correspond to l_g^*, which, except for small deviations resulting from the contribution of the cilia to $\bar{\sigma}_e$, will be a smoothly varying function of ΔT (heavy dashed line in Figure 1, lower diagram). If, on the other hand, isothermal thickening takes place subsequent to the establishment of the initial lamellar thickness l_g^*, as is apt to happen at high crystallization temperatures, the observed lamellar thickness will appear to drop in stepwise fashion as $l_0/2 \rightarrow l_0/3$ at ΔT^*_2, etc., with increasing ΔT (dotted lines in Figure 1, lower diagram).

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Freezing/Melting Transition of Polymer Chains on the Diamond Lattice

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ABSTRACT: A Monte Carlo simulation of polymer chains with gauche/trans energy differences was carried out on the diamond lattice. The Flory mean-field lattice theory predicts a first-order phase transition for such a system. However there has been recent speculation that this could be an artifact of the mean-field approximation. In the present calculation the lattice was fully occupied and Mansfield's method for generating allowed moves via bond breaking/reformation was utilized. It was found that a freezing/melting transition does take place. It appears to be clearly first order. The melting point and the conformational composition of the disordered state are in good accord with the predictions of the mean-field lattice theory (in the Huggins occupational probability approximation).

Lattice calculations have long formed a convenient basis for assessing the statistical properties of polymer chains. One of the more interesting applications was a treatment by Flory[1] of conformationally "stiff" chains (e.g., chains possessing conformational energy differences). With the use of a random approximation for site occupational probabilities, it was found that the partition function factors into a term arising from packing on the lattice and a conformational term identical with that of a free chain. It was demonstrated that this model exhibits a first-order melting/freezing transition. This arises because in the lattice representation of the disordered state, the conformation free energy (which increases with decreasing temperature), can no longer offset the positive free energy of packing. The total free energy becomes positive and thus the zero free energy ordered crystalline state becomes more stable. The model, when generalized to include the second-order conformational energy effects, has been used to discuss the role of polymer conformational structure on the thermodynamics of melting.[2,3]

Recently the model has been the subject of renewed interest. New statistical mechanical arguments have been advanced that have led to questioning the existence of such a transition.[4-6] These arguments and the model in general have recently been discussed by Nagle et al.[7] The case for the prediction of a first-order transition has been reiterated by Flory.[8] Monte Carlo simulations have contributed to clarifying the situation. Baumgaertner and Yoon[9] carried out a simulation on the plane square lattice and found a first-order transition. The quantitative results were not in particularly good agreement with the model predictions, and it has been commented[10] that the results (presumably due to finite system size effects) do not satisfy known bounds. Later Yoon and Baumgaertner reported a simulation on the cubic lattice[11] that showed a transition and gave better agreement with the mean-field model predictions.

The Monte Carlo lattice simulations use periodic boundary conditions with a number of elementary unit cells of the lattice filling a super unit cell or "box". The chains to be simulated are placed in the box and the latter is replicated to approximate an infinite system. In the above simulations,[9,11] Baumgaertner and Yoon used reptation as the move and this was allowed by the presence of a small number of vacant lattice sites. The chain lengths chosen were nearly the linear size of the box. Baumgaertner[12] has reported simulations on both the plane square and cubic lattices where the chain size was much smaller that the box size. Here it was found that at low temperature the system orders into domains of parallel extended chains whose boundaries are defined by surfaces composed of chain ends. The orientation of chain direction from domain to domain was disordered. In other words, the system became polycrystalline with crystallite thickness determined by chain length. However, the chain-ordering process was gradual with decreasing temperature; no transition was found. The disordering due to multiple orientations of the domains apparently was sufficient to prevent it. Since there is no energy penalty associated with surface formation it is apparent that domains whose orientations are disordered can easily have lower free energy than a completely ordered system. However, it seems equally apparent that as the chain size is allowed to increase the contribution of the domain-directional disordering to the free energy on a per bead basis would become small compared to that from the internal chain conformations. The transition would reappear in a really large simulation (presently impractical) of long chains and with box size even much larger and in which the bulk free en-

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ergy within domains would dominate over the interfacial effects. The Baumgaertner and Yoon simulations did not result in domain formation because it is obviously not possible in systems where the chain length is comparable to or larger than the box length.

It is apparent, then, that there are two kinds of low-temperature degeneracy to be considered. One of these is inherently associated with long-chain molecules on a lattice and with the arguments above for and against the adequacy of the mean-field model. The other is associated with degeneracy occasioned by chain ends. In the present work we report results that bear only on the first question, the presence of a transition in systems in which disordering due to domain formation or polycrystallinity resulting from finite chain size is not permitted. The simulation differs from the one carried out by Yoon and Baumgaertner[11] in two significant ways. First, it is done on the diamond lattice. Here the chains can adopt trans/gauche conformations more characteristic of actual polymers (although the packing is still highly unrealistic with respect to intermolecular distances). Second, quite different move rules are used. Finally, as further motivation in studying the diamond lattice, it is worth observing that in their discussion of lattice models, Nagle et al.[7] conjectured that the fully occupied diamond lattice treated here (their "XOD" model) would be the most likely model to show a transition similar to those predicted by mean-field calculations.

Calculational Procedure

It has proven to be quite difficult to simulate polymer chain configurational behavior in dense systems. Ensuring availability of sufficient allowed moves is a severe problem. A way to accomplish this was proposed by Mansfield,[13] who utilized bond breaking and re-forming as a way to generate moves. The bond rearrangements were of two types. One was attack of a free end on a chain segment. The other was bond "flips" that interchanged the connectivity of pairs of parallel bonds. It was emphasized that the bond rearrangements do not represent real physical processes but rather a means of generating moves in a manner that maintains ergodicity. These moves were implemented on the simple cubic lattice in a study of the dependence of root-mean-square end-to-end distance on chain length. No conformational energy differences for different step directions were included.

In the present work it is of course essential to the problem to include conformational energy differences. As stated, in order to provide the realism of the conformations being identifiable as trans and gauche, the calculation was implemented on the diamond lattice. The bond flip moves utilized by Mansfield are not appropriate on the diamond lattice as there are no parallel neighbor bonds. Thus the calculation utilized end atom attacks only. Moves that generated cyclic molecules or chains shorter than six units were prohibited. The system used was made up of a box containing $6 \times 6 \times 6$ diamond unit cells and therefore $8 \times 6^3 = 1728$ units. This box was subject to periodic boundary conditions. At the start of a calculation the chains were loaded on the lattice in the planar zigzag all-trans conformation (in the $\langle 110 \rangle$ direction). Then 8 bond breaks or molecules (16 ends) were generated at random. This leads to a number-average chain length of 216. Then end attack trials proceeded by selecting an end and a neighboring group at random. At this point a check was made to see that the new chains were long enough (at least six units). If the attack satisfied the Metropolis rules[14] (i.e., unconditionally accepted if the energy change was negative but accepted with probability $P = \exp(-\Delta E/k_BT)$ if the energy change, ΔE, was positive), it was temporarily accepted. Then a check was made to see if a cycle was being formed. An otherwise acceptable move was rejected if the latter were the case. The ratio of successful moves to total trials was $\sim {}^1/_2$ at the higher temperatures studied and decreased to $\sim {}^1/_5$ at the lower ones.

The above requirements were accomplished in the following manner. The address of a lattice site can be specified by dividing the sides of the box containing the 6^3 unit cells into 4×6 units. A single integer IJK ($= i \times L^2 + j \times L + k + 1$; where L is the length of a side or 24) records the i, j, k address of a site. A doubly subscripted array $\mathbf{N}(IJK, m)$ ($m = 1, 4$) records the addresses of the four neighbors of the site IJK. Two singly subscripted arrays $\mathbf{N}_1(IJK)$, $N_2(IJK)$ contain the values of the integer m, in $\boldsymbol{N}(IJK, m)$ of the two bonded neighbors of IJK. An array, $\mathbf{N}_e(n)$ records the addresses of the $n = 1, 16$ chain ends. When a possible attack was generated, the changes in the bond vectors at the attack site could be assessed with these arrays and the conformational energy change computed. A list of the complete connectivity of an entire chain was not kept as moves were made. However, a chain can be traced out (a list of addresses of connected beads generated) by starting out at the end of a chain by means of $\mathbf{N}_e$ and using the local connectivity arrays $\mathbf{N}_1$ and $\mathbf{N}_2$ to locate via $\mathbf{N}(IJK, m)$ the neighbors of each succeeding bead in a connected sequence. This procedure was used to check for sufficient chain length and lack of cyclization during each attempted move.

For a calculation at a given temperature, 10^6 moves were attempted (except at the two highest ones, where 3×10^5 sufficed). Each calculation was divided into two equal periods. One was an equilibration period, where no sampling was done, and following this a sampling portion was undertaken, where the system was sampled after every 1000 attempted moves. In part of the calculations where ordering was found the system was first disordered by means of 50×10^3 attempted moves at high temperature before starting the equilibration period at the calculation temperature. This was done to see if the results at low temperature depended on whether the system started from a disordered or ordered state. At the number of attempts used, no hysteresis was observed and true equilibrium appeared to be reached.

Two descriptors of the system state were accumulated during sampling. One was simply the fraction of trans bonds and the other was an order parameter that reflected the directionality of the chains.[9,11] The latter was defined as follows. At each lattice site there are two bond vectors. A given bond vector may point in one of four directions. In a random system there will be equal number of these four directions. In a completely ordered all-trans system only two of the directions will be populated. During sampling, the total numbers of each bond vector direction ($n_d(i)$, $i = 1, 4$) over all the lattice sites were computed (a total of $2N$ vectors, two per site). The order parameter, $\mathbf{O}_p$, defined as

$$\mathbf{O}_p = [\textstyle\sum_{i=1,4}(n_d(i) - N/2)^2/4(N/2)^2]^{1/2} \qquad (1)$$

(where N is the total number of lattice sites) was then calculated. The parameter varies between 0 for a completely disordered system and one for a completely ordered one. In addition to the above parameters, the dispersion of the molecular weight (M_w/M_n) was calculated during sampling. Because of the finite system size fluctuations were noticeable. However, the average ratio was in agreement with the expected value of slightly less than 2.

A comment concerning a characteristic of the calculation is appropriate here. Under the move rules enunciated

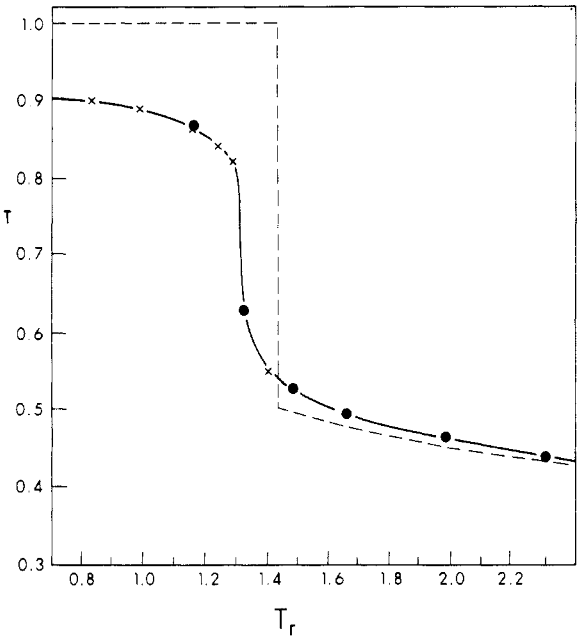

Figure 1. The fraction of trans bonds calculated by the simulation vs. reduced temperature. The filled points are for runs that were first disordered by 50 × 10^3 attempted moves at 500 K. The points marked by crosses were started from an ordered state at the temperature of the run. The dashed curve is the prediction of the Flory mean-field lattice theory (but using the Huggins occupational probability).

above, the longest all-trans sequence possible is equal to the longest all-trans sequence that will fit *inside the box* (this is in the ⟨110⟩ direction and in our case is 24 bonds). Under periodic boundary conditions, an all-trans sequence longer than the box is infinitely long. Since the move rules preserve the number of molecules (via a constant number of ends), an infinite molecule (which has no ends) cannot be formed.

Results and Discussion

The average number of trans bonds as a function of reduced temperature, $T_r = k_B T/\Delta\epsilon$ (where $\Delta\epsilon$ is the gauche/trans energy difference) is shown in Figure 1. The order parameter, O_p, is simlarly displayed in Figure 2. It is evident that a transition to an ordered nearly all-trans state takes place. Although not completely sharp it does without doubt appear to be a first-order transition. The slight diffuseness is no doubt related to the maximum all-trans sequence (24 bonds) allowed and to the polydisperse nature of the molecular length distribution inherent in the method. Some tendency for hysteresis was noted, but it declined with increasing number of moves and was not clearly discernible at the number used in the calculations shown.

To discuss the relationship to the predictions of the mean-field lattice theory we note that the free energy (per bond) of a lattice of chains possessing bond conformation energies written in terms of the Huggins occupational probability[15] rather than the random approximation of the original mean-field theory[1] is according to eq 5a of Starkweather and Boyd[2]

$$\Delta A = -k_B T[(z/2 - 1) \ln (1 - 2/z) + \ln \lambda] \tag{2}$$

where λ is the largest eigenvalue of the second-order statistical weight matrix and z is the lattice coordination number ($z = 4$ for the diamond lattice). In the model treated here with only first-order conformational energies accounted for $\lambda = 1 + 2\,g$, where $g = \exp(-\Delta\epsilon/k_B T)$ and $\Delta\epsilon$ is the gauche/trans energy difference. The transition

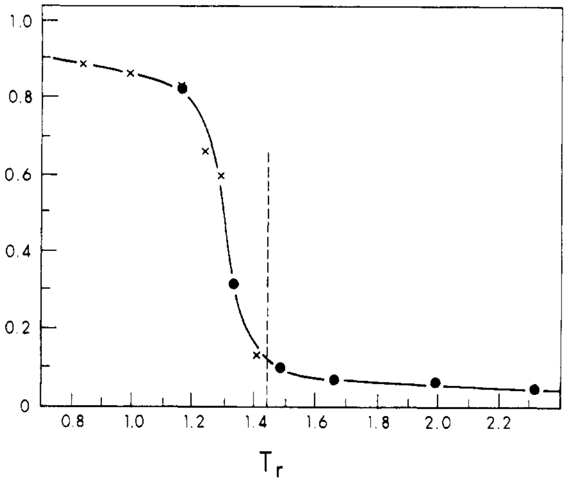

Figure 2. The directional order parameter (see text for definition) vs. reduced temperature. Same runs as in Figure 1.

is located by $\Delta A = 0$ or $\lambda^* = 2$ for $z = 4$, and hence $g^* = {}^1/_2$. The reduced transition temperature is thus $T_r^* = 1/\ln 2 = 1.443$. The fraction of gauche bonds may be found (Starkweather and Boyd, eq 8) from

$$F_g = \mathrm{d} \ln \lambda/\mathrm{d} \ln g \tag{3}$$

as $F_g = 2g/(1 + 2g)$, the obvious free chain result for the first-order bond conformation model. The fraction of trans bonds $F_T = 1 - F_g$ from the model is also shown on Figure 1. It is apparent that the model is in good agreement with the simulation with respect to both the location of the transitiona nd the conformational composition in the disordered state. The mean-field approximation predicts the fraction of trans bonds on the disordered lattice to be the same as for free phantom chains. This appears to be largely verified by the simulation. There does seem to be some tendency for the fraction of trans bonds to be slightly smaller in the disordered state in advance of the transition than the mean-field model predicts. This same tendency was apparent in the cubic lattice simulation of Yoon and Baumgaertner.[11]

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