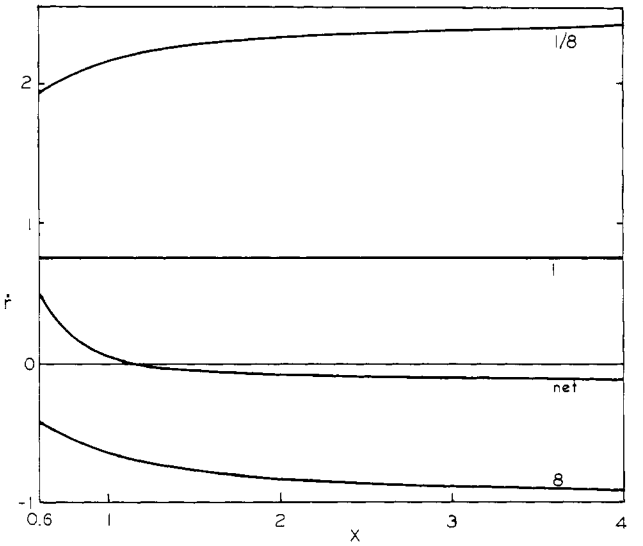

Figure 2. Magnitude of $\dot{r}$ as a function of the distance x between the beads in the equatorial plane, $\theta = \pi/2$. Same parameters as Figure 1. Magnitudes of flow are given relative to the sedimentation rate of the dumbbell without hydrodynamic interaction, $g(m_1 + m_2)/(\rho_1 + \rho_2)$. The curve marked "net" is the net flow rate, the sum of all components, from eq 16; this is independent of the mass ratio. For comparison are shown the curves marked with mass ratios m_2/m_1; these are the flow rates that would occur if only the hydrodynamic terms, the terms in eq 6 that are explicitly multiplied by g, were considered with no spring-force term and no diffusion terms.

that the hydrodynamic component is largely, but in general not completely, canceled by the diffusion terms in the total. The rigid-body approximation, of course, amounts to assuming that the diffusion terms always exactly cancel the hydrodynamic terms, except for steady rotations, which latter do not appear in the present model. Thus the rigid-body approximation appears to be a reasonable, but not perfect, approximation to the truth.

The major potential application of the rigid-body approximation is to long-chain molecules with many interacting segments. These have usually been treated by preaveraging the hydrodynamic interactions. In contrast to preaveraging, the rigid-body approximation has the advantage of setting a definite bound to the viscosity number[9] and apparently to the sedimentatation and diffusion coefficients as well. Moreover, we have found in the case of asymmetric dumbbells with a variety of size ratios that the rigid model gives results that are at least as good as the preaveraged ones. It is interesting that the diagonal approximation, which is actually a simplified version of the rigid-body approximation, gives the best results of all the approximate methods for the dumbbells. However, it must still be recognized that a dumbbell is not an accurate model of a long chain, so more work needs to be done before the situation is clear for such chains.

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Rotational Isomeric Modeling of a Polyethylene-like Polymer between Two Plates: Connection to "Gambler's Ruin" Problem

Charles M. Guttman* and Edmund A. DiMarzio

National Measurement Laboratory, National Bureau of Standards, Washington, D.C. 20234. *Received August 28, 1981*

ABSTRACT: A Monte Carlo simulation of a polyethylene-like polymer chain between two plates has been performed. This continuum treatment augments previous analytical lattice treatments of completely flexible chains between plates. The Monte Carlo results show that the simple concept of statistical length appropriate to unconfined bulk polymer is also appropriate to chain portions residing in the amorphous regions of lamellar semicrystalline polymer. Thus, the "gambler's ruin" method, with the statistical length of the polymer used as the fundamental step length, is a valid method to obtain quantitative estimates of quantities such as length of loops, length of ties, and fraction of loops or ties for moderately stiff polymers. Previous estimates of the amount of chain folding in polyethylene are thus shown to retain their validity for the more realistic isomeric state model.

I. Introduction

Two papers have recently been published in which analytical models for the properties for a homopolymer in the amorphous phase of a lamellar semicrystalline polymer were developed based on the mathematics of the "gambler's ruin" problem of mathematical statistics.[1,2] The conclusion of these works was that gambler's ruin methods correctly model the amorphous region of lamellar semicrystalline polymers. A capsule summary of the physics of these papers is as follows: Experimental evidence suggests that there is little difference between the chain in a melt and the chain in the amorphous phase between lamellae of a semicrystalline polymer.[3] This similarity has been used by Yoon and Flory[4] and by Guttman et al.[5,6] in model calculations of semicrystalline bulk polymers for comparison with SANS data on these polymers. In all the previous modeling and in this work, it is necessary to estimate the properties of an average single chain in the bulk. To this end, we have argued that at equilibrium the time-average spatial density due to an individual chain is a constant.[1] Then the ergodic theorem allows us to conclude that the ensemble-average spatial density due to an individual chain is a constant. The optimum mean field treatment of the amorphous lamella is therefore one in which the average properties of resulting individual polymer chain density is a constant. The absorption boundary condition *with renewal* gives exactly these properties.[1,2] (A chain randomly walks in the amorphous region until it touches the interface, at which point it threads its way into the crystal. This corresponds to the random walk with absorption at the boundary. After forming stems, the chain again emerges into an amorphous lamella. This corresponds to renewal.)

However, in these earlier theoretical works a discrete lattice model for the chain in the amorphous phase was used, and the chains were modeled as perfectly flexible. Although many meaningful physical quantities could be estimated from that discussion, applicability to real polymers was contingent on the validity of the following two implicit assumptions: (1) Formulas derived for a lattice model are valid also for continuum. (2) The bond lengths for the perfectly flexible model correspond to the statistical length of a real polymer even in the presence of the two surfaces. This paper serves to justify these assumptions.

In this paper, the Monte Carlo modeling of a "real chain" between two absorbing boundaries is performed. A continuum rather than lattice treatment is used. Properties of the chains are obtained as a function of thickness of the amorphous phase, l_a, bond length of the chain, b, and characteristic ratio, C_N, for a polyethylene-like backbone chain. From this Monte Carlo study we shall study three different aspects of this problem.

First, we show that the replacement of the statistical step with real chain models leads to the kind of scaling of statistical units predicted in our earlier paper. This will lead us to the conclusion that the general functional form of the various properties describing the amorphous phase in a lamellar structure predicted earlier is correctly measured using the normal definition of the statistical length for a chain in solution even though the polymer is confined between two plates. The two above assumptions are thereby justified; see section IV.

Second, we study the effect of the rotational isomeric modeling (with its emphasis on local structure effects, on the calculation of duration of a run, the average loop size, etc.) on aspects of properties of the real chain near a surface. Our treatment shows little variation in quantitites such as the duration of the run as one changes the starting position (relative to the surface). The use of a statistical step thus is not sensitively dependent on the coupling of chain structure to surface properties; see section V.

Finally, we use this Monte Carlo model to calculate the properties of a switchboard model for a "real chain" model of polyethylene. We find that, as in previous models, we are forced to introduce substantial chain folding in order to avoid a density excess in the amorphous phase.

II. Calculation of the Properties of Polymer Chains in the Amorphous Phase by Gambler's Ruin Methods

As noted earlier we assume in this work that a chain in the amorphous phase of a semicrystalline polymer obeys the same statistics as a chain in the melt. Furthermore, following the ideas of Flory[7] and the experimental evidence of Cotton et al.,[8] we assume the chain in the melt is closely represented by the model of a chain in solution at the Θ point. Thus, we assume our chain obeys the rotational isomeric model of a chain in solution. This is the same model for an amorphous chain in a semicrystalline matrix used by Yoon and Flory[4] and Guttman et al.[5,6] to compare with SANS data.

The model of that portion of the chain that resides in the amorphous phase of a homogeneous semicrystalline polymer is then as follows. The polymer chain emerges from the crystal and then wanders, obeying random walk statistics (or in the case described in the next section "real chain" statistics) until it crosses either of the two planes defining the parallel faces of the amorphous phase. It was shown in earlier papers[1,2] that this model of a chain in an amorphous phase is described by the same mathematics that describes the gambler's ruin problem with renewal. In the remainder of this section we use the concept of statistical step in conjunction with the equations from our earlier paper to obtain equations for the properties of the amorphous phase in terms of the properties of the rotational isomeric chain. In the next section we use the results of a Monte Carlo calculation of these properties to check the relationships obtained here.

In our earlier papers[1,2] it was shown that one could obtain the average number of steps in the walk for each exit from the crystal. This quantity is called the duration of a run, D'. For a cubic lattice in three dimensions we found

$$D' \doteq 3M + 1 \tag{2.1}$$

where D' is the number of statistical steps in the walk and $M + 1$ is the thickness of the amorphous phase in statistical steps. We define the statistical step size on a cubic lattice as b' and the number of statistical steps in the walk on that lattice as N'. Then the end-to-end distance of a chain on that lattice is

$$\langle R^2 \rangle = N'(b')^2 \tag{2.2a}$$

For a "real chain" we have

$$\langle R^2 \rangle = NC_N b^2 \tag{2.2b}$$

where for the "real chain" N is the number of monomers, b is the bond distance, and C_N is the so-called characteristic ratio. One also assumes, as is usual, the stretched lengths of the lattice chain and the real chain are identical. Thus

$$Nb = N'b' \tag{2.3}$$

Thus one can identify the statistical step size, b', and the number of statistical steps, N', as

$$b' = C_N b \tag{2.4a}$$

$$N' = N/C_N \tag{2.4b}$$

The thickness of the amorphous phase in the gambler's ruin problem is $M + 1$ in statistical steps. For a semicrystalline polymer system let us call the amorphous phase thickness l_a. Thus

$$b'(M + 1) = l_a \tag{2.5a}$$

and

$$M + 1 = l_a/C_N b \tag{2.5b}$$

We obtain for D', the duration in statistical steps,

$$D' = 3(l_a/C_N b) - 2 \tag{2.6}$$

But D' is in statistical steps. Thus for D in real monomers we have

$$D' = D/C_N$$

or we obtain

$$D = \frac{3l_a}{b} - 2C_N \tag{2.7}$$

Other quantitites may be derived by using the same arguments. For example, the probability of a tie, P_T, and loop, P_L, is given in statistical units as

$$P_T = 1/(M + 1)$$

$$P_L = M/(M + 1) \tag{2.8}$$

Thus one has from eq 2.5b

$$P_T = C_N b/l_a \tag{2.9}$$

Now the average number of steps in a loop, $\langle L\rangle'$, in statistical steps is given by

$$\langle L\rangle' = 2M + 2 \tag{2.10}$$

By eq 2.5b we obtain

$$\langle L\rangle' = 2l_a/C_N b \tag{2.11}$$

or in true steps the average loop size $\langle L\rangle$ is

$$\langle L\rangle = C_N\langle L\rangle'$$

$$\langle L\rangle = 2l_a/b \tag{2.12}$$

Finally, for the average number of steps in a bridge we obtain in statistical steps $\langle B\rangle'$

$$\langle B\rangle' = (M + 1)^2 - 1 = (l_a/C_N b)^2 - 1 \tag{2.13}$$

Thus the bridge in numbers of monomers, $\langle B\rangle$, is

$$\langle B\rangle = C_N\langle B\rangle'$$

$$\langle B\rangle = (l_a/b)^2/C_N - C_N \tag{2.14}$$

Before we compare these results with the Monte Carlo result, we note that some of these equations are dependent on the regions close to the amorphous–crystal interface. The parts of equations dependent on l_a only should be independent of effects near the interface. Since we anticipate surface effects will cause us some problems, we separate out those parts of eq 2.7 to 2.14 which depend on l_a. These shall be referred to with a subscript B, bulk. Thus, we have

$$D_B = 3l_a/b \tag{2.15a}$$

$$\langle L\rangle_B = 2l_a/b \tag{2.15b}$$

$$\langle B\rangle_B = (l_a/b)^2/C_N \tag{2.15c}$$

$$P_{TB} = C_N b/l_a \tag{2.15d}$$

III. Monte Carlo Calculations

Monte Carlo calculations were made to obtain the properties of the so-called rotational isomeric models of polymer chains in the amorphous phase of a semicrystalline polymer. The model here is similar to other models of chains in the amorphous state. The model is stochastic, with the local structure of the chain included, but long-range self-exclusion in the chain is not included nor is any form of chain exclusion or interaction with other chains included. Programs similar to the one described here have been used to calculate the small-angle neutron scattering of single chains in semicrystalline polyethylene.[5,6]

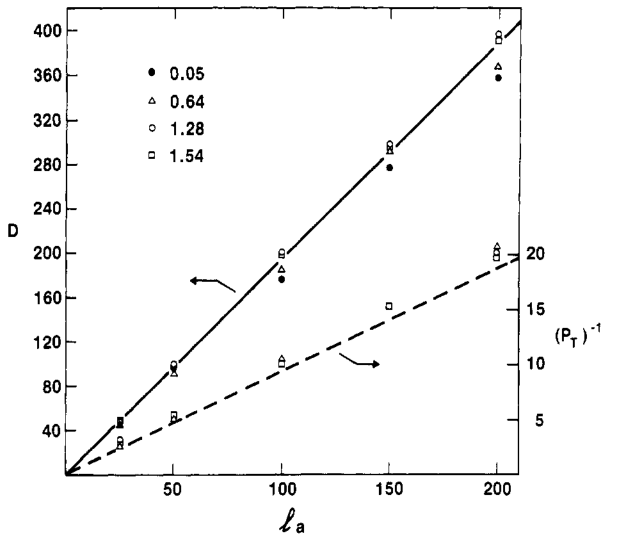

Figure 1. Duration of a run in the amorphous phase of PE, D, vs. l_a, the amorphous phase thickness, and inverse of the probability of a tie P_T^{-1} vs. l_a. Lines are theoretical lines predicted by eq 2.15. Points are from Monte Carlo calculations. Different points at the same l_a refer to differing starting positions in the amorphous phase. See text for discussion.

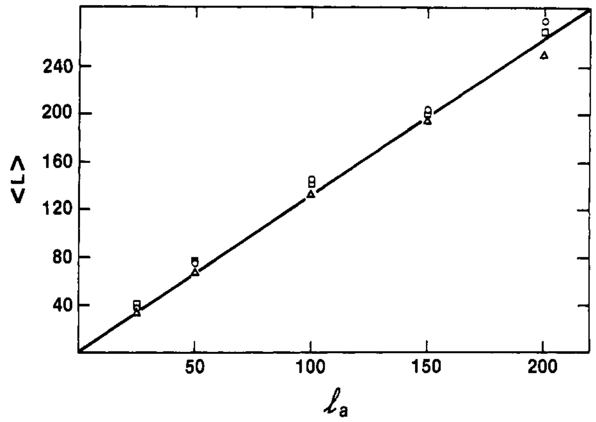

Figure 2. Average loop length, $\langle L\rangle$, vs. l_a for a polyethylene-like chain. Line is predicted by eq 2.15c. Points are from Monte Carlo calculations. See Figure 1 for meaning of points.

Two parallel walls are set up in the computer a distance l_a Å apart. A chain is started at various distances from the lower wall, making its first step always toward the upper wall. Each step is then made following Flory real chain statistics. For the normal case of polyethylene with $C_N = 6.88$ we used $\sigma = 0.54$ and $\delta = 0.088$. Other σ's and δ's were used for other values of C_N. The bond distance was given as b. (For normal PE this is taken as 1.54 Å but b was allowed to vary here to obtain effects of bond length variations.) When the chain touched the lower wall, it was stopped and its duration was recorded as was the fact that it was a loop. Chains that reached the upper wall were, of course, tie molecules. Upon touching either wall, the processes were restarted again.

Calculated results for the average duration, D, the average loop length, $\langle L\rangle$, the average tie length, $\langle B\rangle$, and the probability of a tie are given in Figures 1–5 and are discussed in the next section.

In order to estimate errors in Monte Carlo averages, calculations were made in groups of 500 starts. Ten groups of 500 were averaged together and the standard deviation

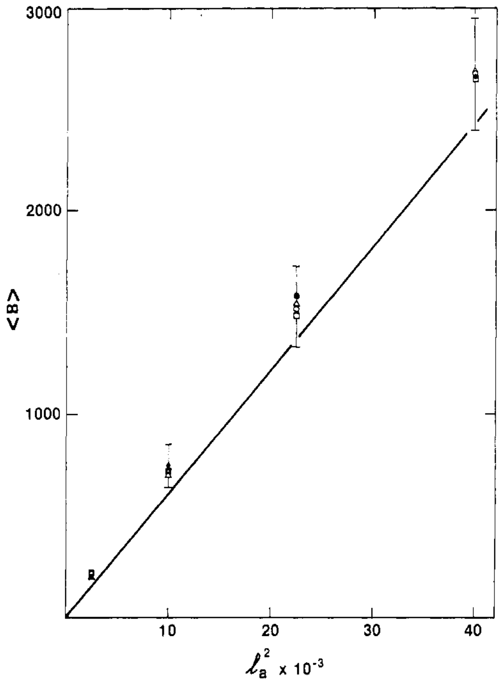

Figure 3. Average bridge length, $\langle B \rangle$, vs. l_a^2 for polyethylene-like chain. Line is predicted by eq 2.15d. Points are from Monte Carlo calculations. See Figure 1 for meaning of points.

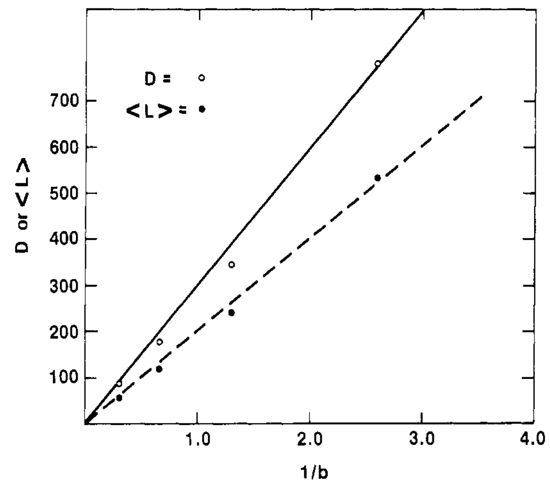

Figure 4. D and $\langle L \rangle$ vs. inverse bond distance. Solid line is eq 2.15a; dashed line is eq 2.15b. Points are Monte Carlo calculations for starting position at 0.68 Å.

and the mean were determined.

In order to see if the standard deviation obtained from these rotational isomeric state models was reasonable, runs were made for six-choice cubic lattices for the same number of chains, and the error estimates were obtained. For lattices of ten statistical steps or larger, the coefficient of variation from the runs on the cubic lattices was the same as those obtained from the rotational isomeric state models, which was 7–14%.

IV. Essential Correctness of Scaling by Statistical Steps

In Figures 1–3 the Monte Carlo results for the duration D, the loop length $\langle L \rangle$, the tie length $\langle B \rangle$, and the probability of a tie, P_T, are presented as a function of l_a, the thickness of the amorphous phase. These results are presented for polyethylene-type chains with $C_N = 6.88$. The lines are theoretical lines for the bulk values based on eq 2.15a–d. As an inspection of the figures shows, there is generally good agreement between asymptotic theory using normal concepts of statistical steps and the Monte Carlo experiment.

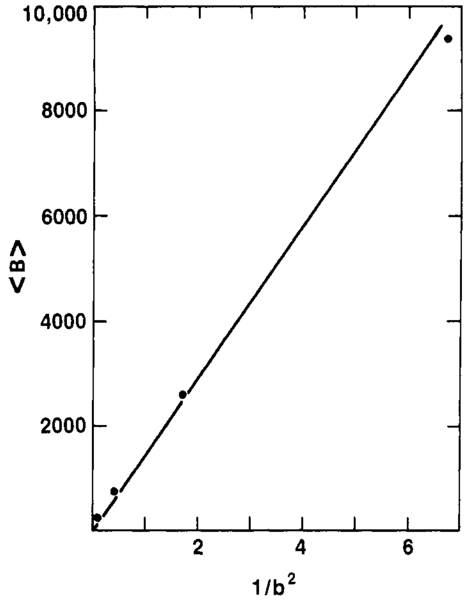

Figure 5. $\langle B \rangle$ vs. inverse squared bond distance. Line is eq 2.15c. Points are Monte Carlo calculations for starting positions at 0.68 Å.

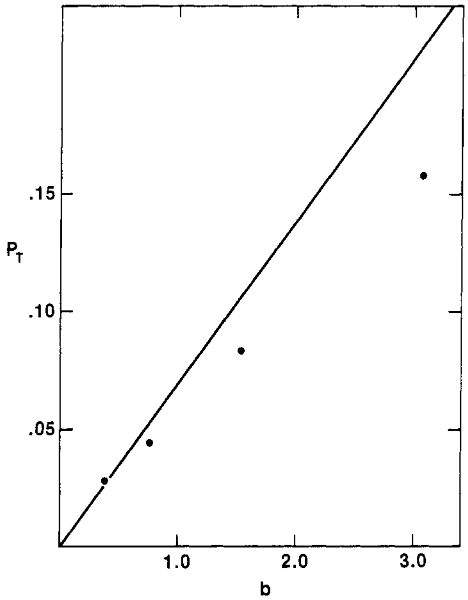

Figure 6. Probability of a tie vs. b. Points are Monte Carlo calculations. Line is eq 2.15d. Deviation of points from line is discussed in section V.

The various points on Figures 1–4 are for values of properties with different starting positions of the first segment. As is seen from the figures, various choices of starting positions do change the value of the properties by, at most, 10%. This small variation of properties of the quantities near the surface is discussed in the next section. Here we need to note that the general functional form for l_a is certainly held to except for minor surface effects, suggesting that the scaling in statistical steps is correct.

In Figures 4–6 the variation with b, the bond distance, is presented as well as the theoretical curves. Again the agreement is excellent except for minor surface effects.

The only significant deviation from theory is seen in Figure 6. Here for large b we see fairly large deviations for the theoretical line. This deviation is the result of the slow approach of the characteristic ratio toward its asymptotic value. This phenomenon is difficult to observe in the other quantitites calculated. It is discussed in the next section.

V. Effect of Local Structure near the Interface

As noted earlier in this paper, the rotational isomeric state model has a variety of inadequacies in relation to its use as a description for a bulk polymer. These shortcomings are most serious when the chains are relatively close to a wall. In this section two of these problems are treated in the context of the rotational isomeric state model itself.

Here we shall not try to rectify any inadequacies of the rotational isomeric model near a surface. Rather we only investigate two of these possible effects and show they do not significantly affect our general overall conclusion.

First we look at the effect of varying the starting position of the first bead of the chain on properties like the duration. Figures 1–3 depict values of various properties such as the duration and the $\langle L \rangle$ and $\langle B \rangle$ for various starting positions. The starting positions tried were as follows: (1) 0.05 Å away from surface—very close to the interface but not on it; (2) 1.54 Å away from surface—a single-bond distance—this is in some respects similar to our starting on a cubic lattice at one step away from surface; (3) 1.28 Å away from surface—here we assumed the first step was a trans step with the chain axis normal to the plane interface; (4) 0.64 Å away from surface—here we try to take into account that, when the last segment is absorbed, all or even a small part of this segment counts as being absorbed. Thus, the first segment should be half of one trans step away from the surface to compensate for this.

As seen in Figures 1–3, all the different starting positions gave the correct functional form with only small corrections for the effect of surfaces. Although we may not have the surface statistics correct, there are only minor contributions to the properties we are interested in due to this inadequacy. Thus, this inadequacy does not affect our general conclusion.

This variation with starting position may be thought to arise from two possible effects. First, there is a measure of uncertainty for the duration or $\langle L \rangle$ for short loops since it is difficult to judge when the off-lattice walk has returned to the wall (the chain seldom returns in an integer number of steps to the wall). This effect should only affect loops or ties by, at most, one or two steps and should not be significant.

Second, an inspection of eq A6 of ref 2, $D_Z = 3Z(M - Z)$, suggests that properties such as the duration might have a strong dependence on starting position Z. If this were so, then whether we start from 0.05 or 1.54 Å from the wall should have an effect on D_Z of a factor of 30 or so. Certainly we do not see an effect of this magnitude. This is due to the fact that the Z in D_Z is only interpretable in full statistical steps. Thus any variation in partial statistical steps will, as we see, have only minor effects.

A second problem relates to the slow approach of the characteristic ratio of the chain between two close absorbing walls to its asymptotic value. An inspection of Figures 1 and 3 show that P_T^{-1} and $\langle B \rangle$ both agree with the theoretical line obtained from eq 15 within the measured statistical error. However, all the Monte Carlo data fall above the line given by eq 2.15. These quantities are strongly dependent on C_N while D and $\langle L \rangle$ are largely independent of C_N. In fact we may use P_T^{-1} and $\langle B \rangle$ to estimate C_N using eq 2.15c and 2.15d:

$$C_N = (l_a/b)^2/\langle B \rangle \quad (5.1)$$

$$C_N = l_a P_T/b \quad (5.2)$$

The C_N so computed are given plotted in Figure 7. Clearly, as l_a increases, one approaches the asymptotic free chain C_N values of 6.88. A slow approach to the asymptotic value of C_N was noted by Flory[9] for modeling rotational isomeric chains in solution. In the case described by Flory the asymptote was reached in 200 or so monomers. Our approach to the asymptote seems to be much slower. For example, for l_a of 100 Å we estimate our C_N to be 6.0. But an l_a of 100 Å yields an average bridge, $\langle B \rangle$, of 700 monomers.

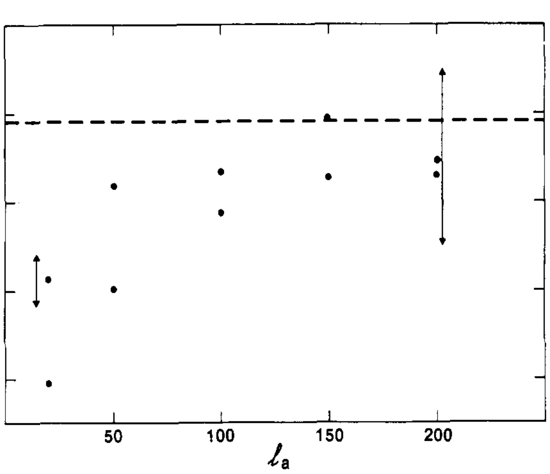

Figure 7. Characteristic ratio computed from eq 5.1 and 5.4 as a function of thickness of amorphous phase. This shows the slow approach to asymptotic C_N of 6.88 discussed in section V.

This slow approach to asymptotic C_N explains the deviation in Figure 6 from the line given by eq 2.15d. For fixed l_a as one increases the bond distance one goes to smaller thicknesses in statistical steps; thus as b increases, one deviates more drastically from the asymptotic value. For example, for l_a = 100 Å and b = 3.08 Å the characteristic ratio is the saame as for l_a = 50 Å and b = 1.54 Å. From Figure 7 this would be a C_N of 5–6. The C_N calculated with eq 2.15d from the point at b = 3.08 Å is 5.1.

The problem of stiff chains (more correctly, semiflexible chains) near a surface has been treated by a number of authors. An early approximate treatment was given by Hoeve, DiMarzio, and Peyser.[10] DiMarzio and Rubin have formally solved the problem in the context of a semiflexible polymer between two plates.[11] An advantage of their method is that energies for the chain stepping straight ahead, back on itself, or sideways can each be assigned arbitrarily. Also the method is easily generalized to include the effects of stiffness energies that are functions of the relative orientations of triplets of successive bonds rather than just pairs of contiguous bonds. Hoeve[12], Birshtein, Zhulina, and Skvortsov,[13] and Birshtein[14] have solved the problem of the adsorption of a semiflexible polymer on a plane surface when the stiffness energy is a function of contiguous pairs of bonds. Their treatments give explicit formulas for the effect of chain stiffness on the location of the critical adsorption energy. Finally, a recent paper by Mattice and Napper studies the effects of a simple plane surface on the shape of polyethylene chain modeled by a Monte Carlo treatment and the isomeric state model.[15]

The treatments of ref 10–12 are all lattice model treatments and are not directly applicable to our continuum Monte Carlo treatment. Nevertheless, our numerical results show that at the critical transition energy the statistics of semiflexible chains are identical with those of competely flexible chains whose fundamental step length is chosen to be the statistical length of the semiflexible chain. We presume this to be true for the discrete as well as the continuum model. For other than critical transition energies we will have a strong coupling of the shape of the (absorbed part of) chain to the energetics of the surface.

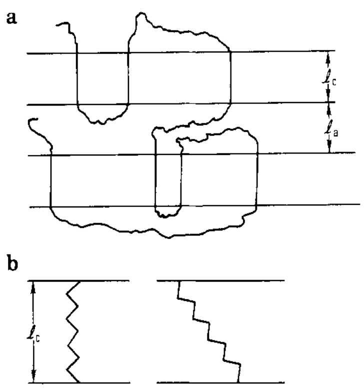

Figure 8. (a) Switchboard model of a single chain in a lamellar system of crystal and amorphous phases. (b) Normal zigzag of polyethylene and a tilted zigzag.

VI. Modeling of Polyethylene Amorphous Phase for a Switchboard Model of a Semicrystalline Polymer

In this section we estimate properties of the switchboard model of a polymer in a semicrystalline matrix for a polyethylene-like chain. The purpose is to obtain in detail the properties of such a model for one specific polymer. The picture of the switchboard model for the amorphous phase of a semicrystalline polymer is, at best, confused. In his 1962 paper, Flory[16] suggested that all chains leaving the crystal surface were behaving as if they were in a genuine amorphous phase. However, he required that 50% of the chains return to the surface that they left "with fairly short loops in the interface". More recently, two other views of the switchboard region have been proposed by Yoon and Flory.[3,4] In one of these views each chain leaving the crystal surface behaves always as a random walker. In the second the chain is a random walker but encounters two semireflecting barriers which are introduced into the amorphous phase. Since the original Flory[16] model gives no detailed model for those chains which return to the original lamellae and since the Yoon and Flory[3,4] model with semireflecting barriers has been shown to yield an unphysical density profile, we choose to model the completely random walk model of the amorphous phase—which we hereafter refer to as the switchboard model.

In what follows, we assume an amorphous phase thickness of 25, 50, and 100 Å since these are in the range of expected amorphous thicknesses in semicrystalline polyethylene.[17] The calculations are made on individual chains obeying, as discussed before, the rotational isomeric state for polyethylene. In the calculation we assume, as is discussed earlier, that the chain in the amorphous phase of a semicrystalline material is describable by the same statistics one uses to describe a chain in the melt and/or a chain in a Θ solvent. As we noted in a earlier section, chains starting at 0.68 Å from the surface seem to be the physically most real situation. Thus all our chains for this calculation will be started at this distance.

All calculations for any amorphous run are made in terms of the quantity per exit from the crystal. To obtain absolute values for these quantities we need to study similar quantities per entrance into the crystal. We now consider these.

For a switchboard model adjacent reentry is minimal.[3,4] There is one exit from the crystal per crystal stem. This is shown in Figure 8a. Thus r_c, the number of segments in a run in a crystal of thickness l_c, is given by

$$r_c = l_c/(1.28\cos\theta) \tag{6.1}$$

where 1.28 is the projection of the zigzag bond distance on the axis normal to the lamellae surface (the length of that normal from surface to surface is l_c) and θ is the angle of tilt of the axis of the zigzag chain to the normal. Chains with $\theta = 0°$ and $\theta = 30°$ are shown in Figure 8b.

Table I[a]

l_a, Å	duration	$\rho_a(\theta = 0°)$, g/cm³	$\rho_a(\theta = 34°)$, g/cm³	$\theta°$, deg
25	52.6	2.69	2.23	71.6
50	108.6	2.79	2.30	72.2
100	205.0	2.62	2.18	71.1
asymptotic value		2.49	2.10	70.0

[a] ρ_a = 0.85 g/cm³ (normally estimated for amorphous PE). ρ_c = 1.0 g/cm³ (normal value given for crystalline PE).

In an earlier paper[1] we derived a relationship between the run length in the amorphous phase, r_a, the run length in the crystal phase, r_c, thicknesses of the phases, l_a and l_c, and the densities of the phases. This relationship was based on crystallinity arguments and yielded

$$\frac{l_a\rho_a}{l_c\rho_c} = \frac{r_a}{r_c} \tag{6.2}$$

where ρ_i is the density of the ith phase. Thus we may obtain the density of the amorphous phase for this model as

$$\rho_a = \left(\frac{r_a}{l_a}\right)\rho_c\left(\frac{l_c}{r_c}\right) \tag{6.3}$$

We may rewrite this equation so that the angle of tilt of the crystal stem is left explicit:

$$\rho_a = \frac{r_a}{l_a}\rho_c 1.28\cos\theta \tag{6.4}$$

In Table I we give values for the duration of a run in the amorphous phase for thicknesses of 25, 50, and 100 Å as well as the asymptotic value from a calculation from eq 2.15a. The density of the amorphous phase of the switchboard model is calculated assuming the density of the crystalline state ρ_c is 1.0 g/cm³. Calculations are made for tilts of $\theta = 0°$ and for $\theta = 34°$, the maximum commonly reported tilt for linear polyethylene.[18] Also reported is the value of $\theta°$, the angle necessary to give a density of the amorphous phase of 0.85 g/cm³,[19] the value usually assigned to amorphous polyethylene.

As is seen from Table I all normally observed tilts give densities of the amorphous phase of polyethylene well over 2 g/cm³. On the other hand, one needs very high tilt angles (ca. 74°) to avoid density problems. Because one never observes such high densities in the amorphous phase or such large tilt angles in the crystalline phase, the random switchboard model for polyethylene yields physically unreal results. We repeat here our earlier observation that the insertion of tight chain folds readily alleviates the serious density paradox inherent in the random switchboard model. The density problem is removed in the case of no tilt if two-thirds of the stems are involved in the formation of tight folds.

VII. Conclusions

We have shown that scaling, using concepts of statistical length, leads to essentially correct estimates of quantities such as duration, loop size, and bridge size for "real chain" models of polymers in the melt in Θ solvent between two absorbing walls. Contributions from the surface, which are thought to be taken into account incorrectly by this model, are shown to be small. We have calculated the properties of a switchboard model of a polyethylene chain and shown that it leads to a density of 2.4 g/cm^3 for the amorphous phase for chains with no tilt or, conversely, that a tilt of 70° to the normal is required in order to achieve the density that is normally accepted for the polyethylene amorphous phase. Neither such densities nor such tilts have ever been observed in linear polyethylene under normal crystallization conditions. This calculation shows the unphysical character of the switchboard model. The density excess can be eliminated by chain folding within the crystal.

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Volume Dependence of the Elastic Equation of State. 3. Bulk-Cured Poly(dimethylsiloxane)

R. W. Brotzman and B. E. Eichinger*

Department of Chemistry, University of Washington, Seattle, Washington 98195.
Received November 2, 1981

ABSTRACT: Vapor sorption measurements for bulk-cured poly(dimethylsiloxane) + cyclohexane and benzene are reported. The Flory–Huggins interaction parameter χ for the cyclohexane system is found to agree, within experimental error, with our previously reported data for this system. For the benzene system, χ is, within experimental error, identical with the results of Shih and Flory. Differential solvent vapor sorption by cross-linked and un-cross-linked PDMS is reported, and the elastic component of the solvent chemical potential is investigated as a function of the degree of dilation for both systems. Comparisons are made between the bulk- and solution-cured PDMS + cyclohexane systems. Results are found to be in quantitative agreement with the current form of Flory's elasticity theory. However, the data demonstrate that the mixing and elastic free energies are not strictly separable.

Introduction

In a previous paper[1] we presented swelling data for a solution-cured poly(dimethylsiloxane) (PDMS) sample with cyclohexane and demonstrated that the elastic component of the solvent chemical potential was qualitatively encompassed by Flory's recent theory[2,3] of elasticity. We concluded that the Flory–Rehner assumption[4,5] of separability of the elastic and mixing free energies in a swollen polymer network was less questionable than had been deduced from earlier work.[6,7] Here we report data for bulk-cured PDMS + cyclohexane and benzene, in which the same PDMS elastomer was used in both runs. Comparisons are also made between the bulk-cured and solution-cured PDMS when swollen with cyclohexane.

According to the theory elaborated by Flory and coworkers,[2,3,8] the elastic contribution to the solvent chemical potential, $\mu_{1,\mathrm{el}}$, is given by

$$\lambda\mu_{1,\mathrm{el}}/V_1 = f(\lambda^2) \qquad (1)$$

where $\lambda = (V/V^0)^{1/3}$ is the extension ratio and V_1 the solvent molar volume. If the Flory–Rehner[4] assumption of separability is combined with the James–Guth[4] theory, $f(\lambda^2)$ = const, but if instead the Wall–Flory[5] elastic equation of state is used, $f(\lambda^2)$ is a monotonically increasing function of λ^2. According to the elasticity theory one adopts, $f(\lambda^2)$ departs from constancy to the extent that the chosen theory departs from the James–Guth isotherm, but for any case the Flory–Rehner assumption gives $f(\lambda^2)$ independent of the nature of the diluent. The purpose of the experiments described here is to test the validity of eq 1 and attendant assumptions.

Flory's recent contributions to elasticity theory have evolved to give ever better agreement with experiment,[2,3,8] both for stress–strain isotherms and for the swelling experiments discussed here. The current form of the theory is briefly reviewed, and its relation to experimental results is discussed.

Experimental Section

The PDMS used for this study was kindly supplied by Professor J. E. Mark. The cross-linked sample had been cured in bulk by irradiation with 4.03 Mrd of γ radiation from a ^{60}Co source. Equilibrium swelling in benzene at 30 °C occurred at 0.242 polymer volume fraction, while in cyclohexane at 25 °C it was at 0.156 polymer volume fraction.[9] The un-cross-linked PDMS

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