polymer papers

Crystals with curved edges: a unified model that mediates between the theories of nucleation-controlled and rough surface growth

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In order to explain the curved outline of some polymer crystals, we start from a slightly modified Frank's system of equations describing nucleation-controlled crystal growth. But we give an alternative and completely new interpretation of these equations with a view to applying them to the description of normal growth of crystals with rough surfaces. We show first that Mansfield's approximate solution of such equations is not exact, does not satisfy absorbing boundary conditions and does not depend on the rate of motion of these boundaries. Because that solution describes the facets of a crystal in terms of arcs of the *same* ellipse, it cannot be used to describe the curvature of 2 0 0 faces of those crystals of large elongation ratio which clearly are not parts of a single ellipse. The most puzzling feature of Mansfield's proposal is, however, that pronounced curvature is obtained solely if the mean distance between steps is assumed to be of the same order of magnitude as the width of a single stem. In such an eventuality, the use of the concept of nucleation-controlled growth becomes meaningless.

We propose, therefore, a completely new interpretation of Frank's equations, which allows us to use these equations to describe nucleation-controlled growth. Then these equations appear as the mathematical formulation of a model that mediates between the approach of Seto and Frank, and that of Gilmer and Sadler. Detailed analysis of the experimental data, mostly those of Labaig and Bassett, shows that the outline of crystals with curved habit is neither elliptic nor made of elliptical arcs. We provide new and exact solutions of our generalized equations with generalized boundary conditions. These solutions account well for the experimental data. In some cases they may be approximated by Mansfield's solution (despite the fact that the change of curvature along the facets differs from that actually observed) or by the solution found independently by Toda and us (33th IUPAC Polymer Symposium at Montreal), despite the fact that it is unusual that near the tips of the crystals the outline of a crystal is well approximated by straight segments. The most important claim is, however, that our model appears as a bridge between the model of nucleation-controlled growth and that of normal growth of rough surfaces.

(Keywords: crystal morphology; crystal growth; modelling; polyethylene)

INTRODUCTION

Morphologists have reported a large variety of crystal shapes. In this paper we deal principally with polyethylene crystals for which a large amount of data about the kinetics of crystallization and about the internal structure are available. As shown by Takamizawa[1], when crystallized from octanol solution, polyethylene crystals may have various morphologies ranging from lozenge to lanceolated shape. From the very beginning it was proposed by Lauritzen and Hoffman[2] and Price[3] that the growth of polyethylene lamellae is nucleation-controlled. However, in 1983 this premise was disputed by Sadler[4]. The disagreement arises from a comparison of the various morphologies observed.

In the current literature it appears that many people think that they are faced with an alternative; either adopt the Hoffman–Lauritzen theory or choose Sadler's approach. We intend to show that, in terms of the ultimate truth, a dichotomy of this sort has little meaning, because the experimental results show first the internal regularity of the crystals and secondly a continuous change from straight to rounded edges.

Moreover, in the nucleation theory the predicted shape of the crystal relies solely on Frank's model[5] of nucleation and not on the various assumptions about zippering, regime, reptation, persistence length, lattice strain effects, etc., which constitute the theories of Hoffman and his coworkers. Symmetrically, in Sadler's approach, the shape of the crystal depends solely on the theory of growth of the two-dimensional (2D) crystal[6] with rough surface and not on the so-called pinning model[7].

Our aim in this communication, when solving the problem of crystal shape, is to differentiate the concepts that are significant (for solving the problem of crystal shape) from the tentative estimation of the physical parameters involved and to construct a unified model that mediates between Frank's and Sadler's approaches. We will also explain all the various possible morphologies of polyethylene crystals.

However, in our discussion on the shape of crystals,

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Table 1

(a) Models by Hoffman and his coworkers[2,12–15]

Assumptions	Remarks
(1) Frank's model	Discussed in this work
(2) Zippering process of the molecule in a nucleus[2,12]	Model not valid at high T[8,9]
(3) Absorption[13] (ψ factor)	There exist other models for limitation of fold length[8]
(4) Increase[13] of σ_e with T	
(5) Decrease[13] *of* σ_e with T	
(6) Persistence length[14]	This length does not exist at all[10]
(7) Regimes transition[14]	No regime transitions[11]
(8) Serrated surfaces[15]	Discussed in this paper

(b) Models by Sadler and Gilmer[6,7]

(1) Growth of 2D crystals with SOS restriction	Discussed in this work
(2) Pinning model	Connectivity of the macromolecules? (numerous papers of various authors). Tapered edges? Bassett

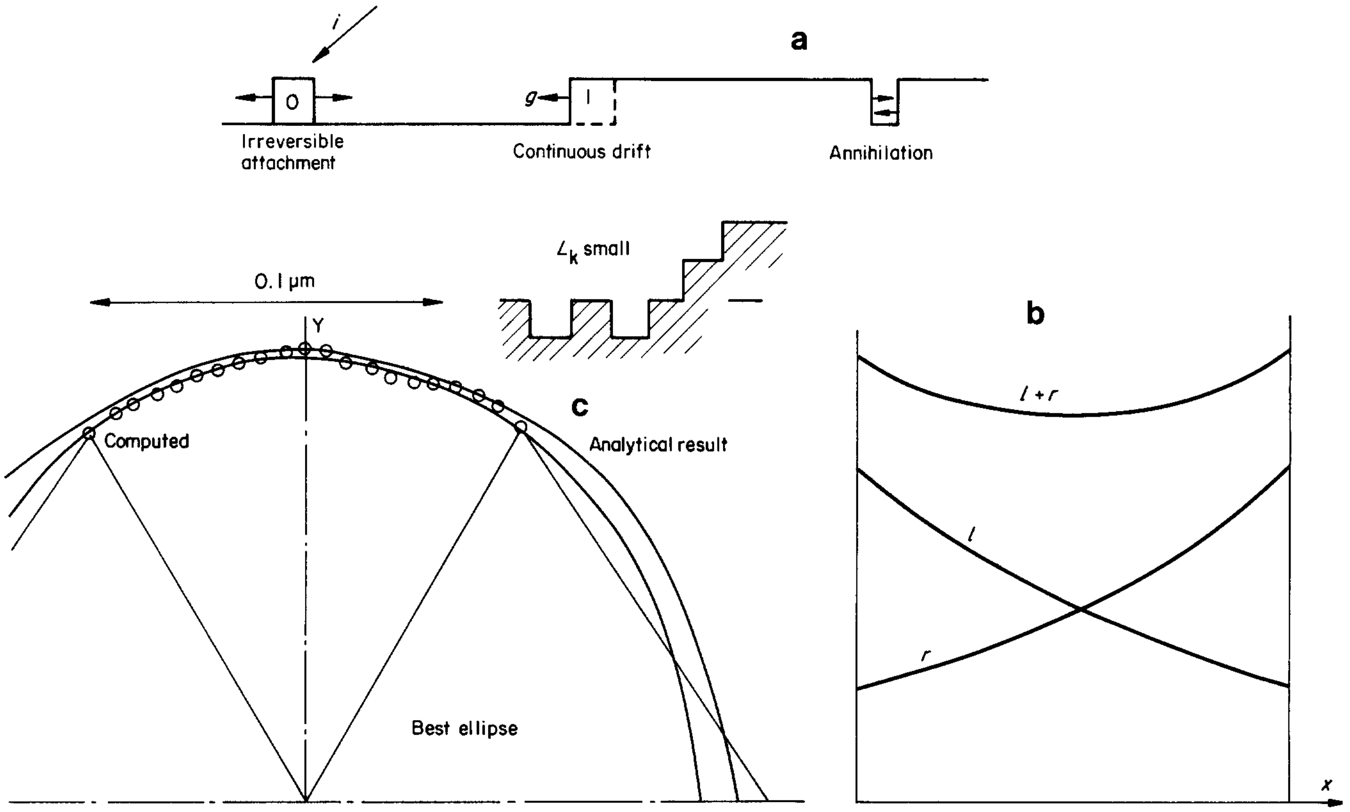

Figure 1 (a) Growth of a 2D crystal according to Frank[5]. (b) In the analytical solution, the values of r and l are of the same order of magnitude everywhere. This is because the conditions at the boundaries ($r = 0$ and $l = 0$) are not taken into account. (c) The result of a simulation (circles) by Mansfield[18] of the growth of a crystal ($g/h = 2$) and the elliptic profile proposed by Mansfield[17]

we are solely concerned with Frank's model and the model of growth of 2D crystals with solid-on-solid (SOS) restriction. All other points are irrelevant (see *Table 1*). It is shown elsewhere[16] that it is very unlikely that the shape of the crystal may result from free-energy minimization or from the effects of thermal (and concentration) gradients.

FRANK'S MODEL

In Frank's model[5] left and right steps run along a crystal face (*Figure 1*). The local variation of the number of left (right) steps is due to convection ($g\,\partial l/\partial x$), ($-g\,\partial r/\partial x$) term), production ($i$ term) and annihilation ($-2glr$ term):

$$\partial l/\partial t = g\,\partial l/\partial x + (i - 2glr) \qquad (1)$$

$$\partial r/\partial t = -g\,\partial r/\partial x + (i - 2glr) \qquad (2)$$

The slope of the crystal facet results from the existence of steps:

$$\partial y/\partial x = b(l - r) \qquad (3)$$

The rate of advance of the facet is due to the movement of steps:

$$\partial y/\partial t = gb(l + r) \qquad (4)$$

At the left (right) end of the substrate:

$$r = 0 \qquad (l = 0)$$

For fixed length of the substrate the profile of the crystal is essentially flat.

MANSFIELD'S ANALYTICAL WORK

In his analytical work, Mansfield[17] chose to replace Frank's equations (1) and (2) by:

$$i - 2glr = 0 \tag{5}$$

That is to say (see Appendix 1) he chose to neglect the time dependence of the density of left and right steps (terms of $\partial r/\partial t$ and $\partial l/\partial t$) and the effect on this density of the movement of steps (terms $g\ \partial l/\partial x$ and $-g\ \partial r/\partial x$). However, the modification by these terms of the balance between production and annihilation of steps is the major idea behind Frank's approach. He evidently conserves equations (4) and (5), and without considering any boundary conditions he exhibits a *particular* solution of the system of equations, which has been modified in this way. This solution is:

$$y = b(2gi)^{1/2}(t^2 - x^2/g^2)^{1/2} \tag{6}$$

To avoid misunderstanding of the result given by Mansfield, it is important to write his solution in the form given in equation (6). If it is simply said that Mansfield predicts that the 200 facets of a polyethylene crystal are elliptical arcs (as shown by equation (44M) of Mansfield[17]), it does not appear that the outline calculated by Mansfield comprises two arcs of the same ellipse (see Appendix 2). The shape of the crystals observed by Labaig, Bassett *et al.* (and others) may readily be approximated by drawing two arcs of two *different* ellipses, but differs widely from any profile obtained by considering two arcs of the same ellipse. This remark holds in the usual case where the crystal has the shape of a laurel leaf (a very common situation according to Labaig[27]).

As expected, this function does not satisfy Frank's equations. Moreover, nowhere (except at $x = gt$ (or $x = -gt$)) do we get:

$$l = 0 \qquad (\text{or } r = 0)$$

despite the fact that Mansfield's intention is to find a profile that satisfies these conditions at:

$$x = ht \qquad (\text{or } x = -ht) \qquad h < g$$

that is to say, at the extremities of the substrate, which are assumed to move in the two opposite directions at a rate h. The rate h, which is the additional physical parameter that Mansfield intends to introduce, does not appear in its 'analytical solution' (6) (see Appendix 2).

We communicated these different comments to Professor Mansfield at the 198th ACS Meeting and he has since published very interesting results on his computer simulations[18]. By simulation Mansfield obtains a profile that displays a pronounced curvature. The mean distance between successive niches is a few times larger than the width of a single stem. Clearly the surface is rough and its growth cannot be described by a nucleation mechanism despite the fact that Frank's equations are intended to describe a nucleation process.

In *Figure 1*, Mansfield's solution is compared with his analytical solution. The profile of the crystal face is found to be very similar and as seen by the simulation the chosen conditions at the boundaries, which move at a rate h, are of little importance. (Nearly) identical profiles were obtained for different values of the ratio g/h.

These results are important. They tend to minimize the role of the boundary conditions (see Appendix 3). They indicate also that Frank's equations, which are intended to describe a nucleation-controlled growth, may also for particular values of the parameters i and g describe another mode of growth, which, however, cannot be taken as the normal growth of a rough surface without a complete revision, at least, of the interpretation of Frank's equations.

This may help us to reach our final goal, a unified model that mediates between Frank's and Gilmer and Sadler's approaches. Unfortunately these results were used by Hoffman and Miller to disparage Sadler's work.

COMPARISON WITH EXPERIMENT

We now have to examine Hoffman and Miller's contention[15] that real crystals have an elliptic outline. A great variety of shapes are known by morphologists, but here the discussion is limited to the case of polyethylene, for which extensive data are available.

Polyethylene crystals with four 110 sectors limited by more or less straight facets and two 200 sectors limited by curved edges are known to grow from xylene, octanol[1], dodecanol[20], tetradecanol[19], hexadecanol, ethyl caproate[19], hexyl acetate[21] and paraffinic solvents[19]. In a few cases, detailed morphological observations show that at least a part of the curvature occurs very likely during the preparation of the sample for electron microscopy (EM)[22]. But this is not the case for the crystals of Lotz and Wittman[23], for Khoury's crystal[20] and for the lenticular crystals grown from solution by Takamizawa[1], Keith[24] and Nagai[25].

The unequal curvature of the two 200 edges of the crystal of *Figure 2*, grown from hexadecanol[21], shows the importance of the deformation of the lamellae during its preparation for EM. For crystals that are diamond-shaped, it is not sufficient to measure the bulge of the 200 faces to prove that the 200 sectors are actually limited by two arcs of the same ellipse. The edges of the lanceolated crystal grown from solution[1,24,25] or from the melt by Bassett *et al.*[26] and Labaig[27] are definitely not elliptic.

Another way to test if crystals are limited by arcs of ellipses is to compare the slope of the edge dx/dy at the tip of the crystal and the elongation ratio (the ratio of half the chord to the bulge of the curved edge). *Figure 3* shows the result of such a comparison. A large majority of the data are due to the pioneering work of Labaig,

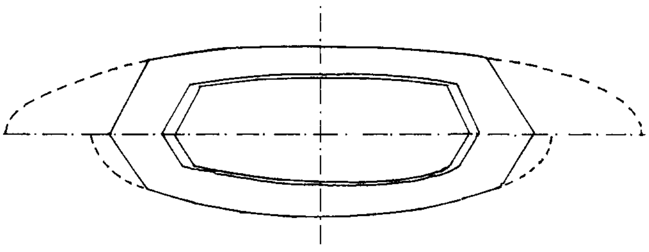

Figure 2 Representation of a crystal grown from a solution of PE in hexadecanol (courtesy of M. Dosière[21]). As a result of mechanical deformation, the two opposite 200 'facets' have unequal curvature

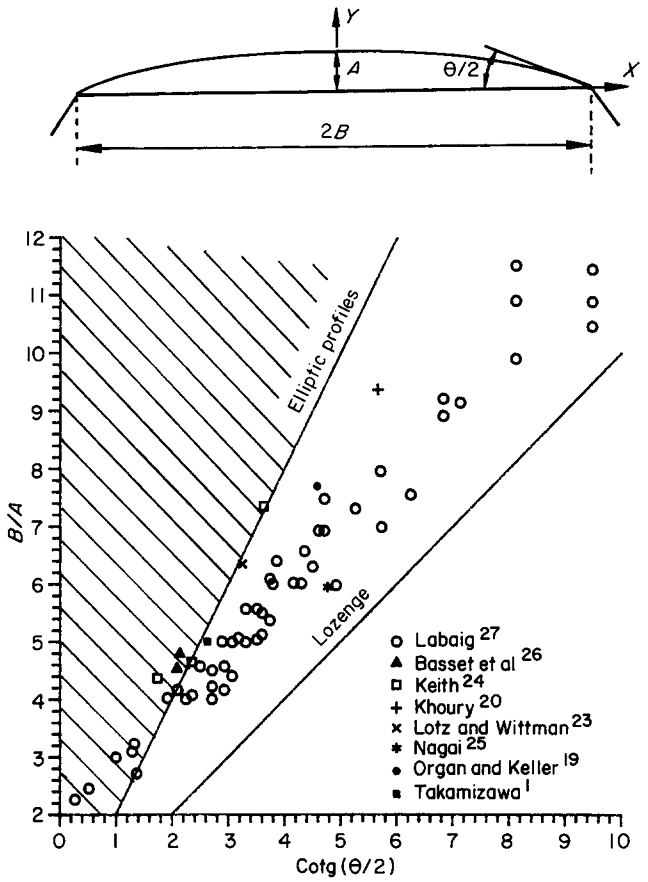

Figure 3 Comparison between the elongation ratio B/A and the maximum of the slope $\partial x/\partial y$ of the edge of all the crystal on which we make precise measurements (most of them are from Labaig, the others from the quoted references). The hatched area shows all the possible values predicted for an arc of an ellipse, the domain defined by the inequality $B/A > 2\cot(\theta/2)$. The straight line denoted 'lozenge' corresponds to a lozenge-shaped crystal (with any possible value of the apex angle) (see text of 'Epilogue')

and others were measured on crystals prepared by Organ and Keller[19], Bassett *et al.*[26], Lotz and Wittman[23] and others. In the same graph, the shaded area corresponds to all possible situations corresponding to elliptic crystals. The figure expresses mathematically the clearly seen morphological properties of the lanceolated crystals of high elongation ratio. The radius of curvature of the edge of the crystal *increases* when we go from the centre to the tips of the crystal, and this is definitive proof that this non-elliptic edge is even not made of arcs of an ellipse.

HOFFMAN AND MILLER'S MODEL

Disregarding the fact that the curved edges of polyethylene crystals, when measurable with precision, are definitely not elliptic, we now have to discuss Hoffman and Miller's claim[15] that the observations of curved habits have been given an explanation by a development of Hoffman and Lauritzen's theory.

The controversy does not pertain to Frank's model, which is solely a constituent part of Hoffman and Lauritzen's approach, but:

(i) to the values of i, g, and the nature of the nucleation barrier;

(ii) to the zippering process, which in Hoffman's view describes the formation of a stable nucleus, and explains the limitation of fold length; and

(iii) to the compatibility between the observation of curved facets and Lauritzen's assumption about the existence of regime I and of a regime I–regime II transition.

One of us[22] has previously disputed in detail these various points, but we now have to reanalyse these assumptions in the framework of the study of a crystal with curved edges.

(i) According to Hoffman and Miller, the curved edges of polyethylene crystals represent a steady-state profile of 2 0 0 subsidiary surfaces formed under regime II whose length along the b axis is controlled by planar 1 1 0 dominant facets growing either in regime I or in regime II. According to them, there is no longer any nucleation barrier to form niches on stepped $\{200\}$ faces serrated at a molecular level. A free-energy barrier is still taken to exist because of lattice strain due to the expansion of the lattice to accommodate folds.

This free-energy barrier $s\sigma_s$ replaces the lateral surface free energy $2bl\sigma$, in the expression of i and also limits the value of g. This modifies the value of the distance between the niches $L_k = (2g/i)^{1/2}$. From the Hoffman and Miller estimation of the ratio g_{200}/G_{200} (which is of the order of magnitude of 2), the value of L_k is approximated to be four times the width of a single stem.

This is another confirmation of our remark about Mansfield's calculation[17]: the mechanism of crystallization must be at the borderline of nucleation-controlled growth.

(ii) However, in Hoffman and Miller's view, we no longer have nucleation at all. The replacement in the expression for i of $2bl\sigma$ by $s\sigma_s$ modifies the familiar diagram relative to the zippering process. The graph of *Figure 4* gives the free energy of adding v stems to a 2 0 0

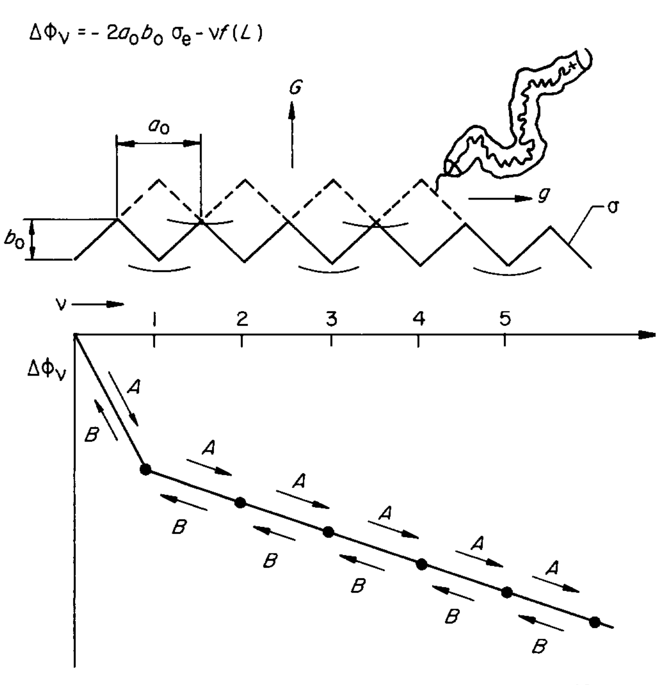

Figure 4 Serrated surface according to Hoffman and Miller[15], and free-energy change on formation of a nucleus of fixed length as a function of the number of stems. In the notation of ref. 15 (and by using L in place of l to designate the thickness of the lamellae) $f(L) = 2a_0b\sigma_e + 2\sqrt{2}b_0\sigma_s - a_0b_0L(\Delta G)$

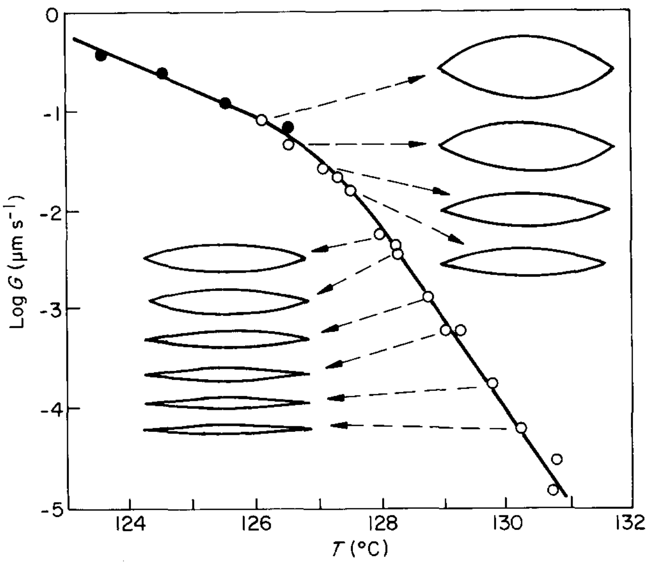

Figure 5 Growth rate and morphology of crystals obtained from the melt of PE ($M_w = 50900$) according to Labaig (communicated by Labaig, Lotz and Wittman). The 'dominant 1 1 0 facets which according to Hoffman and Miller govern the change from regime I to regime II' are not seen

face as a function of v and leads to a situation that is commonly known as the 'δl catastrophe'[13].

In fact, the attachment of the first stem leads to a decrease of the free energy, which becomes larger as the lamellae get thicker. The attachment of the first stem is easier than the attachment of further stems, and the basic argument of the Hoffman and Lauritzen zippering model is lost.

(iii) Hoffman and Miller introduce the idea that, although the 200 facets grow on regime II, these faces are subordinate to dominant 1 1 0 facets, which in turn govern the regime I–II transitions as shown by *Figure 5*, drawn from Labaig's data. These hypothetical 1 1 0 facets are not seen below the break in the log G *versus* $1/T\,\Delta T$ curve nor above this break.

Despite the fact[14] that from the Gargagno Meeting in 1988 the persistence length was reduced from 1 μm to 20 nm, we do not believe that these omnipresent, dominant, phantom facets exist (see Appendix 4). From our point of view, these apparent paradoxes may be ruled out by discarding the concepts of regime I[11] and of the zippering nuclei[8]. There are other approaches to the problem of limitation of fold length at high supercooling[7–9].

In conclusion, the various developments given by Hoffman and Miller do not seem to be consistent. Nevertheless this does not make Mansfield's major result any less interesting: 'Despite the fact that the Frank's model is intended to describe a nucleation controlled growth, the Frank's equation may be used to construct rough surfaces.'

SADLER'S APPROACH

The premise that nucleation was the rate-controlling factor in kinetic theories was first disputed by Sadler in 1983. He states that in some circumstances poly(ethylene oxide) crystals have a rounded habit as do polyethylene crystals grown from the melt or grown in a solution with higher dissolution temperature.

The approach proposed by Sadler to replace the theory of nucleation control may be divided into two parts:

The first one[7] is related to Sadler's concept of pinning. As a molecule attaches itself, it does not necessarily choose a conformation that is suitable for a later stage of growth. It forms chain folds and loops, which constitute pinned surface sites. Therefore, growth tends to get frustrated. The simple two-dimensional version of this model, the row model, allows the rate constants and value of the fold length to be calculated. In such a model, a row of stems is cut out of the crystal *perpendicular* to the growth face, neglecting all lateral correlations. This problem is completely disconnected from the second topic and is not discussed here.

The second part of Sadler's approach[6] concerns the problem of the overall external shape of polymer lamellae and is now scrutinized and compared to Frank's approach.

Consider (*Figure 6*) the surface of a two-dimensional crystal with a square lattice which grows in the direction y. Impose the solid-on-solid (SOS) restriction: The only 'on' sites allowed are those in position y where there is an existing occupied site at $y-1$. There are three kinds of sites, namely sites 0, 1 and 2 according to the number of lateral neighbours of the unit. Rate constants A_0, A_1, A_2 for addition and B_0, B_1, B_2 for removal may be defined, and their ratio depends on the corresponding changes in free energy. It is clear (*Figure 5*) that by defining the rate constants i and g Frank has also differentiated the sites 0 from the sites 1. However, Frank's theory ignores the removal of a unit from a site 2. Removal and addition in such sites are rare events when the situation is a nucleation-controlled growth.

The most important difference between the two models is that in Frank's model the rate of advance of a step is

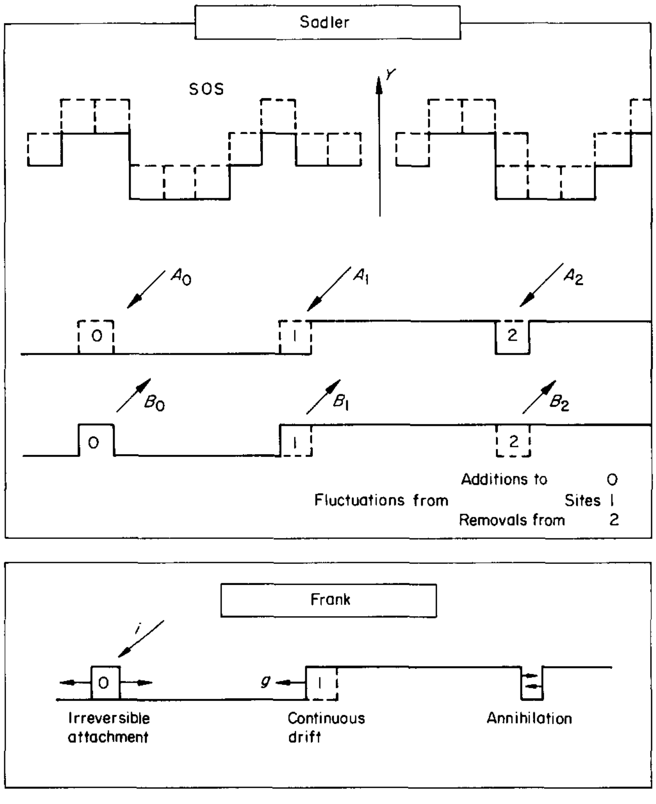

Figure 6 Growth of a 2D crystal according to Sadler[6]

a constant, but in Sadler's model fluctuations will be superimposed on a systematic drift of the step. A more or less biased random walk of the steps is assumed. On the contrary, similarities exist between the models. More specifically, Sadler considers in a part of his work the extreme situation where the mean distance between steps, the kinetic length $L_k = (2g/i)^{1/2}$ of Frank's model, is much larger than the width of the individual stem and also much larger than the amplitude of the fluctuations of the position of a niche. In such a situation, simulations show that nuclei form on the surface, which grows systematically outwards, with little probability of total removal before they encounter a second nucleus. Thus Sadler indicates the possibility of a continuous transition from a situation of normal growth of a rough surface to a nucleation-controlled growth. This remark of Sadler is symmetrical with our own conclusion about Mansfield's work: 'When disentangled from other considerations about reptation, persistence length, regime transition, zippering up of the molecule, Frank's equations may paradoxically produce a rough surface.'

NEED FOR A UNIFIED MODEL

Instead of using, as Hoffman and Miller did, Mansfield's result to disparage the Sadler approach, it may be possible to construct a unified model that mediates between Frank's model and the theory of growth of 2D crystals disconnected from the consideration of the pinning model. To do this, we first have to return to the experiment and to scrutinize the facts.

(i) The rounded habit of some poly(ethylene oxide) crystals of Kovacs[28] and of methoxy poly(ethylene oxide) of Cheng[29] does not result from thermal roughening. When grown at the highest practicable temperature of crystallization, the crystals display polygonal shapes.

(ii) An impressive set of experimental data shows that polyethylene may grow by a mechanism that ranges continuously from nucleation-controlled growth to normal growth. The isochronous decoration in some six facetted polyethylene crystals[10] and the existence of rectangular 200 sectors are interpreted in ref. 22 as proof of nucleation control. This was also previously demonstrated by Bassett, Keller and others for lozenge crystals with distinct sectors and with systematically distorted lattices. The sectorized crystal of Khoury with curved facet[20], the polyethylene crystal with curved edges and decorated by paraffinic crystals described by Lotz and Wittman[23], the sectorized crystal with curved edges of Organ and Keller[19] and the isochronously decorated crystal with rounded habit grown from hexadecanol by Dosière[21] display a high degree of internal regularity. Lanceolated polyethylene crystals grown by Takamizawa[1], Keith[24] and Nagai[25], and those of Bassett in which distinct sectors were identified by diffraction contrast[26], grow at the borderline of normal growth but have, however, internal regularity.

All these facts dictate in an imperative tone what must be our ultimate goal. Our precise targets are (i) to construct equations that generalize Frank's model and include some of the constituent ingredients of the model of normal growth of 2D crystals and (ii) to solve exactly the just-mentioned restated system of equations.

THE MODEL

We start from Frank's equations (1) and (2), and to account for the possible removal of units from site 0, we replace i by its mean value $\langle i \rangle$. Similarly because in the rough surface model, as a consequence of adding and removing units in site 1, the positions of the niches fluctuate, we first replace g by its mean value g/p but only in the convective term. Because this more or less biased random walk of the niches leads to an increasingly large number of encounters between facing steps, a modification of the expression of the annihilation term is required. A second reason to revise this term is that we are dealing with crystals of polymer instead of atomic crystals such as those considered in the original model of Hillig[30], Calvert and Uhlman[31] and Frank[5].

In the study of the concentration effect in crystallization from solution, Sanchez and Di Marzio[32], Toda *et al.*[33] and others have explained in various ways the role played by the two cilia or dangling ends of molecules that result from the encounter of two nuclei. They stressed the fact that these cilia may nucleate, for instance, another layer, and took this into consideration by modifying the value of the initiation rate. It may also be envisaged that two dangling ends of molecules cooperate in creating two new steps in the further layer, just when colliding. In this case the probability that, if they encounter one another, two opposite steps disappear is less than one. It remains, however, that annihilation may be an increasing, and very likely a linearly increasing, function both of the concentration of left steps and of the concentration of right steps. We therefore express the annihilation term as $2wlr$, where w has the same dimension as a rate of displacement. Note that w has a value that may depend noticeably on the temperature and on the molecular weight and may differ widely from g/p.

Along the same line, we have to discuss what happens when a step reaches the extremity of the substrate. In an atomic crystal, annihilation of the step is predicted; in a polymer crystal, the dangling end of the attaching molecule must cooperate with a cilia incoming from the intersecting facet with a view to lengthening the substrate. Another eventuality is that the molecule folds back on itself and pursues its deposition on the original crystal facet. In this case a left step is created at the expense of a right step or vice versa. This last opportunity may be called a reflection, the reflecting power of the end of the substrate being 1 or less than 1.

These considerations open the possibility of using other boundary conditions than those assumed by Mansfield[17] and Frank[5]. Note the following nuance: in the work of Mansfield and of Hoffman and Miller[15], the mobility of the extremities of the substrate, for instance of a 200 facet of PE crystal, is governed from, say, the outside, essentially by the movement of the dominant 110 facets. In the present view, this motion is related, at least partially, to the mode of growth of the 200 facet itself. We return to these points later.

In conclusion, in order to mediate between Frank's and Gilmer and Sadler's models, we profoundly modify the meaning of the physical parameters used in Frank's equations and we stress that various boundary conditions may be assumed (for instance the condition $h < g/p$ does not necessarily hold). But we restate, however, the formally nearly identical system of equations, although the range of physical interpretation has been extended.

At first sight this may appear deceptive because the only known solutions of Frank's equations are as follows:

(i) The solution given by Frank himself:

$$y = b\{\log[\cos(2\pi kx)] + \omega t\}$$

We use k and ω in this expression to draw attention to the fact that, ultimately, the resolution of the problem implies the resolution of a Klein–Gordon equation. In this view, k may be used to design a wavenumber. We may use G instead of $b\omega$ to underline that ω is the growth rate. Note also that k and ω are not independent quantities: $\omega^2 = 2ig - 4\pi^2k^2g^2$. From this, it appears that the amplitude of modes with smaller wavenumbers increases more rapidly than the others.

(ii) The (from a strict mathematical point of view erroneous) analytical solution given by Mansfield[17].

(iii) Mansfield's solutions[18] resulting from computer simulation.

We have now to discuss these solutions and to see if we can find other more appropriate and exact solutions.

RESULTS

Effect of the reduction of the probability of annihilation

The logarithmic term that appears in Frank's solution may be assumed to be comprised between 0 and a few negative units. Thus b being smaller than 1 nm and the length of a facet being, for instance, several micrometres, Frank's solution describes a very flat profile. Reduction of the annihilation probability by a factor of, say c, increases by a factor c the ordinate scale (or the apparent value of b). This increases the curvature of the profile. For sufficiently large value of c, we can get a curve that fits the shape of lanceolated crystals of elongation ratio smaller than 4.

Effect of reflecting boundary conditions

We have shown that Mansfield's solution is a good approximation of an exact solution of Frank's problem, but for completely different boundary conditions than those used by Mansfield himself. If appropriate and very special reflecting moving boundary conditions are assumed:

$$y = b\log I_0[(2ig)^{1/2}(t^2 + x^2/g^2)^{1/2}]$$

where I_0 is the modified Bessel function of zero order. Then y is an exact solution of Frank's equations. Similar results are obtained from generalized equations. These changes in the analytical expression of y and of the boundary conditions rehabilitate Mansfield's analytical solution (because for large values of x, $I_0(x) \simeq 0.398\,942\,28x^{-1/2}e^x$). A remaining difficulty is that an appropriate correlation between the reflecting power of the boundaries and their motion must be assumed. Another apparent paradox is that reflecting boundary conditions were not used by Mansfield when performing his computer simulations. From our point of view, both paradoxes are solved by considering that the effect of local modifications of the values of the densities of steps does not propagate deeply along the profile because the kinetic length is much smaller than the length of the substrate. At this stage, Mansfield's work and our new interpretation of the physical parameters involved appear as good premises in our task to mediate between Frank's and Sadler's approaches. It appears that the same equations may be used to describe a nucleation-controlled growth (an already known result) and also to describe a certain mode of growth of rough crystals in which the distance between consecutive niches is only a small multiple of the width of a single stem (the original Frank's model being patently unsuited[5] to describe such a situation). But the task is not achieved because the solutions obtained cannot explain the shape of all the very common lanceolated crystals, which do not have measurable or even visible 1 1 0 facets and are definitely not elliptic. From Labaig's work and Bassett's investigations, this lanceolated shape is the only one observed when PE crystallizes in the orthorhombic phase from the melt either below and after the break in the log G *versus* T curve. Therefore, we have searched for and found all the solutions of our system of equations in the framework of its new interpretation.

Search for other non-elliptic profiles

Passing on the mathematical details, we first demonstrate that the initial system of equations is equivalent to the following system of equations:

$$\left(\frac{b}{w}\right)\left(\frac{g}{p}\right)\frac{\partial^2 y}{\partial t^2} + \left(\frac{\partial y}{\partial t}\right)^2 = 2i\left(\frac{g}{p}\right)^2\frac{b^2}{w} + \left(\frac{g}{p}\right)^2\left[\left(\frac{g}{w}\right)\left(\frac{g}{p}\right)\frac{\partial^2 y}{\partial x^2} + \left(\frac{\partial y}{\partial x}\right)^2\right]$$

$$\frac{\partial y}{\partial t} = \left(\frac{g}{p}\right)b(l + r)$$

$$\frac{\partial y}{\partial x} = b(l - r)$$

made up of a non-linear hyperbolic differential equation and two ordinary equations. However, these last two equations may be, from a formal point of view, considered as the definitions of l and r, and the problem is thus reduced to the resoluton of a single equation.

By an appropriate new choice of variables, this equation was further reduced to a linear hyperbolic equation very similar to a Klein–Gordon equation. Then it was shown (S. Alinhac) that this last equation may be solved by the study of a set of integral equations, which was finally performed (D. Villers) by numerical analysis (see ref. 34). We now discuss the exact solutions for different values of the physical parameters.

Figure 7 shows the various shapes obtained and displays the successive outlines of the crystal at equal intervals of time. We see a crystal similar to those observed by Khoury[20], Organ and Keller[19], Lotz and Wittman[23] and many others in *Figure 7a*. *Figure 7b* shows a fairly lanceolated crystal where the external parts of the curved edges are fairly straight, as some crystals of Keith[24], many of Labaig[27] and of Nagai[25]. All these results show the predictive ability of our unified approach for the description of crystals, the shape of which ranges from lozenge to lanceolated crystals with very large elongation ratios. We have hit our target.

The influence of the various parameters on crystal shape merits a long discussion. Some important results, explicitly established elsewhere[34], are the following. Lanceolated crystals are obtained solely if the rate h of the moving boundaries exceeds the mean rate g/p of the step and if we have reflecting boundaries. For absorbing boundaries, the crystals have the shape of a truncated lozenge with curved 2 0 0 faces. Appreciable curvature is obtained solely if $(2w/i)^{1/2}$ is of the same order of magnitude as b.

Note carefully that our model does not mediate between Hoffman, Lauritzen and Miller's views[15] and Sadler's pinning theory[7], but that it does mediate between Frank's model[5] and Gilmer and Sadler's model[6] for 2D crystal growth when these theories are disentangled from other very controversial and complicated considerations.

EPILOGUE

So, we can forget Bessel functions, partial differential and integral equations, all these complicated mathematical topics. We can forget serrated faces, reptation, regimes, zippering, lattice strains and all these complicated physical topics and look at a *lanceolated crystal.*

We have to decide if it grows homothetically (an idea of a mathematician because a molecule has a constant size and because the persistence length, and all the submicroscopic dimensions, does not increase with the size of the crystal) or by a motion parallel to the y axis (*Figures 8a* and *8b*). The answer was given recently by Bassett *et al.*[26]. Because these lanceolated crystals are bisectorized, it seems very likely that each molecule is deposited in a layer roughly parallel to the 200 crystallographic plane. The second solution seems to be the right one.

We have now to ask why the crystal is larger at $x = 0$ than at some distance from the crystal centre. If we have any common sense, our answer is that near the centre it has grown from the beginning for a larger interval of time than in any other place. Therefore, the crystal is nearly lozenge-shaped and the elongation ratio is roughly equal to the cotangent of half the theta angle (*Figure 8c*).

If we return to the experimental data, essentially those of Labaig[27], we see that this conclusion is qualitatively founded but nevertheless not exactly verified. Then we look at the unique equation we have stated equivalent to those of the generalized Frank's model. As the linear size of the crystal increases by a factor of 10, neither $\partial y/\partial x$ nor $2igb$ are modified, but the curvature is divided by 10. We may thus write, as Mansfield does implicitly and without a convincing physical explanation:

$$\left(\frac{\partial y}{\partial t}\right)^2 = 2i\left(\frac{g}{p}\right)^2\frac{b^2}{w} + \left(\frac{g}{p}\right)^2\left(\frac{\partial y}{\partial x}\right)^2$$

and a particular solution of this equation is made up of one ellipse with four segments tangent to it (*Figure 8d*). This shape was also found by Toda[35] and presented at the 33rd IUPAC Polymer Symposium.

This is, to the precision of the measurements, the shape of many crystals. The experimental shape is obtained by solving exactly the master equation, as we do it. The last problem is to explain why the solutions do not depend greatly on the assumed density of steps at the boundaries but solely on the motion of these boundaries. This is simply because the conditions on l and r relax into few persistence lengths, i.e. some tens of nanometres.

This is all the story. It relies solely on the following:

(i) Our generalized Frank's model.

(ii) The bisectorization of lanceolated crystals observed by Bassett.

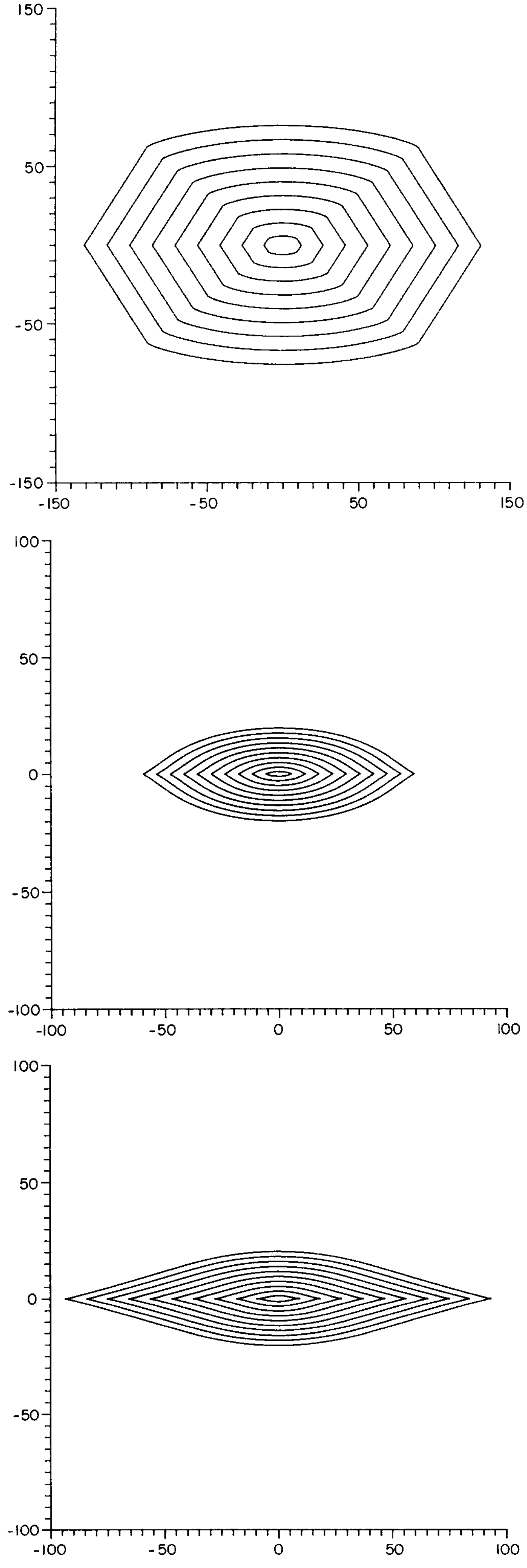

Figure 7 Exact solutions of the equations of the new model for various values of the involved physical parameters. The shapes given in (b) and (c) are respectively similar to those of crystals obtained by Bassett[26] and Nagai[25]

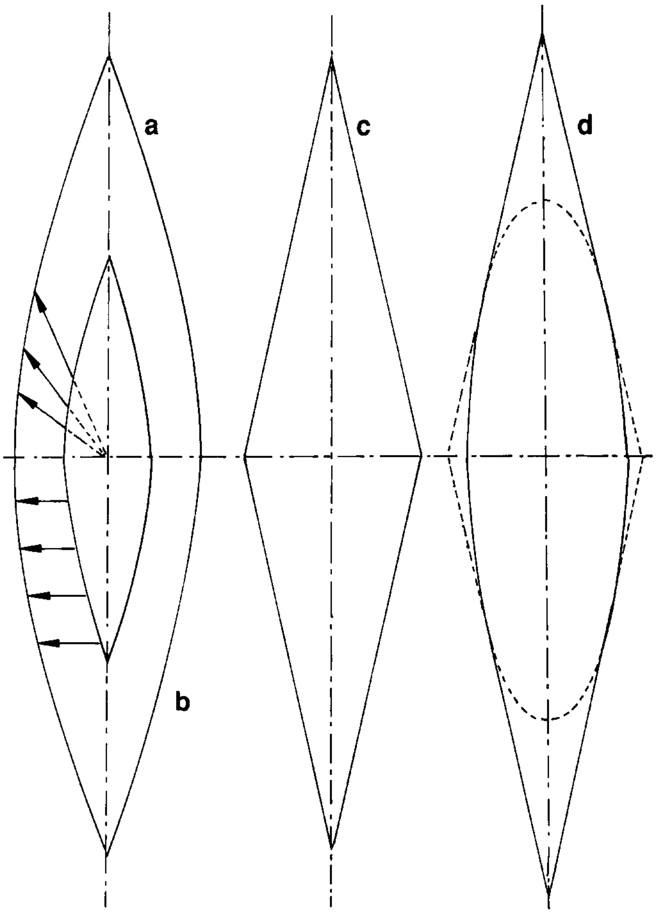

Figure 8 A qualitative justification of the shape of a crystal with a curved edge

(iii) The relation between the elongation ratio and theta angle found by Labaig and given by us as a proof that the crystals are not limited by arcs of ellipses.

(iv) The observation by Sadler, which recognizes that rough surface models may produce in some instances a nucleation mode of growth.

(v) Mansfield's computer simulations, which construct rough surfaces from Frank's equations.

(vi) The remark that the boundary conditions on r and l are unimportant.

(vii) Many other observations by experimentalists and theoreticians.

It also relies on this work in which we scrutinize all experimental facts, we make a new interpretation of Frank's equations disembodied from the sophisticated Hoffman–Lauritzen theory, and we solve exactly the single equation of a suitably generalized model.

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APPENDIX 1

Because one reviewer (and Mansfield himself) thinks erroneously that equation (14) of Mansfield's paper[17]:

$$u\frac{\mathrm{d}\phi_2}{\mathrm{d}u} = g\frac{\mathrm{d}\phi_1}{\mathrm{d}u} \qquad (14\mathrm{M})$$

expresses the balance between the various causes of changes in the density of steps, we give here a detailed account of Mansfield's work. Mansfield defines the functions

$$\phi_1 = (l + r)/2 \qquad \text{and} \qquad \phi_2 = (r - l)/2$$

We first establish that Frank's equations (3) and (4) lead to equation (14M). From equations (3) and (4) we get:

$$\partial y/\partial x = b(l - r) = -2b\phi_2$$

and

$$\partial y/\partial t = gb(l + r) = -2gb\phi_1$$

From the identity $\partial^2 y/\partial x\, \partial t = \partial^2 y/\partial t\, \partial x$ we get (14M) without considering equations (1) and (2) (which express the balance between creation, annihilation and convection of steps). Therefore it is incorrect to think that equation (14M) takes these facts into account.

The sum of equations (1) and (2):

$$\left(\frac{\partial l}{\partial t} - g\frac{\partial l}{\partial x}\right) + \left(\frac{\partial r}{\partial t} + g\frac{\partial r}{\partial x}\right) = 2i - 4glr$$

is equivalent to equation (13M) of Mansfield:

$$\left(\frac{\partial \phi_1}{\partial t}\right)_x = g\left(\frac{\partial \phi_2}{\partial x}\right)_t = i - 2g(\phi_1^2 - \phi_2^2)$$

or

$$\frac{1}{t}\left(g\frac{\mathrm{d}\phi_1}{\mathrm{d}u} - u\frac{\mathrm{d}\phi_1}{\mathrm{d}u}\right) = i - 2g(\phi_1^2 - \phi_2^2)$$

In the first step of his calculation, Mansfield (as he explicitly states) neglects the transformation terms, which constitute the left-hand side of this equation, and this leads to the result expressed by equation (6). In a second step of his calculation he tries (see Appendix 3) to show that this oversimplification has no consequences.

APPENDIX 2

Because one reviewer thinks that the rate h appears in Mansfield's solution[17] and because his equation (44M) would mislead the reader, we explicitly demonstrate the very important equation (6), which expresses that the two 2 0 0 facets of Mansfield's solution are arcs of a *single* ellipse.

Consider the equations (17M) and (18M) of Mansfield at $x = 0$; these equations give $r = l = (i/2g)^{1/2}$ and on integration of equation (4):

$$y(0, t) = b(2gi)^{1/2}t$$

For $x \neq 0$, integration of equations (17M) and (18M) give in the notation of Mansfield $y = y(-ht, t) + \Gamma(x, t)$ where $\Gamma(x, t)$ is given by equation (44M) of Mansfield.

At first sight the right-hand of this equation depends on h, because $y(-ht, t)$ and $\Gamma(x, t)$ both depend on h. However, by substitution of the values of $y(-ht, t)$ and $\Gamma(x, t)$ by their values, we get equation (6), which gives at $x = 0$ the expression just found. In this expression the additional parameter introduced, h, the rate of motion of the ends of the substrate, does not appear. This is not a great surprise, because in this part of his work, Mansfield does not use boundary conditions.

APPENDIX 3

It is, however, not established that, for long times, the effects of the boundary conditions are unimportant. First of all, as demonstrated elsewhere, they are important for a large value of h ($h > g$) (a case not considered by Mansfield). Let us now discuss the case $g > h$. The boundary conditions have been shown to be unimportant for small times (Mansfield[18]). Moreover, in his work[17], Mansfield intends to demonstrate that they are negligible for large times. But, as shown below, first his demonstration is invalid and, secondly, numerical calculation at intermediate times makes doubtful the validity of Mansfield's theorem itself. Let us examine this point in some detail. In a second step of his calculation (the first is described in Appendix 1), Mansfield assumes that the effective solution of the problem may be expressed in the form:

$$r = [\phi_1(u) - \phi_2(u)]/2 + f_1(x + ht) + f_2(ht - x) \qquad (19\text{M})$$

$$l = [\phi_1(u) + \phi_2(u)]/2 + f_1(ht - x) + f_2(ht + x) \qquad (20\text{M})$$

From this premise, Mansfield demonstrates that taking into account the full Frank's system of equations, and the boundary conditions, he can neglect f_1 and f_2 in the expressions of r and l. Unfortunately, the premise of his calculation (equations (19M) and (20M)) is wrong, because the exact solution of a particular problem given here in the second subsection of the 'Results' does not lead to values of r and l that would be expressed by equations (19M) and (20M) and therefore the demonstration of Mansfield's claim is obsolete.

The next question is to know if, the demonstration being unfounded, Mansfield's theorem itself (that is to say 'The difference between exact value of y and that given by equation (6) varies as the logarithm of t') is true or false. We do not know the answer. However, for intermediate time, numerical calculation shows that the difference between the actual value of y and that given by equation (6) increases more rapidly with time than $\ln(t)$ and the theorem itself may be presumed wrong even when $h < g$ (the case considered by Mansfield).

APPENDIX 4

The *facts* are that during the growth, the length of the crystal along the b axis increases. As stated in the section on 'The model', when a step reaches an extremity of the substrate, the dangling end of the attaching molecule may cooperate with a cilia incoming from the intersecting facet in order to lengthen the substrate. If submicroscopic 1 1 0 'facets' (or even 0 2 0 facets or serrated surfaces) exist, they also offer the opportunity for attachment of molecules coming from the solution. If we see nothing, we may imagine everything. What is open to criticism is the notion of a dominant 1 1 0 facet. As discussed later, the curvature of the 2 0 0 facets implies that the mean distances between nearest nuclei or steps on the 2 0 0 facet is small. This is an intrinsic property of the 2 0 0 facet, which has nothing to do with the value of h. Briefly speaking, the terms 'dominant facets', 'subsidiary facets' and the assumption of the existence of 'submicroscopic 1 1 0 facets' may lead to assigning the curvature of the 2 0 0 facet to a sole cause without explicit reference to the nature of the 2 0 0 facet itself.