A model for chain folding in polymer crystals: rough growth faces are consistent with the observed growth rates

D. M. Sadler* and G. H. Gilmer
Bell Laboratories, Murray Hill, New Jersey 07974, USA
(*Received 14 December 1983*)

The hypothesis that growth surfaces of polymer crystals can be molecularly rough has been tested using models designed to predict lamellar thicknesses and crystal growth rates. Monte Carlo methods used for crystallization of atomic growth units have been adapted to take account of the connectedness along the chains by including two types of restrictions for adding units to the crystal. Firstly new units cannot be added to an established fold surface. Secondly the effect of loops created at the growth surface is simulated by 'pinning' points generated at random along the crystalline stem, corresponding to stems growing from chains which are attached elsewhere on the growing face. No interruptions are allowed along crystalline stems. The trends in the results do not depend on the precise nature of the restrictions, and agree with the experimental ones. Crystal thicknesses vary approximately inversely with supercooling at small supercooling, and then level off to an approximately constant 'plateau' (no 'catastrophic' increase). They are smaller in magnitude than experimental ones since high fold energies are not included. The growth rates obey equations derived for secondary nucleation, though nucleation is certainly not present. The explanation is related to the high free energy (low entropy) states that are required for overall advance of the crystal. The low entropy depends on the crystal thickness as does the high enthalpy states in secondary nucleation. These results resolve the problem that both the existence of lamellae and the growth rate curves were explained on the assumption of molecularly smooth growth surfaces, whereas polymer crystals are often curved.

(Keywords: polymer; crystallization; rough growth surfaces; nucleation; growth rates; chain folding; lamellae)

INTRODUCTION

We develop here a model of polymer crystallization, which allows for the crystal growth surfaces being molecularly rough because of equilibrium effects[1]. We are then able to explain the existence of lamellae[2-4] and the form of the growth kinetics[5,6] without invoking surface nucleation.

In the usual nucleation models[7-9] the free energy barrier for initiating a new layer of the crystal is minimized (and hence the growth rate maximized) if the length of the nucleus in the chain direction is only slightly greater than that required for stability of the final crystal. On the basis of a nucleation mechanism being the rate controlling step, one would anticipate faceted crystals is the limit of slow growth[10]. Facets in the strict sense refer only to infinite 'singular' surfaces which are in equilibrium with the medium[11]. The angle of tilt of the surface with respect to a crystallographic direction is then strictly zero since steps then have a finite free-energy per unit length. The crystallographic direction usually involves a surface structure which is close packed. When the term 'facet' is applied to polymer crystals it must be understood in a less than strict sense since, appart from the lack of equilibrium, the growth faces are only 100 Å or so wide. On the nucleation model the nearest approach to strict facets is to be expected in the limit of low supercooling and slow growth of the lamellae. Departures from faceting from the existence of surface steps (two are created during each nucleation event) should become increasingly apparent as the supercooling ΔT is increased. In fact tge observations show almost the inverse to be the case[1]: for polyethylene 'facets' can be seen for low temperatures of crystallization T_x, but at high T_x (including conditions where growth is very slow) characteristic curvature is seen which is smooth on the scale of 100 Å and greater. Such curvature proves the existence of many surface steps crossing the lamellar edge, and suggests that initiation of new layers i not in fact an unlikely event. Gradients of temperature or concentration do not appear to be a general explanation of the curvature, since the curvature is not always associated with high growth rates. (Moreover, typical dimensions of polymer crystals are only $0.01 \times 1.0 \times 1.0\ \mu$ which tends to minimize gradient effects).

It has been proposed[1] that for many polymer crystals curvature indicate the absence of any singular surface orientations. In this case the introduction of individual steps on low-index orientations does not increase the system free energy. For this reason, even an infinitely wide surface does not follow low index planes. A surface roughness (and hence entropy) has been associated with such surfaces. For a more detailed discussion of the roughening transition see, for example, references 13–15.

Detailed arguments concerning the morphology of polyethylene have already been described[1]. A further publication[16] concentrates on some of these questions, in

---

* Permanent address: H. H. Wills Physics Laboratory, University of Bristol, Tyndall Avenue, Bristol, BS8 1TL.

0032–3861/84/101446–07$03.00

particular the effects of re-entrant corners on twin morphology. Enhanced growth rates at such corners is important evidence of nucleation, and is seen at *low* T_x. An observation probably specific to polyethylene is the high 'intrinsic' growth rate along the *b* crystal axis, the origin of which is yet to be elucidated.

The secondary nucleation theory for explaining the almost universal lamellar form for polymer crystals was conceived when all observations showed facets. At the present time as many instances of curved as faceted crystals have been reported[17] including polyethylene[18] and it is clearly necessary to develop a more general approach which does not rely on facets.

Principal requirements of a model

1. Applicability for both rough and faceted growth faces.

2. Explanation of lamellar thickness: an equation of the form

$$l = a/\Delta T + \delta l \tag{1}$$

(where a and δl are constants and ΔT the supercooling) seems adequate to describe the experiments[17,19].

3. Explanation of speed of advance of the growth front G of the form

$$G = c\exp(-K_g/T_x\Delta T) \tag{2}$$

where c and K_g are quantities which are constant at least for some range(s) of T_x[5,6,8].

4. Generality. Since lamellae are so prevalent it is desirable to aim for a simple model which does not incorporate features which are specific only to some systems.

Secondary nucleation is at least partly successful on requirements 2 and 3 but does not appear to be appropriate for non-faceted crystals for the reasons outlined above. The model to be described below can be applied either to rough or faceted surfaces (requirement 1). It also differs from many previous models since it depends explicitly on the coiled conformations existing prior to crystallization.

Outline of the model

Method of analysis. The characteristic of our approach is to include in the model a large number of processes and possible configurations, and to use simulation methods to help identify those which are most frequent. In this way a model can be established which makes simplifications in quite a different manner from existing theories. In particular, it has been found necessary to include many simultaneous events at different locations on the growth face. This is in contrast to the analytic models[7-9], which treat a single 'active' site which advances by the addition of stems[7,8] or segments of stems[9,20]. (A stem is that part of a chain that traverses the lamella.) Even for non-polymers the static and dynamic properties of the growth surface (especially those involving rough surfaces) often require Monte Carlo simulation techniques[12] so this method is the basis of our initial work.

Details of the techniques are given elsewhere[21]. The crystal is set up as a simple rectangular lattice, and energy calculated according to nearest neighbour interaction. It is assumed that segments or 'flexibility units' of the molecule are the basic crystallizing units, and these consist of several monomers in consecutive positions along the chain[9,20]. Random number generators are used to specify the coordinates of the surface sites where units are to be added or subtracted. Rules restricting these events are described below. Once a site is selected, whether this event occurs depends on a comparison between a probability value and a random number. The probabilities are specified as follows: the probability of addition is independent of the nature of the site and of temperature. The probability of removal is calculated according to a Boltzmann weighting factor with the energy determined by the sum of bond energies with nearest neighbours. These bond energies ε_i are proportional to the enthalpy of fusion or dissolution of the polymer. The subscript on ε_1 indicates the direction in the lattice. In this model the heat of fusion Δh is $\sum_i \varepsilon_i$. It is convenient to imagine a surface 'kink site' (three nearest neighbours) for which addition and removal involves no change in the crystal surface area. In this special case the ratio of, on to off, events is unity at the melting point of the infinite crystal T_m°. At lower temperatures $T_x(=T_m^\circ - \Delta T)$, the ratio is:

$$\exp(-\Delta f/kT_x)$$

where k is Boltzmann's constant. Δf is the difference in the Gibbs free energy per unit in the two bulk phases, usually approximated by:

$$\begin{aligned}\Delta f &= \Delta h(1 - T_x/T_m^\circ) \\ &= \Delta h \Delta T/T_m^\circ.\end{aligned} \tag{3}$$

The outcome of the simulation studies indicated that a simplified version of this model would exhibit some of the essential features. In this case analytic calculations are possible, and results of these will be reported elsewhere.

Geometry. The crystallization of a stem is imagined as a sequence of units adding along the vertical direction as shown in *Figure 1*. No interruptions are allowed along the stem; i.e., partial stem attachment is allowed but two or more partial attachments at the same stem position are not permitted. This effectively introduces a 'solid on solid' (SOS) restriction in the chain direction (for a definition of this term see ref. 13) and simplifies the computations. For simplicity, no distinction is made between adjacent stems that belong to the same or different molecules.

Previous SOS calculations refer only to one growing surface. The opposite parallel face is considered to be infinitely far away, and other surfaces are effectively removed by the use of cyclic boundary conditions in the two lateral directions (x,y). For polymer crystals we include a second surface, similar to the first. A third face (perpendicular to the x-axis) consists of sides of stems, to which new stem units can be added or existing units subtracted. In the y-direction cyclic boundary conditions mimic the effect of an infinitely wide crystal.

Restrictions. The aim is to extend the methods used for non-polymers in as simple a way as possible, but it is of course necessary to take account of the connectivity of different units in chains and the restrictions this will impose on crystallization. A description of the restrictions, which involves the same molecule being incorporated in different places in the crystal, will be followed by a more detailed description of the physical basis. The results of the simulations indicate that changing the precise form of the restrictions does not lead to essentially different results.

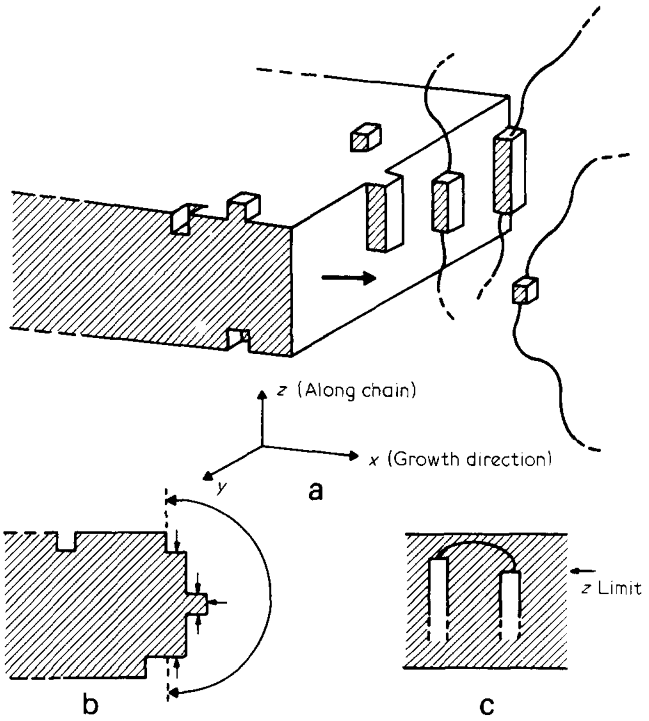

Figure 1 Schematic representations of polymer lamellae during crystallization. (a) The growth direction along the x-axis is indicated by the arrow. Stems add to the advancing face and expand along the z-axis, in both directions. (b) A cross-section through a lamella (perpendicular to the y-axis) illustrates restriction (i). Stems in the region to the left of the dotted line are frozen by the two active stems on the right. (c) Pinning of an active stem resulting from crystallization of a molecule in two locations (restriction (ii)). The type of folding[1,22] which may follow from (c) is not essential to restriction (ii)

(i) The simplest restriction is to limit the values of x for which stems can be lengthened. For example, consider a row of stems in the x direction up to an x value of x_0. The most severe form of this restriction is to allow adding and removal of units only at x_0, thus 'freezing' the underlying stems at their current length, but essentially similar results are given if the active region is expanded (e.g., including stems located at x_0 and $x_0 - 1$, where units of length are in lattice repeat distances). New stems are initiated by adding a single unit on the side of a pre-existing stem. When this happens the active regions change since x_0 has increased by unity. For a restriction to adding only at x_0, the length of the underlying stem becomes frozen by the new addition, although it could become active again if the unit were removed.

(ii) Pinning. When a new stem is initiated, a restriction is created in a random way such that that stem will have maximum and minimum z values to which it can grow in the future (z_+ and z_-). A Poisson distribution was chosen for the distribution. Typically, only a few of the z_+ and z_- occur within the region in which the lamella actually grows. If the stem is completely removed by fluctuations during growth, the values of z_+ and z_- are eliminated and new values are selected when another unit is deposited in that position.

Both (i) and (ii) are conceived as the result of different parts of a molecule attaching independently to the crystal, the loop (fold) so formed making it impossible for both incipient stems to lengthen beyond a certain limit. These 'freezing' processes have their counterpart in the previous (secondary nucleation) models: when a new stem was initiated alongside of the previous one, the two stems were imagined as being from the same molecule. Clearly, in this model no further extensions of the stems beyond the fold so formed were possible without considerable reorganization. One difference here is that the process is not strictly sequential since new units are being added in many places in a random way over the growth face.

Restriction (ii) applies when a new section of chain approaches the growth surface and attaches at two or more places along its length. The average distance between z_+ and z_- is related to the degree of coiling in the liquid. (For the less rough surfaces the attachments will tend to be in adjacent stem positions: for a discussion of this and its relevance to neutron scattering studies on types of folding see refs. 1 and 22.) Restriction (i) reflects the fact that the ends of stems are unlikely to continue as dangling chains from the top or bottom surface. Hence the stems there do not, in general, have units available for their extension. In the extreme case, it is not possible to add new units to a pre-existing fold surface. In a sense the folds 'poison' that crystal face and prevent further crystal growth.

In previous models a stem is frozen only after the creation of a fold with the same free energy as in the final crystal. This (for polyethylene) involves energies of about 8 kT[8]. Hence even when individual units (rather than stems) are treated[20] the freezing is intrinsically unlikely. Here by contrast the freezing occurs before the fold had a high free energy, when the molecule is in a state similar to an adsorbed chain (loops plus partly attached stems)[8,23,24]. In fact, the simulations do not involve a high fold energy at all: the (fold) surface energy of the final crystal is only $\varepsilon/2$ per stem site (about 1.0 kT).

Restrictions (i) and (ii) appear to give qualitatively similar results when used either singly or in combination even though they are very different in their detailed mechanisms. Restriction (i) is simple enough from the computational point of view to permit an analytic approach (to be published). It is reasonable that these restrictions should limit crystal dimensions along z. It is not obvious *a priori* why they should be sufficient to give l and G values of the correct form (see requirements 2 and 3 above).

RESULTS

Although the simulation has been discussed in terms of a lamellar structure (*Figure 1*), each run was in fact started using as a 'seed' crystal a large half-cylinder (*Figure 2(a)*). With the application of a sufficiently large supercooling ΔT, the seed spontaneously extended in the x direction to form a lamella (*Figure 2(b)* and *(c)*) with an approximately constant stem length. *Figure 2* shows two configurations for the ratio ε/kT_m° of 1/0.55 and 1/0.7, where ε was the same for all bond orientations x, y and z. For an infinite surface the transition from an atomically smooth structure (with long range correlations in the plane of the surface) to a rough one (without these correlations) occurs at $kT_m^\circ/\varepsilon \simeq 0.62$[15]. The difference in surface roughness is very apparent in the Figures. It is noticeable that, especially for the smaller value of ε/kT_m° there is no very clear demarcation between faces with normals along x and along z. This is to be expected[25] since a crystal corner or a crystal apex can never be entirely regular for $T > 0$ K. This 'rounding off' of corners seems to have a crucial influence on the growth process (see below).

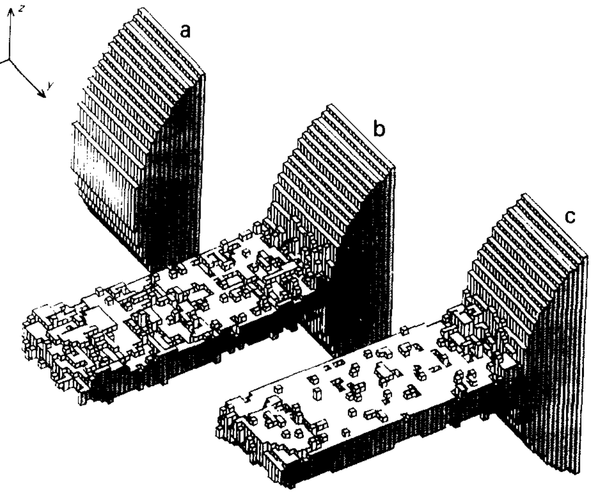

Figure 2 Computer drawings of the 'seed' crystal (a), and the lamellar crystals generated by the simulation at two different ε values. The lamellar crystal on the left (b) corresponds to $kT^{\circ}_{m}/\varepsilon=0.7$, and that on the right (c) corresponds to $kT^{\circ}_{m}/\varepsilon=0.55$. Crystal width along y is 20 units

Values of l *and* G

The average value of the stem length l was computed over those regions of the crystal away from the original 'seed' (to the left of the Figures) and from the growing edge ($x=x_0$). The growth rate G was measured as the linear rate of advance along x. The units impinge on the simulated surface at a constant arbitrary rate. This rate was used to measure 'time' during crystal growth and hence enables a growth rate to be calculated in arbitrary units. *Figures 3* and *4* show some simulation results which are in accord with the trends observed experimentally (equations (1) and (2)). The l values are rather small in comparison to those observed for polyethylene (see below).

The minimum value of lamellar thickness

The well known equation for the melting of polymer crystals[26] can be used to calculate the minimum value l_m below which the lamella would have a higher free energy than the liquid (or solution) state for a given value of ΔT. We can be certain that this is a necessary condition for growth. This value of l can be written as:

$$l_m=\frac{2\sigma_e}{\Delta f} \tag{4}$$

where σ_e is the (fold) surface free energy per surface site. For a completely smooth surface in the simulation σ_e is $\varepsilon_3/2$. In practice, of course, σ_e is less than this because of an entropy contribution which more than compensates for the increase in surface energy as a result of the roughness. From equations (3) and (4) we therefore have:

$$l_m \lesssim \varepsilon_3 T^{\circ}_m \Big/ \sum_i \varepsilon_i \Delta T \tag{5}$$

At this stage we do not address the question as to whether the 'melting' or 'no growth' condition could depart from equation (4) for kinetic reasons. The thermodynamic condition (equation (4)) can be considered a 'mean field' result in the sense that the excess surface free energy is averaged over the whole crystal. It should also be stressed that l_m has been derived for the Monte Carlo model rather than from actual polymer crystals. In order for growth surface roughness to be possible, ε_3 must be about equal to kT and similar to ε_1 and ε_2. Equation (5) for a ΔT of 30°C gives $l_m \leqslant 4$ units. For polyethylene, a 'unit' is likely to be several monomers (for example six), in which case l_m is calculated to be about a factor of five less than observed for experimentally measured melting points. In other words the model does not allow for relatively high fold energies in the final crystal (σ_e larger than the 'side' surface free energy σ)[8]. This omission may be less severe for polymers such as nylon-6,6 than it is for polyethylene.

Interpretation of crystal thickness values

It can be seen that equation (5) contains the ΔT^{-1} dependence which is prominent in equation (1). We may anticipate that a successful model would be achieved, at low ΔT at least, if growth were such that l is only slightly greater than l_m. This appears to be the case for our simulation results shown in *Figure 3*. It may be noted that many theories could successfully give the ΔT^{-1} dependence, as long as some mechanism serves to minimize l; secondary nucleation is only one possibility. In the simulation, the restrictions (i) and/or (ii) are sufficient in minimizing l. Growth proceeds in the x-direction at such a rate that the stem becomes immobilized before its length is extended much behond l_m. The disfavouring of thick crystals is evidenced further by the steeply decreasing growth rate as l_m is increased (see below). At large ΔT most models for secondary nucleation predict a 'catastrophic' increase in l[7] which is not observed in experiments[27]. It is reasonable to associate this with a growth regime where it is assumed that there is no rise in free energy as a stem is added to a smooth face, and hence with there being no nucleation events. This has been avoided by the additional hypotheses of (a) supposing another high free energy step (adsorption)[8] or (b) increasing the probability of folding as l increases beyond l_m, together with the basic unit for crystallization being small units rather than whole stems[20]. In the simulation results of the present model (*Figure 3*) a 'plateau' in l is predicted at high ΔT which is well in line with experiment. A correlation between the plateau level of l (l_p) and the random coil characteristics of the chain has been noted[28]. The origin of the pinning mode of restriction (ii) can be taken to be the independent attachment of the same molecule to different

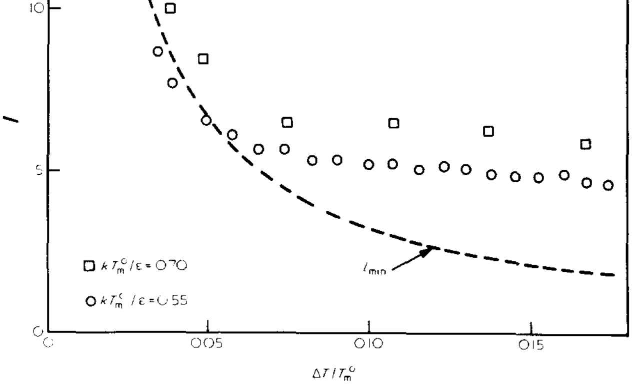

Figure 3 A plot of the lamellar thickness *versus* supercooling for two different values of the equilibrium melting temperature. The dashed curve is a plot of equation (5). Crystal width is 10 units

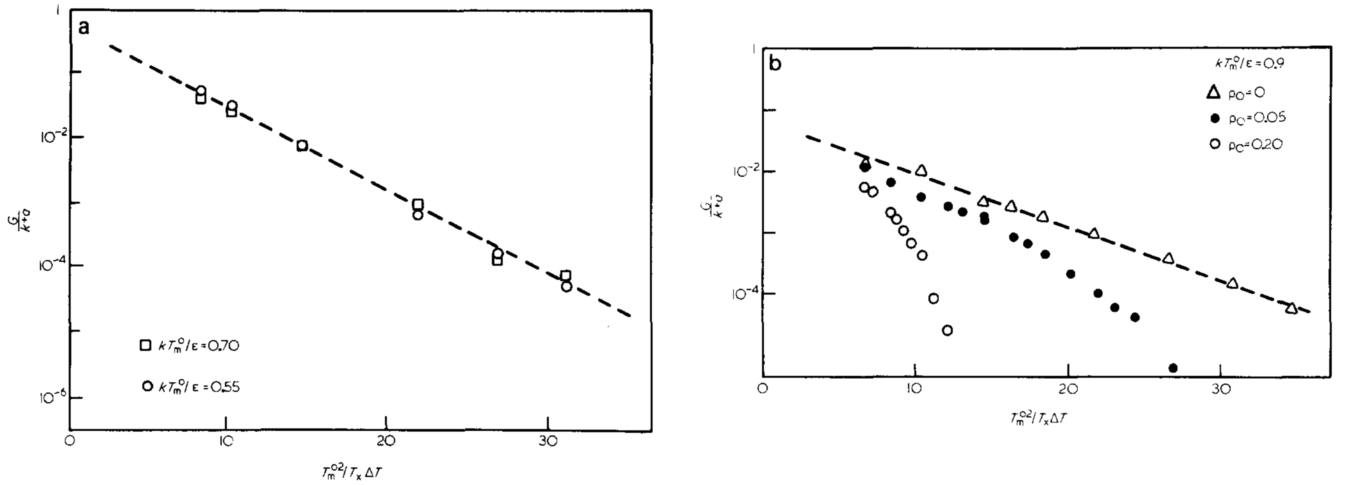

Figure 4 The dimensionless growth rate is plotted on a logarithmic scale as a function of the reciprocal of the product of the supercooling and the temperature. (a) Growth rates without pinning at (□) $kT_m^\circ/\varepsilon=0.7$ and (○) $kT_m^\circ/\varepsilon=0.55$. (b) Growth rates with different values of the density of pinning sites, ρ_0, for $kT_m^\circ/\varepsilon=0.90$. (△) $\rho_0=0$, (●) $\rho_0=0.05$, (○) $\rho_0=0.20$. k^+ is the rate of arrival of units per surface site and a the repeat distance in the growth direction

parts of the crystal face. Clearly the probability of this happening will depend on the coil characteristics.

The trends in the *l versus* ΔT curve agree well with experiment, but detailed adjustment of parameters is required in order to achieve quantitative agreement for any one polymer. The most significant omission concerns the low absolute values for l, at least for polyethylene. These can be traced to the lack of an energy contribution from a fold in the final crystal as opposed to that from a partially attached chain. Analytic calculation and simulation studies on impurity trapping show that it is very important whether a mismatch energy is involved as soon as the impurity arrives at a site on the crystal surface[29], or whether it occurs later[30] (e.g. as a result of lattice distortion involving several unit cells). In an analogous manner, if the energy contributions from the fold (e.g. lattice distortion) occur well after the initial multiple attachment, folds will probably only be disfavoured to the extent that l_m will be higher.

Interpretation of the growth rate G

The usual theories for crystal growth for globular molecules (see above) show that continuous growth occurs on rough surfaces ($G\alpha\Delta f$), whereas secondary nucleation occurs on facets in the absence of dislocations (equation (2)). For the simulations on polymer crystallization, equation (2) appears to hold when the surfaces are all rough (*Figure 2*) as well as when they are relatively smooth. It seems paradoxical that equation (2) is applicable to simulation results where (surface) nucleation is certainly not occurring. It was surmised[1] that the growth of curved crystals might obey equation (2) if there was a free energy barrier (in particular low entropy) to growth. The height of the barrier would have to increase with l. This possibility was studied by running the simulation under a range of conditions as described below, so as to identify what the barriers could be; they were not obvious from *Figure 2*. The conclusion was that the absence of sharp corners demarcating the top and bottom (fold) surface from the growth face ('rounding off') imposes an entropy barrier for the attachment of long stems. This serves both to minimize δl and make growth very slow at high l_m.

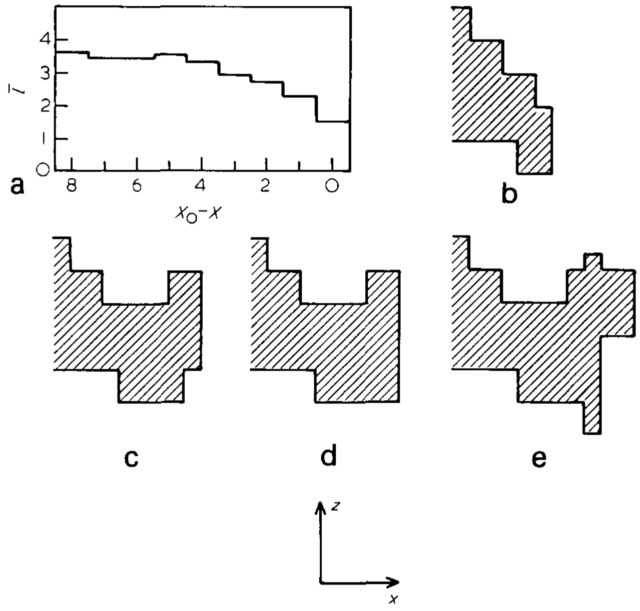

Figure 5 (a) Data for the average stem length $\bar{l}$ plotted for different positions relative to the end stem at x_0. Here $kT_m^\circ/\varepsilon_l=0.36$, $\varepsilon_2=0$ and $\Omega T/T_m^\circ=0.038$. (b)–(e) Typical configurations of the stem during growth, with $kT_m^\circ/\varepsilon_l=0.36$, $\varepsilon_2=0$ and $\Omega T/T_m^\circ=0.038$

Figure 5 shows stem lengths as a function of x_0-x, averaged over a number of stem rows along x. The tapering is very pronounced. Rounding of crystal corners is to be expected. *Figure 5(b)* shows a typical individual arrangement. Consider now restriction (i). For stems to form a viable crystal they must average to about l_m or more in length, yet at the positions where they are allowed to add units (e.g. x_0 and x_0-1) the stems are usually much shorter. These stems can only progress to become incorporated into the body of the lamella if the crystal edge is momentarily square so that a relatively long stem can be added, as in *Figure 5(d)*. If a very short stem is incorporated (e.g. to $x=x_0-3$) by addition of new stems further growth will be inhibited until a backwards fluctuation of the growth front enables it to grow. *Figures 5(b)*, (*c*) and (*e*) show configurations only a few time steps away from the configuration in *Figure 5(d)*.

This idea was tested by using the simulation program for simple two dimensional models by putting $\varepsilon_2=0$ (and increasing ε_2 values). Each row along x then grows independently. It was found that the kinetics were of the exponential type (as in *Figure 4*) as long as ε_1 was sufficiently large. For $\varepsilon_1 = 1.4\ kT_m^\circ$ or less the kinetics were linear, but for $\varepsilon_1 = 2.8\ kT_m^\circ$ or greater the exponential law (equation (2)) was obeyed. For $\varepsilon_2 = 0$ and small ε_1 the stems have enough randomness in length that there is no longer an entropy barrier. A short stem at $x_0 - 2$ does not block further growth, since the small energy interaction ε_1 permits a longer stem to be deposited in the next position. Histograms of stem lengths also illustrate the idea: *Figure 6* shows the number of times a stem at x_0 has a given length during several short simulated growth 'experiments'. It can be seen that the probability of finding stems at x_0 which are long enough to fit in the final crystal is indeed small (note the logarithmic scale). Even in those cases where a long stem is present, some will involve short stems at $x < x_0$, and others are likely to be removed by spontaneous fluctuations. (Hence the histogram of stem lengths for the final crystal, broken line, always lies below that for stems at x_0 during growth). It can be seen that, especially at the low ΔT (a), very nearly all the stem lengths which are observed by sampling randomly at $x = x_0$ are too small to make viable stems. They serve to freeze stems at smaller values of x which are also not viable. Before the row os stems can progress, there must be a spontaneous fluctuation which allows 'bad' stems ($l \ll l_m$) to be lengthened and then refrozen before they shorten again. For restriction (ii) the fluctuation may have to remove the 'bad' stem completely.

Consider now the situations which will occur when roughness decreases and the number of steps crossing the growth front is diminished. The 'rounding off' of the lamellar edge is then less pronounced (*Figure 2(b)*). Even so, there will be a compensating increase in free energy as a result of a requirement for squaring off to occur simultaneously for a number of adjacent stems on the growth face. In the limit of high enough ε/kT_m° one would anticipate a smooth surface and secondary nucleation. Direct morphological evidence shows that this is the case[1,16] for $T_x \lesssim 60°C$ for polyethylene crystallized from solution: $\{110\}$ twins show growth rates which are suppressed for the faces which do not adjoin a re-entrant corner, which is a hallmark of nucleation control[31,32].

The dependence of G on ΔT can be seen to arise very simply from the step of high free energy ϕ during secondary nucleation[8]. To a first approximation:

$$G \sim \exp(-\phi/kT) \tag{6}$$

For a single stem on an ideally smooth surface, ϕ contains a term:

$$l\varepsilon_2 \simeq l_m\varepsilon_2 \simeq \frac{\varepsilon_2\varepsilon_3 T_m^\circ}{\sum_{i=1}^{3} \varepsilon_i \Delta T} \tag{7}$$

$\varepsilon_2\varepsilon_3$ corresponds to the quantity$\sigma\sigma_e$[8]. This gives equation (2) directly. In order for ϕ to affect the slope in *Figure 4* it must be dependent on l. The entropy term for 'squaring off' a rounded crystal edge in two dimensions clearly satisfies this condition. *Figure 4b* shows other examples for $kT_m^\circ/\varepsilon = 0.9$, with rougher surfaces, where there is very distinct rounding off. Three different pinning densities are shown. One plot even shows a passing resemblance to data which have previously been interpreted[33] in terms of a transition from Regime I to Regime II (i.e. two types of surface nucleation growth behaviour). More details of this effect will be published elsewhere. Evidently it is difficult to extract unique interpretations from such plots without direct morphological information on the growth surface structure.

The slopes of the plots in *Figure 4* can be used to derive the quantity K_g in equation (2). From the simulations in *Figure 4(a)* K_g is about 2.4 if T_x and ΔT are expressed as fractions of T_m°. Higher or lower values than this are obtained in *Figure 4(b)* according to the degree of pinning. The experimental values are 1.4 – 0.7. No special attempt has been made to achieve even this degree of numerical agreement, since the model is schematic in many ways, but at least there is not a very large quantitative disagreement.

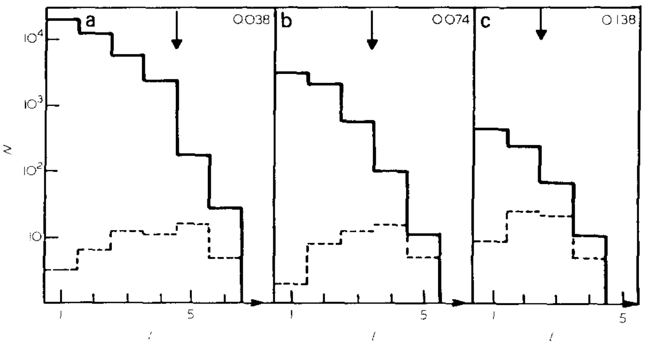

Figure 6 The number of lamellae N in an ensemble in which the stem at x_0 has length l. The dashed lines indicate the distribution of stem lengths in the bulk of the lamellae. Note the logarithmic scale for N. The arrow indicates the average stem length in the final crystal. Here $kT_m^\circ/\varepsilon_1 = 0.36$, $\varepsilon_2 = 0$ and values of $\Omega T/T_m^\circ$ are shown in the Figure

The origin of folding

Folding and hence lamellar growth follows if there are sufficient restrictions on crystal growth along the chain direction. The relatively simple model here shows that restrictions (i) and/or (ii) are sufficient for this, and in addition that they give very reasonable trends in l and G values *versus* ΔT for a wide range of roughness on the growth surface. The section on the interpretation of the restrictions (above) relates (i) and (ii) to multiple attachments of the same molecule. On the growth face one could imagine a multiple attached molecule as being in a kind of adsorbed state, such that the creation of an extended chain crystal would involve the unlikely process of detachment of all but one of the attached sequences before they were covered by stems from another molecule. High degrees of roughness are not essential for this process: for example several parts of the same molecule could participate in the formation of a secondary nucleus on a molecularly smooth surface. (However, the process is not sequential as in the secondary nucleation models[7–9]. Because of this difference a high free energy fold is not required before the restrictions can operate, as in the previous models.) The implication is that multiple attachment (and hence folding) is related to coiled conformations. If coiling prior to crystallization could be avoided (e.g. by flow) partly extended chain crystals might be expected, as is observed. In our model the dimensions of the coils are not very directly related to the lamellar thicknesses, although the degree of pinning (related to flexibility) does appear to have some effect on l values.

ACKNOWLEDGEMENTS

The authors are grateful to H. D. Keith and K. A. Jackson for enthusiastic support and many helpful discussions. D.M.S. wishes to thank Bell Laboratories for support as a Resident Visitor during the summer of 1983. We thank Antwi Nyanin for assistance with the computer graphics.

REFERENCES

1 Sadler, D. M. *Polymer* 1983, **24**, 1401
2 Keller, A. *Phil. Mag.* 1957, **2**, 1171
3 Fischer, E. W. *Z. Naturforsch.* 1957, **129**, 753
4 Till, P. H. *J. Polym. Sci.* 1957, **24**, 301
5 Flory, P. J. and McIntyre, A. D. *J. Polym. Sci.* 1955, **18**, 592
6 Burnett, B. B. and McDevit, W. F. *J. Appl. Phys.* 1957, **28**, 1101
7 Lauritzen, J. J. and Hoffman, J. D. *J. Res. Natl. Bur. Stds.* 1960, **64A**, 73
8 Hoffman, J. D., Davis, G. T. and Lauritzen, J. I. in 'Treatise on Solid State Chemistry' (Ed. N. B. Hannay), Plenum, New York, 1976, Vol. 3, Ch. 7
9 Frank, F. C. and Tosi, M. *Proc. Roy. Soc., London* 1961, **263A**, 323
10 Gibbs, J. W. in 'The Scientific Works of J. Willard Gibbs', Vol. I, Longmans Green, New York, 1906, p. 219
11 Herring, C. *Phys. Rev.* 1951, **82**, 87
12 Burton, W. K. and Cabrera, N. *Discuss Faraday Soc.* 1949, **5**, 33
13 Leamy, H. J., Gilmer, G. H. and Jackson, K. A. in 'Surface Physics of Materials', (Ed. J. M. Blakeley), Academic Press, New York, 1975, Vol. I, p. 121
14 Weeks, J. D., Gilmer, G. H. and Leamy, H. J. *Phys. Rev. Lett.* 1973, **31**, 549
15 Weeks, J. D. in 'Ordering in Strongly Fluctuating Condensed Matter Systems', (Ed. T. Riste), Plenum, London, 1980
16 Sadler, D. M. *Polymer* 1984, (*Commun*) 1984, **25**, 196
17 Wunderlich, B. 'Macromolecular Physics', Academic Press, New York, 1973, Vol. I
18 Keith, H. D. *J. Appl. Phys.* 1964, **35**, 3115
19 Kawai, T. and Keller, A. *Phil. Mag.* 1965, **11**, 1165
20 Point, J. J. *Macromolecules* 1979, **12**, 770
21 Gilmer, G. H. and Bennema, P. *J. Appl. Phys.* 1972, **43**, 1347
22 Sadler, D. M. in 'Structure of Crystalline Polymers' (Ed. I. Hall), Applied Science, 1984, p. 125
23 Jenkel, E. and Rumbach, B. *Z. Electrochem.* 1951, **55**, 612
24 Simha, R. and Eirich, F. R. *J. Phys. Chem.* 1953, **57**, 584
25 Frank, F. C. in 'Metal Surfaces' (Eds. W. D. Robertson and N. A. Gjostein), American Society for Metals, Metals Park, Ohio, 1963, p. 1
26 Hoffman, J. D. and Weeks, J. J. *J. Res. Natl. Bur. Stand.* 1962, **66A**, 13
27 Jones, D. H., Latham, A. J., Keller, A. and Girolamo, M. *J. Polym. Sci., Polym. Phys. Edn.* 1973, **11**, 1759
28 Raoult, J. *J. Macromol. Sci. Phys.* 1978, **B15**, 567
29 Jackson, K. A., Gilmer, G. H. and Leamy, H. J. in 'Laser and Electron Beam Processing of Materials' (Eds. C. W. White and P. S. Peercy), Academic Press, New York, 1980
30 Gilmer, G. H. in 'Laser-Solid Interactions and Transient Thermal Processing of Materials. (Eds. J. Naryan, W. L. Brown and R. A. Lemons), North-Holland, Amsterdam, 1983, p. 249
31 Stranski, I. N. *Disc. Faraday Soc.* 1949, **5**, 69
32 Frank, F. C. *Disc. Faraday Soc.* 1949, **5**, 186
33 Hoffman, J. D., Frolen, G. S. Ross and Lauritzen, J. I. *J. Res. Natl. Bur. Stand.* 1975, **79A**, 671