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Effect of Chain Transport in the Secondary Surface Nucleation Based Flux Theory and in the Lauritzen−Hoffman Crystal Growth Rate Formalism

Chad R. Snyder and Hervé Marand*

Department of Chemistry, Department of Materials Science and Engineering, and National Science Foundation for High Performance Polymeric Adhesives and Composites, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061-0212

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ABSTRACT: A previous study (Snyder, C. R.; Marand, H.; Mansfield, M. L. *Macromolecules* **1996**, *29*, 7508) by the authors suggested that, within the context of the Lauritzen−Hoffman secondary surface nucleation theory, the apportionment factor for the free energy of crystallization (ψ_{LH}) and the retardation factor due to transport of chain segments (β_{LH}) may differ for placement of the first vs all subsequent stems. In this manuscript, we investigate the consequences of this treatment on the crystal growth rate of polyethylene in regimes I, II, and III. It has been impossible so far to find an analytical solution for the secondary nucleation rate, i, and the average lamellar thickness, $\langle l\rangle$, when the apportionment and the retardation factors for the first stem (ψ' and β') are treated as being different from those used for all subsequent stems (ψ and β). It is shown in this work that approximate solutions, which cover most conditions, can be obtained by assuming two extreme cases. In the first case, it is assumed that the rate constant for initial stem removal (B_1) is larger than the difference between the rate constants for subsequent stem placement and removal ($A - B$); *i.e.* $A - B \ll B_1$. Such an approximation leads to the conclusion that the crystal growth rate in regimes I and II is only dependent upon the retardation factor for subsequent stem placement. In the second case, it is demonstrated that if $(A - B) \gg B_1$, the resulting flux equation is valid over most other circumstances where the first assumption ($B_1 \gg A - B$) does not hold. This leads to the conclusion that the crystal growth rate in regime I is only dependent upon the path followed for initial stem placement whereas in regime II it is dependent upon both the initial and subsequent stem placement paths. Conversely, it is shown, without any assumption regarding the relative magnitudes of β' and β, that in regime III the crystal growth rate is dependent upon the path of initial stem placement and independent of the path of subsequent stem placement. Under these conditions, the molecular weight dependency of the crystal growth rate in regimes I and II vs III may differ substantially. Finally, some remarks are given on the consequences of this approach for the crystallization of other polymers at larger undercoolings than encountered for poly(ethylene).

I. Introduction

During primary crystal growth, two of the most significant temperature dependent quantities are the initial lamellar thickness ($\langle l\rangle$) and the isothermal crystal growth rate (G). One of the most frequently used and most comprehensive kinetic theories which attempts to model, and predict, these quantities is the Lauritzen−Hoffman (LH) secondary surface nucleation theory.[1] Additionally, the classical LH theory provides a sound explanation for the presence and origin of “breaks” in the crystal growth rate curve, known as “regime transitions”. Three crystal growth regimes are generally predicted by the LH theory, and therefore two regime transitions. Regime I occurs typically at low undercoolings where the secondary nucleation rate (i), the rate of placement of an isolated stem onto the crystal growth face, is much less than the lateral substrate completion rate (g), the rate at which subsequent crystal stems are added adjacent to the first. As the undercooling increases, i increases until it is of the same order of magnitude as g. This is designated as regime II. Finally, when the undercooling increases sufficiently, the secondary nucleation rate becomes much larger than g. This is designated as regime III. It should be noted that all three regimes may not be observable for all polymers as the location of regime transitions is a function of (1) the relative magnitude of the force of crystallization and the monomeric friction coefficient and (2) the ability of the chain to undergo forced reptation over a sufficiently large number of repeat units that the substrate completion process is not aborted at an early stage. The second condition relates to the fact that when the chain dimensions (i.e. the polymer molecular weight) become fairly large, multiple nucleation events of a given chain at multiple sites become unavoidable and forced reptation of whole chains can no longer occur. In this case, reptation of slacks sets in and a regime III-A is predicted.[2] In addition to predicting these three regimes, the LH theory in its present state also attempts to provide some insight into the effect of molecular weight on both G and the degree of tight adjacent or near-adjacent reentry folding and therefore on the degree of crystallinity.[2]

At the basis of the LH theory is a set of rate constants which attempt to describe in a coarse-grained fashion the activated state for stem placement and removal (see Figure 1). The classical LH theory gives the rate constant for placement of the first stem (A_{o}) as

$$A_{\mathrm{o}} = \beta_{\mathrm{LH}} \exp\left\{\frac{-2b_{\mathrm{o}}l\sigma}{kT_{\mathrm{x}}} + \frac{\psi_{\mathrm{LH}}a_{\mathrm{o}}b_{\mathrm{o}}l\Delta G_{\mathrm{f}}}{kT_{\mathrm{x}}}\right\} \qquad (1a)$$

where a_{o} and b_{o} are the crystal stem width and thickness, l is the stem length, ΔG_{f} is the free energy of fusion at the crystallization temperature, σ is the lateral crystal/melt interfacial free energy, k is the Boltzmann constant, T_{x} is the crystallization temperature, and β_{LH} is the retardation factor for transport of chain segments to crystallographic sites, which will be expanded upon later. In eq 1a the first term in the exponential is

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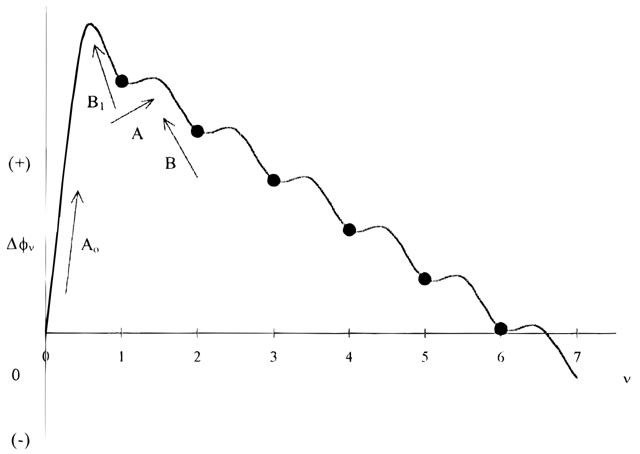

Figure 1. Free energy as a function of the number of crystalline stems. $\Delta\phi_\nu$ is the net free energy of formation of an embryo containing ν adjacent stems. See the text for definitions of A_o, B_1, A, and B.

associated with the free energy required for formation of two new lateral surfaces, while the second term is the fraction of the total bulk free energy of crystallization which is allocated (or apportioned) to the activated state. Because of this, ψ_{LH} is known as the apportionment factor for the free energy of crystallization and can have values ranging from zero to unity.

Recently, the nature of the lateral crystal/melt interfacial free energy (σ) in the LH theory has been expanded upon by Hoffman and co-workers.[3] In this new approach, σ has been attributed solely to the change in entropy associated with the localization, in the activated state, of chain segments onto the crystal growth front. Additionally, a relationship was presented which physically links the lateral crystal/melt interfacial free energy to the chain characteristic ratio (C_∞). This approach is consistent with the negentropic model of Turnbull and Spaepen[4] for *n*-paraffins and the work of Spaepen and co-workers[5−8] on the interfacial tension (free energy) in homogeneously nucleated metals. Furthermore, this approach displays similarities[9] to the "row model" of Sadler and Gilmer[10,11] and the "multipath" model of Point[12] and Dupire.[13]

The rate constant for initial stem removal (B_1) is given by

$$B_1 = \beta_{LH} \exp\left\{\frac{-(1-\psi_{LH})a_o b_o l \Delta G_f}{kT_x}\right\} \tag{1b}$$

where the exponential is the remainder of the bulk free energy obtained upon crystallization. After the first stem has been placed, the rate constants for all subsequent stems are treated as being equivalent. The rate constant for subsequent stem placement is

$$A = \beta_{LH} \exp\left\{\frac{-2a_o b_o \sigma_e}{kT_x} + \frac{\psi_{LH} a_o b_o l \Delta G_f}{kT_x}\right\} \tag{1c}$$

where the first term in the exponential is due to the formation of a chain fold. In eq 1c, σ_e is the fold crystal/melt interfacial free energy. Similarly, in the classical Lauritzen−Hoffman theory, the rate constant for subsequent stem removal is

$$B = \beta_{LH} \exp\left\{\frac{-(1-\psi_{LH})a_o b_o l \Delta G_f}{kT_x}\right\} \tag{1d}$$

It should be noticed immediately that $B_1 = B$, *i.e.* the rate of removal of the first stem is the same as the rate of removal of all subsequent stems. This equality results from the assumption in the traditional version of the Lauritzen−Hoffman theory that β_{LH} and ψ_{LH} are identical for the first and all subsequent stems. In the above equations (eq 1a−d) the term β_{LH} accounts for the decrease in the coarse grained[20] rate constants (or the retardation in stem deposition) due to the necessity of transporting chain segments to the crystallographic sites at the growth front.

In a recent paper,[14] hereafter referred to as paper I, we showed that for consistency of the Lauritzen−Hoffman theory with the DiMarzio *et al.*[15] approach for the lateral substrate completion rate, the retardation factor associated with transport processes for the first stem (β') vs all subsequent stems (β) must be different. That these two processes are very different can be readily envisioned if one associates the formation of the first stem with the partial localization of chain segments at crystallographic sites on the growth front and the formation of subsequent stems with a reeling-in process in which the polymer chain is pulled through the melt. It should be quite apparent that the use of two distinct retardation terms β and β' can render the crystal growth equation cumbersome and the analysis of crystal growth rate data more convoluted. It has been impossible so far to find an analytical solution to the secondary nucleation rate, *i*, and the average lamellar thickness, $\langle l \rangle$ when the apportionment and the retardation factors for the first stem (ψ' and β') are treated as being different from those used for all subsequent stems (ψ and β). We will determine under these conditions how the presence of two distinct retardation factors affects the flux equations in regimes I, II, and III, and we will compare these results to those obtained by the classical LH theory. We will show that considerations of the magnitude of the ratio β'/β and of the quantity $\Delta\psi = \psi' - \psi$ allow us to define two limiting conditions, $(A - B)$ much larger or much smaller than B_1, under which the general flux equation (see eq 3 below) can be approximated and integrated analytically. From the flux equations, the secondary nucleation rate (*i*) will be derived and thus, the crystal growth rate *G*. We will show that different dependencies of the crystal growth rate (*G*) on the retardation factors β and β' should be expected in regimes I, II, and III. Specifically, when $B_1 \gg A - B$ the crystal growth rate in regimes I, II, and III will be dependent upon β, β, and β', respectively. Furthermore, it is shown that when $B_1 \ll A - B$ the crystal growth rate in regimes I, II, and III is dependent upon β', $(\beta'\beta)^{1/2}$, and β', respectively. Through considerations of the force of crystallization, when for polyethylene the molecular weight ranges from 15 000 to 90 000, β has been shown to scale with $1/n$, where n is the number of repeat units in the polymer chain.[2,14,15] The molecular weight dependency of β' is expected to be much weaker than $1/n$ due to the fact that Rouse-like motions are envisioned to govern placement of the first stem; *i.e.*, only localized rearrangements should occur rather than curvilinear diffusion of the entire chain. This difference in the modes of transport for the first stem vs all subsequent stems lends credibility to the assumption that β' should be different from β. Therefore, the regime III crystal growth rate *may* follow a quite different molecular weight dependency than the $1/n$ dependency in regimes I and II. It is thus the goal of this work to develop crystal growth rate equations whose preexponentials are in terms of β' and β. Thus, crystal growth rate equations which have been derived analytically will be presented in a form which can be

Table 1. Polyethylene Input Parameters[a]

Δh_f (J/m^3)	2.80×10^{8}	b_o (m)	4.15×10^{-10}
σ (J/m^2)	1.18×10^{-2}	T_m (K)	418.7
σ_e (J/m^2)	9.00×10^{-2}	l_u (m)	1.27×10^{-10}
a_o (m)	4.55×10^{-10}		

[a] From ref 2.

utilized when, in a future manuscript, explicit expressions are derived which describe the molecular weight dependency of β' and β.

Arguments may be brought forward regarding our examination of the apportionment factors for the first and all subsequent stems. Clearly, a number of papers in the literature have attempted to discuss the free energy apportionment factors for the barriers for the first and subsequent stems. For example, Frank and Tosi[20] chose to use a ψ equal to unity for the first stem and ψ equal to zero for the second stem while Sanchez and DiMarzio[16] and Hoffman *et al.*[1] have chosen to have ψ for both stems equal to zero. Furthermore, it is clear that the current trend in crystallization theory is the refinement of fine-grained models such as that of Point.[12] However, DiMarzio and Guttman[17] have stated that it would be all but impossible to account for all the possible paths to crystallization, which is required by such a fine-grained theory. Furthermore, they state that the difficulties in obtaining a small advance in such a theory is discouraging. Therefore, we are attempting to generalize even further the Lauritzen–Hoffman crystallization theory so that its utility is extended, specifically as it pertains to the molecular weight dependence or independence of crystal growth rates. By allowing for two ψ's and two β's, we are helping the theory approximate even more closely the results of a thorough fine-grained analysis. Regarding the previous works on the apportionment factor, values of ψ were *a priori* selected so that closed form solutions were obtained. By keeping this theory as general as possible (not overspecifying expressions for β and values for ψ) and finding analytical solutions to the crystal growth rate equations, we are allowing for future advances in the understanding of the nature of the transport and nucleation processes.

II. Theoretical

A. Rate Constant Expressions. In order to determine the consequences of using two different β's on the crystal growth rate, we must first define the various rate constants that govern the crystallization process (see Figure 1). The rate constants for addition and removal of the first stem on the crystal substrate are given by

$$A_o = \beta' \exp\left\{\frac{-2b_o l\psi}{kT_x} + \frac{\psi' a_o b_o l \Delta G_f}{kT_x}\right\} \tag{2a}$$

$$B_1 = \beta' \exp\left\{\frac{-(1-\psi')a_o b_o l \Delta G_f}{kT_x}\right\} \tag{2b}$$

The rate constants for all subsequent stems are given by

$$A = \beta \exp\left\{\frac{-2a_o b_o \sigma_e}{kT_x} + \frac{\psi a_o b_o l \Delta G_f}{kT_x}\right\} \tag{2c}$$

$$B = \beta \exp\left\{\frac{-(1-\psi)a_o b_o l \Delta G_f}{kT_x}\right\} \tag{2d}$$

where ψ' is the fraction of the bulk free energy apportioned to the activated state for placement of the first stem and ψ is the apportionment factor for placement of each of the subsequent stems. Comparison of eqs 1a–d to eqs 2a–d shows the differences between the traditional Lauritzen–Hoffman secondary surface nucleation model and our treatment.

B. Flux Equations for Regimes I, II, and III. 1. Dependence of the Regimes I and II Flux Equations on $\boldsymbol{\beta}$. To obtain the crystal growth rate equations, expressions for the secondary nucleation rate must first be derived. For this, the flux, which is the rate at which polymer segments go from sites in the melt to sites on the crystal face, must be determined. Frank and Tosi[20] and Lauritzen and Hoffman[18] have independently shown that the flux is given, for a sufficiently large number of adjacent reentry stems, by

$$S(l) = N_o A_o \left(\frac{A - B}{A - B + B_1}\right) \tag{3}$$

where N_o is the number of initially reacting species, given by $N_o = C_o n_L$ (where C_o is the configurational path degeneracy and n_L is the number of stem sites on the crystal growth face between defects).[1,19] As was mentioned in the introduction, consideration of the transport processes for the first stem vs all subsequent stems leads one to the intuitive assumption that β' should be different from β. It should also be intuitively obvious that depending on the magnitude of the ratio β'/β, the expression for the flux can be simplified. We will consider two extreme cases: $(A - B) \ll B_1$ and $(A - B) \gg B_1$, for which the flux can be integrated analytically to yield the nucleation rate and the average lamellar thickness. We will then define the conditions (in terms of β, β', and $\Delta\psi = \psi' - \psi$) under which these approximate flux equations can be justifiably used.

If we first consider $B_1 \gg (A - B)$, then the flux in eq 3 can be rewritten as

$$S_I = S_{II} \cong N_o\left(\frac{A_o}{B_1}\right)(A - B) \tag{4a}$$

where S_I and S_{II} refer to the flux in regimes I and II, respectively. To determine under which conditions eq 4a is valid, let us require that the relative error in the flux generated by eq 4a is less than or equal to ϵ. More formally, we are requiring that

$$\frac{|S(\text{eq 3}) - S(\text{eq 4a})|}{S(\text{eq 3})} \leq \epsilon \tag{5}$$

By substituting eqs 3 and 4a into the above inequality, we obtain

$$\frac{A - B}{B_1} \leq \epsilon \tag{6a}$$

when $(A - B)$ is positive. Before exploring the implications of the above inequality, we will consider the results of the opposite approximation, *i.e.* $A - B \gg B_1$. This approximation results in a flux equation of

$$S_I = S_{II} \cong N_o A_o \tag{4b}$$

If we apply eq 5 to eq 4b, we obtain

$$\frac{A - B}{B_1} \geq \frac{1}{\epsilon} \tag{6b}$$

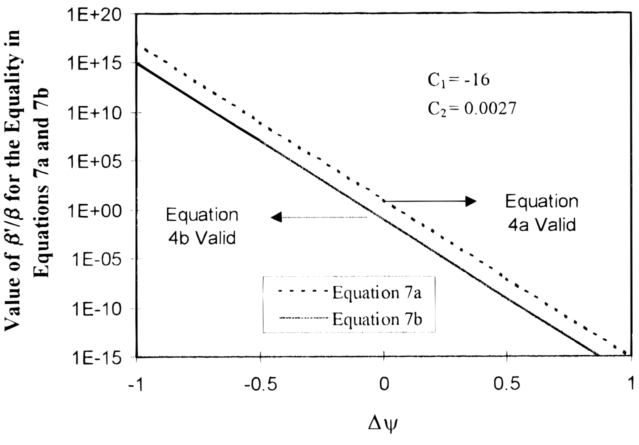

Figure 2. β'/β ratio required for the equality in eqs 7a and 7b to hold (for $\epsilon = 0.1$) at an undercooling of 27 °C (regime II → III transition) for polyethylene for varying values of $\Delta\psi = \psi' - \psi$. Note that to the right of the dashed line eq 4a is valid, whereas to the left of the solid line eq 4b is valid.

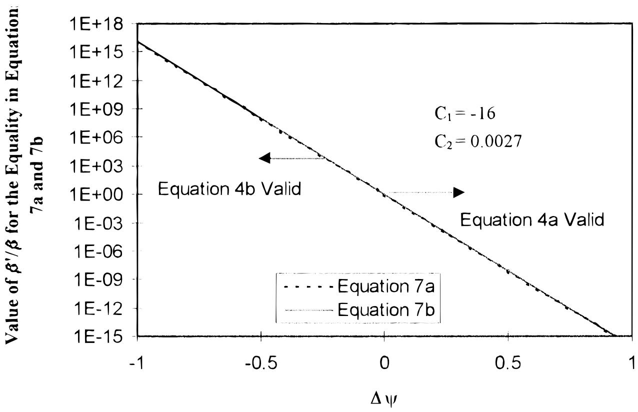

Figure 3. β'/β ratio required for the equality in eqs 7a and 7b to hold (for $\epsilon = 1$) at an undercooling of 27 °C (regime II → III transition) for polyethylene for varying values of $\Delta\psi = \psi' - \psi$. Note that the two lines are coexistent. To the right of the the line eq 4a is valid, whereas to the left eq 4b is valid.

Examination of eqs 6a and 6b shows that, as expected, the conditions under which the two approximations (eqs 4a and 4b) are valid are governed by the relative error in the flux which is deemed acceptable. As the relative error is decreased, there is a larger range of conditions over which neither of the two approximations holds. It should be apparent that if we were to allow the relative error in the flux to increase to 100% (*i.e.* $\epsilon = 1$), the two equations, eqs 6a and 6b, would coincide at the equality. This result will be examined in detail later in this work. It is also extremely important to note that these equations are not dependent upon the Lauritzen–Hoffman model; they are valid for the Frank and Tosi[20] formalism as well. The result is very important because it seems that it is impossible to obtain an analytical solution to the secondary nucleation rate and average lamellar thickness for the flux given by eq 3 when $\psi \neq \psi'$ and $\beta \neq \beta'$. However, analytical solutions can be easily obtained for the approximate equations, eqs 4a and 4b.

Let us now direct our attention to the range of applicability of the approximated flux equations. For $B_1 \gg (A - B)$, we showed with eq 6a that a maximum relative error of ϵ for the approximated flux is guaranteed if $(A - B)/B_1 \leq \epsilon$. Using eqs 2b–d to express the various rate constants and approximating the lamellar thickness by $l = \langle l \rangle \cong 2\sigma_e/\Delta G_f + kT_x/b_o\sigma$ leads to

$$\log\left(\frac{\beta'}{\beta}\right) \geq C_1\Delta\psi + C_2 - \log(\epsilon) \qquad (7a)$$

where

$$C_1 = \frac{-4.606 a_o b_o \sigma_e}{kT_x} + \frac{-2.303 a_o \Delta G_f}{\sigma}$$

and

$$C_2 = \log\left[\exp\left(\frac{-a_o \Delta G_f}{2\sigma}\right) - 1\right]$$

Similarly, when $(A - B) \gg B_1$ we obtain

$$\log\left(\frac{\beta'}{\beta}\right) \leq C_1\Delta\psi + C_2 + \log(\epsilon) \qquad (7b)$$

with C_1 and C_2 defined as previously. To illustrate the above concepts, we have plotted in Figure 2 eqs 7a and 7b for the case of polyethylene at an undercooling slightly below that of the regime II → III transition ($\Delta T = 27$ K)[2] for a relative error of $\epsilon = 10\%$. Figure 3 gives the corresponding plots for ϵ=100%. Equation 4a will hold for conditions to the right of the dashed line in Figure 2 and Figure 3, whereas eq 4b will hold to the left of the solid line. Note that in Figure 3 the two lines are coexistent. The vertical separation between the lines associated with eqs 7a and 7b provides an estimate of the range of conditions in which neither "simplified" flux equation (eqs 4a and 4b) is a good approximation of the original flux (eq 3). This vertical separation is given by $d = -2\log(\epsilon)$ in units of $\log(\beta'/\beta)$. When $d \leq 0$ (*i.e.* $\epsilon \geq 100\%$), the simplified flux equations provide an approximation (within an uncertainty ϵ) of the original flux equation for all values of β'/β and $\Delta\psi$. On the other hand, for $d > 0$ (*i.e.* for $\epsilon < 100\%$) the original flux equation (eq 3) should be used and integrated numerically for the range of β'/β and $\Delta\psi$ values between the two straight lines (eqs 7a and 7b—Figure 2).

Clearly, while indeed the region in which neither equation holds spans 2 orders of magnitude in the value of the β'/β ratio, it should be recalled that this region can be eliminated by increasing the allowable error in the flux. Ordinarily this would seem to be a problematic solution; however, it should be recalled that in the basic LH theory the temperature dependence of the crystal growth rate arises predominantly from the secondary nucleation rate term "*i*", which is proportional to the integrated flux. For most polymers, and for polyethylene in particular, the temperature dependence of the crystal growth rate, and thus that of the secondary nucleation rate and flux, spans many orders of magnitude in the crystallization temperature range of interest (see Figure 4 for instance). A 100% relative error in the flux will have a fairly negligible impact on the analysis of a growth rate which changes by many orders of magnitude over the temperature range of interest. As was stated earlier, if a more accurate flux is required, then flux eq 3 must be integrated numerically.

Finally, it is extremely interesting to note that in the classical LH theory the rate constant for removal of the initial stem (B_1) is treated as being equal to that for removal of all subsequent stems (B). This results in a flux equation of[1]

$$S(l) = N_o A_o\left(1 - \frac{B}{A}\right) \qquad (8)$$

which differs from the expressions presented in eqs 4a and 4b. The significance of the differences between

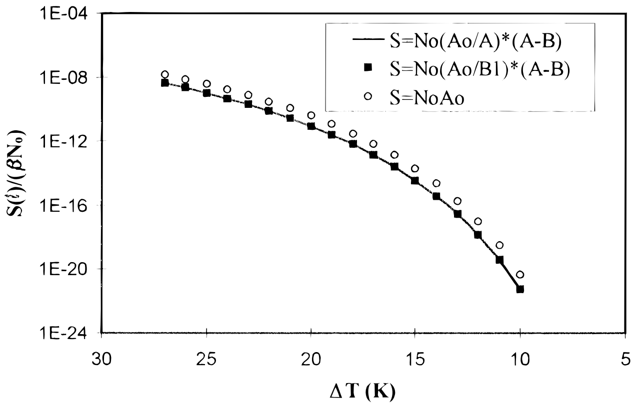

Figure 4. Temperature dependence of the three different flux equations (eqs 4a, 4b, and 8) with $\psi' = \psi = 0$ and $\beta' = \beta$. Equations 4a and 4b used the rate constants given by eqs 2a–d, and eq 8 used the rate constants given by eqs 1a–d.

these three equations will be examined in detail in the following section.

2. Comparison to the Traditional Lauritzen–Hoffman Flux Equation. Since some of our arguments are based upon conclusions drawn from the classical LH analysis, it is important to further examine the difference in the results from eqs 4a, 4b, and 8. To compare the Lauritzen–Hoffman flux equation (eq 8) with the approximated flux equations (eqs 4a and 4b), we must examine them under *identical* conditions. For this we set $\psi' = \psi = 0$ and $\beta = \beta'$ in eqs 4a and 4b. A plot of $S/N_o\beta$ for the three different flux expressions is given in Figure 4, where we have utilized the expression for l which was used to generate Figure 2 and Figure 3. Note that the classical LH equation and eq 4a produce essentially coexistent data, whereas flux eq 4b produces data that are approximately parallel but shifted upward on the y-axis. The reason for this becomes apparent when we ratio the flux given by eq 4a to that given by eq 8

$$\frac{S(\text{eq 4a})}{S(\text{eq 8})} \cong \exp\left(\frac{a_o \Delta H_f \Delta T}{\sigma T_m}\right) \cong 1 \quad \text{for low } \Delta T$$

where we have utilized $\Delta G_f \cong \Delta H_f \Delta T/T_m$, where ΔH_f is the heat of fusion at the equilibrium melting temperature. Therefore, we have demonstrated that, for low undercoolings, the two equations are essentially identical, when compared under similar conditions, and will therefore produce equivalent results, in the limit of $\psi = \psi' = 0$ and $\beta' = \beta$. Furthermore, if we ratio the flux given by equation 4b to that given by eq 8, we obtain

$$\frac{S(\text{eq 4b})}{S(\text{eq 8})} \cong \frac{\sigma T_m}{a_o \Delta H_f \Delta T}\left(\frac{1}{1 - \dfrac{a_o \Delta H_f \Delta T}{2\sigma T_m}}\right) > 1 \quad \text{for low } \Delta T$$

This is why eq 4b is displaced upward on the *y*-axis in Figure 4. It should be noted that since all three curves are essentially parallel, their temperature dependence should be practically identical (*i.e.* the three flux equations have the same exponential temperature dependence and differ in their prefactor, which exhibits only a weak temperature dependence).

3. Regime III Flux Equation. The expression for the flux given by eq 3, is only valid when the distance between secondary nuclei on the growth face is large.[18,20] Upon entering Regime III, the distance between nuclei has been suggested to decrease[24,21] to approximately $1.5a_o$ to $2.5a_o$, and therefore a new expression for the flux is required. Hoffman,[21] through his variable cluster model of chain folding, has suggested that in regime III the flux is governed by the following equation:

$$S_{III} = N_o A_o \left\{\frac{1}{1 + \dfrac{B_1}{A} + \dfrac{B_1 B}{A_c A}}\right\} \cong N_o A_o \qquad (9)$$

A_c is the rate of placing the stem which completes the local substrate ($A_c \cong A$). In the above equation, Hoffman has stated that the approximation resulting in the right-hand side of eq 9 can be made because $A > B_1$ and $A_c A > B_1 B$.

C. Expressions for the Flux in Terms of the Modified Rate Constants. The flux equation governing regime I and II growth (S_I and S_{II}) is obtained by substituting eqs 2a–d into eqs 4a and 4b. If the condition in eq 7a is satisfied, then use of the approximated flux equation, eq 4a, leads to

$$S_I = S_{II} = N_o\left(\frac{A_o}{B_1}\right)(A - B) \cong N_o\beta \exp\left[\frac{-2b_o l\sigma}{kT_x}\right] \exp\left[\frac{(1+\psi)a_o b_o l \Delta G_f}{kT_x}\right] \times \left\{\exp\left[\frac{-2a_o b_o \sigma_e}{kT_x}\right] - \exp\left[\frac{-a_o b_o l \Delta G_f}{kT_x}\right]\right\} \qquad (10a)$$

By the principle of detailed balance, it can be seen that the above equation is the product of the number of initially reacting species, the equilibrium constant for placement of the first stem (first exponential), and the difference in the rates of the forward and reverse reactions for subsequent stem placement and removal. Therefore, the flux is only affected by the path of reaction followed for placement of subsequent stems. Comparison with equation 8 shows that, previously,[1] the flux was treated as a function of the number of initially reacting species, the equilibrium constant for placement of *subsequent* stems, and the rate of the forward reaction for initial stem placement; *i.e.* the flux was only affected by the path of the reaction for *initial stem placement*.

When the condition in eq 7b is satisfied, use of the approximated flux equation, eq 4b, leads to

$$S_I = S_{II} \cong N_o A_o = N_o\beta' \exp\left[\frac{-2b_o l\sigma}{kT_x}\right] \exp\left[\frac{+\psi' a_o b_o l \Delta G_f}{kT_x}\right] \qquad (10b)$$

which is obviously only affected by the path of reaction for *initial stem placement*.

The regime III flux can be calculated by substituting eqs 2a–d into eq 9:

$$S_{III} \cong N_o\beta' \exp\left[\frac{-2b_o l\sigma}{kT_x}\right] \exp\left[\frac{+\psi' a_o b_o l \Delta G_f}{kT_x}\right] \qquad (11)$$

Notice that in regimes I and II, the flux equations are functions of β and ψ for the conditions given by eq 6a, and β' and ψ' for the conditions given by eq 6b. This should be contrasted to the above equation (eq 11) for regime III, which is always a function of β' and ψ'.

D. Secondary Nucleation Rate and Crystal Growth Rate. To obtain the crystal growth rate equations, the secondary nucleation rate and the lateral substrate completion rate must first be determined. Using the approximated flux equations, the secondary nucleation rate (i) can be calculated for each regime through the following expression:

$$i = \frac{S_{\mathrm{T}}}{n_{\mathrm{L}} a_{\mathrm{o}}} = \frac{1}{n_{\mathrm{L}} a_{\mathrm{o}} l_{\mathrm{u}}} \int_{2\sigma_{\mathrm{e}}/\Delta G_{\mathrm{f}}}^{\infty} S(l)\, \mathrm{d}l \qquad (12)$$

S_{T} is the total flux, and l_{u} is the projection of the bond length onto the c-crystallographic axis. Substitution of the appropriate flux equation (eq 10a or 10b) into eq 12, yields

$$i_{\mathrm{I}} = i_{\mathrm{II}} = \frac{C_{\mathrm{o}}\beta}{a_{\mathrm{o}} l_{\mathrm{u}}}\left[\frac{kT_{\mathrm{x}}}{2b_{\mathrm{o}}\sigma - (1+\psi)a_{\mathrm{o}}b_{\mathrm{o}}\Delta G_{\mathrm{f}}} - \frac{kT_{\mathrm{x}}}{2b_{\mathrm{o}}\sigma - \psi a_{\mathrm{o}}b_{\mathrm{o}}\Delta G_{\mathrm{f}}}\right] \exp\left(\frac{-4b_{\mathrm{o}}\sigma\sigma_{\mathrm{e}}}{kT_{\mathrm{x}}\Delta G_{\mathrm{f}}}\right) \exp\left(\frac{+2\psi a_{\mathrm{o}}b_{\mathrm{o}}\sigma_{\mathrm{e}}}{kT_{\mathrm{x}}}\right) \qquad (13a)$$

for regimes I and II, when the condition given by eq 6a is valid. Alternately, the secondary nucleation rate is given by

$$i_{\mathrm{I}} = i_{\mathrm{II}} = \frac{C_{\mathrm{o}}\beta'}{a_{\mathrm{o}} l_{\mathrm{u}}}\left[\frac{kT_{\mathrm{x}}}{2b_{\mathrm{o}}\sigma - \psi' a_{\mathrm{o}}b_{\mathrm{o}}\Delta G_{\mathrm{f}}}\right] \times \exp\left(\frac{-4b_{\mathrm{o}}\sigma\sigma_{\mathrm{e}}}{kT_{\mathrm{x}}\Delta G_{\mathrm{f}}}\right) \exp\left(\frac{+2\psi' a_{\mathrm{o}}b_{\mathrm{o}}\sigma_{\mathrm{e}}}{kT_{\mathrm{x}}}\right) \qquad (13b)$$

when the condition given by eq 6b is valid. For regime III the secondary nucleation rate, calculated by substituting eq 11 into eq 12, is given by

$$i_{\mathrm{III}} = \frac{C_{\mathrm{o}}\beta'}{a_{\mathrm{o}} l_{\mathrm{u}}}\left[\frac{kT_{\mathrm{x}}}{2b_{\mathrm{o}}\sigma - \psi' a_{\mathrm{o}}b_{\mathrm{o}}\Delta G_{\mathrm{f}}}\right] \exp\left(\frac{-4b_{\mathrm{o}}\sigma\sigma_{\mathrm{e}}}{kT_{\mathrm{x}}\Delta G_{\mathrm{f}}}\right) \times \exp\left(\frac{+2\psi' a_{\mathrm{o}}b_{\mathrm{o}}\sigma_{\mathrm{e}}}{kT_{\mathrm{x}}}\right) \qquad (14)$$

It is important to recall that although we have treated β and β' as being independent of lamellar thickness, the authors have shown in paper I that this is only an approximation. (Note: Examination of eq 13a shows that singularities exist at critical undercoolings of $\Delta T_{\mathrm{c}} = 2\sigma T_{\mathrm{m}}/[(1 + \psi)a_{\mathrm{o}}\Delta H_{\mathrm{f}}]$ and $\Delta T_{\mathrm{c}} = 2\sigma T_{\mathrm{m}}/(\psi a_{\mathrm{o}}\Delta H_{\mathrm{f}})$. The latter singularity is also present in eqs 13b and 14 with ψ replaced by ψ'. The implications of these singularities are discussed briefly in the Appendix.)

The lateral substrate completion rate (g) is defined through the LH theory to be

$$g = a_{\mathrm{o}}(A - B) \qquad (15)$$

and the crystal growth rate (G) is defined[22,23] to be

$$G_{\mathrm{I}} = a_{\mathrm{o}}b_{\mathrm{o}}n_{\mathrm{L}}\mathbf{i} \qquad (16)$$

for regime I

$$G_{\mathrm{II}} = b_{\mathrm{o}}(2\mathbf{ig})^{1/2} \qquad (17)$$

for regime II, and

$$G_{\mathrm{III}} = a_{\mathrm{o}}b_{\mathrm{o}}n_{\mathrm{III}}\mathbf{i} \qquad (18)$$

for regime III,[21] where n_{III} is the number of stems between secondary nuclei (which has a value close to 1.5 according to Guttman and DiMarzio[24] or a value close to 2.5 according to Hoffman[21] in regime III). Substitution of the appropriate secondary nucleation rate expressions into the respective crystal growth rate equations results in

$$G_{\mathrm{I}} = \beta\left(\frac{b_{\mathrm{o}}n_{\mathrm{L}}C_{\mathrm{o}}}{l_{\mathrm{u}}}\right)\left[\frac{kT_{\mathrm{x}}}{2b_{\mathrm{o}}\sigma - (1+\psi)a_{\mathrm{o}}b_{\mathrm{o}}\Delta G_{\mathrm{f}}} - \frac{kT_{\mathrm{x}}}{2b_{\mathrm{o}}\sigma - \psi a_{\mathrm{o}}b_{\mathrm{o}}\Delta G_{\mathrm{f}}}\right] \exp\left(\frac{-4b_{\mathrm{o}}\sigma\sigma_{\mathrm{e}}}{kT_{\mathrm{x}}\Delta G_{\mathrm{f}}}\right) \exp\left(\frac{+2\psi a_{\mathrm{o}}b_{\mathrm{o}}\sigma_{\mathrm{e}}}{kT_{\mathrm{x}}}\right) \qquad (19a)$$

$$G_{\mathrm{II}} = \beta b_{\mathrm{o}}\left(\frac{2C_{\mathrm{o}}}{l_{\mathrm{u}}}\right)^{1/2}\left\{\left[\frac{kT_{\mathrm{x}}}{2b_{\mathrm{o}}\sigma - (1+\psi)a_{\mathrm{o}}b_{\mathrm{o}}\Delta G_{\mathrm{f}}} - \frac{kT_{\mathrm{x}}}{2b_{\mathrm{o}}\sigma - \psi a_{\mathrm{o}}b_{\mathrm{o}}\Delta G_{\mathrm{f}}}\right]\left[1 - \exp\left(\frac{-a_{\mathrm{o}}b_{\mathrm{o}}\delta l\Delta G_{\mathrm{f}}}{kT_{\mathrm{x}}}\right)\right]\right\}^{1/2} \times \exp\left(\frac{+\psi a_{\mathrm{o}}b_{\mathrm{o}}\delta l\Delta G_{\mathrm{f}}}{2kT_{\mathrm{x}}}\right) \exp\left[\frac{(2\psi - 1)a_{\mathrm{o}}b_{\mathrm{o}}\sigma_{\mathrm{e}}}{kT_{\mathrm{x}}}\right] \exp\left(\frac{-2b_{\mathrm{o}}\sigma\sigma_{\mathrm{e}}}{kT_{\mathrm{x}}\Delta G_{\mathrm{f}}}\right) \qquad (20a)$$

for Regimes I and II under the conditions described by eq 6a and

$$G_{\mathrm{I}} = \beta'\left(\frac{b_{\mathrm{o}}n_{\mathrm{L}}C_{\mathrm{o}}}{l_{\mathrm{u}}}\right)\left[\frac{kT_{\mathrm{x}}}{2b_{\mathrm{o}}\sigma - \psi' a_{\mathrm{o}}b_{\mathrm{o}}\Delta G_{\mathrm{f}}}\right] \times \exp\left(\frac{+2\psi' a_{\mathrm{o}}b_{\mathrm{o}}\sigma_{\mathrm{e}}}{kT_{\mathrm{x}}}\right) \exp\left(\frac{-4b_{\mathrm{o}}\sigma\sigma_{\mathrm{e}}}{kT_{\mathrm{x}}\Delta G_{\mathrm{f}}}\right) \qquad (19b)$$

$$G_{\mathrm{II}} = (\beta'/\beta)^{1/2} b_{\mathrm{o}}\sqrt{\frac{2C_{\mathrm{o}}}{l_{\mathrm{u}}}}\left\{\left[\frac{kT_{\mathrm{x}}}{2b_{\mathrm{o}}\sigma - \psi' a_{\mathrm{o}}b_{\mathrm{o}}\Delta G_{\mathrm{f}}}\right] \times \left[1 - \exp\left(\frac{-a_{\mathrm{o}}b_{\mathrm{o}}\delta l\Delta G_{\mathrm{f}}}{kT_{\mathrm{x}}}\right)\right]\right\}^{1/2} \exp\left(\frac{+\psi a_{\mathrm{o}}b_{\mathrm{o}}\delta l\Delta G_{\mathrm{f}}}{2kT_{\mathrm{x}}}\right) \times \exp\left[\frac{(\psi + \psi' - 1)a_{\mathrm{o}}b_{\mathrm{o}}\sigma_{\mathrm{e}}}{kT_{\mathrm{x}}}\right] \exp\left(\frac{-2b_{\mathrm{o}}\sigma\sigma_{\mathrm{e}}}{kT_{\mathrm{x}}\Delta G_{\mathrm{f}}}\right) \qquad (20b)$$

under the conditions described by eq 6b. For regime III the crystal growth rate is given by

$$G_{\mathrm{III}} = \beta'\left(\frac{b_{\mathrm{o}}C_{\mathrm{o}}n_{\mathrm{III}}}{l_{\mathrm{u}}}\right)\left[\frac{kT_{\mathrm{x}}}{2b_{\mathrm{o}}\sigma - \psi' a_{\mathrm{o}}b_{\mathrm{o}}\Delta G_{\mathrm{f}}}\right] \times \exp\left(\frac{+2\psi' a_{\mathrm{o}}b_{\mathrm{o}}\sigma_{\mathrm{e}}}{kT_{\mathrm{x}}}\right) \exp\left(\frac{-4b_{\mathrm{o}}\sigma\sigma_{\mathrm{e}}}{kT_{\mathrm{x}}\Delta G_{\mathrm{f}}}\right) \qquad (21)$$

In the above equations, δl is the increment in the lamellar thickness above the minimum lamellar thickness which allows the nucleus to enter the region of thermodynamic stability at a finite rate. Analytical expressions for δl are derived in the Appendix. From the above equations it can be seen that the crystal growth rate equation in regimes I and II is a function of β when eq 6a holds and in regime III it is a function of β'. Alternately, when eq 6b is valid, the crystal growth rate will be a function of β' in regime I and a function of $(\beta'\beta)^{1/2}$ in regime II. Therefore, it should be apparent that if β' has a weaker molecular weight dependency than $1/n$, then it is possible that the molecular weight dependency in regime III could be very different from that of regimes I and II.

Thus far, we have attempted to keep the assumptions regarding the crystallization model within this paper to a minimum. If for a moment we allow ourselves some latitude regarding the proposed molecular weight dependencies of β' and β, the importance of the preceding conclusions immediately comes to light. Let us first, in the manner of DiMarzio *et al.*,[15] assign an n^{-1} dependency to β. Let us then attribute to β' an n^{0} molecular

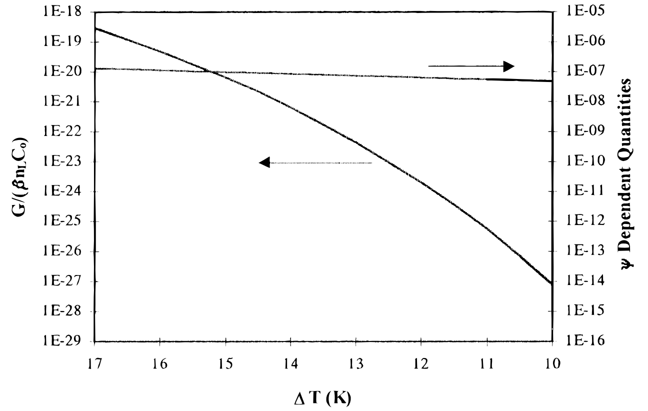

Figure 5. Regime I crystal growth rate as a function of undercooling. $G/(\beta n_L C_o)$ from eq 19a (left-hand axis) and the product of the ψ-dependent quantities in eq 19a (right-hand axis) plotted against undercooling. Note that both axes span the same order of magnitude, *i.e.* 10^{11}.

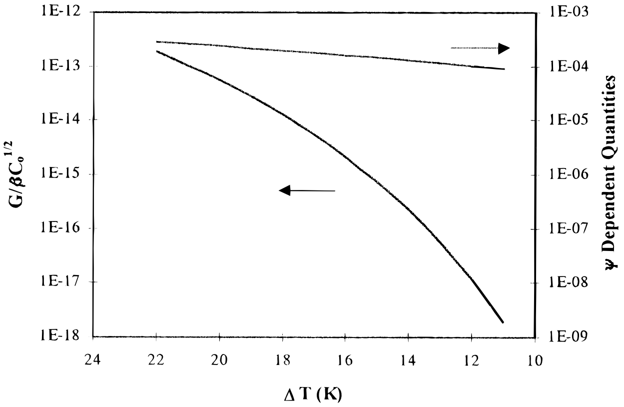

Figure 6. Regime II crystal growth rate as a function of undercooling. $G/(\beta C_o^{1/2})$ from eq 20a (left-hand axis) and the product of the ψ-dependent quantities in eq 20a (right-hand axis) plotted against undercooling. Note that both axes span the same order of magnitude, *i.e.* 10^6.

weight dependence, a not unreasonable assumption if the concept of reptation of slack is considered.[2,25] Under these assumptions, when condition 6a is valid, the crystal growth rates in regimes I, II, and III will be proportional to n^{-1}, n^{-1}, and n^0, respectively. Alternately, when condition 6b is valid, the crystal growth rate in regimes I, II, and III will be proportional to n^0, $n^{1/2}$, and n^0, respectively. Although we would be hesitant to draw any definitive conclusions from such nonexplicit assumptions, it is interesting to note that polyethylenes of moderate molecular weight approximately obey the molecular weight dependencies described under the condition in eq 6a for regimes I, II, and III.

Again, we wish emphasize that we have attempted to keep our solutions as general as possible and therefore, excluding the above exercise, we *shall not* put forth any statements regarding the relative molecular weight dependence of β' vs β. We have only stated that intuitively they should be different; however, our conclusions are still valid if $\beta' = \beta$. To decide whether eq 4a or 4b is the appropriate choice under a given set of experimental conditions or whether the system is in the region where the approximations are relatively (ϵ < 100%) inaccurate, analytical expressions for β', β, ψ', and ψ *must be determined.*

E. Utility of Crystal Growth Rate Equations. At first glance, eqs 19−21 appear to make an analysis of crystal growth rates far more difficult than the classical LH approach. It should first be recalled that the simple LH growth rate equation with a constant prefactor G_o is only a good approximation at very low undercoolings, *i.e.* only strictly applicable to the case of isothermal crystallization of PE at $\Delta T < 25$ K. To decide whether or not eqs 19−21 are as tractable as the LH analysis, it must be determined whether or not the "ψ"-containing terms can be treated as temperature independent. To examine the largest effect of ψ' or ψ on the crystal growth rate equation, both ψ' and ψ have been set equal to unity in our calculations.

In Figure 5, $G/(\beta n_L C_o)$ from eq 19a (regime I) is plotted on the left-hand axis vs undercooling. On the right axis, the product of all ψ-containing terms in eq 19a is plotted over the same range of magnitudes as the left-hand axis. Figure 6 is a similar plot of $G/(\beta C_o^{1/2})$ using eq 20a (regime II). Finally, in Figure 7, $G/(\beta C_o n_{III})$ is plotted using eq 21 (regime III), where the right hand axis now contains the product of all ψ'-dependent terms. Inspection of Figures 5−7 shows that the "ψ"-dependent terms have a very weak temperature dependence relative to the overall crystal growth rate and therefore can be approximated as constants for low to moderate undercoolings. (Similar trends can be shown for eqs 19b and 20b.) The crystal growth rate equations, eqs 19a, 19b, 20a, 20b, and 21, can then be written, respectively, as

$$G_I = \beta G_{o,I,a} \exp\left(\frac{-4b_o\sigma\sigma_e}{kT_x\Delta G_f}\right) \tag{22a}$$

$$G_I = \beta' G_{o,I,b} \exp\left(\frac{-4b_o\sigma\sigma_e}{kT_x\Delta G_f}\right) \tag{22b}$$

$$G_{II} = \beta G_{o,II,a} \exp\left(\frac{-2b_o\sigma\sigma_e}{kT_x\Delta G_f}\right) \tag{23a}$$

$$G_{II} = (\beta'\beta)^{1/2} G_{o,II,b} \exp\left(\frac{-2b_o\sigma\sigma_e}{kT_x\Delta G_f}\right) \tag{23b}$$

$$G_{III} = \beta' G_{o,III} \exp\left(\frac{-4b_o\sigma\sigma_e}{kT_x\Delta G_f}\right) \tag{24}$$

where $G_{o,I,a}$, $G_{o,I,b}$, $G_{o,II,a}$, $G_{o,II,b}$, and $G_{o,III}$ are treated as constants. With the exception of their dependence on the transport terms β and β', these growth rate expressions are identical to those given by Hoffman and Miller.[2] It is important to note that, at high undercoolings, these terms will begin to play a significant role in the temperature dependence of the crystal growth rate and can therefore no longer be treated as constants. The formalism developed here suggests that experiments focusing on the molecular weight dependency of the crystal growth rate for polymers exhibiting the three crystal growth regimes should be carried out.

III. Conclusions

It has been demonstrated that in regime III the crystal growth rate will be a function of the pathway for placement of the first stem. Furthermore, if the molecular weight dependency of β' is different from that of β, then the molecular weight dependency of the crystal growth rate in regime III may be different from that of regimes I and II. It is the goal of a future manuscript to provide an extension of this work to different polymers. To attain this goal, it must be determined which of eq 6a or eq 6b is applicable for the polymer of interest. Thus in a subsequent manuscript,

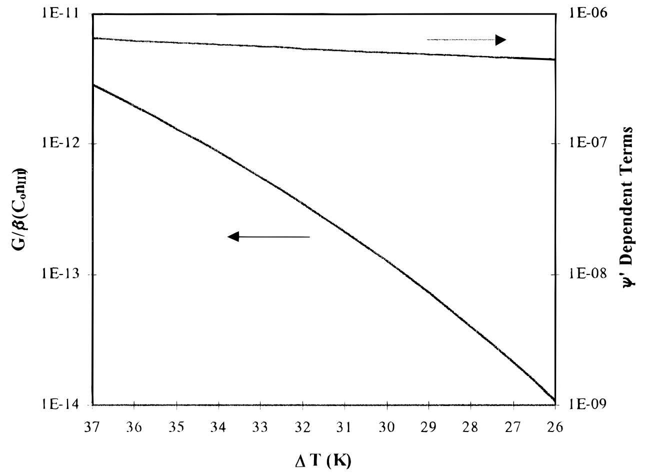

Figure 7. Regime III crystal growth rate as a function of undercooling. $G/(\beta n_{\mathrm{III}}C_o)$ from eq 21 (left-hand axis) and the product of the ψ' dependent quantities in eq 21 (right-hand axis) plotted against undercooling. Note that both axes span the same order of magnitude, *i.e.* 10^3.

expressions for β' and β will be presented to allow for a determination of the experimental conditions under which eqs 4a and 4b are to be utilized.

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Appendix

Determination of δl for Regimes I, II, and III. Expressions for δl, the increment in lamellar crystal thickness above the minimum lamellar thickness, which allows the nucleus to enter the region of thermodynamic stability at a finite rate, can be easily determined by calculating the average lamellar thickness through the equation

$$\langle l\rangle = \frac{2\sigma_e}{\Delta G_f} + \delta l = \frac{\dfrac{1}{l_u}\displaystyle\int_{2\sigma_e/\Delta G_f}^{\infty} lS(l)\,\mathrm{d}l}{\dfrac{1}{l_u}\displaystyle\int_{2\sigma_e/\Delta G_f}^{\infty} S(l)\,\mathrm{d}l} \tag{25}$$

Equation 10a (Regimes I and II) yields an expression for δl of

$$\delta l = kT_x\left\{\frac{4b_0\sigma - (1+2\psi)a_0b_0\Delta G_f}{[2b_0\sigma - (1+\psi)a_0b_0\Delta G_f][2b_0\sigma - \psi a_0b_0\Delta G_f]}\right\} \tag{26a}$$

and eqs 10b and 11 (regimes I, II, and III) yields

$$\delta l = \frac{kT_x}{2b_0\sigma - \psi' a_0b_0\Delta G_f} \tag{26b}$$

Equation 26a, like eq 13a, shows that a "δl catastrophe" is predicted to occur slightly below the regime II → III transition for $\psi = 1$. This is confusing since the classical δl catastrophe is predicted to occur when the barrier to displacement of the first stem is equal to zero while eq 26a displays a singularity under different conditions, *i.e.* $\Delta T_c = 2\sigma T_m/[(1+\psi)a_0\Delta H_f]$. (It is of interest to note that for $\psi = 1$, this singularity occurs at the same critical undercooling as the "δl catastrophe" of the Lauritzen–Passaglia crystallization model.[26]) However, in regime III the catastrophe is governed by ψ', and Lauritzen and Hoffman have demonstrated that this is definitely below unity for undercoolings of up to $\Delta T = 80$ K (regime III). Furthermore, because the relationship between σ and C_∞ alluded to in the introduction[3] has been demonstrated to be valid for polyethylene, as well as several other polymers, the low ψ_{LH} (or ψ') model (i.e. $\psi_{\mathrm{LH}} < 0.2$) must be valid. The reasoning behind this statement is as follows: a large apportionment of the free energy of fusion to the activated state would indicate a zippering down type motion rather than a segmental localization/adsorption model upon which the aforementioned relationship is based, and hence agreement would not be obtained between theory and experiment. Because of this, if the condition in eq 6a is valid for the appropriate undercoolings, examination of the crystal growth rates of materials which display a II → III transition should provide an upper bound on ψ. However, at this point we prefer not to make any definitive statements regarding whether or not this singularity in the regimes I and II equations is a mathematical artifact or whether it is arising because of some physical process that we have not yet visualized.

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