Intramolecular Nucleation Model for Polymer Crystallization

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ABSTRACT: We report a numerical study of the free energy barrier for crystallization and melting of a single homopolymer chain. The simulations show that the free energy barrier separating the crystalline and molten states at the same free energy level strongly depends on the chain length. However, at a fixed temperature the barrier for single-chain crystallization is independent of chain length. This observation is in agreement with recent experiments on multichain bulk-polymer systems and can be understood theoretically if we assume that the primary nucleation of polymer crystals is determined by intramolecular nucleation. If we further assume that the subsequent growth of polymer crystals is controlled by two-dimensional intramolecular nucleation on the growth front, we can even account for the experimentally observed molecular segregation during crystal growth as well as the chain-length independence of the free energy barrier for secondary nucleation.

Introduction

The mechanism by which polymer crystals form from a quiescent liquid involves several steps. In the absence of impurities or other seeds for heterogeneous nucleation, the first step of the crystallization process is the nucleation of a small crystallite.[1,2] The critical crystal nucleus may consist of only a small fraction of a single macromolecule. The rate G of this primary nucleation is usually described in terms of the classical nucleation theory (see e.g. ref 3):

$$G = G_0 \exp[-\Delta F_c/(k_B T)] \qquad (1)$$

where k_B is Boltzmann's constant, T the absolute temperature, G_0 a kinetic prefactor, and ΔF_c the free energy barrier for critical nucleus formation. After primary nucleation has taken place, the step that limits the rate of subsequent crystal growth is the incorporation of polymers in the growth front.[4] Under conditions where the growth front is smooth, the crystal exhibits layer-by-layer growth, the rate of which is limited by the secondary two-dimensional nucleation of new crystal layers on the growth front. The Lauritzen−Hoffmann (L−H) theory for polymer-crystal growth assumes that, at relatively large supercooling, the deposition of a single polymer stem initiates the growth of a new layer, which then grows by reeling-in and folding of the remainder of the chain.[5,6] At higher temperatures, the growth front may be rough and growth is limited by the entropic cost to form a sufficiently flat surface by thermal fluctuations—this is the situation considered by the Sadler−Gilmer model.[7−9]

Although there exist several theoretical models for the mechanism of polymer crystallization, the role of molecular weight in polymer crystallization is still poorly understood. For instance, we have no satisfactory explanation for the phenomenon of polymer-size segregation during crystal growth.[4] Another aspect that is mysterious is the following: in order to have an appreciable rate of both primary nucleation[10,11] and crystal growth,[12] long-chain polymers typically require larger supercooling than short chains. Somewhat surprisingly, while the linear crystal growth rate of polymers depends significantly on the chain length,[13,14] this effect appears to be exclusively due to chain-length dependence of the kinetic prefactor G_0 in eq 1—the free energy barrier ΔF_c for secondary nucleation is effectively independent of chain length.[15] In addition, recent experiments on the primary nucleation rates of both extended-chain and folded-chain crystals of polyethylene also suggest that the barrier for crystallization is independent of molar mass.[16,17]

For long-chain polymers, the critical crystal nucleus may involve far fewer monomers than are contained in a single polymer chain. Under these conditions, it is natural to consider the role of intramolecular nucleation in polymer-crystal nucleation. We should expect that intramolecular nucleation differs from intermolecular nucleation in two important respects: first of all, it should be fairly insensitive to the overall concentration of macromolecules, and second, it may depend explicitly on the molar mass of the polymer.

Crystallization in a single homopolymer chain has been observed in experiments[18,19] and has been studied extensively in simulations.[20−23] In particular, Muthukumar and collaborators have reported a detailed study of the way in which a single chain incorporates into a crystal growth front. This work provided evidence for the existence of an entropic barrier for polymer crystal growth.[23] Here, we will argue that much of the phenomenology of polymer crystallization and melting can be understood on the basis of a single or multiple free energy barrier for the melting and crystallization behavior within a single chain. Recently, we have shown that it is possible to compute the free energy barrier separating the solid and the "liquid" state of a single-chain molecule.[24] In the present paper, we exploit this approach to study the chain-length dependence of single-chain crystal nucleation. Below we show that our simulations allow us to understand why the free energy barriers, for both primary and secondary nucleations, hardly depend on polymer chain length.

The rest of this paper is organized as follows. First, we briefly discuss the simulation techniques. Then we

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discuss the numerical calculation of barriers for single-chain crystallization. These numerical results are analyzed in terms of a simple theoretical model. We present dynamic Monte Carlo simulations that show the difference in single-chain crystallization/melting for long and short chains. We discuss these results in the context of available experimental data. We then use the same theoretical framework to discuss the chain-length dependence of secondary nucleation in polymer-crystal growth and fractionation during crystal growth.

Simulation Techniques

In our Monte Carlo simulations, we consider a single polymer chain "living" on a lattice. The size of simulation box was 256^3 lattice sites. This box was repeated periodically. For chains that we have studied in our simulations (containing 1024 units or less), the linear size of the box was large enough to make contacts between periodic images of a single chain extremely unlikely. To let the conformations of the polymer chain be controlled by the local interactions, we used a Metropolis scheme. The trial moves that we used were those of the so-called "microrelaxation" model.[25] This is a dynamic Monte Carlo scheme that allows for partial sliding diffusion of the polymer chains. Trial moves of single monomers can be either along the main axes of the lattice or along the plane or body diagonals. The total number of neighbors joined by these links to a lattice point is $6 + 12 + 8 = 26$. Polymer bonds cannot cross. In addition, there is an energetically favorable term to have parallel (nonbonded) bonds on neighboring sites. The energetic cost for breaking up such a pair is denoted by E_p.[26] We use E_p as our unit of energy. The reduced temperature of the system is given by k_BT/E_p.

In our simulations, we considered single chains of length 16, 32, 64, 128, 256, 512, and 1024. Initially, we prepared the single chains in a regularly folded state for a lamella with small thickness; for instance, the initial crystallite of the 1024-mer has a fold length of 4 units and lateral dimensions of 16 × 16 lattice sites. The chain conformation was then equilibrated at the desired temperature by spontaneous thickening. The structure of this well-equilibrated crystallite was found to depend only on the temperature. In all cases, the surface of the equilibrated crystallite was quite disordered. As the crystallite melts, this disorder increases. We can trace the progress of melting by counting the number of disordered ("molten") units, i.e., polymer bonds having less than five parallel, nonbonded neighbors. In our simulations, we computed the free energy of the chain as a function of the number of molten units using

$$\Delta F/(k_BT) = -\ln P(n) \tag{2}$$

where $P(n)$ is the probability to find n molten units in the chain. To be able to probe free energy barriers that are much larger than k_BT, we used umbrella sampling.[27] In our umbrella sampling, we use several overlapping "windows" (defined by parabolic biasing potentials with different minima[28]). To improve equilibration of the chain conformations, we combined the multiwindow umbrella sampling with parallel tempering.[29]

Theoretical Estimation

Before reporting the results of the simulations, we first consider a simple theoretical model that serves as a framework to discuss the simulation results. The model that we consider is, in essence, the single-chain equivalent of classical nucleation theory. In this model, we can estimate how the free energy of a single chain depends on the degree of melting. As the coexistence of a part of the polymer melt with the crystallite, the free energy changes due to (1) the difference in bulk free energy between crystal and disordered state and (2) the surface free energy associated with the existence of an interface between the ordered and disordered parts of the chain. In the present lattice model, we can easily estimate the energetic and entropic contributions to the bulk free energy difference. The potential energy cost per molten unit is approximately given by $\Delta E = E_p(q - 2)/2$, where q is the coordination number of a regular lattice. Here, we have ignored the small probability that, in the disordered state, two neighboring bonds will be parallel. The entropy gain per molten unit is $\Delta S = \ln(q - 1) + (\gamma - 1)(\ln n)/n$. Here, $q - 1$ denotes the number of possible directions for each step of an ideal (non-self-avoiding but nonreversing) random walk on the lattice. The second term takes self-avoidance into account, and γ is the appropriate critical exponent for a three-dimensional self-avoiding random walk.[30] This correction is expected to be much smaller than the first term, and we shall ignore it in what follows. We expect that the surface free energy for a chain of length N, containing n molten units, will be proportional to $(N - n)^{2/3}$: $\Delta F_s \approx \sigma(N - n)^{2/3}$. We refer to the constant of proportionality σ as the "interfacial free energy density", though several prefactors (e.g., $36\pi/\rho^2$ for a spherical crystallite where ρ is the density) have been absorbed into σ. The free energy of a single-chain system can then be written as a function of molten units, n, as

$$\begin{aligned} F(n) &= \frac{q-2}{2}nE_p + \sigma(N-n)^{2/3} - k_BTn\ln(q-1) \\ &= n\Delta f + \sigma(N-n)^{2/3} \end{aligned} \tag{3}$$

where $\Delta f \equiv E_p(q - 2)/2 - k_BT \ln(q - 1)$ is the bulk free energy change per molten unit. For our model in simulations, $q = 26$. We treat σ as a fit parameter. The point where the free energies of the disordered coil and the compact, single-chain crystallite are equal defines the single-chain "equilibrium temperature".

The main difference between crystallization and melting in a bulk system and in a system consisting of a single chain is that the latter is finite in size. This implies that the stable crystalline "phase" of the single chain should have chain folding to minimize the surface free energy of the crystallite. The melting temperature of such a crystallite is, by definition, equal to the temperature where the free energies of the fully crystalline and the fully disordered states of the single chain are equal: $N\Delta f = \sigma N^{2/3}$ or $\Delta f = \sigma N^{-1/3}$. The shape of the free energy barriers near equilibrium is shown schematically in Figure 1.

From eq 3 we can estimate the free energy of the critical nucleus, using $\partial F(n)/\partial n = 0$. This yields $F_{\max} = N\Delta f + 4\sigma^3/(27\Delta f^2)$. When we compare this free energy to the fully disordered state ($n = N$), we find that the free energy barrier for crystallization is $4\sigma^3/(27\Delta f^2)$. Note that, at fixed Δf (or fixed crystallization temperature), this barrier is independent of N. At the point where the crystalline and disordered states have the same probability to occur, the equilibrium free energy barrier for both crystallization and melting is

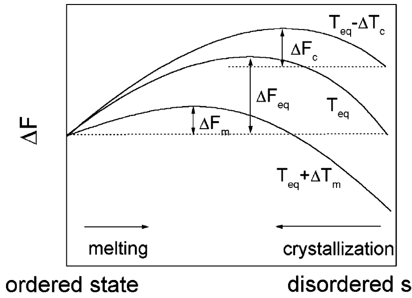

Figure 1. Schematic picture showing free energy curves in the vicinity of equilibrium melting temperature T_{eq}, the equilibrium free energy barrier ΔF_{eq}, and the free energy barriers for melting ΔF_m with a superheating ΔT_m and for crystallization ΔF_c with a supercooling ΔT_c.

$$\Delta F_{eq} = \frac{4}{27}\sigma N^{2/3} \tag{4}$$

Results and Discussion

Primary Nucleation. With the above picture in mind, let us consider the simulation results. Figure 2 (reproduced from Figure 4 in ref 24) shows the computed free energy barrier for the native-to-coil transition of a single 1024-mer. In this figure, we have chosen the free energy of the crystalline state as the reference value. For this chain length, the crystalline and coil states have equal free energies at a temperature of $2.967E_p/k_B$. Note that the free energy minimum in the crystalline state does not correspond to a situation where there are only crystalline units. This is not surprising, as under the equilibrium condition there is a considerable disorder at the surface of the crystallite and as bonds located at the fold ends are counted as disordered. We find that, for a chain of 1024 units, some 20% of all units are disordered. In our crude theoretical analysis, we simply ignore these molten units when we fit our theoretical expression to the height of the free energy barrier (see Figure 2).

Similar simulations were performed for chains of length 16, 32, 64, 128, 256, and 512. In every case, we located the equilibrium transition temperature, and then we computed the height of the equilibrium free energy barrier.

According to the simple barrier model described in the previous section, the equilibrium free energy barrier should vary with N as $(4/27)\sigma N^{2/3}$ (see eq 4). As shown in Figure 3, the simulation results for the height of equilibrium free energy barrier can be fitted reasonably well with this expression, using a single fit parameter: $\sigma \approx 15E_p$ obtained from Figure 2.

The observed chain-length dependence of the equilibrium free energy barrier implies that for short chains thermal fluctuations are sufficient to induce the transition between crystalline and disordered conformations. In other words, short polymer chains will crystallize and melt without hysteresis. In contrast, longer chains are much less likely to cross the high barrier at the equilibrium temperature. Hence, the crystallization and melting of long chains should exhibit hysteresis. This is indeed what is observed in Figure 4, where we show dynamic MC simulations of the phase transformations during heating and cooling of both short and long single chains.

In the vicinity of the equilibrium temperature of 64-mer (see Figure 5), the system frequently jumps between the disordered and the crystalline states. Changing the temperature just shifts the relative probability of these two states. This results in a continuous transition from the ordered to the disordered structure. Of course, the magnitude of the barrier beyond which the system shows hysteresis depends on the time scale of the simulations. From Figure 3, we can deduce that, on the time scale of our simulations, barriers of height $10k_BT$ to $15k_BT$ can still be crossed by spontaneous thermal fluctuations.

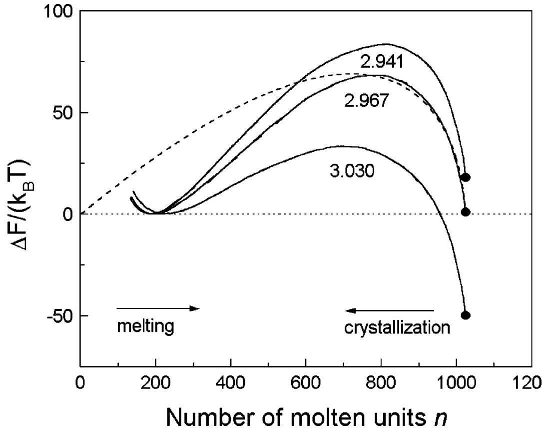

Figure 2. Free energy curves vs the number of molten units for 1024-mer at the denoted temperatures with the unit of E_p/k_B. The numerical results (solid lines) are calculated by umbrella sampling with 15 windows.[24] The dashed line is calculated from eq 3 with $\sigma = 15E_p$ and the fitted equilibrium melting temperature $3.2657E_p/k_B$.

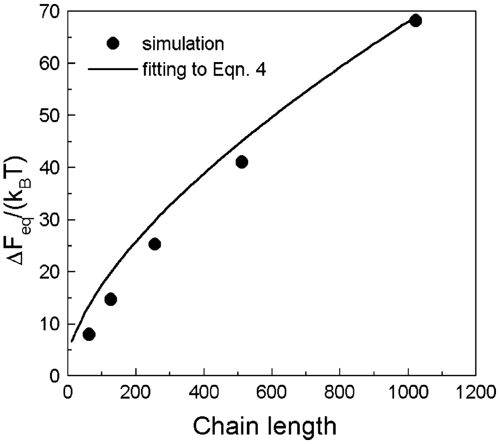

Figure 3. Height of equilibrium free energy barrier vs chain length. The solid curve is calculated from eq 4 with $\sigma = 15E_p$.

Away from equilibrium, our model predicts that the height of free energy barrier for melting is given by

$$\Delta F_m = \Delta f\, N - \sigma N^{2/3} + \frac{4\sigma^3}{27\Delta f^2} \tag{5}$$

while the free energy barrier for crystallization remains:

$$\Delta F_c = \frac{4\sigma^3}{27\Delta f^2} \tag{6}$$

At a fixed temperature (i.e., at fixed Δf), ΔF_m depends on the chain length, but ΔF_c does not. Figure 6 shows the free energy barrier for crystallization and melting for a number of different chains at a fixed temperature. The figure demonstrates that, indeed, the barrier for crystallization is chain-length-insensitive while the barrier for melting depends strongly on chain length.

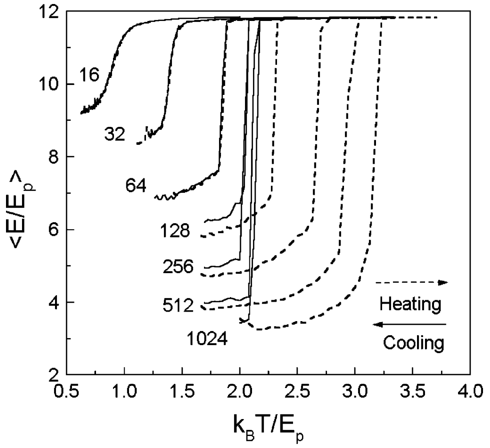

Figure 4. Heating and cooling curves (dashed and solid lines, respectively) of the potential energy with the denoted variable chain length (number of units). The potential energy is defined as the mean value of $24 - p$, where p is the number of parallel bonds packing around each bond. The heating and cooling programs are the steps in the value of $E_p/(k_BT)$, each having a length of 0.01 and a period of 10^6 Monte Carlo (MC) cycles. One MC cycle is defined as one jump for each chain unit on average. The reported data are averaged over 1000 samples, each with 1000 MC cycle interval.

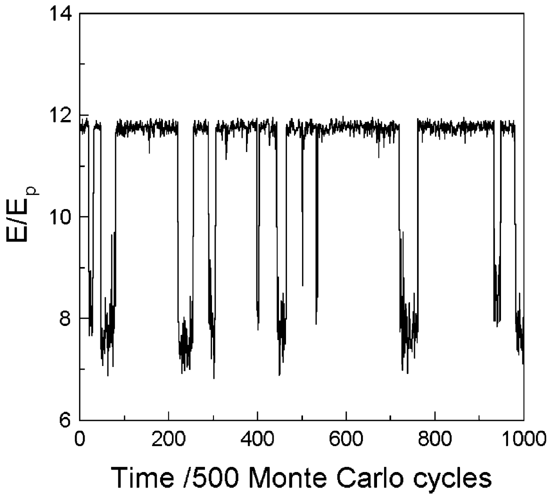

Figure 5. Isothermal curve of the potential energy for 64-mer at $T = 1.845E_p/k_B$. The initial state was picked up from the corresponding heating curve in Figure 4 after 10^6 MC cycles annealing at this temperature step.

This provides a simple explanation for the chain-length dependence of the kinetics shown in Figure 4, where at a constant cooling rate all chains containing at least 128 units crystallize within a narrow temperature range, but on heating, they melt at different temperatures, depending on the chain length.

The picture that emerges from the present simulations is that the crystallization of long chains is initiated by intramolecular nucleation. Such nucleation will not take place at the equilibrium melting point, since the equilibrium free energy barrier is quite high for long chains, but rather at a much lower temperature region where the barrier for crystallization can be crossed by spontaneous thermal fluctuations. At fixed temperature, the barrier height for nucleation is effectively independent of chain length. This would seem to imply that all polymers of a given family should start to crystallize at the same supercooling. This, however, is an oversimplification: the equilibrium melting temperature itself depends on chain length (see e.g. ref 31), and in addition, the nucleation of very short polymers may be affected by the presence of ordered mesophases. Moreover, for sufficiently short chains, single-chain nucleation is no longer possible as the single-chain crystal state is less stable than the disordered state at the spontaneous-crystallization temperature of the bulk system. Experimentally, it is observed that for long chains crystallization occurs at constant supercooling, but for short chains (less than 150 backbone atoms), this supercooling rapidly decreases down to zero.[10,11] The vanishing supercooling may be attributed to the fact that the free energy barriers for both melting and crystallization of short chains including their mesophases are lower than the spontaneous thermal fluctuations.

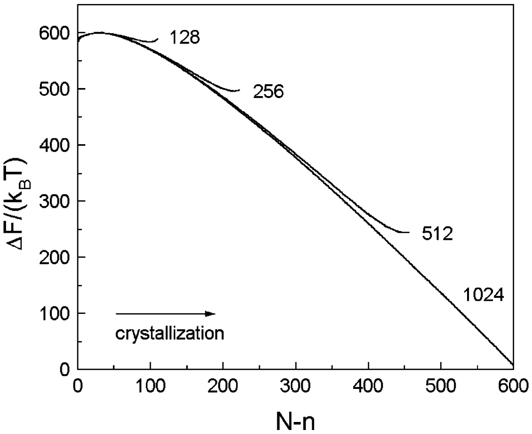

Figure 6. Free energy changes of single-chain systems with the denoted chain length (number of units) at the fixed temperature $T = 2.174E_p/k_B$. Curves are shifted to meet at their tops.

For sufficiently short chains the picture changes because at the temperature where single-chain crystallization becomes kinetically allowed, the single-chain crystallite is still less stable than the disordered state. This would suggest that a large supercooling is required to initiate crystallization. Therefore, the mechanism for primary nucleation will change from single-chain to multichain. In other words, at a given supercooling, the barrier for multichain nucleation is presumably somewhat higher than for single-chain nucleation, but a multichain nucleus can grow to become a stable crystallite. In any event, the comparison for the crystallization of short-chain polymers is complicated by the fact that intermediate mesophases may play a role in the crystal nucleation of short-chain molecules, such as paraffins.[32]

Secondary Nucleation. Let us next consider two-dimensional analogue of single-chain crystallization, namely the deposition of a single polymer molecule on a smooth growth front. The expression for the free energy of single-chain deposition is

$$F(n) = n\Delta f + \sigma(N - n)^{1/2} \qquad (7)$$

where both Δf and σ have different values than in three-dimensional case.

In this case, the height of the free energy barrier for melting is

$$\Delta F_m = N\Delta f - \sigma N^{1/2} + \frac{\sigma^2}{4\Delta f} \qquad (8)$$

while the free energy barrier for crystallization is

$$\Delta F_c = \frac{\sigma^2}{4\Delta f} \qquad (9)$$

As before, for a fixed value of Δf (i.e., at a fixed temperature), ΔF_c does not depend on chain length. This is consistent with the experimental observations.[15]

The existing models for polymer crystallization do not explain size fractionation, although Wunderlich[33] pointed out that molecular nucleation could play an important role in size fractionation. Below, we show that, if we assume that secondary nucleation proceeds through the nucleation of two-dimensional single-chain crystals, we can understand the observed temperature dependence of size fractionation. At a fixed temperature, polymer chains of all lengths should have the same barrier for secondary nucleation but different barriers for melting (see eqs 8 and 9). The longer the chains, the higher the barrier for melting (the analogous three-dimensional case is shown in Figure 6). At a specific temperature, there is a well-defined chain length N_c for which the two-dimensional crystalline state is in equilibrium with the fully disordered state. Under these conditions, the equilibrium free energy barrier for crystallization (and melting) is

$$\Delta F_{eq} = \frac{\sigma^2}{4\Delta f_{eq}} \qquad (10)$$

where $\Delta f_{eq} = \sigma N_c^{-1/2}$. Polymer chains longer than $N_c = (\sigma/\Delta f)^2$ can form stable surface crystallites. Shorter chains will, most likely, dissolve again due to thermal fluctuations. This observation suggests that there should exist a simple relation between chain length and crystallization temperature, namely $N_c^{-1/2} \sim a - bT_c$. Figure 7 shows that the relation is, in fact, well satisfied by the experimental data on the melt fractionation of polyethylene.

Intramolecular Nucleation Model. Thus far, we have only discussed the initial stages of nucleation and crystal growth of a single chain. At a later stage of long chains, the growth of two-dimensional crystallites may be arrested, either by impingement on other crystallites or by reaching the edge of the substrate. In that case, the remainder of the chain needs to nucleate a second crystallite. This would lead to a free energy landscape for nucleation and growth of a single chain, as sketched in Figure 8. Note that, for long chains, the free energy barrier for secondary nucleation is still independent of the (remaining) chain length, as long as it exceeds N_c. In fact, in an earlier publication[34] we have observed the stepwise crystal growth of a single-chain polymer, under conditions where the growth was interrupted by the finite size of the growth front. Morphological evidence for the nucleation of many crystallites on a growth front comes from a recent AFM study of the lateral surface of polymer-crystal lamellae.[35] The AFM images reveal a granular texture of the lateral surface that may be due to the presence of multiple crystallites. It is not even necessary that all two-dimensional crystallites belonging to the same chain are located on the same growth front. If crystallite growth is blocked and the remainder of the chain is shorter than the critical chain length, it will become a cilium emerging from the fold surface or the lateral surface of the lamellar crystal. This scenario would lead to lamellar crystals where most folds correspond to adjacent reentries, but some (those that go from one crystallite to the next) would be "random switchboard"-like.[36]

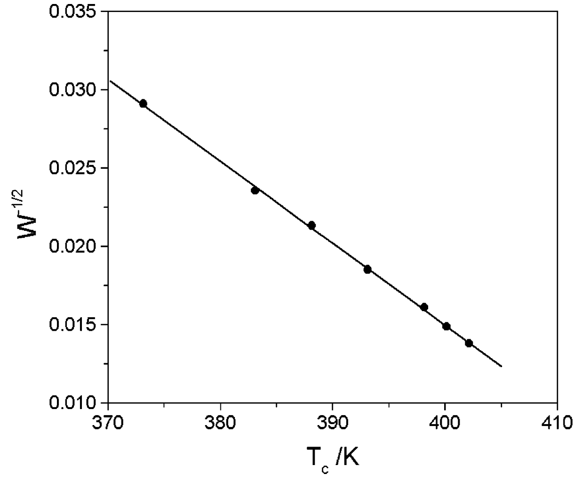

Figure 7. Critical molecular weight $W^{-1/2}$ of melt polyethylene in equilibrium fractionation as a function of crystallization temperature T_c. The data points are reproduced from ref 4, p 101 in Table V-7, type M series, excluding the low-molecular-weight end. The fitting line shows a correlation coefficient of 0.9997.

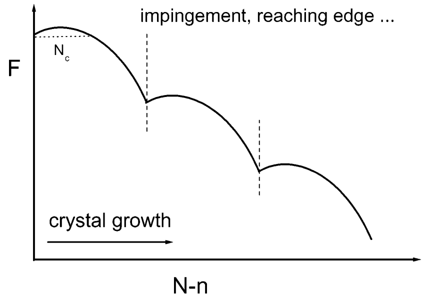

Figure 8. Schematic representation of the free energy landscape associated with a multiple nucleation process of single-chain crystal growth. The dashed vertical lines indicate the points where crystal growth is arrested, for instance when a nucleus reaches the edge of the growth front or when two nuclei impinge.

Conclusions

In this paper, we have presented simulations of the free energy barrier for the nucleation of single-chain polymer crystallites. The simulation results suggest that a simple thermodynamic model may be used to describe the dependence of the nucleation barrier on temperature and chain length. Using this intramolecular nucleation model—and its two-dimensional analogue—we can account for a number of features of polymer crystallization. In particular, we can explain the chain-length independence of the free energy barrier for both primary and secondary nucleation, and we can account for molecular segregation during polymer crystal growth. Of course, the molecular weight dependence of the polymer crystal growth rate is also affected by the change in the kinetic prefactor that determines the rate of "reeling in" of long-chain molecules. This prefactor, which depends both on the chain length and on the crystal morphology, is not discussed in the present paper. We stress that our description, based on single-chain nucleation, does not rule out the possibility that multichain nuclei will form under suitable circumstances. In fact, we expect the latter mechanism to be dominant for short chains and, a fortiori, for small molecules.

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