooling, this result correctly predicts the band spacing to increase with crystallization temperature. The model is not sufficiently highly developed to say more than this: that the band spacing is placed in the right quantitative range and that the qualitative trends of band spacing with temperature and molecular weight are correct.

There are several extrapolative comments to be made. These are:

1. The model is based on the twist of the lath being accommodated by homogeneous elastic stresses. If no mechanism exists to maintain the twist after the crystallization front passes, the crystal should revert to an untwisted state. Several possibilities for maintaining the twisted state exist: (a) irreversible shearing of the chains, as in the models of Bassett and Hodge [10,11] or Keith and Padden [15–17], (b) creation of giant screw dislocations, or (c) geometrical constraint from surrounding crystals. The first two of these possibilities amount to the transformation of elastic to plastic strain. The shearing mechanism would cohere to the experimental findings reviewed in Section 1. In this context, the role of anisotropic surface stress would be to direct the handedness of the twisting and to lock in the deformation. The possibility of constraint by adjacent crystals is also possible, since the growing crystal is not fully disassociated from the adjacent crystals to which it is attached by tie chains and giant screw dislocations. A final possibility is that the macroscopically observed twisting is not an actual twisting of crystals, but rather a cumulative change in the azimuth of short crystals. It is not yet possible to sort among these alternatives. Nevertheless, the totally elastic approach used here is the worst-case solution and indicates that even in this scenario, rotation of the growth face about the growth axis gives increases in growth velocity sufficient to produce macroscopic twist and banding in spherulites.

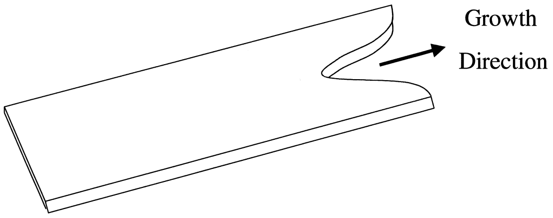

Fig. 8. Sketch of the effect of the lateral velocity gradient on the shape of the growth surface of the crystal.

2. In the above analysis, it has been assumed that the ribbon's cross-section is not curved, whereas Bassett and coworkers report S-shaped cross-sections for primary crystallites in banded polyethylenes. The uncurved cross-section was assumed above, to simplify the computation and to test whether the predicted result satisfies the basic tests of comparison to experiment. But now consider what would happen if the cross-section could reconfigure its shape. The growth surface should protrude as far out of the high concentration regions as possible. This could be facilitated if the ends of the cross-section were to bend into the direction of twist, as sketched in Fig. 7. In this way, the S-shaped cross-sections will grow faster than would uncurved cross-sections. And the direction of the S-acting as if it were a scoop for the melt it encounters as it twists-is as observed [11]. In this scenario, U-shaped crystal cross-sections would be a priori as likely as would S-shaped sections. The selection of S over U would require the action of an anisotropic surface energy, as we would in any case expect.

3. For uncurved cross-sections, there must be a gradient of growth velocity from the centerline of the section outward to the edges, since the concentration of solute in the melt increases along that trajectory. This condition would be aggravated for S-sections. This gradient indicates that the edges of the lath outrace the centerline. The situation would appear as sketched in Fig. 8. As the concavity fills in during growth, there would be opportunity for the two 'wings' of the growth front to overlap, creating giant screw dislocations, as observed some time ago by Reneker and Geil [51]. This could account for the queues of such screw dislocations suggested by Bassett and Hodge [11].

4. As mentioned earlier, the analytical scheme given above should not be confined to concentration fields. Indeed, it is expected that stress fields resulting from the step-change in density as the melt transforms to solid will give rise to similar results. In this case, the crystal twists to move portions of the growth face to regions of lower stress in the melt. It would be useful to carry out such a simulation, but this is beyond the scope of the present work.

5. The analysis was performed for a single lathlike crystal. This may be appropriate for some systems, in which

the growth of primary lamellae is followed later by more general filling in of the consequent skeletal growth front. However, it is possible that in some situations, the primary extension of the growth front may occur by stacks, or bundles, of thin crystals. The analysis for this case would proceed just as in the present case, with a new set of cross-section dimensions and a more complex elastic analysis.

6. A growing lath could also use bending about the *y*-axis (the widthwise axis) as a means to encounter lower field values. Eventually such misdirected growth would encounter adjacent growing crystals (or their fields) and would either halt or be redirected radially. Although the literature shows many high-resolution micrographs of spherulite fine structure, for several polymer systems, it is not clear whether or not such bending takes place. The classical electron micrographs of Eppe et al. [52], and of Bassett and Hodge ([11; Fig. 7]) show apparent changes of direction, ending in termination of lamellae. However, it is not evident whether these apparent directional changes represent actual bending or if they are artifacts of width or observation direction changes.

5. Summary

A conceptual model is proposed, whereby a lathlike crystal (or bundle of crystals) twists so as to move portions of the growth face into regions of lower field magnitude. This action accelerates the crystal growth velocity and should occur spontaneously. The twisting is opposed by elastic strain within the crystal. The situation has been modeled for a compositional field for the situation in which a component which cannot crystallize is excluded from the growing crystal. The diffusion of this solute in front of a twisting crystal has been computed, based on extension of a moving point source analysis. The composition in the melt at the growth face is then used to define the growth velocity of the crystal. The effect of lattice strain also enters the growth velocity expression as a decrease in the melting point, and hence a lowering of the undercooling. The model has been used to simulate the crystal growth in a crystallizable/uncrystallizable polyethylene blend. The results are quantitatively and qualitatively consistent with experimentally observed behavior. A gradient of growth velocity across the width of the growth face could result in both the observed S-shaped lamellae and would provide a reentrant growth-face concavity, the latter possibly leading to formation of a giant screw dislocation.

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