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Monte Carlo Study of Chain Folding in Melt-Crystallized Polymers

Marc L. Mansfield

Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523.
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ABSTRACT: The amorphous region between two crystalline lamellae is simulated with a set of chains on a simple cubic lattice. The model takes account of steric interactions between individual chains (no two chains occupying the same lattice site), has the correct density (no vacant lattice sites), and for properly chosen model parameters, exhibits a partially ordered layer between each crystalline lamella and the amorphous region. (Such a layer is considered important in determining the nature of chain folding.) An energy term destabilizing tight folds is also included. In the absence of this energy term a high degree of adjacent reentry, greater than about 50% or 60%, is observed, even in the presence of the above-mentioned partially ordered layer. When tight folds are destabilized, adjacent reentry can become much less important, but the combined adjacent and next-nearest-neighbor reentry never falls below about 50% in the examples considered. The model is compared to a simpler model, consisting of random walks on a simple cubic lattice between two absorbing barriers, and it is found that the random walk model gives a correct qualitative picture.

I. Introduction

The nature of chain folding in melt-crystallized polymers has been a controversial subject from the time that it was first recognized that such polymers crystallize in a lamellar habit. Two opposing opinions[1] have been presented: One holds that a high degree of regular or adjacent folding occurs, while the other, the "switchboard" model, holds that different polymer stems within the crystal are connected randomly by chains in the amorphous phase.

Steric arguments favoring a high degree of adjacent folding have been given.[2] Basically stated, these hold that the amorphous phase between two crystalline lamellae would have much too large a density if a large number of chains from the two crystals were permitted to enter the amorphous phase and perform random walks. For example, models[3,4] based on random walk statistics predict that each walk in the amorphous region would be on the average about three times too long. One way to compensate for this within the context of these models is to have about two-thirds of the chains turn abruptly about and reenter the crystal along an adjacent site, never entering the amorphous region. Such steric arguments have been countered by arguing that they apply only to cases where the loss of order upon passage from the crystal to the amorphous region is abrupt, while polymers actually exhibit an interfacial layer, on the order of 10 Å thick, between the crystal and the amorphous region that retains some of the order of the crystal.[5,6] Also, the random walk models suffer from the well-known fact that ideal chains are perturbed by the presence of boundaries,[2,7] so that random walks may not well characterize the chains in the amorphous region near the crystal.

It has also been argued that crystallization proceeds too rapidly for chains in the melt to disentangle and form crystals with a large degree of adjacent reentry.[8,9] This, as well as the fact that the radius of gyration does not change much with crystallization,[9,10] has led to various models (the "*Erstarrungsmodell*",[11] or the "freezing-in" model[12]) in which the chains more or less line up in place during crystallization. However, disagreement exists on this point as well. Theoretical and experimental evidence has been given that the chains in the melt can rearrange quickly enough to produce adjacent reentry.[13–15] It also appears that the lack of change in the gyration radius cannot be taken as evidence for a lack of adjacent reentry. (See next paragraph.)

Neutron scattering experiments permit study of the conformation of polymer chains but seem inadequate to resolve the present controversy. Models have been proposed exhibiting both small[9,16] and large[17] amounts of adjacent reentry that agree well with the same set of small-angle neutron scattering data.[18] Since the scattering data at small angles are used to yield the gyration radii, arguments based on these radii are also inconclusive. Recent wide-angle results[19,20] do show promise of providing additional answers, however.

In this article we present Monte Carlo calculations of a simple cubic lattice model of the amorphous region between two crystalline lamellae. This model treats properly the steric interactions between individual chains, the density is not excessive, for certain values of the model parameters it exhibits the partially ordered interfacial layer mentioned above, and in contrast to the simple random walk models, it is able to account for deviations from ideality due to the crystalline boundary. The model includes an energy term representing the resistance of a chain to folding tightly. Reentry is predominantly adjacent for this model when this energy term is absent. When it is present, adjacent reentry becomes less important but the combined contribution from both adjacent and next-nearest-neighbor reentry retains significance. Reentry is not adjacent in this case, but neither is it random.

In section II we describe the model considered here. In section III we review the results of random walk models[3,4] given by Guttman et al. to facilitate a comparison between those models and the present one. In sections IV and V we present results obtained in the absence or presence, respectively, of the partially ordered interfacial region and the energy of destabilization of tight folds. Finally in section VI, we present a summary and a discussion of the results.

II. Description of the Model

The model discussed here is similar to one employed previously to study the dependence of root-mean-square end-to-end distance on chain length for chains in the molten state.[21] We model the amorphous phase between two crystalline lamellae as a set of chains on a simple cubic lattice as shown schematically in Figure 1. The chains lie in a box of dimension L in the x and y direction and dimension N in the z direction. We assume the bottom of the box corresponds to $z = 0$ and the top to $z = N$. The crystalline regions are not directly modeled; the effect of the crystal is simulated by requiring the chains to be anchored in either the $z = 0$ or the $z = N$ plane; i.e., we assume that the two crystalline lamellae lie in the regions $z \leq 0$ or $z \geq N$, and we require all the chain ends present in the box to lie on the two faces $z = 0$ or $z = N$. No other chain ends are present in the box; this corresponds to a large molecular weight limit in which the concentration of chain ends is small. (However, using the techniques given in ref 21, it will be possible to include additional chain ends in this model.) We require that every lattice site be visited once and only once by a chain. In order to create the partially ordered interfacial layer discussed in the Introduction, we include a set of energy differences. We assume that every pair of parallel, neighboring (i.e., forming the opposing sides of a square whose side is one lattice unit) bonds contributes a value $-ak_BT$ to the total energy of the system and that every 180° bond angle contributes a value $-bk_BT$ while 90° angles contribute nothing. Taking both a and b positive permits us to model attractive van der Waals interactions between different chain segments and rotational isomerization leading to helix bending, respectively, and will produce partially ordered regions in the vicinity of the two crystal surfaces. In order to simulate the resistance of a chain to folding tightly, each such fold contributes a value ck_BT to the total energy of the system. Statistical averages for this model are computed by using the well-known Metropolis Monte Carlo sampling technique,[22] with new configurations of the system being generated by breaking and re-forming the chains in the following manner: A pair of parallel bonds is located (such as those circled on chains d and e or on g and f in Figure 1) and flipped to the dashed-line positions as shown in Figure 1. Additional details are given in ref 21; we only add that to suppress cyclization, such bond flips are not permitted within the same chain and that bond flips can occur anywhere within the box, including at the crystal surfaces. The initial state of the system either is a completely ordered array (all chains parallel to the z axis) or is taken from a previous run with different a, b, and c values. After an initial equilibration period, the system is sampled at regular intervals and averages of quantities of interest are generated. During the equilibration period the number of tight loops, the ratio of accepted moves to attempted moves, and the CPU time required to attempt a given number of moves were all monitored. When these three values stabilized, it was deemed safe to proceed sampling the system. We point out that Dill[23] has discussed the abstraction of breaking and re-forming chains but apparently did not consider using it as the basis of practical calculations. Note that the two-dimensional representation of Figure 1 is only schematic; the system is three-dimensional, and bonds can occur in all three directions. We also employ periodic boundary conditions across the x and y faces of the box. We should also point out that some question still remains concerning the ergodicity of this Monte Carlo technique.[24]

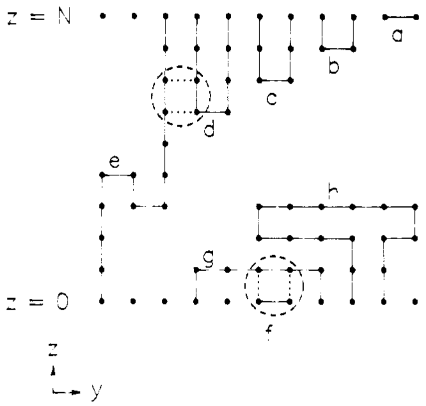

Figure 1. Schematic diagram of model.

In this paper we will use the term *loop* to refer to chains such as a, b, c, d, f, g, and h that return to the same crystal face and *tie* to refer to chains such as e that span the amorphous layer. Loops such as a, b, c, d, f, and h that return to a neighboring lattice site will be called *adjacent reentrant loops*. Those adjacent reentrant loops such as a–d in Figure 1 which contain only one x or y bond will be called *tight loops*. When it is necessary to differentiate among these, we will refer to chains such as a, b, c, or d as zeroth-, first-, second-, or third-order tight loops, respectively. At the risk of introducing potentially confusing nomenclature, we will refer to structures in which three consecutive bonds lie on three sides of a square as *tight folds*. Chains e and h in Figure 1 each contain two tight folds, chains a, b, c, d, and f each contain one, and chain g contains none. As noted above, each such tight fold is assigned an energy ck_BT. We will observe the convention that the $z = 0$ or $z = N$ surfaces lie within the crystal, so that zeroth-order tight folds are not part of the amorphous component, and we will let the term *amorphous loop* refer to any loop that is part of the amorphous component, i.e., any loop that is not a zeroth-order tight loop. We will let M denote the length in bonds of any chain (e.g., $M = 1$ for zeroth-order tight loops).

III. A Random Walk Model

A simpler, similar model is provided by the problem of a random walk between two absorbing barriers. There are a number of treatments of this problem[25,26] and it has recently been interpreted by Guttman et al.[3,4] in the context of semicrystalline polymers. In this section we summarize several properties of this model in order to compare it with the model described in section II. The reader interested in a more detailed discussion should consult the above cited references.

We consider random walks on a simple cubic lattice with absorbing boundaries at $z = 0$ and $z = N$. The random walks begin at the point (0,0,1) and continue until they are absorbed at one of the two boundaries. If the walk is absorbed at $z = 0$, it represents an amorphous loop, while if it is absorbed at $z = N$, it represents a tie chain. If from the point (0,0,1) to $(x,y,0)$ or (x,y,N) the walk takes n steps, we assume it represents a chain of $M = n + 1$ bonds since we include the step (0,0,0) to (0,0,1) as part of the chain. The probability that a given walk is an amorphous loop is $(N - 1)/N$ while the probability that it is a tie is $1/N$, so that there are $N - 1$ times as many loops as ties present. The probability that an amorphous loop has length M is

$$P_{\text{loop}}(M) = 3^{1-M}N^{-1}\sum_{\nu=1}^{N-1}(2 + \cos(\pi\nu/N))^{M-2}\sin^2(\pi\nu/N) \tag{3.1}$$

and the probability that a tie has length M is

$$\begin{aligned} P_{\text{tie}}(M) &= 0 \qquad \text{for } M < N \\ &= 3^{1-M}N^{-1}\sum_{\nu=1}^{N-1}(-1)^{\nu+1}(2 + \\ &\qquad \cos(\pi\nu/N))^{M-2}\sin^2(\pi\nu/N) \qquad \text{for } M \geq N \end{aligned} \tag{3.2}$$

The probability that any walk (either an amorphous loop or a tie) has length M, $P_{\text{walk}}(M)$, is given by the sum of eq 3.1 and 3.2. The average number of bonds in either an amorphous loop, a tie, or a walk (either amorphous loop or tie) is given by

$$\langle M\rangle_{\text{loop}} = 2N - 1 \tag{3.3}$$

$$\langle M\rangle_{\text{tie}} = N^2 \tag{3.4}$$

$$\langle M\rangle_{\text{walk}} = (3N^2 - 3N + 1)/N \tag{3.5}$$

The fraction of the amorphous density resulting from amorphous loops is

$$(2N - 2)/(3N - 1) \tag{3.6}$$

or $^2/_3$ for large N, and the fraction resulting from ties is one less this.

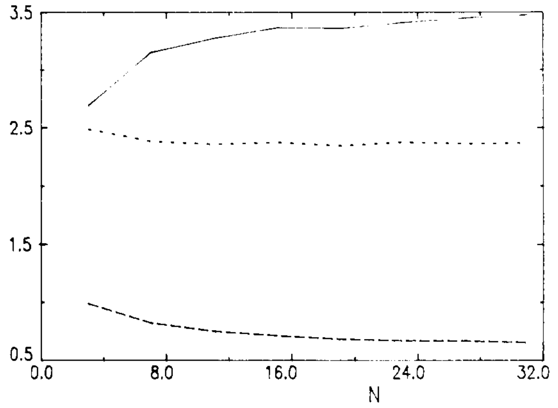

Figure 2. Average number of bonds in each of three different types of chains. Dashed curve, $\langle M\rangle_{\text{tie}}/N^2$; dotted curve, $\langle M\rangle_{\text{loop}}/N$, amorphous loops only; solid curve, $\langle M\rangle_{\text{walk}}/N$, amorphous loops and ties.

From eq 3.5 we see that the average length of the chains entering the amorphous component is $3N$ for N large. If we were to permit one such chain in the amorphous component for every two crystalline stems, then the density of the amorphous component would be three times too high.[3] The only way to compensate for this with the present model is to permit only about $^1/_3$ of the stems to enter the amorphous component and require $^2/_3$ to form tight loops. This model, therefore, gives a prediction of $^2/_3$ for the degree of adjacent reentry, not counting those walks that return to an adjacent site after entering the amorphous region.

IV. Results for $a = b = c = 0$

A number of computations were performed for $a = b = c = 0$ for N varying from 3 to 31 and for $L = 31$. (A few additional computations were performed for $L = 15$ to test the effect of periodic boundary conditions. No measurable effect was seen.) A large degree of adjacent reentry was observed: 72% of the chains were zeroth-order tight loops (independent of N for all N values considered) and there were an additional 5% of all other tight loops (measured for $N = 27$ but not expected to vary with N except for N very small) and 2% adjacent reentrant loops that were not tight (once again measured for $N = 27$), for a total of 79% adjacent reentry. All other loops constituted $(21 - 55/N)$% of the chains, and $(55/N)$% of the chains were ties (for $N > 10$). We see that the number of amorphous loops, $(28 - 55/N)$%, and the number of tie chains exhibit the same N dependence as for the model described in section III. However, the ratio of amorphous loops to tie chains for the present model is about $N/2$ or less by about a half. Figure 2 gives plots of $\langle M\rangle_{\text{loop}}/N$ (for amorphous loops only), $\langle M\rangle_{\text{tie}}/N^2$, and $\langle M\rangle_{\text{walk}}/N$. From the curves in Figure 2 we have that

$$\langle M\rangle_{\text{loop}} \cong 2.4N \tag{4.1}$$

$$\langle M\rangle_{\text{tie}} \cong 0.6N^2 \tag{4.2}$$

$$\langle M\rangle_{\text{walk}} \cong 3.5N \tag{4.3}$$

By comparing eq 4.1 to 4.3 with eq 3.3 to 3.5, we see that the model discussed in section III gives the correct N dependence but errs by a numerical factor. Figures 3–5 compare the results for $P_{\text{loop}}(M)$, $P_{\text{tie}}(M)$, and $P_{\text{walk}}(M)$ for the two models.

Although the number of amorphous loops is greater than the number of tie chains by a factor of order N, the lengths of tie chains exceed those of amorphous loops by a factor of the same order, so that the fractions of lattice sites in the amorphous region belonging to amorphous loops or tie

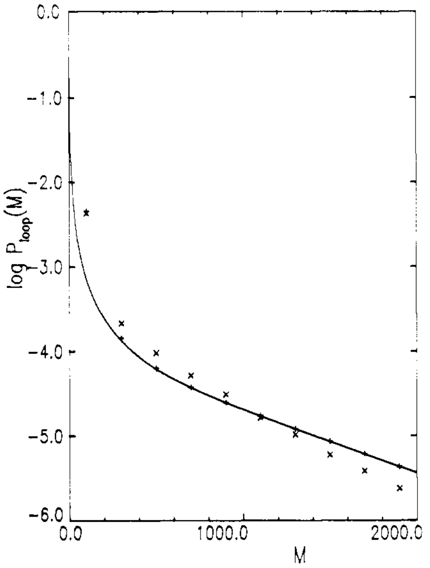

Figure 3. Decimal logarithm of the probability that an amorphous loop contains M bonds. Solid curve, eq 3.1, random walk model; (+) probabilities given by eq 3.1 averaged over intervals of 200; (×) probabilities given by the present model averaged over intervals of 200.

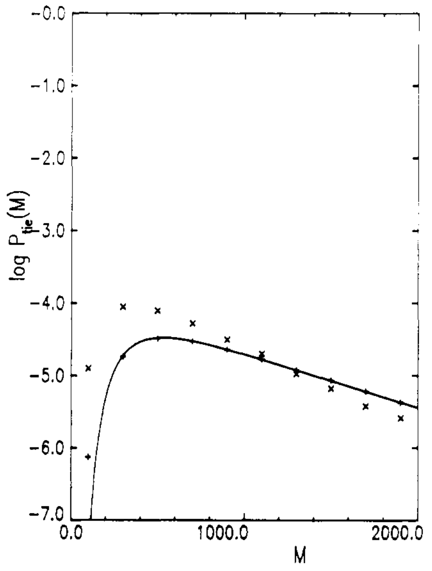

Figure 4. Same as Figure 3 for tie molecules.

chains respectively are of the same order of magnitude. This is seen in Figure 6, where the fraction of lattice sites on amorphous loops agrees with eq 3.6 to within several percent. In Figure 7 we display the probability as a function of z that a lattice site is in either a tie chain or an amorphous loop, respectively, for $N = 27$. The two functions pass through $^1/_2$ and $^1/_4$ at the midpoint, respectively, since a lattice site at the center of the amorphous region has equal probability of being attached to either face of the crystal.

In Figure 8 is plotted the probability that a lattice site at a given value of z is attached to either an x, y, or z bond for $N = 27$. The probabilities are equal to $^1/_3$ to within sampling error, except when $z = 1$ or 26, for which z bonds are slightly less probable. This is interpreted as due to the large number of zeroth-order tight loops on the two crystal faces.

V. Calculations for *a*, *b*, or *c* Nonzero

A. $c = 0$. Effect of Partially Ordered Interfacial Region. The results presented in the previous section

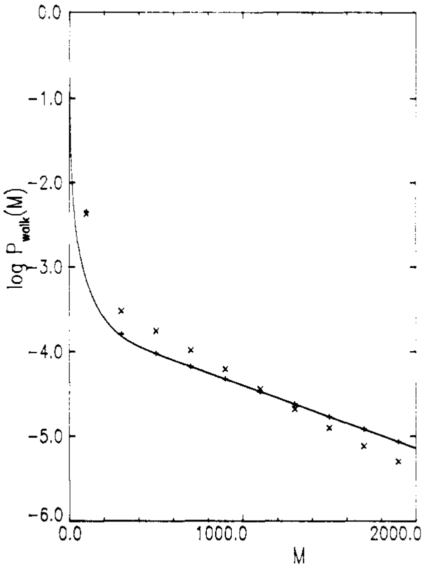

Figure 5. Same as Figure 3 for both amorphous loops and tie molecules.

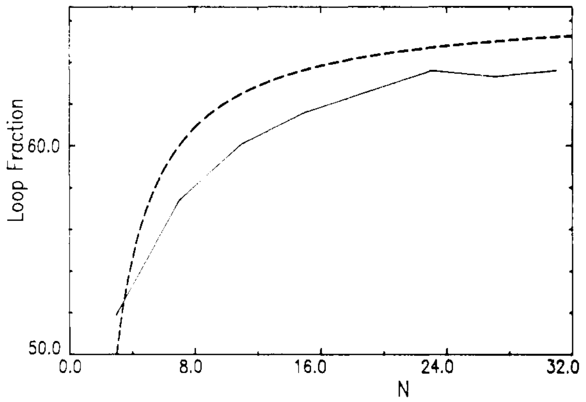

Figure 6. Fraction (in percentage units) of lattice sites in the amorphous region belonging to loop chains. Solid curve, the present model; dashed curve, expression 3.6.

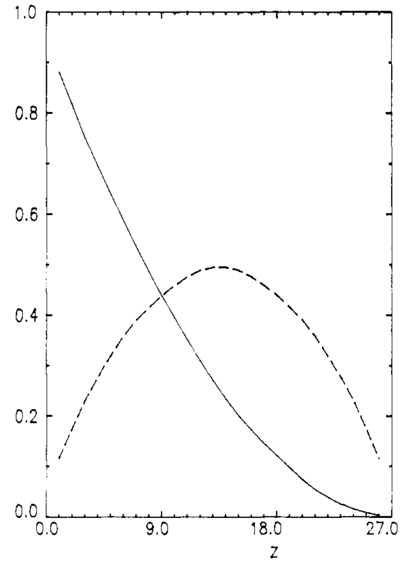

Figure 7. Probability that a lattice site at a given value of z is visited by either a loop (solid curve) or a tie (dashed curve). The solid curve represents only the contribution from the $z = 0$ face. The contribution from the $z = 27$ face is the same curve, inverted about the center of the graph.

favor a high degree of adjacent reentry. It has been argued, however, that different results should be expected when a partially ordered interfacial layer exists between the

Table I
Percentages of Different Types of Chains as a Function of Energy Parameters a and b with $c = 0$[a]

a	0.00	0.25	0.30	0.35	0.37	0.10	0.00	0.00	0.10	0.50
b	0.00	0.25	0.30	0.35	0.37	0.60	0.75	1.00	0.75	0.10
TL0	72.0	58.1	43.5	31.8	18.2	46.2	48.9	29.8	36.2	33.2
TL1	4.4	10.0	14.4	15.5	13.1	11.0	8.1	8.6	10.8	15.4
TL2	0.3	1.9	4.9	8.0	10.7	3.5	2.8	6.6	5.4	8.8
TL3	0.0	0.4	1.4	3.5	7.1	0.8	0.8	3.3	2.3	4.1
TL4	0.0	0.1	0.4	1.3	3.4	0.2	0.2	1.5	0.9	1.6
TL5	0.0	0.0	0.1	0.4	2.0	0.1	0.1	0.5	0.3	0.6
TL6	0.0	0.0	0.0	0.1	0.9	0.0	0.0	0.2	0.1	0.2
TL7	0.0	0.0	0.0	0.0	0.3	0.0	0.0	0.1	0.0	0.0
TL8	0.0	0.0	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.0
TL	76.8	70.4	64.7	60.6	56.4	61.9	61.0	50.7	56.0	63.9
ANT	1.9	3.2	4.5	5.2	6.0	3.1	2.8	3.5	3.9	5.9
AAL	78.7	73.6	69.2	65.8	62.4	65.0	63.7	54.2	59.9	69.8
NAL	19.3	24.6	28.8	32.0	35.1	32.8	33.8	42.5	37.5	28.3
T	2.0	1.8	2.0	2.2	2.5	2.2	2.5	3.3	2.6	1.8

[a] TLn, tight loop of order n; TL, all tight loops (sum of the TLn); ANT, adjacent, but not tight, loops; AAL, all adjacent loops (TL + ANT); NAL, nonadjacent loops; T, ties.

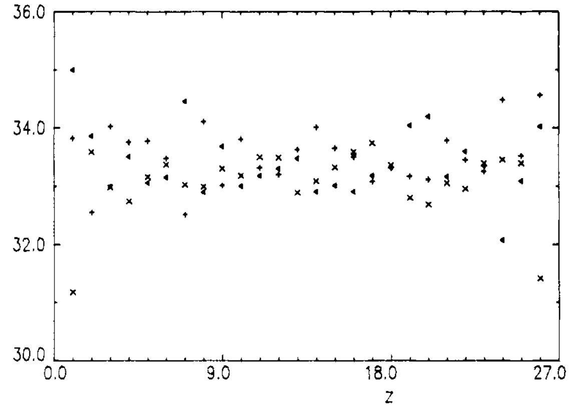

Figure 8. Probability (in percentage units) that a lattice site on a given z plane is connected to a bond oriented in the x (▲), y (+), or z (×) direction for $a = b = 0$.

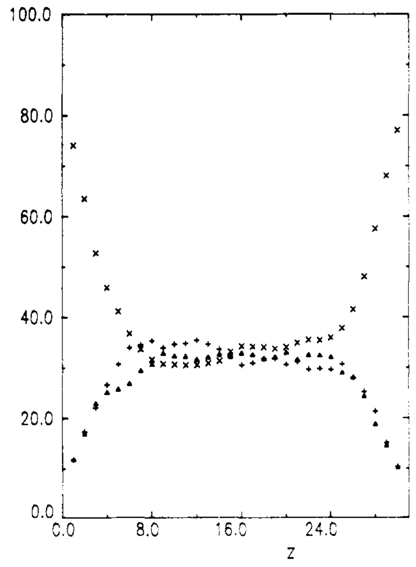

Figure 9. Same as Figure 8 for $a = b = 0.37$.

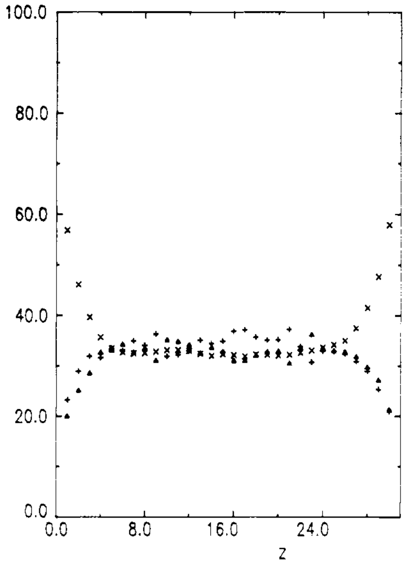

Figure 10. Same as Figure 8 for $a = 0.1$, $b = 0.75$.

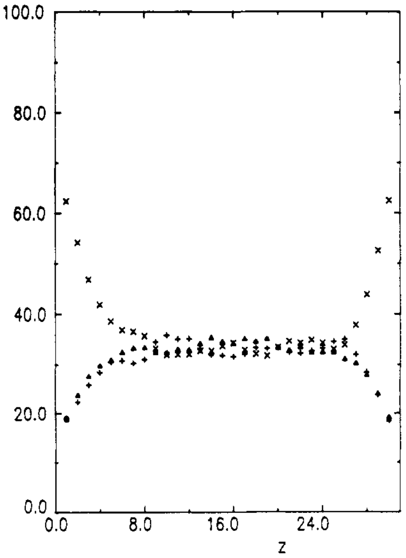

Figure 11. Same as Figure 8 for $a = 0.5$, $b = 0.1$.

crystalline and amorphous regions.[5,6] As we stated in section II, the present model will exhibit such an interfacial region for appropriately chosen values of the parameters a and b. Calculations have been performed at the following seven points on the a–b plane: $(a,b) = (0.25,0.25)$, $(0.3,0.3)$, $(0.35,0.35)$, $(0.37,0.37)$, $(0.1,0.6)$, $(0.1,0.75)$, $(0,0.75)$, $(0,1)$, and $(0.5,0.1)$ and for $N = L = 31$. Calculations were also attempted at $(a,b) = (0.4,0.4)$, $(0.1,1.0)$, $(0,1.1)$, and $(0.6,0.1)$ but these gave crystalline, or at least very anisotropic structures. These points were chosen to obtain representative results in each of the three regions $a \ll b$, $a = b$, and $a \gg b$. Figures 9–11 display the probability that a lattice site at a given value of z is attached to either an x, y, or z bond for the $(0.37,0.37)$, $(0.1,0.75)$, and $(0.5,0.1)$

Table II
Percentages of Different Types of Chains as a Function of Energy Parameters a, b, and c[a]

a	0.00	0.00	0.30	0.30	0.00	0.00	0.50	0.50
b	0.00	0.00	0.30	0.30	0.75	0.75	0.10	0.10
c	5.00	10.00	5.00	10.00	5.00	10.00	5.00	10.00
TL0	31.9	28.7	13.8	15.7	15.4	16.9	9.3	10.7
TL1	3.5	2.3	5.2	5.5	4.2	5.5	4.6	7.6
TL2	0.2	0.2	1.5	0.9	0.8	0.7	2.4	1.7
TL3	0.0	0.0	0.3	0.2	0.2	0.2	1.2	0.3
TL4	0.0	0.0	0.1	0.0	0.1	0.1	0.2	0.1
TL	35.6	31.2	21.0	22.3	20.8	23.3	17.9	20.4
ANT	1.0	1.3	1.4	1.3	1.4	1.2	1.6	1.0
AAL	36.6	32.5	22.4	23.6	22.2	24.5	19.5	21.4
N20	10.6	11.8	14.8	12.8	13.0	12.6	13.5	13.0
N11	14.8	17.2	15.1	14.9	12.1	12.1	14.7	13.9
ANL	62.0	61.5	52.3	51.3	47.2	49.2	47.6	48.3
T	3.3	3.2	4.4	3.9	4.1	4.2	4.4	4.2

[a] TLn, tight loop of order n; TL, all tight loops (sum of the TLn); ANT, adjacent, but not tight, loops; AAL, all adjacent loops (TL + ANT); N20, loops spanning vectors $(0,\pm 2)$ or $(\pm 2,0)$ on crystal surface; N11, loops spanning vectors $(\pm 1,\pm 1)$ on crystal surface; ANL, adjacent and next-nearest-neighbor loops (AAL + N20 + N11); T, ties.

calculations, respectively. In each of the profiles displayed in Figures 9–11 a well-developed interfacial region exists. In Table I we display the probabilities of obtaining each different type of chain. We observe that the degree of adjacent reentry does decrease with either increasing a or b but in no case does the degree of adjacent reentry become negligible. It appears that the number of tight loops will always be greater than about 50% and attempts to force it below this value by increasing a or b will crystallize the system. It also appears that the lower bound of 50% will be obtained only for physically unrealistic thicknesses of the interfacial region.

B. $c \neq 0$. Effect of Energetic Tight Folds. Calculations with $L = N = 31$, $a = b = 0$, and $0 < c \leq 10$ were performed, with results displayed in Figure 12. Curve I in Figure 12 gives the probability of finding a tight fold in regions distant from the two crystal faces ($7 \leq z \leq 24$) and demonstrates that increasing c beyond about 4 or 5 completely suppresses tight folds in those regions. We also observe that once these tight folds have been removed, i.e., for c above about 5, the structure of the system becomes practically insensitive to the value of c. We see that the amount of adjacent reentry (curve C) falls from near 80% at $c = 0$ to about 30% for $c > 5$. At the same time, the amount of next-nearest-neighbor reentry (curves D and E) grows, so that the amounts of combined adjacent and next-nearest-neighbor reentry (curve F) only falls from about 80% to about 60%. The bulk of the adjacent reentry comes from tight loops (curve B lies near curve C), and surprisingly enough, the system seems willing to tolerate very energetic tight folds near the crystal faces while rejecting them away from the faces. Of course, the only reason the system would accept such energetic states is that they are preferred entropically, and we have to conclude that a much greater portion of configuration space is available to the system as a whole if tight loops are permitted. Of course, in the limit $c \rightarrow \infty$ the number of tight loops must fall to zero. But it appears from Figure 12 that that will not happen until $c \gg 10$, and such values are probably not physically realistic.

Calculations with $L = N = 31$, $c = 5$ or 10, and a or b nonzero were also performed. These are summarized in Table II. These calculations all exhibited a partially ordered interface. Once again we observe that although the amount of adjacent reentry can be made quite small (about 20%), next-nearest-neighbor reentry becomes more important and the combined contribution is near 50% for all the examples considered. Also, the results are once again practically independent of the value of c.

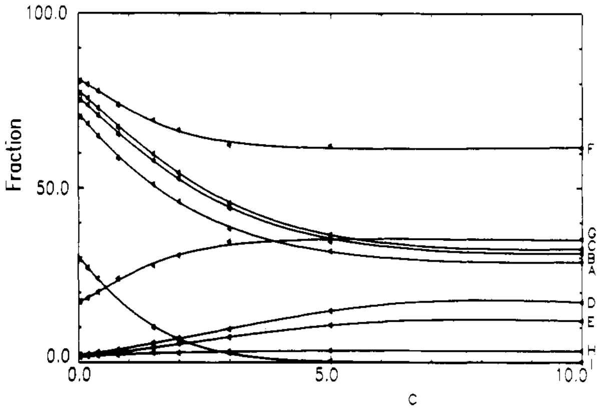

Figure 12. Curves A–H give as a function of c for $a = b = 0$ the fraction of chains (in percentage units) that are (A) zeroth-order tight loops, (B) tight loops, (C) adjacent reentrant loops, (D) next-nearest-neighbor reentrant loops spanning a vector $(\pm 1,\pm 1)$ on the crystal faces, (E) next-nearest-neighbor reentrant loops spanning a vector $(\pm 2,0)$ or $(0,\pm 2)$ on the crystal face, (F) all adjacent and next-nearest-neighbor adjacent loops, C + D + E, (G) all loops other than adjacent or next-nearest-adjacent], and (H) ties. Curve I is the probability (in percentage units) of finding a tight fold in the interior of the system ($7 \leq z \leq 24$) calculated by assigning a weight of $^1/_2$ to each lattice site that forms the central bond of a tight fold and dividing by the total number of lattice sites sampled.

VI. Summary and Discussion

The present model indicates a high degree of adjacent reentry or next-nearest-neighbor reentry in melt-crystallized polymers. The degree of adjacent reentry is about 80% in the absence of a partially ordered interface between crystalline and amorphous domains and an energy of destabilization for tight folds. In the presence of a partially ordered interface this value drops to somewhere around 50% before the system crystallizes completely, and states of the system with adjacent reentry near 50% probably have unphysically large interfacial regions. When tight folds are destabilized, adjacent reentry becomes less important but combined adjacent and next-nearest-neighbor reentry never dropped below about 50% in the calculations performed. In this case, it appears that neither of the two extremes, adjacent or random reentry, are entirely correct. These calculations also indicate that a related, simpler model[3,4] based on random walk statistics is qualitatively correct.

It is important to remember that Metropolis Monte Carlo calculations only provide results at thermodynamic equilibrium, a state only rarely achieved by solid polymers.

In these calculations we have had to maintain a temperature above the melting point (e.g., small values of *a* and *b*) to prevent the system from crystallizing, so it could be argued that we have failed to model the true thermodynamic state of the amorphous domain. However, it is generally considered that the amorphous material is liquid-like in structure, and if this is the case, the present calculations should be correct. One should also remember, in attempts to apply this work to real systems, that lattice models may not give an accurate representation.

Ironically, these calculations (especially those for $a = b = 0$ and $c > 0$) appear to indicate that entropic forces are acting to favor adjacent and near-adjacent reentry, i.e., by permitting adjacent and near-adjacent reentry the system as a whole can access more configuration space. They seem to support the steric arguments[2] opposing a high degree of random reentry. If the structure of the amorphous domain is indeed liquid-like, then it is impossible for it to contain all the chains available from the two crystal faces. Either there is a high degree of near-adjacent reentry or we do not really understand the structure of the amorphous domain in these polymers.

Recent wide-angle neutron scattering results[19,20] indicate that no more than about four or five adjacent stems within either the (100) or the (010) crystallographic planes belong to the same chain. This is not necessarily inconsistent with the results reported here. From the present calculations we may expect a nonnegligible number of adjacent pairs of stems, but if the probability of finding n adjacent stems behaves something like p^{n-1}, then it will be improbable that any more than a few stems from the same chain be adjacent unless p is very near 1.

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Brownian Dynamics Computer Simulations of a One-Dimensional Polymer Model. 1. Simple Potentials

Robert Cook*
Lawrence Livermore National Laboratory, Livermore, California 94550
Lawrence L. Livornese, Jr.†
Department of Chemistry, Lafayette College, Easton, Pennsylvania 18042.

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ABSTRACT: Brownian dynamics computer simulation results are presented on a simple one-dimensional polymer model that contains the essential features of rotational angle flexibility. Comparison is made with analytical treatments of the model.

I. Introduction

In the last few years there have been a significant number of computer simulations of polymeric systems. Many of these simulations use the method of Brownian dynamics, which involves the numerical solution of Langevin equations in order to deal with the diffusive motion of the chain brought about by the solvent. The focus of these studies has been varied. For simple polymethylene-type chains, workers seem to have focused either on the dynamics of conformational transitions[1,2] or upon various relaxation

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† Present address: University of Medicine and Dentistry of New Jersey, Newark, NJ.

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