

Rate-Theory Model of Polymer Crystallization

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A new lattice model of polymer crystallization is described. Results of numerical solutions of rate equations for crystallization of a two-dimensional "crystal" are presented. It is shown that the crystal thickness varies inversely with supercooling and that kinetics similar to secondary nucleation occurs. This is true even though the growth face is intrinsically rough and hence there cannot be any nucleation. The presence of a low-entropy saddle point during growth is explained, and its influence on the crystal thickness and lamellar morphology is discussed.

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Crystals of long-chain molecules invariably grow as lamellae that are usually much thinner than the length of the chains.^{1,2} Molecules traverse the lamellae many times; the geometry is described in detail below. The precise manner of this folding has been the subject of considerable debate, but the emphasis of this paper is instead the origin of the lamellar habit. This phenomenon has been explained by models that invoke secondary nucleation; i.e., the nucleation of new layers of the crystal on the advancing edge of the lamella.³⁻⁵ The kinetics is also consistent with this mechanism,⁵⁻⁷ yet the crystals do not always have the faceted edges required for the nucleation process.^{2,8} In those cases where crystals of a polymer can be grown with either straight or smoothly rounded morphologies, the latter tend to occur at higher temperatures. It has been proposed that this change is associated with surface roughening.^{9,10} At the higher temperatures the surface is intrinsically rough on a microscopic scale, since steps across the growth faces and other favorable growth sites are generated by thermal fluctuations in equilibrium. Nucleation of a new layer is not required under these conditions. For growth faces of infinite extent, the theory of the roughening transition is now well established,¹¹⁻¹⁴ and experimental verification has been obtained.¹⁵ We now develop further a model of polymer crystallization that applies to rough growth faces and which could also be relevant when the faces are straight. The model reproduces the principal trends in experimental measurements of lamellar thickness and growth rates.

The growth face can only be sufficiently rough if the stems (the straight sequences of chain which traverse the crystal) are allowed to vary in length and if short stems are allowed. Our model considers the basic unit of crystallization to be a short sequence of chain (e.g., six CH₂ units of polyethylene; cf. Refs. 4 and 9 and Point¹⁶); stems differ in length according to how many units they contain.

The geometry of the crystals is described schematically in Fig. 1(a) with each stem corresponding to a prism. The ends of the stems should be imagined as

having attached chains emerging from the crystalline region. In many cases (e.g., to the left of the diagram) the chains will be folded back into the lamella. Partly attached chains with loops are indicated at the growth surface. Effects of polymer chain connectivity and coiling in the fluid phase are included by the introduction of "pinning points." These represent points on the crystal boundary which are not able to extend, e.g., because the emerging chain is trapped elsewhere as happens during folding. If a three-dimensional (3D) Monte Carlo simulation¹⁷ is performed, the roughness is typically as shown in Fig. 1(b). In contrast to the nucleation theories, there is only a weak correlation between stems and partial stems in the direction parallel to the growth face (coordinate y in Fig. 1).

We now simplify the model further so as to neglect

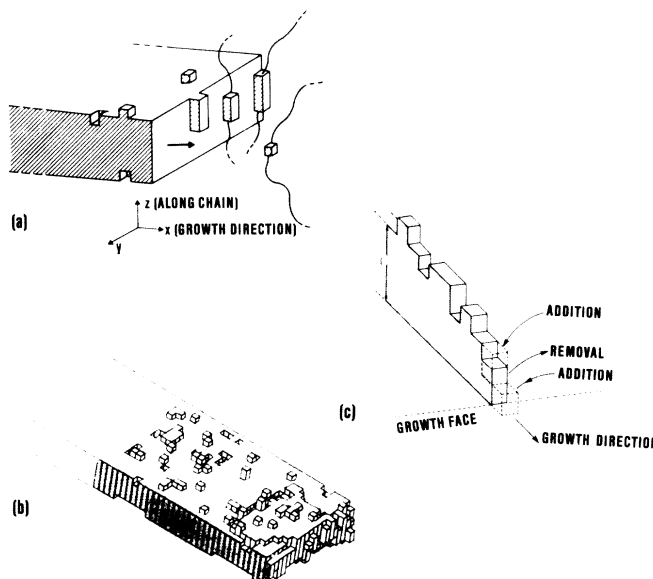


FIG. 1. (a) Schematic diagram of the three-dimensional model used for Monte Carlo calculations (see text). (b) Simulated crystal (Ref. 17) ("substrate" not shown). (c) Two-dimensional model which is the basis for the rate equations in this paper.

lateral correlations entirely. The result is a 2D model as in Fig. 1(c). n is the sequence number of stems, $n=1$ corresponding to the stem with the largest x coordinate. The exact form of the pinning was not found to have a fundamental effect, and for this study we have employed a particularly simple one: Additions and removals can occur *only* at the outermost stem positions (i.e., at $n=1$). The following changes are allowed. (1) Initiation of a new stem by addition of a single unit beyond the outermost position. (In this case $n=1$ refers to the new stem, and the previous outermost stem corresponds, after the addition, to $n=2$.) (2) Extension of a stem by one unit. (3) Reduction of a stem by one unit. In the case where the existing outermost stem only has one unit, that unit is removed and a stem is destroyed. Figure 1(c) describes all but the stem removal events. The rules which result have the great advantage that there is a strictly sequential set of processes. Such systems are tractable by using sets of rate equations (see, e.g., Volmer¹⁸), which permits accurate calculations of the properties of the system; e.g., growth rates and lamellar thicknesses. Unambiguous data can be obtained from numerical solutions of the set of rate equations. Monte Carlo simulations, while more generally appli-

cable, always involve a significant amount of statistical uncertainty. This uncertainty in the data often obscures the trends that would reveal the nature of the mechanism that is being investigated.

The rate constants for the various possible events are as follows. Both types of additions, those to an existing stem or creation of a new stem of unit length, have the rate k^+ . Removal rate constants are given by

$$k^- = k^+ e^{(\Delta f - \epsilon n')/kT_c}, \quad (1)$$

where T_c is the crystallization temperature, $-\Delta f$ is the bulk energy change on crystallization multiplied by T_c/T_m^0 , with T_m^0 the melting point of an infinite crystal, ϵ is the energy associated with breaking a bond, and n' is the number of bonds broken when a unit is removed. $C_n(i)$ is the fraction of stems at position n behind the "growth face" which have length i . It is also necessary to specify a function which determines the correlations in probabilities for adjacent stems; $f_n(i,j)$ is the conditional probability that the $(n+1)$ th stem is of length j given that the n th stem is of length i . It turns out¹⁹ that $f_n(i,j)$ is independent of n . The probability $P_n(i,j)$ of having stems of length i at n and j at $n+1$ is then $f(i,j)/C_n(i)$. The rate equations are then constructed as follows: For $i > 1$,

$$\frac{dP_1(i,j)}{dt} = k^+ P_1(i-1,j) + k^- (i+1,j) P_1(i+1,j) - k^+ P_1(i,j) - k^- (i,j) P_1(i,j) + P_1(1,i) k^- (1,i) f(i,j) - k^+ P_1(i,j); \quad (2)$$

for $i=1$,

$$\frac{dP_1(1,j)}{dt} = \{k^+ C_1(j) - k^+ P_1(1,j)\} + k^- (2,j) P_1(2,j) - k^+ P_1(1,j) - k^- (1,j) P_1(1,j) + P_1(1,1) k^- (1,1) f(1,j). \quad (3)$$

The rate constants for removal, from Eq. (1), are given by, for example,

$$k^- (i,j) = \exp\{(\Delta f - 2\epsilon)/kT_c\} \quad (i > 1, j > i), \quad (4a)$$

$$k^- (i,j) = \exp\{(\Delta f - \epsilon)/kT_c\} \quad (i=1, j > i). \quad (4b)$$

The various terms on the right in Eqs. (2) and (3) originate from the various possible processes, as listed as follows for the case $i=1$. The first and second terms [in braces, right-hand side of Eq. (3)] correspond to finding a stem of length j not equal to 1 at $n=1$ and adding to it a stem (the model only allows new stems to have length 1). The third term accounts for removal of one unit from a stem of 2, and the fourth, adding onto a stem of 1 so as to create a stem of 2 (thus eliminating a stem of length 1). The fifth and sixth terms allow for the removal of a stem of length one in the case where the stem in position 2 is

not of length 1, and in the case where it is of length 1, respectively.

Initial values of the $P(i,j)$ were chosen (e.g., all stems the same length) and then their changes after a small increment in time were calculated from Eqs. (2) and (3). Values of i and j were considered up to a maximum N , which was chosen in each case to give small values of $P(N,j)$. The updated $P(i,j)$ were then used in turn to calculate another set of differentials. By this means transients in stem configurations can be studied. Clearly a case of special interest is that of the steady state where the differentials become zero. This could commonly be attained after about 1000 iterations. The growth rate is given by the difference in attachment and detachment rates for stems at $n=1$:

$$G = k^+ \sum_{i=1}^N C_1(i) - \sum_{i=1}^N k(1,i) i C_1(i). \quad (5)$$

The average thickness l was taken to be the average

stem length at $n = 20$:

$$\sum_{i=1}^N i C_{20}(i) \left(\sum_{i=1}^N C_{20}(i) \right)^{-1}.$$

For n less than about 8, the average stem length decreases as n decreases to 1. With n as large as 20, this tapering effect is negligible and a measure of the stem length in the body of the "crystal" is obtained.

Figures 2 and 3 show the results for l and G ($\epsilon/kT_m^0 = 1.8$) in the same format as is usual for polymer crystals. N was in general about twice l . Clearly the trends are those found in experiment and in previous theories based on quite different models: $l \sim \Delta T^{-1}$ and $G \sim \exp(K_g/T_c \Delta T)$, where K_g is a constant.²⁰ The absolute values for l are small compared with experiment for the case of polyethylene: This is because¹⁷ suitably high fold energies have not been incorporated. The broken line corresponds to the minimum l value with the assumption that (fold) surface free energy is equal to surface energy [i.e., use of Eq. (5) of Ref. 17]. l can be smaller than this because of surface entropy. The plot of G is concave; this is found for some actual polymer crystal systems. These results compare with straight or convex G plots for the Monte Carlo 3D model.¹⁷

The explanation of these results is as follows. There is a free-energy barrier to growth, whose magnitude

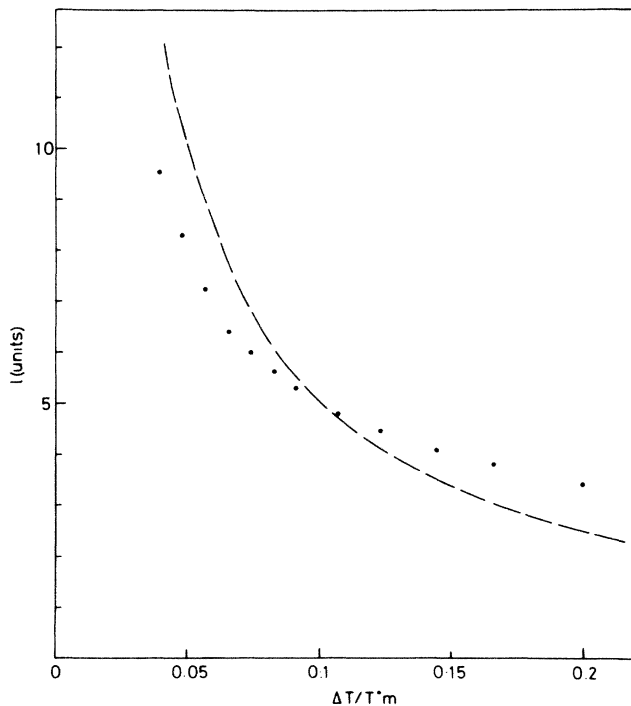


FIG. 2. Average stem length l subsequent to growth obtained from the rate equations. The dashed line indicates $T_m^0/2\Delta T$ (see text).

increases with l , as in the nucleation model. However, on rough surfaces the saddle point is a state of low entropy instead of the high-energy state of nucleation theory. In the majority of states accessible to the growth face, the 2D crystal is tapered at the edge, with the average stem in this region shorter than the average lamellar thickness. Furthermore, many of these stems are pinned as a consequence of the presence of additional stems in the direction of growth (i.e., they are not at position $n = 1$). Since they are in general too short to produce a stable crystal, they effectively block the growth at that point. Growth can proceed only by fluctuations that remove some of the material in the edge, thereby freeing the stems for extension. These fluctuations become much less likely in the case of thick lamellae that are formed at small values of ΔT , because so many more configurations are then available for the tapered region. It seems likely that the number of tapered configurations will go up approximately exponentially with l . Hence G will decrease exponentially with l , and if $l \sim \Delta T^{-1}$, the exponent is proportional to ΔT^{-1} as is observed. In terms of a free-energy barrier ΔF^* which is entropic, ΔF^* should be roughly linear in l (cf. the energy barrier arising from the creation of steps in the growth face which is also proportional to l in nucleation theories). It is the dependence of G on l which is the primary effect, and the dependence on ΔT is mainly a consequence of this. When l values are constrained to be constant for at least some range of ΔT , the dependence of G on ΔT is then found to be only linear, both for experimental data²¹ on polyethylene oxide and for results of simulation.²²

In conclusion, the model presented here is consistent with experimental observations for polymer lamellae growing with either straight or curved (stepped) growth faces. It appears to reproduce the two striking observations concerning these crystals:

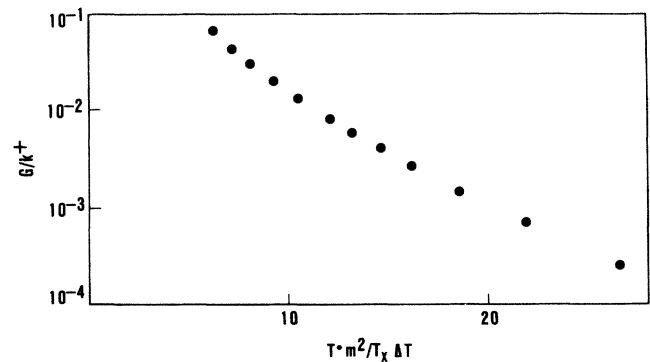


FIG. 3. Growth rate G plotted in a form appropriate for nucleation-limited growth (Refs. 3 and 20). The uncertainty in the data points is small compared with the size of the symbols.

(i) the decrease in thickness with supercooling ΔT , and (ii) the steep exponential dependence of growth rate with ΔT . These trends have previously been explained by the existence of a high energy (enthalpy) barrier to growth due to the creation of steps in the growth face. However, very high values for this barrier must be included (about $10kT$) which are not compatible with the observation that such steps are often very numerous. An entropic barrier has been identified for growth on rough growth faces, and it is proposed that this mechanism can occur during polymer crystallization.

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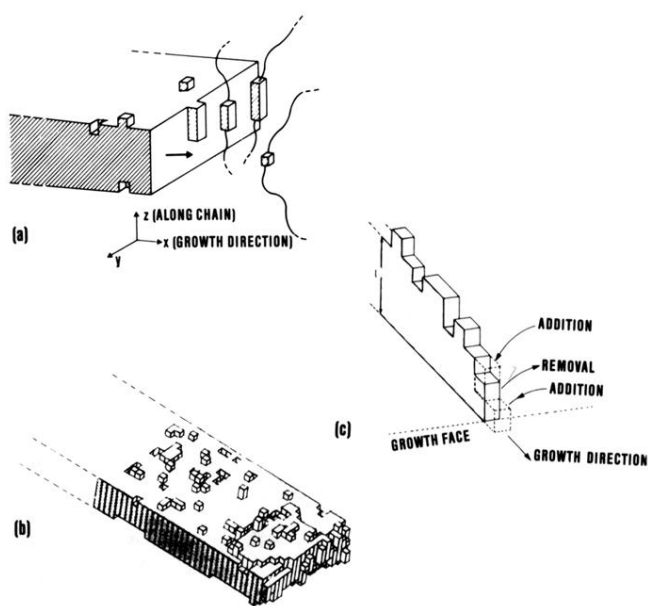


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