Lateral Substrate Completion Rate in the Lauritzen−Hoffman Secondary Surface Nucleation Theory: Nature of the Friction Coefficient

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ABSTRACT: In this paper it is demonstrated that, within the context of the Lauritzen−Hoffman (LH) secondary surface nucleation theory, the nature of the friction factor governs whether or not a fraction of the total bulk free energy is apportioned to the activated state during secondary nucleation. The friction coefficient (ζ) associated with reeling the chain onto the growth front, when equated to that measured through self-diffusion studies, forces the apportionment factor (ψ) to be equal to zero. On the other hand, assuming that ζ is a function of the shape of the free energy barrier allows ψ to take on nonzero values. In the first instance, the "δl catastrophe" is eliminated, whereas in the second case the "δl catastrophe" is associated with the substrate completion process (in contrast to the classical LH theory, which associates it with the deposition of the first stem). It is shown that both occurrences are mathematical artifacts which arise because the apportionment factor is treated as being equivalent for the first and all subsequent stems, and thus two different ψ's are required. Furthermore, it is suggested that two different expressions for β (the transport term) are required for the first versus all subsequent stems.

Introduction

The vast majority of polymer crystallization kinetic investigations rely on the Lauritzen−Hoffman (LH) flux-based surface nucleation theory for the analysis of the temperature dependence of polymer crystal growth rates. The LH theory is a comprehensive treatment of the kinetics of polymer crystallization that enables the modeling of, or the accounting for, a large number of experimental observations.[1] Among these are the undercooling dependence of both the initial lamellar thickness and the crystal growth rate and the existence and origin of breaks in growth rate curves. In its present state the LH theory also attempts to provide some insight into the effect of molecular weight on both the isothermal crystal growth rate and the degree of tight folding, and thus on the degree of crystallinity.[1] One of the perceived concerns with the surface nucleation theory lies in the prediction of a critical undercooling, ΔT_c, above which the nucleation barrier vanishes and the secondary nucleation rate diverges. No such divergence or upswing in either the crystallization rate or the lamellar crystal thickness has been observed experimentally. This potential problem with the nucleation theory has been referred to in the literature as the "δl catastrophe".[2−15,27] This problem can be circumvented by setting ψ, the fraction of the bulk free energy of crystallization released during the deposition of the first stem, equal to zero.[16] In a recent theoretical treatment by Hoffman *et al.*,[22] it was suggested that the lateral melt-crystal interfacial free energy (σ) is of entropic origin and can be calculated *a priori* in terms of the polymer chain characteristic ratio and the entropy of fusion. Comparison of model predictions with experimental data[22] on *n*-alkanes, polyethylene, poly(propylene), and poly(L-lactic acid) indicates that, for flexible chain polymers, choosing $\psi = 0$ for placement of the first stem is in agreement with the σ−C_∞ correlation. Such an argument is fully in accord with the negentropic model of Turnbull and Spaepen[23] and the work on atomic systems by Spaepen.[24]

In this paper, through an examination of the Lauritzen−Hoffman theory we will present two very different approaches for evaluation, in regimes I and II, of the transport factor β which describes the retardation of the crystallization process due to the necessity of transporting polymer chain segments to the crystal growth front. In both instances, we will assume that (1) the transport factor β and the crystallization free energy apportionment factor ψ are identical for deposition of the first and subsequent stems and (2) the substrate completion rate obtained from the secondary nucleation theory g_{nucl} is equal to that derived from the force of crystallization using the approach of Di Marzio *et al.*[21] In the first approach, we consider the ratio of the force of crystallization to the reeling-in rate to be identical with the chain friction coefficient as is commonly defined for the diffusion coefficient in a polymer melt. In this case, the LH surface nucleation theory no longer leads to a "δl catastrophe" for any value of the apportionment factor, ψ. Additionally, under the same conditions it will be shown that the $\psi = 0$ assumption constitutes a very good approximation of the solution outlined in this paper. Differences of less than 1% are observed for polyethylene in either the secondary nucleation rate, *i*, or the average initial lamellar thickness, l_g*, between the regime II → III transition and the melting temperature when comparing the approach of Hoffman and Miller[1,17] to the first approach presented in this work. In the second treatment, we define an apparent friction coefficient which is dependent on the shape of the free energy barrier (*i.e.* on the apportionment factor ψ). In this case, the classical LH theory is approximately regenerated with preservation of the "δl

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catastrophe". In both instances, polymer melt dynamical considerations imply that the flux contains an inverse square lamellar thickness contribution which was previously neglected. Finally, this exercise suggests that the apparently opposite conclusions reached by the two distinct approaches result directly from the implicit assumption that the apportionment factors for the first and subsequent stems are identical.

Modified Lauritzen−Hoffman Surface Nucleation Theory

The change in the free energy associated with ν stem attachments in the classical Lauritzen−Hoffman (LH) surface nucleation theory is given by

$$\Delta\phi_\nu = (2bl\sigma - a_0b_0l\Delta G) - (\nu - 1)(a_0b_0l\Delta G - 2a_0b_0\sigma_e) \qquad (1)$$

where a_0 and b_0 are the crystal stem width and thickness in the basal plane of the crystal, l is the lamellar thickness, ΔG is the free energy of fusion at the crystallization temperature, and σ and σ_e are the lateral and fold melt−crystal interfacial free energies, respectively.

The force of crystallization is given by

$$^1f_c = \frac{1}{l}\left[\frac{-\mathrm{d}\Delta\phi_\nu}{\mathrm{d}\nu}\right] \qquad (2)$$

One should note that eq 2 differs from that obtained in the classical treatment by Di Marzio *et al.*[21] in that we are not assuming that the lamellar thickness, l, in eqs 1, 2, and 4 is the *average* initial fold length at the crystallization temperature of interest. (The preceding assumption is the only difference between the treatment given here and that of Di Marzio *et al.*[21]) The fact that the fold length is a variable in eq 2 implies that reeling-in effects contribute directly to the flux distribution $S(l)$. This force is then substituted into the expression for the rate at which the chain is reeled from the melt onto the crystal substrate (reeling-in rate):[21]

$$r_{re} = \frac{^1f_c}{\zeta n} \qquad (3)$$

which is the classical relationship for drift of a Brownian particle subjected to an external force[25] where ζ is the friction coefficient per chain repeat unit at the crystallization temperature (T_x) and n is the number of repeat units in the polymer chain. It should be recalled that this linear relationship holds only for low forces, which restricts this treatment to low undercoolings (i.e. regimes I and II). Additionally, this relationship will hold only for molecular weights which are low enough such that the chains do not form multiple attachments at distant sites on the same or different growth fronts (according to Hoffman and Miller, for PE this corresponds to a molecular weight of less than *ca.* 100 000)[1] and high enough such that the friction coefficient is not molecular weight dependent.[20] Through the reeling-in rate, the lateral substrate completion rate, g_{re}, is defined by[21]

$$g_{re} = r_{re}\left(\frac{a_0}{l}\right) \qquad (4)$$

where (a_0/l) accounts for the fact that a length "l" of the chain must be reeled onto the substrate to allow the niche to move laterally by a distance a_0. Combination of eqs 1−4 yields

$$g_{re} = \frac{a_0^{\,2}b_0}{l^2\zeta n}(l\Delta G - 2\sigma_e) \qquad (5)$$

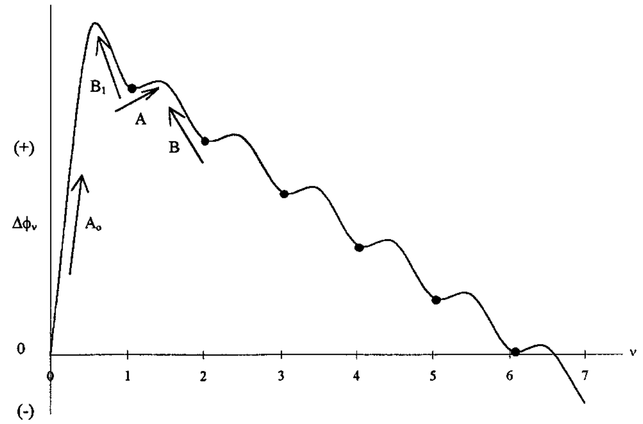

Figure 1. Free energy as a function of the number of stems.

With this expression for the lateral substrate completion rate, a comparison can be made to that obtained from the LH secondary nucleation model. The various rate constants for stem attachment and removal,[19] as shown in Figure 1, are

$$A_0 = \beta\,\exp\left\{\frac{-2b_0l\sigma}{kT_x} + \frac{\psi a_0b_0l\Delta G}{kT_x}\right\} \qquad (6a)$$

$$A = \beta\,\exp\left\{\frac{-2a_0b_0\sigma_e}{kT_x} + \frac{\psi a_0b_0l\Delta G}{kT_x}\right\} \qquad (6b)$$

$$B_1 = B = \beta\,\exp\left\{\frac{-(1-\psi)a_0b_0l\Delta G}{kT_x}\right\} \qquad (6c)$$

where β describes the retardation associated with the necessity of transporting the polymer chain segments to the growth front and where the ψ associated with the attachment/detachment of the first stem has been assumed to be the same as for all subsequent stems. Using these rate constants, the lateral substrate completion rate, g_{nucl}, can be defined by the LH nucleation theory to be

$$g_{nucl} = a_0(A - B) \qquad (7)$$

which upon substitution of A and B, from eqs 6b and 6c, becomes

$$g_{nucl} = a_0\beta\,\exp\left[\frac{\psi a_0b_0l\Delta G}{kT_x}\right]\exp\left(\frac{-2a_0b_0\sigma_e}{kT_x}\right)\left\{1 - \exp\left[\frac{-a_0b_0}{kT_x}(l\Delta G - 2\sigma_e)\right]\right\} \qquad (8)$$

At this point, there are two possible pathways for determining the expression for β in eq 8.

Approach 1. The first approach, like that of Hoffman and Miller,[17] treats the monomeric friction coefficient in eq 5 as being the same as that in self-diffusion studies. The Arrhenius law is used to describe the temperature dependence of the monomeric friction coefficient for temperatures in excess of $T_g + 100$ K. (The Vogel−Fulcher−Tammann−Hesse law is used to describe the temperature dependence of the monomeric friction coefficient for temperatures between T_g and $T_g + 100$ K.) Denoting by T_0 a reference temperature where the monomeric friction coefficient is ζ_0, the following expression is obtained for the substrate completion rate (from eq 5):

$$g_{\mathrm{re}} = \frac{a_0^{\,2} b_0}{l^2 \zeta_0 n}(l\Delta G - 2\sigma_e) \exp\left[\frac{+Q^*}{RT_0}\right] \exp\left[\frac{-Q^*}{RT_x}\right] \tag{9}$$

where Q^* is the activation energy for viscous flow and R is the gas constant.[18,26] It can be seen that g_{re} has no dependence on ψ, which is inherent in the definition of ζ. Equating the "reptation" (g_{re}) and nucleation (g_{nucl}) expressions for the lateral substrate completion rate, an expression for β is obtained:

$$\beta = Y\left(\frac{1}{l^2}\right)(l\Delta G - 2\sigma_e)\frac{\exp\left(\dfrac{-\psi a_0 b_0 l \Delta G}{kT_x}\right)}{1 - \exp\left[\dfrac{a_0 b_0}{kT_x}(l\Delta G - 2\sigma_e)\right]} \tag{10}$$

where Y contains all terms that are independent of l:

$$Y = \frac{a_0 b_0}{\zeta_0 n} \exp\left[\frac{+Q^*}{RT_0}\right] \exp\left[\frac{-Q^*}{RT_x}\right] \exp\left(\frac{+2a_0 b_0 \sigma_e}{kT_x}\right) \tag{11}$$

Note that β now has a ψ dependence. At this point, we will define a new term β^* as

$$\beta^* = Y\left(\frac{1}{l^2}\right)\frac{l\Delta G - 2\sigma_e}{1 - \exp\left[\dfrac{a_0 b_0}{kT_x}(l\Delta G - 2\sigma_e)\right]} \tag{12}$$

with Y maintaining its previous definition. Upon substitution of β from eq 10 into the rate constants in eqs 6a–c and simplifying, we obtain the following expressions for the rate constants:

$$A_0 = \beta^* \exp\left\{\frac{-2b_0 l \sigma}{kT_x}\right\} \tag{13a}$$

$$A = \beta^* \exp\left\{\frac{-2a_0 b_0 \sigma_e}{kT_x}\right\} \tag{13b}$$

$$B_1 = B = \beta^* \exp\left\{\frac{-a_0 b_0 l \Delta G}{kT_x}\right\} \tag{13c}$$

which are now independent of ψ.

Approach 2. The second approach is based upon the assumption that the apparent friction experienced by the chain, as it is reeled onto the growth face, is a function of the structure of the free energy "ripples" shown in Figure 1—which indicates that ζ is therefore a function of ψ. The force we have used was derived from the gradient of a coarse-grained free energy (eq 1). It is well known that the effects of the finer details of the free energy surface, *e.g.*, the drift of the system into unproductive configurations, can be included in the friction coefficient. Therefore, it follows that ζ is a function of ψ.

Since the linear relationship between the reeling-in rate (rate of displacement) (eq 3) and the applied force is valid only for small forces, *i.e.*, ${}^1f_c l/kT_x \ll 1$, it can be stated that

$$\exp\left(\frac{-{}^1f_c l}{kT_x}\right) \cong 1 - \frac{{}^1f_c l}{kT_x} = 1 - \frac{a_0 b_0}{kT_x}(l\Delta G - 2\sigma_e) \tag{14}$$

Rewriting eq 5 as

$$g_{\mathrm{re}} = \frac{a_0 k T_x}{l^2 \zeta n}\left\{1 - \left[1 - \frac{a_0 b_0}{kT_x}(l\Delta G - 2\sigma_e)\right]\right\} \tag{15}$$

and using the approximation given by eq 14, we obtain

$$g_{\mathrm{re}} = \frac{a_0 k T_x}{l^2 \zeta n}\left\{1 - \exp\left[\frac{-a_0 b_0}{kT_x}(l\Delta G - 2\sigma_e)\right]\right\} \tag{16}$$

where the quantity in brackets should be recognizable as $(1 - B/A)$ in the LH nucleation approach. Comparison of this equation with eq 8 indicates that

$$A = \frac{kT_x}{l^2 \zeta n} \tag{17}$$

Before proceeding further into the implications of this conclusion, we must consider the nature of β. Since β contains the effects of reeling in the chain, it must contain the Arrhenius law dependence on temperature (for $T_x > T_g + 100$ K), the n^{-1} dependence, and the $1/l^2$ dependence, since as the lamellar thickness is increased, the number of individual conformational transitions necessary to lay down a stem in partial crystallographic registry (state $\nu \rightarrow$ state $\nu + 1$) is increased and therefore the retardation is increased (*i.e.*, β decreases). We can therefore rewrite β with these considerations in mind as

$$\beta = \frac{\beta_0}{nl^2} \exp\left[\frac{+Q^*}{RT_0}\right] \exp\left[\frac{-Q^*}{RT_x}\right] \tag{18}$$

where β_0 is a constant. It should also be noted that the $1/l^2$ dependence is the gambler's ruin result that the average tie length goes as the square of the distance between the faces.

Setting eq 6b equal to eq 17, with the above expression for β in mind, results in

$$\zeta = \frac{kT_x}{\beta_0} \exp\left(\frac{q}{kT_x}\right) \exp\left(\frac{-\psi a_0 b_0 l \Delta G_f}{kT_x}\right) \exp\left[\frac{-Q^*}{RT_0}\right] \times \exp\left[\frac{+Q^*}{RT_x}\right] \tag{19}$$

This result is then very similar to that of the Hoffman–Miller version of the secondary surface nucleation theory, with the exception of the $1/l^2$ and the ψ dependence. This second approach appears to be more physically realistic for the following reasons. First, in this coarse-grained approach, we are considering the multitude of nonviable configurations which the chain explores and which do not lead to crystallization. Second, because of these considerations, the apparent friction coefficient increases with the work of chain folding. Finally, this equation also indicates that the "apparent friction coefficient" should decrease with increasing magnitude of the apportionment factor, ψ. It must be clear that the "friction coefficient" as described by eqs 3 and 19 may be significantly different from that encountered in self-diffusion studies as it reflects the multitude of conformational transitions required for the polymer chain to reach the activated adsorbed state on the crystal surface. Furthermore, one may also question whether Q^* which enters eq 19 is identical to that derived from relaxation experiments on liquids, as the transport process may be affected by the vicinity of the crystal substrate.

Secondary Nucleation Rate and Average Lamellar Thickness. With expressions for β, it is now possible to consider the flux distribution. The flux is given by the classical LH theory to be

$$S(l) = N_0 A_0 \left(1 - \frac{B}{A}\right) \tag{20}$$

when $B_1 = B$ and where N_0 is the number of initial reacting species. ($N_0 = C_0 n_L$, where C_0 is the configurational path degeneracy and n_L is the number of segments, in units of stem width, between nucleation sites.) Since the equations derived by the second approach are basically those of the classical LH approach, we will limit ourselves primarily to those generated by the first approach. Substitution of eqs 13a, 13b, 13c, and 12 into eq 20 yields (first approach)

$$S(l) = C_0 n_L Y \left(\frac{1}{l^2}\right) \exp\left(\frac{-2b_0 l\sigma}{kT_x}\right)(l\Delta G - 2\sigma_e) \tag{21.1}$$

while substitution of eqs 6a, 6b, 6c, 17, 18, and 19 into eq 20 yields (second approach)

$$S(l) = \frac{C_0\beta_0 n_L}{nl^2} \exp\left(\frac{-(2b_0\sigma l - \psi a_0 b_0 l\Delta G)}{kT_x}\right) \times \exp\left[\frac{+Q^*}{RT_0}\right] \exp\left[\frac{-Q^*}{RT_x}\right]\left[1 - \exp\left(\frac{-a_0 b_0 l\Delta G + 2a_0 b_0\sigma_e}{kT_x}\right)\right] \tag{21.2}$$

both of which should be contrasted with the following equation that is obtained with the classical Lauritzen–Hoffman approach:[19]

$$S(l) = C_0\beta n_L \exp\left(\frac{-(2b_0\sigma l - \psi a_0 b_0 l\Delta G)}{kT_x}\right) \times \left[1 - \exp\left(\frac{-a_0 b_0 l\Delta G - 2a_0 b_0\sigma_e}{kT_x}\right)\right] \tag{22}$$

Note that, previously, solutions to the integral of the classical equation (22) were obtained by assuming that β was independent of l; *i.e.*, l was replaced by $l_g^* = \langle l\rangle$ in eq 22. In other words, the proposed modification to the LH theory considers explicitly the influence of reeling in the polymer chain on the weighting factor associated with a given lamellar thickness in the expression for the total flux, secondary nucleation rate, and average initial lamellar thickness. With the flux equations, the secondary nucleation rate can be obtained by summing fluxes for all possible lamellar thicknesses.

$$i = \frac{1}{n_L a_0 l_u}\int_{2\sigma_e/\Delta G}^{\infty} S(l)\,dl \tag{23}$$

where l_u is the projection of the main chain bond length onto the *c* crystallographic axis. The average lamellar thickness can be obtained similarly with

$$\langle l\rangle = l_g^* = \frac{\frac{1}{l_u}\int_{2\sigma_e/\Delta G}^{\infty} S(l)\,dl}{\frac{1}{l_u}\int_{2\sigma_e/\Delta G}^{\infty} S(l)\,dl} \tag{24}$$

Equation 21.1 leads to the following expression (using the first approach) for the secondary nucleation rate:

$$i = \frac{C_0 Y}{a_0 l_u}\int_{2\sigma_e/\Delta G}^{\infty}\left[\left(\frac{\Delta G}{l}\right)\exp\left(\frac{-2b_0 l\sigma}{kT_x}\right) - \left(\frac{2\sigma_e}{l^2}\right) \times \exp\left(\frac{-2b_0 l\sigma}{kT_x}\right)\right] dl \tag{25}$$

the solution of which is a power series, while the previous approach (eq 22) results in the well-known expression for the secondary nucleation rate:

$$i = \frac{C_0\beta}{a_0 l_u}\left[\frac{kT_x}{2b_0\sigma - \psi a_0 b_0\Delta G} - \frac{kT_x}{2b_0\sigma + (1-\psi)a_0 b_0\Delta G}\right]\exp\left(\frac{-4b_0\sigma\sigma_e}{kT_x\Delta G}\right) \tag{26}$$

Examination of the above equation (26) shows a singularity when $2b_0\sigma = \psi a_0 b_0\Delta G$ (*i.e.* when the free energy barrier for placement of the first stem is zero). This singularity, or divergence, is present, as well, in the lamellar thickness for infinite chain length and is the well-known "δl catastrophe". By substituting the approximation $\Delta G \approx \Delta H\Delta T/T_m$, we can see that the singularity is present at a critical undercooling, $\Delta T_c = 2\sigma T_m/\psi a_0\Delta H$. It should be apparent that if $\psi = 0$, $\Delta T_c = \infty$ and therefore no "δl catastrophe" should be observed. Examination of eq 25 shows no such divergence and hence no "δl catastrophe", since the $\psi = 0$ assumption is inherent to the first approach.

Similarly, in the second approach the $1/l^2$ term in eq 21.2 makes a tractable analytical solution difficult to obtain. With the exception of the $1/l^2$ term, the integral is essentially the same as that of the classical LH theory. Since ψ is still present in the flux equation there *will* still be a singularity in the equation, resulting in a "δl catastrophe". It should be noted that the "δl catastrophe" occurs at the critical undercooling, ΔT_c, where the free energy barrier for deposition of the first stem vanishes. Such an event may occur in theory at a finite undercooling only if the apportionment factor for the first stem is nonzero.

In the two approaches presented in this paper, the existence or absence of a "δl catastrophe" is linked to the exact description of the apparent friction coefficient relating the reeling-in rate of segments to the growth front to the force of crystallization. Equating the apparent friction coefficient with the true friction coefficient of a polymer chain is mathematically equivalent to assuming that the apportionment factor for stem deposition during the substrate completion process is zero; clearly this is what has been done by Hoffman *et al.*[17] Conversely, accounting for the structure of the free energy ripples in the definition of the apparent friction coefficient is mathematically equivalent to the assumption that the apportionment factor associated with substrate completion is nonzero. In this treatment, as in all versions of the LH theory, the crystallization free energy apportionment factor for the first and subsequent stems are taken to be identical. Under these conditions, it becomes clear why the first approach does

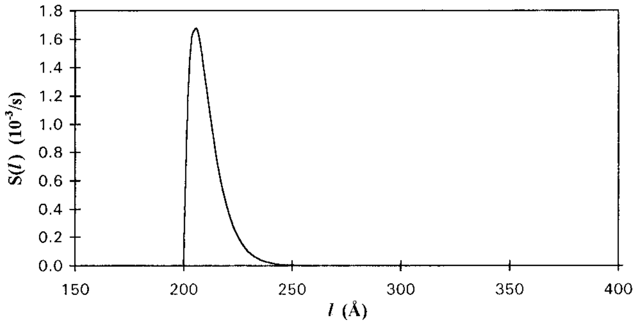

Figure 2. Flux of stems of length, *l*, over the energy barrier as a function of *l* for polyethylene at 131 °C.

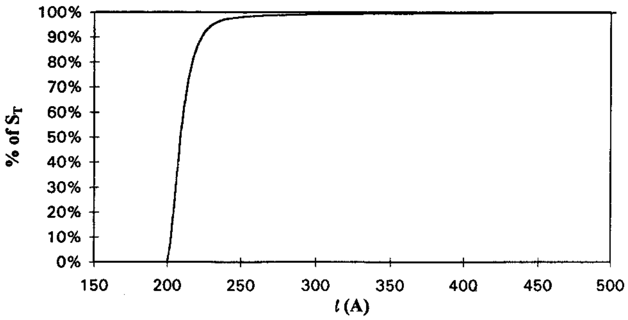

Figure 3. Contribution of the flux, $S(l)$, at length l (as given by Figure 2), to the integral given in eq 25.

not lead to a "δl catastrophe" (*i.e.*, $\psi = 0$) while the second one does (*i.e.*, $\psi > 0$).

In the classical Lauritzen–Hoffman secondary surface nucleation theory, the "δl catastrophe" arises from the nature of the barrier to placement of the first stem; *i.e.*, ΔT_c corresponds to an undercooling at which the free energy barrier for deposition of the first stem is zero. However, because we have assumed that g_{nucl} is equivalent to g_{re} and that ψ is the same for the first stem as for all subsequent stems, the "δl catastrophe" in the second approach is essentially arising from the substrate completion process. It should therefore be apparent that the absence of the "δl catastrophe" in the first approach and its origin in the second approach are mathematical artifacts which arise from our assumption that the expressions for ψ for placement of the first stem and ψ associated with substrate completion are the same. The only way to eliminate these artifacts is to assume that there are two different ψ's, *i.e.*, ψ' for placement of the first stem and ψ for placement of all subsequent stems. Additionally, since β (in the first approach) and ζ (in the second approach) were functions of the apportionment factor (ψ), it is logical that we treat the transport processes for the first stem versus all subsequent stems differently; *i.e.*, we define expressions for β' and β, respectively. Furthermore, it should be simple to picture that the two transport processes should be quite different. Since it is ordinarily assumed that the polymer chain is already at the growth front prior to the initial stem placement, the transport process should consist solely of localized rearrangements which result in the activated state, whereas in the lateral substrate completion process, the chains are being pulled through the melt, and therefore the entire chain is experiencing the force of crystallization. It should therefore be apparent that β will maintain its $1/n$ dependence while β' will have a far weaker (if any) molecular weight dependence.

Although our conclusion is that two ψ's and two β's were required for a self-consistent theoretical treatment, it will be shown that important information can be obtained from the solution of the secondary nucleation rate (eq 25) and the average lamellar thickness (eq 24) integrals. Since a tractable analytical solution for the integral in eq 25 is not readily available, this equation was integrated numerically using Simpson's rule over a range of l, from $2\sigma_e/\Delta G$ to around 2000 Å with 1 Å increments. This upper bound on l was set to accelerate the calculations and was judged appropriate since there was negligible contribution to the total integral above this lamellar thickness; see Figures 2 and 3. Figure 4 shows an excellent agreement between eqs 25 (with $\psi = 0$) and 26 for polyethylene using the input parameters given in Table 1. (*N.B.*: Since we have stated that the results of this work are limited to regimes I and II, the plots for i and l_g^* are only given down to the II → III transition. Over the range examined, the percent error between eqs 25 and 26 reaches only a maximum of 0.9% at the II → III transition.) This result has important implications. The first is that it demonstrates our conclusion that the first approach is mathematically equivalent to setting $\psi = 0$. The second is that we have demonstrated that over the ranges of integrated quantities, the $1/l^2$ term has negligible effects upon the integral. (Note that this conclusion can be extended to the integral of the flux equation produced by the second approach as well.) Similar agreement was achieved for the results obtained for the predictions of the lamellar thickness (see Figure 5). Note that the lamellar thickness still follows an equation of the form $\langle l \rangle = 2\sigma_e/\Delta G_f + \delta l$, although this expression cannot be obtained analytically, as was the case with the secondary nucleation rate. It should be stressed that our conclusion regarding the absence of the "δl catastrophe" in the first approach is essentially only a reaffirmation of the conclusion of Lauritzen and Hoffman,[16] that setting $\psi = 0$ results in an elimination of the "δl catastrophe".

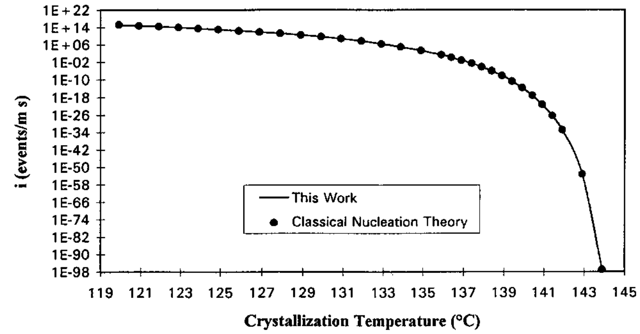

Figure 4. Secondary nucleation rate as a function of crystallization temperature, for polyethylene, by the method of this work and by classical nucleation theory with $\psi = 0$.

Table 1. Polyethylene Input Parameters (from Ref 1)

ΔH_f (J/m³)	2.80×10^{8}	T_m (K)	418.7
σ (J/m²)	1.18×10^{-2}	Q^* (cal/mol)	5736
σ_e (J/m²)	9.00×10^{-2}	l_u (m)	1.27×10^{-10}
a_0 (m)	4.55×10^{-10}	M_0 (g/mol)	14
b_0 (m)	4.15×10^{-10}	n	2000
ζ_0 (kg·s)	2.20×10^{-12}	$L = n_L a_0$ (m)	7.20×10^{-8}
T_0 (K)	450	C_0	4.08×10^{5}

Conclusions

The most important result of this work was that we have clearly demonstrated a need for separate crystallization free energy apportionment factors (ψ's) and transport terms (β's) for the first stem versus all subsequent stems in the Lauritzen–Hoffman secondary

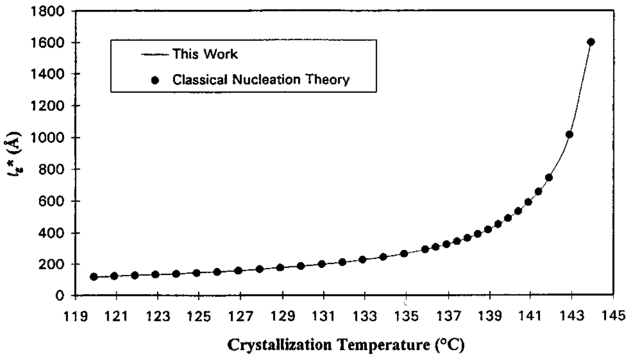

Figure 5. Average lamellar thickness as a function of crystallization temperature, for polyethylene, by the method of this work and by classical nucleation theory with $\psi = 0$.

surface nucleation theory. Additionally, we have demonstrated that within the framework of the LH theory, equating the apparent friction coefficient (ζ) to that obtained from self-diffusion measurements is mathematically equivalent to setting the apportionment factor for substrate completion equal to zero, while an approach which defines ζ to be a function of the shape of the free energy barrier is equivalent to assuming a nonzero value for ψ. Finally, as a result of this work, it has been shown that β has a $1/l^2$ dependence which has been (and ordinarily can be) ignored, but which must be considered for any analysis to be rigorous. Consideration of the implications of different ψ's and β's on the crystal growth rate will be presented in a subsequent paper.

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