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Chain Conformations at Semicrystalline Interphases

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ABSTRACT: The structure of a semicrystalline interphase is obtained from an enumeration of all the chain conformations at the crystal surface. In our model study, 40% of the chains exiting the crystal immediately reenter its surface at an adjacent site. Our study also indicates that the amorphous phase retains some of the order present in the crystal over a distance much larger than previously anticipated.

Introduction

It has long been recognized that the conformations of the chains exiting the crystal phase in semicrystalline homopolymers play a major role in determining material properties.[1,2] Experimental evidence strongly suggests that these chains retain some of the order present in the crystal and create inside the amorphous domain a thin interphase with modulus higher than in the bulk.[3,4] The presence of such ordered interphases is of importance in a wide variety of materials, including ethylene copolymers,[5,6] binary polymer blends,[7] carbon black reinforced elastomers,[8] lipid monolayers and bilayers,[9] micelles and vesicles[10] and biopolymers.[11]

Several models have been proposed for describing the chain conformations at the boundaries between amorphous and crystalline domains (for a concise review, see ref 12). All these models clearly recognize the fact that the transition from an ordered to a random coil configuration at the crystal/amorphous boundary imposes serious steric constraints on the chains exiting a crystal. In order to avoid an anomalous increase in density, a large number of chains must turn abruptly about and reenter the crystal. In the so-called gambler's ruin or random walk statistics models,[13-15] the amorphous phase is assumed to be homogeneous and isotropic; i.e., the interphase is neglected. That assumption leads to the prediction that two-thirds of the chains exiting the crystalline phase return to the crystal at an adjacent site. The existence of an interphase has been accounted for in more refined models.[16-19] These studies are based on mean field estimations of the entropy of the chains exiting the crystalline phase. Maximization of the entropy, assuming the density in all phases is uniform, leads to the prediction of a very thin interphase with an amount of adjacent reentry ranging from 42 [16] to 73%.[17] The discrepancy between these two values has been attributed[17] to the use of a poor approximation in the entropy calculation of ref 16. In a third type of approach,[6,20] the structure of the interphase has been simulated on a simple cubic lattice entirely filled-in with a set of chains in an extended and oriented conformation. Chain segments in the amorphous phase are then progressively randomized by a Monte Carlo process in which chains are broken and reformed according to a set of prescribed rules. The process, however, is not ergodic,[20] which casts some doubts on the validity of the approach. Results indicate a 72% adjacent reentry, assuming that the amorphous phase has the same density as that of the crystal.

In the present work, the structure of the interphase is obtained from an enumeration of all the configurations of chains of length α, exiting the crystal surface. For large enough values of α ($\alpha \geq 5$), our approach allows one to accurately estimate the probability of immediate adjacent reentry of the chains into the crystal. As in all previous work,[6,13-20] our model is based on static equilibrium considerations and it neglects the influence of kinetic factors, such as crystallization rate, on the morphology of semicrystalline polymers. The study is nevertheless of great value since it clearly identifies the direction in which spontaneous changes must occur.[21] For simplicity, our approach is on the scale of a statistical segment length and it therefore also neglects the influence of chain-bending energies which prevent the formation of tight fold conformations. These considerations will be the object of future work.

Model

In our approach, the conformations of the chains exiting the crystal surface are generated on a lattice. The lattice unit length is set equal to that of a statistical chain segment which, for polyethylene, is about 10 Å.[22] Since the chains are mutually self-avoiding, every lattice site can be occupied once and only once by a chain. The crystal surface is oriented perpendicular to the y-axis; see Figure 1. The numbers of sites along the x- and z-axes are denoted by L_x and L_z, respectively. In order to easily characterize the degree of order of the chains in the amorphous phase, we also define a series of layers one lattice unit thick and labeled 1, 2, ... from the crystal surface; see Figure 1.

In order to study the probability of immediate adjacent reentry, we start by generating all possible chain conformations in layer 1. For a crystal with $L_x = 2$ and free boundary conditions, there are $m = 5$ possible conformations (one with adjacent reentry) which do not violate the excluded-volume condition; see bottom of Figure 1. These conformations have statistical weights proportional to the number of configurations of chains of length α that can be grown from them. This is illustrated in Figure 1 for a choice $\alpha = 1$. Thus, the conformation on the bottom left of Figure 1 has $n = 5$ possible continuations, the next has $n = 9$, etc., whereas that on the bottom right has $n = 0$. From these results, we infer that, for a choice $\alpha = 1$, the probability for a single immediate adjacent reentry has value $p_1 = 0/(5 + 9 + 9 + 9) = 0$. The accuracy of our determination of that probability of course improves at larger α. Large α values, however, also lead to a dramatic increase in the number of chain configurations to be

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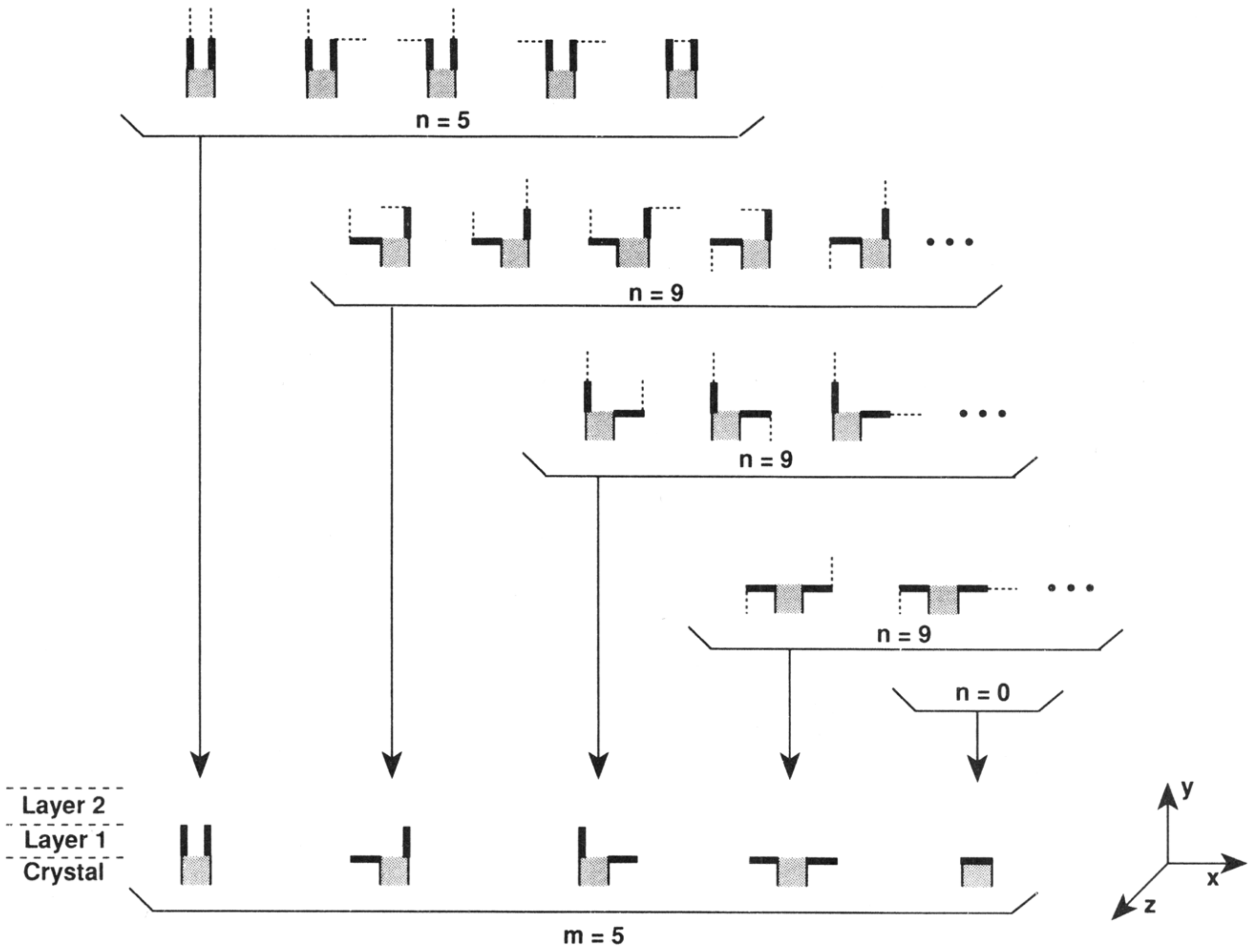

Figure 1. Model setup for a crystal/amorphous interphase. The crystal phase is represented by a bundle of $L_x = 2$ chain segments oriented along the *y*-axis. The amorphous phase is described through a series of layers one lattice unit thick and parallel to the crystal surface. Bottom: ensemble of $m = 5$ possible conformations in layer 1. Middle and top: ensemble of *n* possible continuations of chains of length $\alpha = 1$.

generated. As an example, for a two-dimensional periodic crystal with $L_x = 9$ chains, we have counted $m = 76$ conformations in layer 1. The number of configurations of chains of length α that can be grown from these *m* conformations roughly increases as m^α so that, for a typical length $\alpha = 5$, ensembles of up to 2×10^9 configurations need to be generated!

Results and Discussion

Chain Conformations in Layer 1. Figure 2 shows the effect of chain length α on the convergence of our values for the probability of immediate chain reentry at the interphase. The figure is for a two-dimensional periodic lattice with $L_x = 9$. The results are for the probabilities p_0, p_1, p_2, and p_3 having respectively 0, 1, 2, and 3 adjacent reentry loops in the first layer of the amorphous phase; see Figure 1a. Figure 2 clearly reveals convergence of our results for α values as low as 5. Similar conclusions have been reached for three-dimensional systems.

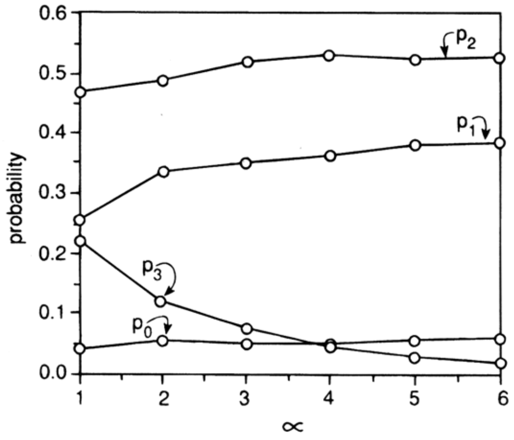

Figure 2. Effect of the chain length α on the probabilities p_0, p_1, p_2, and p_3 of having 0, 1, 2, and 3 adjacent reentry loops in the first layer of the amorphous phase; see Figure 1. The calculations are for a two-dimensional periodic crystal with $L_x = 9$.

Figures 3 and 4 show the dependence of the loop probabilities *p* on size L_x and L_x and L_z for two- and three-dimensional periodic lattices, respectively. From the location of the maxima in these curves, we easily infer that there is approximately one loop for every five chains exiting the crystal surface. Our model therefore predicts a ~40% immediate adjacent reentry in the limit of infinitely wide crystals, in agreement with Flory's result.[16] We note that our value is much smaller than the 70% prediction of refs 17 and 20. Further investigation of our model results also reveals no additional loops in the subsequent layers 2 and 3.

All the results of Figures 2–4 are for periodic lattices, i.e., for infinitely thick crystals. We now turn to a study of the importance of finite crystal size. Figure 5 shows the dependence of the loop probabilities *p* on crystal size L_x for two-dimensional lattices with free boundaries. Comparing with Figure 3, we observe that the only

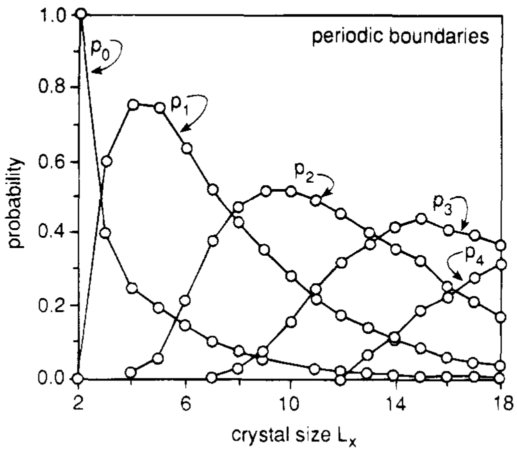

Figure 3. Dependence of the loop probabilities p on size L_x for two-dimensional periodic crystals. The results are for $\alpha = 3$.

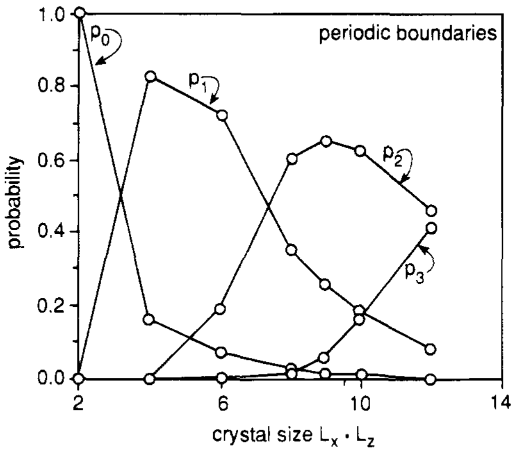

Figure 4. Dependence of the loop probabilities p on size $L_x \times L_z$ for three-dimensional periodic crystals. The results are for $\alpha = 3$.

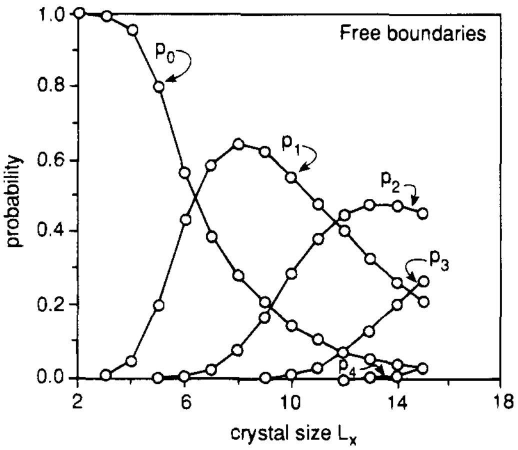

Figure 5. Dependence of the loop probabilities p on size L_x for two-dimensional crystals with free boundaries. The results are for $\alpha = 3$.

effect of finite crystal size is to delay the onset of adjacent reentry loop formation; i.e., $p_1 \sim 0$ for all $L_x < 4$. The absence of any folding for $L_x < 4$ is due to the fact that, for small crystals, the spatial constraints at the interphase are readily dissipated by dispersing the chains in directions transverse to the crystal axis.[21] At higher $L_x > 4$, our results of Figure 5 again indicate a ~40% immediate adjacent reentry in the first layer, in agreement with our previous findings for infinitely thick crystals (see Figure 3).

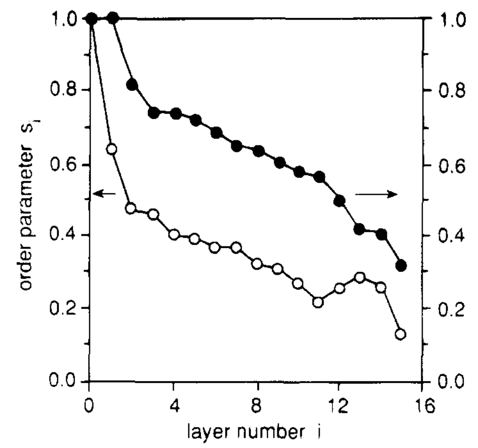

Figure 6. Variation of the order parameter s (eq 1) and density in consecutive interfacial layers. The results are for a two-dimensional periodic crystal with $L_x = 12$. The results denote average values over 150 chain configurations in the interfacial region. The figure is for $\alpha = 3$.

Chain Conformations in Subsequent Layers. We now turn to a detailed study of the chain conformations away from the interphase, i.e., in the subsequent layers 2, 3, etc. This has been obtained as follows. We start by generating the possible conformations in layer 1, and their weights are estimated from the ensemble of possible continuations of chains of length $\alpha = 3$. A random number is then generated, and one conformation in layer 1 is selected according to its weight. Starting from that conformation, we generate all possible conformations in layer 2. Their weights are estimated and used to select the conformation within layer 2. And so on and so forth. We note that our procedure is, in effect, similar to the scanning method of Meirovitch.[23]

Our results are presented in Figure 6 for a two-dimensional periodic crystal with $L_x = 12$. Within each layer i, we define an order parameter s_i through[16]

$$s_i = 1 - 2q_i \qquad (1)$$

in which q_i denotes the average fraction of horizontal chain segments per lattice site between layers $i - 1$ and i. Clearly, for a disordered chain in two dimensions, $q_i = 0.5$ so that $s_i = 0$ for all i. The figure clearly indicates a sharp drop in the order parameter, s, within the first layer $i = 1$. This can be attributed to the 40% immediate adjacent rentry discussed in connection with Figure 3. Our observations are again in agreement with those of ref 16. In contrast to all previous theories, however, Figure 6 also indicates a slow decrease in s through the subsequent layers $i = 2, 3$, etc. Taking a unit lattice length of 1 nm, our results in Figure 6 predict an interphase thickness of the order of 10 nm. Such a rather high value indicates that these ordered interfacial layers cannot be neglected, and as previously anticipated, they could play an important role in the mechanical properties of carbon-reinforced elastomers[8] and semicrystalline biopolymers.[11] Also represented in Figure 6 are our model predictions for the decrease in density away from the crystal surface. It should be noted that, in more realistic simulations involving several crystals, our density values are expected to be higher as some of the lattice voids are likely to be filled with chains emanating from other crystals.

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