Diamond Lattice Model of Semicrystalline Polyethylene in the Amorphous Region

Zhong-Hui Duan and Louis N. Howard*

Department of Mathematics
Florida State University
Tallahassee, Florida 32306

Abstract

The statistics of polyethylene chains in the amorphous region between two crystallites have been computed, modeling the chains as random walks on a diamond lattice with two absorbing boundaries. The probabilities of *trans* and *gauche* states are considered, thereby determining some effects of temperature, e.g. at higher temperature more loops are formed and the average length of loops is shorter, in contrast to less ties formed with longer average length. It is also found that the lower bound on the adjacent reentry is 49% at very high temperature and it increases to 55% at about 400K, assuming the interface normal to the crystalline chains in the crystal.

Introduction

Random walks on a cubic lattice have been extensively used as models of the chain molecules in the amorphous region of semicrystalline polyethylene, both for the analytical investigation of some statistical properties and as a basis for computational simulation studies. [1-6] As Flory and Yoon remarked, [7] the geometry in the amorphous region is probably approximately the same as that which existed previously in the melt, with the chains forming random coils, although the angle between adjacent carbon-carbon bonds is usually restricted to a small neighborhood of the tetrahedral angle. Because of this, the 'step' of the random walk on the cubic lattice cannot be interpreted as a C-C bond; it is generally regarded as corresponding to three or four such bonds, the idea being that because of the possibility of rotation about bonds, even though the angle between adjacent bonds is always about 109°, after 3 or 4 bonds the direction of the chain can be almost arbitrary. Actually with just 4 carbon atoms we may regard the first three as defining a plane and the 'rotational state' may then be described by the rotation of the fourth

* corresponding author

about the middle bond, out of this plane. But this rotation is not entirely free — there is an energy minimum with the fourth atom in the plane of the other three, forming a planar zig-zag, and two subsidiary minima with rotations about 120°, to either side, these latter minima being roughly 500 cal/mol higher than the absolute minimum. If the maxima between these minima provide a sufficient energy barrier, then one may expect the molecule to remain in one of these minimum basins for a long time; it is rather as if there were just 3 rotational states, corresponding to the three minima. These are the planar zig-zag or *trans* state and the two enantiomorphs $gauche^{+}$ and $gauche^{-}$.

To the extent that this 3-state picture is acceptable, we may describe the spatial configuration of the polyethylene chain as determined by a sequence of rotational states. In the model to be investigated here, we take this idealization quite literally, and suppose that the carbon chain in the amorphous region has bonds all of the same length, all adjacent pairs meeting at the tetrahedral angle, and all adjacent triplets of bonds exactly in the ideal *trans*, $gauche^{+}$, or $gauche^{-}$ states — planar zig-zag or with a rotation from this, about the middle bond, of exactly 120°. Such a chain can readily be seen to lie on the lattice on which every vertex is tetrahedrally surrounded by its four neighbors — the lattice of the diamond (also silicon) crystal. We shall model the chains in the amorphous region of semicrystalline polyethylene by random walks on the diamond lattice. Unlike the cubic lattice model, here the unit step of the lattice *is* interpreted as a carbon-carbon bond. We shall also restrict the random walks by certain probabilistic considerations. When a row of 5 carbon atoms of the chain is considered, we may expect 6 distinguishable *rotational isomers,* tt, tg^{+}, tg^{-}, $g^{+}g^{+}$, $g^{-}g^{-}$, $g^{+}g^{-}$, where t stands for *trans* and $g^{+/-}$ for $gauche^{+/-}$. Energies of these isomers are affected not only by the first order intrachain interactions associated with 4 carbon segments, but also by second order ones involving interactions between two CH_2 groups separated by four C-C bonds. In the melt, where disorder prevails, it was argued in [7] that the intrachain interactions represent average effects and interchain effects can be ignored. We suppose this true also of the amorphous region, which is regarded as a sort of fossil melt.

The energy of a tg^{+} or tg^{-} pair relative to tt is known to be $E_\sigma = 430-590 \text{cal mol}^{-1}$, the energy of a $g^{+}g^{+}$ or $g^{-}g^{-}$ pair relative to $g^{+}t$ to be the same as E_σ and the energy of a $g^{+}g^{-}$ or $g^{-}g^{+}$ pair relative to $g^{+}g^{+}$ to be $E_\omega = 1700-2000 \text{cal mol}^{-1}$.[8-9] Let u_{ij} be the statistical weight to assign a bond k to a rotational state j (one of the three minima) with its two preceding bonds $k-1$ and $k-2$, given the bond $k-1$ being in the state i with its two preceding bonds $k-2$ and $k-3$. The statistical weight matrix for the kth bond ($k \geq 4$) has the form [8-9]

$$U = (u_{ij}) = \begin{pmatrix} 1 & \sigma & \sigma \\ 1 & \sigma & \sigma\omega \\ 1 & \sigma\omega & \sigma \end{pmatrix} \tag{1}$$

with rows and columns indexed in the order of states t, g^+ and g^-, where $\sigma = e^{-\frac{E_\sigma}{RT}}$ and $\omega = e^{-\frac{E_\omega}{RT}}$ are functions of temperature.

The physical meaning of this temperature is unfortunately not entirely clear; it is presumably a temperature at which the chains were in thermal equilibrium, e. g. the temperature of the melt if we would be concerned with the statistical weights (or associated probabilities) of different chain configurations in the melt. Perhaps this is the appropriate "temperature" for the chains in the amorphous region in a polymer that has been crystallized by rapid quenching from the melt to a fairly low temperature. The appropriate interpretaion for a polymer crystallized slowly at a temperature not too much below the melting point might instead be the crystallization temperature. We shall give results for a range of temperatures; for the most part the results do not vary much over what seems to be a reasonable range of temperatures.

Diamond Lattice Model

We consider a diamond lattice with two parallel absorbing boundaries in a rectangular coordinate system. The lattice angles of 109.47° resemble the bond angles in polyethylene chains. The lattice bonds (resembling carbon-to-carbon bonds) of unit length fall into the vector set $\mathbf{B} = \{\mathbf{b}_1, \mathbf{b}_2, \mathbf{b}_3, \mathbf{b}_4, \mathbf{b}_5, \mathbf{b}_6, \mathbf{b}_7, \mathbf{b}_8\}$, where

$$\mathbf{b}_1 = (0, \sqrt{\tfrac{1}{3}}, \sqrt{\tfrac{2}{3}}),\ \mathbf{b}_2 = (0, \sqrt{\tfrac{1}{3}}, -\sqrt{\tfrac{2}{3}}),\ \mathbf{b}_3 = (0, -\sqrt{\tfrac{1}{3}}, \sqrt{\tfrac{2}{3}}),\ \mathbf{b}_4 = (0, -\sqrt{\tfrac{1}{3}}, -\sqrt{\tfrac{2}{3}}),$$
$$\mathbf{b}_5 = (\sqrt{\tfrac{2}{3}}, \sqrt{\tfrac{1}{3}}, 0),\ \mathbf{b}_6 = (\sqrt{\tfrac{2}{3}}, -\sqrt{\tfrac{1}{3}}, 0),\ \mathbf{b}_7 = (-\sqrt{\tfrac{2}{3}}, \sqrt{\tfrac{1}{3}}, 0),\ \mathbf{b}_8 = (-\sqrt{\tfrac{2}{3}}, -\sqrt{\tfrac{1}{3}}, 0),$$

but not all the sequences of the vectors are on the lattice. In particular, it can be shown that a bond vector $\mathbf{a}$ may be followed by another vector $\mathbf{b}$ if and only if $\mathbf{a} \cdot \mathbf{b} = 1/3$. The two parallel absorbing boundary planes at $z = 0$ and $z = M \cdot \sqrt{\frac{2}{3}}$ resemble the two adjacent crystalline lamellae M bonds apart (reasonable values for M is between 25 and 140, since the thickness of the amorphous region is between 30Å- 180Å[10] and the length of C-C bonds is about 1.54Å).

We now consider a random walk initiated at the site $(0, 0, 0)$ on the diamond lattice with each step resembling one carbon-to-carbon bond. The first step of the walk takes either $\mathbf{b}_1$ or $\mathbf{b}_3$ with equal probabilities to step into the amorphous region. We assume that it forms a *trans* with its two preceding bonds inside the crystal (i.e. assume that the interface is normal to the crystalline chains in the crystal). The walk is continued on the lattice with certain transition probability of proceeding to one of the adjacent lattice points until it reaches $z = 0$, where a *loop* is formed, or $z = M \cdot \sqrt{\frac{2}{3}}$, where a *tie* is formed. Along its way, a sequence of *trans*, *gauche*$^+$ and *gauche*$^-$ is formed. As no two carbon atoms can occupy the same site, no reverse step in the random walk is allowed. It can be shown that two vectors $\mathbf{a}$ and $\mathbf{b}$ form a *trans* if the succeeding vector is $\mathbf{a}$, or they form a *gauche*$^+$ or a *gauche*$^-$ with a succeeding vector

$$\frac{1}{2}(\mathbf{b}-\mathbf{a}) - \frac{\sqrt{3}}{2}\mathbf{b}\times\mathbf{a} \qquad \text{or} \qquad \frac{1}{2}(\mathbf{b}-\mathbf{a}) + \frac{\sqrt{3}}{2}\mathbf{b}\times\mathbf{a},$$

respectively. Therefore, the random walks described in this model have three step memory. Table I shows all the possible vector representations of a rotational state in a random walk. The transition probability t_{ij} from a rotational state i to a state j in one step can be obtained directly by normalizing the statistical weight matrix, Eq. (1). Hence the transition matrix for the kth step of the random walk has the form

$$T_k = (t_{ij})_k = (u_{ij}/\sum_i u_{ij})_k = \begin{pmatrix} \frac{1}{1+2\sigma} & \frac{\sigma}{1+2\sigma} & \frac{\sigma}{1+2\sigma} \\ \frac{1}{1+\sigma+\sigma\omega} & \frac{\sigma}{1+\sigma+\sigma\omega} & \frac{\sigma\omega}{1+\sigma+\sigma\omega} \\ \frac{1}{1+\sigma+\sigma\omega} & \frac{\sigma\omega}{1+\sigma+\sigma\omega} & \frac{\sigma}{1+\sigma+\sigma\omega} \end{pmatrix} \tag{2}$$

with rows and columns indexed in the order of states t, g^+ and g^-.

A Mathematical Simplification

Eq. (2) gives the conditional probabilities for t, g^+ and g^- to occur given the preceding state being t (first row), g^+ (second row) or g^- (third row). For mathematical simplicity, we wish to consider random walks with only two step memory. We shall ask what the probability of the occurrence of each rotational state is, rather than considering all the conditional probabilities. Now let p_t, p_+ and p_- be the probabilities of the rotational states *trans*, *gauche*$^+$ and *gauche*$^-$ to occur, respectively. Using the total probability formula and the notation of Eq. (2) we have,

$$\begin{cases} p_t + p_+ + p_- = 1, \\ p_t = P(t|t)p_t + P(t|g^+)p_+ + P(t|g^-)p_- = t_{tt}p_t + t_{g^+t}p_+ + t_{g^-t}p_-, \\ p_+ = t_{tg^+}p_t + t_{g^+g^+}p_+ + t_{g^-g^+}p_-, \\ p_- = t_{tg^-}p_t + t_{g^+g^-}p_+ + t_{g^-g^-}p_-. \end{cases}$$

Solving the above linear system gives

$$\left.\begin{aligned} p_t &= \frac{1+2\sigma}{1+4\sigma+2\sigma^2+2\sigma^2\omega}, \\ p_+ &= p_- = \frac{1-p_t}{2}, \end{aligned}\right\} \tag{3}$$

in which both the first and the second order intrachain interactions have been included.

Statistics of the Random Walks

We can now consider random walks with only two step memory on a diamond lattice with two parallel absorbing boundaries. We are ready to formulate them mathematically. As we shall see, the walks are actually homogeneous Markov chains of order 3. For simplicity, we first rescale the coordinate system by multiplying the x, y, and z coordinates of the vectors in the vector set **B** by $\sqrt{\frac{3}{2}}$, $\sqrt{3}$ and $\sqrt{\frac{3}{2}}$, respectively (the basic vectors of this new coordinate system are orthogonal, but not normalized). We thus have a new vector set **A** such that

$$\mathbf{a}_1 = (0,1,1),\ \mathbf{a}_2 = (0,1,-1),\ \mathbf{a}_3 = (0,-1,1),\ \mathbf{a}_4 = (0,-1,-1),$$
$$\mathbf{a}_5 = (1,1,0),\ \mathbf{a}_6 = (1,-1,0),\ \mathbf{a}_7 = (-1,1,0),\ \mathbf{a}_8 = (-1,-1,0).$$

The random walks will now take the vector step in **A** and terminate at $z = 0$ or $z = M$. Consider a state space $\{X_n, n \geq 0\}$ which is formed by all the possible positions of the restricted random walk. We define a process whose value Y_n at time n is given by the ordered triplet of states (X_{n+2}, X_{n+1}, X_n), where X_n is the position of a random walk after n steps. It is easy to show that $\{Y_n, n \geq 0\}$ is a Markov chain, though $\{X_n, n \geq 0\}$ is not. The transition probabilities are (for $n \geq 1$):

$$P\{Y_n = (X,Y,Z)|Y_{n-1} = (A,B,C)\}$$
$$= \begin{cases} p_t & \text{if}\quad Y = A,\ Z = B,\ \text{and } X,\ A,\ B,\ \text{and } C \text{ forms a } \textit{trans}, \\ p_+ & \text{if}\quad Y = A,\ Z = B,\ \text{and } X,\ A,\ B,\ \text{and } C \text{ forms a } \textit{gauche}^+, \\ p_- & \text{if}\quad Y = A,\ Z = B,\ \text{and } X,\ A,\ B,\ \text{and } C \text{ forms a } \textit{gauche}^-, \\ 0 & \quad \text{otherwise.} \end{cases} \tag{4}$$

The Fractions of Loops and Ties. Let $f\{Y_n = (X,Y,Z)|Y_0 = (A,B,C)\}$ stand for the probability that in a process $\{Y_n\}$ starting from (A,B,C), the first entry to (X,Y,Z) occurs at time n. That is, for $n \geq 1$ and $1 \leq j \leq n-1$,

$$f\{Y_n = (X,Y,Z)|Y_0 = (A,B,C)\} = \\ P\{Y_n = (X,Y,Z); Y_j \neq (X,Y,Z)|Y_0 = (A,B,C)\}.$$

Hence the probability that, starting from (A,B,C), the process will ever pass through (X,Y,Z) may be written as

$$\sum_{n=1}^{\infty} f\{Y_n = (X,Y,Z)|Y_0 = (A,B,C)\}.$$

And the fraction of loops and the fraction of ties may be written as

$$\sum_{n=1}^{\infty} f\Big\{Y_n \in \{(X,Y,Z)|X \in \mathcal{N}^2 \times \{0\}, Y \in \mathcal{N}^3, Z \in \mathcal{N}^3\} \\ |Y_0 = ((0,0,1),(0,-1,0),(0,0,-1))\Big\}$$

and

$$\sum_{n=1}^{\infty} f\Big\{Y_n \in \{(X,Y,Z)|X \in \mathcal{N}^2 \times \{M\}, Y \in \mathcal{N}^3, Z \in \mathcal{N}^3\} \\ |Y_0 = ((0,0,1),(0,-1,0),(0,0,-1))\Big\}$$

respectively. Where $\mathcal{N}$ denotes the set of nonnegative integers. By the properties of homogeneous Markov chain and conditional probability, we must have (for $n \geq 2$ and $2 \leq j \leq n-1$)

$$\begin{aligned}
&f\{Y_n = (X,Y,Z)|Y_0 = (A,B,C)\} = \\
&\quad P\{Y_n = (X,Y,Z); Y_j \neq (X,Y,Z); Y_1 \neq (X,Y,Z)|Y_0 = (A,B,C)\} = \\
&\quad P\{Y_n = (X,Y,Z); Y_j \neq (X,Y,Z)|Y_1 \neq (X,Y,Z); Y_0 = (A,B,C)\}\cdot \\
&\qquad\qquad P\{Y_1 \neq (X,Y,Z)|Y_0 = (A,B,C)\} = \\
&\quad P\{Y_n = (X,Y,Z); Y_j \neq (X,Y,Z)|Y_1 \neq (X,Y,Z)\}\cdot \\
&\qquad\qquad P\{Y_1 \neq (X,Y,Z)|Y_0 = (A,B,C)\} = \\
&\quad f\{Y_n = (X,Y,Z)|Y_1 \neq (X,Y,Z)\}P\{Y_1 \neq (X,Y,Z)|Y_0 = (A,B,C)\}.
\end{aligned} \tag{5}$$

For $n = 1$, we have

$$f\{Y_n = (X,Y,Z)|Y_0 = (A,B,C)\} = P\{Y_1 = (X,Y,Z)|Y_0 = (A,B,C)\}. \tag{6}$$

We now simplify our notation by letting

$$P_k(0|\mathbf{a}_i\mathbf{a}_j) = \sum_{n=1}^{\infty} f\Big\{Y_n \in \big\{(X,Y,Z)|X \in \mathcal{N}^2 \times \{0\}, Y \in \mathcal{N}^3, Z \in \mathcal{N}^3\big\} \\ |Y_0 \in \big\{(A,B,C)|A \in \mathcal{N}^2 \times \{k\}, B = A - \mathbf{a}_i, C = A - \mathbf{a}_i - \mathbf{a}_j\big\}\Big\}$$

and

$$P_k(M|\mathbf{a}_i\mathbf{a}_j) = \sum_{n=1}^{\infty} f\Big\{Y_n \in \big\{(X,Y,Z)|X \in \mathcal{N}^2 \times \{M\}, Y \in \mathcal{N}^3, Z \in \mathcal{N}^3\big\} \\ |Y_0 \in \big\{(A,B,C)|A \in \mathcal{N}^2 \times \{k\}, B = A - \mathbf{a}_i, C = A - \mathbf{a}_i - \mathbf{a}_j\big\}\Big\}.$$

We interpret $P_k(a|\mathbf{a}_i\mathbf{a}_j)$ as the probability for a walk to terminate at $z = a$ ($a = 0$ or M) given that it starts at $z = k$ $(0 < k < M)$ with two preceding steps $\mathbf{a}_i$ and $\mathbf{a}_j$ (where $\mathbf{a}_j$ occurs before $\mathbf{a}_i$). Since each step has three possible succeeding steps, by Table I and Eqs. (4-6) we have (for $1 < k < M-1$)

$$
\begin{aligned}
P_k(0|\mathbf{a}_1\mathbf{a}_3) = \sum_{n=1}^{\infty} f\Big\{ & Y_n \in \{(X,Y,Z)|X \in \mathcal{N}^2 \times \{0\}, Y \in \mathcal{N}^3, Z \in \mathcal{N}^3\} \\
& |Y_0 \in \{(A,B,C)|A \in \mathcal{N}^2 \times \{k\}, B = A - \mathbf{a}_1, C = A - \mathbf{a}_1 - \mathbf{a}_3\}\Big\} \\
= \sum_{n=2}^{\infty} f\Big\{ & Y_n \in \{(X,Y,Z)|X \in \mathcal{N}^2 \times \{0\}, Y \in \mathcal{N}^3, Z \in \mathcal{N}^3\} \\
& |Y_1 \notin \{(X,Y,Z)|X \in \mathcal{N}^2 \times \{0\}, Y \in \mathcal{N}^3, Z \in \mathcal{N}^3\}\Big\} \cdot \\
P\Big\{ & Y_1 \notin \{(X,Y,Z)|X \in \mathcal{N}^2 \times \{0\}, Y \in \mathcal{N}^3, Z \in \mathcal{N}^3\} \\
& |Y_0 \in \{(A,B,C)|A \in \mathcal{N}^2 \times \{k\}, B = A - \mathbf{a}_1, C = A - \mathbf{a}_1 - \mathbf{a}_3\}\Big\} \\
+ P(& Y_1 \in \{(X,Y,Z)|X \in \mathcal{N}^2 \times \{0\}, Y \in \mathcal{N}^3, Z \in \mathcal{N}^3\} \\
& |Y_0 \in \{(A,B,C)|A \in \mathcal{N}^2 \times \{k\}, B = A - \mathbf{a}_1, C = A - \mathbf{a}_1 - \mathbf{a}_3\}) \\
= \sum_{n=2}^{\infty} f\Big\{ & Y_n \in \{(X,Y,Z)|X \in \mathcal{N}^2 \times \{0\}, Y \in \mathcal{N}^3, Z \in \mathcal{N}^3\} \\
& |Y_1 = (A + \mathbf{a}_3, A, A - \mathbf{a}_1)\Big\} \cdot P\Big\{Y_1 = (A + \mathbf{a}_3, A, A - \mathbf{a}_1) \\
& |Y_0 \in \{(A,B,C)|A \in \mathcal{N}^2 \times \{k\}, B = A - \mathbf{a}_1, C = A - \mathbf{a}_1 - \mathbf{a}_3\}\Big\} \\
+ \sum_{n=2}^{\infty} f\Big\{ & Y_n \in \{(X,Y,Z)|X \in \mathcal{N}^2 \times \{0\}, Y \in \mathcal{N}^3, Z \in \mathcal{N}^3\} \\
& |Y_1 = (A + \mathbf{a}_5, A, A - \mathbf{a}_1)\Big\} \cdot P\Big\{Y_1 = (A + \mathbf{a}_5, A, A - \mathbf{a}_1) \\
& |Y_0 \in \{(A,B,C)|A \in \mathcal{N}^2 \times \{k\}, B = A - \mathbf{a}_1, C = A - \mathbf{a}_1 - \mathbf{a}_3\}\Big\} \\
+ \sum_{n=2}^{\infty} f\Big\{ & Y_n \in \{(X,Y,Z)|X \in \mathcal{N}^2 \times \{0\}, Y \in \mathcal{N}^3, Z \in \mathcal{N}^3\} \\
& |Y_1 = (A + \mathbf{a}_7, A, A - \mathbf{a}_1)\Big\} \cdot P\Big\{Y_1 = (A + \mathbf{a}_7, A, A - \mathbf{a}_1) \\
& |Y_0 \in \{(A,B,C)|A \in \mathcal{N}^2 \times \{k\}, B = A - \mathbf{a}_1, C = A - \mathbf{a}_1 - \mathbf{a}_3\}\Big\} \\
= p_t P_{k+1}&(0|\mathbf{a}_3\mathbf{a}_1) + p_- P_k(0|\mathbf{a}_5\mathbf{a}_1) + p_+ P_k(0|\mathbf{a}_7\mathbf{a}_1).
\end{aligned}
$$

Similarly we have, for $1 < k < M-1$,

$$\left.\begin{aligned}
P_k(a|\mathbf{a}_1\mathbf{a}_3) &= p_t P_{k+1}(a|\mathbf{a}_3\mathbf{a}_1) + p_- P_k(a|\mathbf{a}_5\mathbf{a}_1) + p_+ P_k(a|\mathbf{a}_7\mathbf{a}_1),\\
P_k(a|\mathbf{a}_1\mathbf{a}_5) &= p_+ P_{k+1}(a|\mathbf{a}_3\mathbf{a}_1) + p_t P_k(a|\mathbf{a}_5\mathbf{a}_1) + p_- P_k(a|\mathbf{a}_7\mathbf{a}_1),\\
P_k(a|\mathbf{a}_5\mathbf{a}_1) &= p_t P_{k+1}(a|\mathbf{a}_1\mathbf{a}_5) + p_- P_k(a|\mathbf{a}_6\mathbf{a}_5) + p_+ P_{k-1}(a|\mathbf{a}_2\mathbf{a}_5),\\
P_k(a|\mathbf{a}_5\mathbf{a}_6) &= p_+ P_{k+1}(a|\mathbf{a}_1\mathbf{a}_5) + p_t P_k(a|\mathbf{a}_6\mathbf{a}_5) + p_- P_{k-1}(a|\mathbf{a}_2\mathbf{a}_5),\\
P_k(a|\mathbf{a}_5\mathbf{a}_2) &= p_- P_{k+1}(a|\mathbf{a}_1\mathbf{a}_5) + p_+ P_k(a|\mathbf{a}_6\mathbf{a}_5) + p_t P_{k-1}(a|\mathbf{a}_2\mathbf{a}_5),\\
P_k(a|\mathbf{a}_2\mathbf{a}_5) &= p_t P_k(a|\mathbf{a}_5\mathbf{a}_2) + p_- P_{k-1}(a|\mathbf{a}_4\mathbf{a}_2) + p_+ P_k(a|\mathbf{a}_7\mathbf{a}_2),\\
P_k(a|\mathbf{a}_2\mathbf{a}_4) &= p_+ P_k(a|\mathbf{a}_5\mathbf{a}_2) + p_t P_{k-1}(a|\mathbf{a}_4\mathbf{a}_2) + p_- P_k(a|\mathbf{a}_7\mathbf{a}_2).
\end{aligned}\right\} \tag{7}$$

By the symmetry of the lattice, we have

$$\begin{aligned}
&P_k(a|\mathbf{a}_1\mathbf{a}_3) = P_k(a|\mathbf{a}_3\mathbf{a}_1), \quad P_k(a|\mathbf{a}_5\mathbf{a}_1) = P_k(a|\mathbf{a}_7\mathbf{a}_1), \quad P_k(a|\mathbf{a}_5\mathbf{a}_6) = P_k(a|\mathbf{a}_6\mathbf{a}_5),\\
&P_k(a|\mathbf{a}_5\mathbf{a}_2) = P_k(a|\mathbf{a}_7\mathbf{a}_2), \quad P_k(a|\mathbf{a}_2\mathbf{a}_4) = P_k(a|\mathbf{a}_4\mathbf{a}_2).
\end{aligned}$$

In addition, we let p_g denote both p_+ and p_-, since $p_+ = p_-$, and E be the shift operator such that $E^n k = k + n$. Eq. (7) can then be written in a matrix form as

$$\mathbf{CP} = \mathbf{0}, \tag{8}$$

where $\mathbf{C} =$

$$\begin{pmatrix}
1-p_tE & 0 & -2p_g & 0 & 0 & 0 & 0\\
-p_gE & 1 & -p_t-p_g & 0 & 0 & 0 & 0\\
0 & -p_tE & 1 & -p_g & 0 & -p_gE^{-1} & 0\\
0 & -p_gE & 0 & 1-p_t & 0 & -p_gE^{-1} & 0\\
0 & -p_gE & 0 & -p_g & 1 & -p_tE^{-1} & 0\\
0 & 0 & 0 & 0 & -p_t-p_g & 1 & -p_gE^{-1}\\
0 & 0 & 0 & 0 & -2p_g & 0 & 1-p_tE^{-1}
\end{pmatrix}$$

and $\mathbf{P} =$
$(P_k(a|\mathbf{a}_1\mathbf{a}_3), P_k(a|\mathbf{a}_1\mathbf{a}_5), P_k(a|\mathbf{a}_5\mathbf{a}_1), P_k(a|\mathbf{a}_5\mathbf{a}_6), P_k(a|\mathbf{a}_5\mathbf{a}_2), P_k(a|\mathbf{a}_2\mathbf{a}_5), P_k(a|\mathbf{a}_2\mathbf{a}_4))^T$, (i.e. the column $\mathbf{P}$ is the transpose of this row.) We define the boundary conditions of the above system so that it is valid also for $k = 1$ and $k = M-1$. That is

$$\left.\begin{aligned}
&P_0(0|\mathbf{a}_2\mathbf{a}_5) = 1, \quad P_0(0|\mathbf{a}_2\mathbf{a}_4) = 1, \quad P_0(M|\mathbf{a}_2\mathbf{a}_5) = 0, \quad P_0(M|\mathbf{a}_2\mathbf{a}_4) = 0,\\
&P_M(0|\mathbf{a}_1\mathbf{a}_3) = 0, \quad P_M(0|\mathbf{a}_1\mathbf{a}_5) = 0, \quad P_M(M|\mathbf{a}_1\mathbf{a}_3) = 1, \quad P_M(M|\mathbf{a}_1\mathbf{a}_5) = 1.
\end{aligned}\right\} \tag{9}$$

Clearly, the probability for a walk to be a loop is $P_1(0|\mathbf{a}_1\mathbf{a}_3)$ and to be a tie is $P_1(M|\mathbf{a}_1\mathbf{a}_3)$.

The Average Lengths of Loops and Ties. We let $P_k(n|\mathbf{a}_i\mathbf{a}_j, a)$ be the probability that a walk has length n given that the walk starts at $z = k$ with two preceding steps $\mathbf{a}_i$ and $\mathbf{a}_j$ and terminates at $z = a$ and $P_k(a, n|\mathbf{a}_i\mathbf{a}_j)$ be the probability that a walk terminates at $z = a$ and has length n given that the walk starts at $z = k$ with two preceding steps $\mathbf{a}_i$ and $\mathbf{a}_j$. By an argument similar to that used in the last section, we have, for $1 < k < M-1$ and $n > 1$,

$$\left.\begin{aligned}
&P_k(a,n|\mathbf{a}_1\mathbf{a}_3) = p_t P_{k+1}(a,n-1|\mathbf{a}_1\mathbf{a}_3) + 2p_g P_k(a,n-1|\mathbf{a}_5\mathbf{a}_1),\\
&P_k(a,n|\mathbf{a}_1\mathbf{a}_5) = p_g P_{k+1}(a,n-1|\mathbf{a}_1\mathbf{a}_3) + (p_t+p_g) P_k(a,n-1|\mathbf{a}_5\mathbf{a}_1),\\
&P_k(a,n|\mathbf{a}_5\mathbf{a}_1) =\\
&\qquad p_t P_{k+1}(a,n-1|\mathbf{a}_1\mathbf{a}_5) + p_g P_k(a,n-1|\mathbf{a}_5\mathbf{a}_6) + p_g P_{k-1}(a,n-1|\mathbf{a}_2\mathbf{a}_5),\\
&P_k(a,n|\mathbf{a}_5\mathbf{a}_6) =\\
&\qquad p_g P_{k+1}(a,n-1|\mathbf{a}_1\mathbf{a}_5) + p_t P_k(a,n-1|\mathbf{a}_5\mathbf{a}_6) + p_g P_{k-1}(a,n-1|\mathbf{a}_2\mathbf{a}_5),\\
&P_k(a,n|\mathbf{a}_5\mathbf{a}_2) =\\
&\qquad p_g P_{k+1}(a,n-1|\mathbf{a}_1\mathbf{a}_5) + p_g P_k(a,n-1|\mathbf{a}_5\mathbf{a}_6) + p_t P_{k-1}(a,n-1|\mathbf{a}_2\mathbf{a}_5),\\
&P_k(a,n|\mathbf{a}_2\mathbf{a}_5) = (p_t+p_g) P_k(a,n-1|\mathbf{a}_5\mathbf{a}_2) + p_g P_{k-1}(a,n-1|\mathbf{a}_2\mathbf{a}_4),\\
&P_k(a,n|\mathbf{a}_2\mathbf{a}_4) = 2p_g P_k(a,n-1|\mathbf{a}_5\mathbf{a}_2) + p_t P_{k-1}(a,n-1|\mathbf{a}_2\mathbf{a}_4).
\end{aligned}\right\} \qquad (10)$$

In analogy with the boundary conditions of Eq. (8), we wish to define the boundary conditions of Eq. (10) so that the equations are valid also for $k = 1$, $k = M-1$ and $n = 1$. We therefore define

$$\left.\begin{aligned}
&P_0(0,0|\mathbf{a}_2\mathbf{a}_5) = 1, \quad P_0(0,0|\mathbf{a}_2\mathbf{a}_4) = 1, \quad P_0(M,0|\mathbf{a}_2\mathbf{a}_5) = 0, \quad P_0(M,0|\mathbf{a}_2\mathbf{a}_4) = 0,\\
&P_M(0,0|\mathbf{a}_1\mathbf{a}_3) = 0, \quad P_M(0,0|\mathbf{a}_1\mathbf{a}_5) = 0, \quad P_M(M,0|\mathbf{a}_1\mathbf{a}_3) = 1, \quad P_M(M,0|\mathbf{a}_1\mathbf{a}_5) = 1,
\end{aligned}\right\} \qquad (11)$$

and

$$P_0(a,n|\mathbf{a}_2\mathbf{a}_5) = 0, \quad P_0(a,n|\mathbf{a}_2\mathbf{a}_4) = 0, \quad P_M(a,n|\mathbf{a}_1\mathbf{a}_3) = 0, \quad P_M(a,n|\mathbf{a}_1\mathbf{a}_5) = 0, \quad (12)$$

for $n > 0$. We now let

$$L_k(a|\mathbf{a}_i\mathbf{a}_j) = \sum_{n=0}^{\infty} P_k(a,n|\mathbf{a}_i\mathbf{a}_j)n.$$

From Eq. (10), we have, for $0 < k < M$,

$$L_k(a|\mathbf{a}_1\mathbf{a}_3) = \sum_{n=0}^{\infty} P_k(a,n|\mathbf{a}_1\mathbf{a}_3)n = \sum_{n=1}^{\infty} P_k(a,n|\mathbf{a}_1\mathbf{a}_3)n$$

$$
\begin{aligned}
&= p_t \sum_{n=1}^{\infty} P_{k+1}(a, n-1|\mathbf{a}_1\mathbf{a}_3)n + 2p_g \sum_{n=1}^{\infty} P_k(a, n-1|\mathbf{a}_5\mathbf{a}_1)n \\
&= p_t \sum_{n=0}^{\infty} P_{k+1}(a, n|\mathbf{a}_1\mathbf{a}_3)(n+1) + 2p_g \sum_{n=0}^{\infty} P_k(a, n|\mathbf{a}_5\mathbf{a}_1)(n+1) \\
&= p_t \sum_{n=0}^{\infty} P_{k+1}(a, n|\mathbf{a}_1\mathbf{a}_3)n + 2p_g \sum_{n=0}^{\infty} P_k(a, n|\mathbf{a}_5\mathbf{a}_1)n \\
&\quad + p_t \sum_{n=0}^{\infty} P_{k+1}(a, n|\mathbf{a}_1\mathbf{a}_3) + 2p_g \sum_{n=0}^{\infty} P_k(a, n|\mathbf{a}_5\mathbf{a}_1) \\
&= p_t L_{k+1}(a|\mathbf{a}_1\mathbf{a}_3) + 2p_g L_k(a|\mathbf{a}_5\mathbf{a}_1) + p_t P_{k+1}(a|\mathbf{a}_1\mathbf{a}_3) + 2p_g P_k(a|\mathbf{a}_5\mathbf{a}_1) \\
&= p_t L_{k+1}(a|\mathbf{a}_1\mathbf{a}_3) + 2p_g L_k(a|\mathbf{a}_5\mathbf{a}_1) + P_k(a|\mathbf{a}_1\mathbf{a}_3),
\end{aligned}
$$

(using the first equation in Eq. (8) in last step). Similarly, we can show that,

$$
\begin{aligned}
L_k(a|\mathbf{a}_1\mathbf{a}_5) &= p_g L_{k+1}(a|\mathbf{a}_1\mathbf{a}_3) + (p_t + p_g) L_k(a|\mathbf{a}_5\mathbf{a}_1) + P_k(a|\mathbf{a}_1\mathbf{a}_5), \\
L_k(a|\mathbf{a}_5\mathbf{a}_1) &= p_t L_{k+1}(a|\mathbf{a}_1\mathbf{a}_5) + p_g L_k(a|\mathbf{a}_5\mathbf{a}_6) + p_g L_{k-1}(a|\mathbf{a}_2\mathbf{a}_5) + P_k(a|\mathbf{a}_5\mathbf{a}_1), \\
L_k(a|\mathbf{a}_5\mathbf{a}_6) &= p_g L_{k+1}(a|\mathbf{a}_1\mathbf{a}_5) + p_t L_k(a|\mathbf{a}_5\mathbf{a}_6) + p_g L_{k-1}(a|\mathbf{a}_2\mathbf{a}_5) + P_k(a|\mathbf{a}_5\mathbf{a}_6), \\
L_k(a|\mathbf{a}_5\mathbf{a}_2) &= p_g L_{k+1}(a|\mathbf{a}_1\mathbf{a}_5) + p_g L_k(a|\mathbf{a}_5\mathbf{a}_6) + p_t L_{k-1}(a|\mathbf{a}_2\mathbf{a}_5) + P_k(a|\mathbf{a}_5\mathbf{a}_2), \\
L_k(a|\mathbf{a}_2\mathbf{a}_5) &= (p_t + p_g) L_k(a|\mathbf{a}_5\mathbf{a}_2) + p_g L_{k-1}(a|\mathbf{a}_2\mathbf{a}_4) + P_k(a|\mathbf{a}_2\mathbf{a}_5), \\
L_k(a|\mathbf{a}_2\mathbf{a}_4) &= 2p_g L_k(a|\mathbf{a}_5\mathbf{a}_2) + p_t L_{k-1}(a|\mathbf{a}_2\mathbf{a}_4) + P_k(a|\mathbf{a}_2\mathbf{a}_4).
\end{aligned}
$$

In matrix form, this is

$$
\mathbf{CL} = \mathbf{P}, \tag{13}
$$

where $\mathbf{L} =$
$(L_k(a|\mathbf{a}_1\mathbf{a}_3), L_k(a|\mathbf{a}_1\mathbf{a}_5), L_k(a|\mathbf{a}_5\mathbf{a}_1), L_k(a|\mathbf{a}_5\mathbf{a}_6), L_k(a|\mathbf{a}_5\mathbf{a}_2), L_k(a|\mathbf{a}_2\mathbf{a}_5), L_k(a|\mathbf{a}_2\mathbf{a}_4))^T$.
Eqs. (11) and (12) give

$$
L_0(a|\mathbf{a}_2\mathbf{a}_5) = 0, \quad L_0(a|\mathbf{a}_2\mathbf{a}_4) = 0, \quad L_M(a|\mathbf{a}_1\mathbf{a}_3) = 0, \quad L_M(a|\mathbf{a}_1\mathbf{a}_5) = 0. \tag{14}
$$

It follows from the property of the conditional probability $P(A|BC) = \dfrac{P(AB|C)}{P(B|C)}$ (i.e. the conditional probability of A for given B and C is equal to the conditional probability of the occurrence of both A and B for given C divided by the conditional probability of B on the hypothesis C) that

$$
P_k(n|\mathbf{a}_i\mathbf{a}_j, a) = \frac{P_k(a, n|\mathbf{a}_i\mathbf{a}_j)}{P_k(a|\mathbf{a}_i\mathbf{a}_j)}.
$$

Therefore, the expected length of a loop may be written as

$$\sum_{n=0}^{\infty} P_1(n|\mathbf{a}_1\mathbf{a}_3, 0)n = \frac{L_1(0|\mathbf{a}_1\mathbf{a}_3)}{P_1(0|\mathbf{a}_1\mathbf{a}_3)}$$

and the expected length of a tie as

$$\sum_{n=0}^{\infty} P_1(n|\mathbf{a}_1\mathbf{a}_3, M)n = \frac{L_1(M|\mathbf{a}_1\mathbf{a}_3)}{P_1(M|\mathbf{a}_1\mathbf{a}_3)}.$$

The rth Order Moments of the Loop Length and the Tie Length. Similarly, the rth order moment of the expected length can be calculated. Let $r \geq 1$ be an integer. The rth moment of the loop length and the tie length are

$$\sum_{n=0}^{\infty} n^r P_k(n|\mathbf{a}_i\mathbf{a}_j, 0) \quad \text{and} \quad \sum_{n=0}^{\infty} n^r P_k(n|\mathbf{a}_i\mathbf{a}_j, M),$$

respectively. We let

$$M_k^r(a|\mathbf{a}_i\mathbf{a}_j) = \sum_{n=0}^{\infty} n^r P_k(a, n|\mathbf{a}_i\mathbf{a}_j).$$

It can be shown that, for $0 < k < M$,

$$\mathbf{C}\mathbf{M}^r = \mathbf{P} + \sum_{i=1}^{r-1} \frac{r!}{i!\,(r-i)!}\mathbf{M}^i, \tag{15}$$

where $\mathbf{M}^j =$
$(M_k^j(a|\mathbf{a}_1\mathbf{a}_3), M_k^j(a|\mathbf{a}_1\mathbf{a}_5), M_k^j(a|\mathbf{a}_5\mathbf{a}_1), M_k^j(a|\mathbf{a}_5\mathbf{a}_6), M_k^j(a|\mathbf{a}_5\mathbf{a}_2), M_k^j(a|\mathbf{a}_2\mathbf{a}_5), M_k^j(a|\mathbf{a}_2\mathbf{a}_4))^T$.
We similarly define

$$M_0^r(a|\mathbf{a}_2\mathbf{a}_5) = 0, \quad M_0^r(a|\mathbf{a}_2\mathbf{a}_4) = 0, \quad M_M^r(a|\mathbf{a}_1\mathbf{a}_3) = 0, \quad M_M^r(a|\mathbf{a}_1\mathbf{a}_5) = 0. \tag{16}$$

The rth moment of the expected loop length is therefore given by

$$\sum_{n=0}^{\infty} P_1(n|\mathbf{a}_1\mathbf{a}_3, 0)n^r = \frac{M_1^r(0|\mathbf{a}_1\mathbf{a}_3)}{P_1(0|\mathbf{a}_1\mathbf{a}_3)}$$

and the rth moment of the expected tie length by

$$\sum_{n=0}^{\infty} P_1(n|\mathbf{a}_1\mathbf{a}_3, M)n^r = \frac{M_1^r(M|\mathbf{a}_1\mathbf{a}_3)}{P_1(M|\mathbf{a}_1\mathbf{a}_3)}.$$

Solutions of the Systems of Difference Equations

One Limit Case. The limit case, temperature $\to \infty$, corresponds to the amorphous region being completely isotropic. Since the probabilities for *trans*, *gauche*$^{+}$ and *gauche*$^{-}$ to occur are equal as temperature $\to \infty$, Eq. (8) is reduced to:

$$\begin{pmatrix} 1-\frac{2}{3}E & -\frac{1}{3}E^{-1} \\ -\frac{1}{3}E & 1-\frac{2}{3}E^{-1} \end{pmatrix} \begin{pmatrix} P_k(a|\mathbf{a}_1\mathbf{a}_3) \\ P_k(a|\mathbf{a}_2\mathbf{a}_4) \end{pmatrix} = \mathbf{0} \tag{17}$$

together with relations expressing the other probabilities in terms of these two. And we have the boundary conditions:

$$P_0(0|\mathbf{a}_2\mathbf{a}_4)=1, \quad P_0(M|\mathbf{a}_2\mathbf{a}_4)=0, \quad P_M(0|\mathbf{a}_1\mathbf{a}_3)=0, \quad P_M(M|\mathbf{a}_1\mathbf{a}_3)=1. \tag{18}$$

Similarly Eq. (13) is reduced to

$$\begin{pmatrix} 1-\frac{2}{3}E & -\frac{1}{3}E^{-1} \\ -\frac{1}{3}E & 1-\frac{2}{3}E^{-1} \end{pmatrix} \begin{pmatrix} L_k(a|\mathbf{a}_1\mathbf{a}_3) \\ L_k(a|\mathbf{a}_2\mathbf{a}_4) \end{pmatrix} = \begin{pmatrix} P_k(a|\mathbf{a}_1\mathbf{a}_3) \\ P_k(a|\mathbf{a}_2\mathbf{a}_4) \end{pmatrix} \tag{19}$$

with the boundary conditions:

$$L_0(a|\mathbf{a}_2\mathbf{a}_4)=0, \qquad L_M(a|\mathbf{a}_1\mathbf{a}_3)=0, \tag{20}$$

and Eq. (15) is reduced to

$$\begin{pmatrix} 1-\frac{2}{3}E & -\frac{1}{3}E^{-1} \\ -\frac{1}{3}E & 1-\frac{2}{3}E^{-1} \end{pmatrix} \begin{pmatrix} M_k^r(a|\mathbf{a}_1\mathbf{a}_3) \\ M_k^r(a|\mathbf{a}_2\mathbf{a}_4) \end{pmatrix}$$

$$= \begin{pmatrix} P_k(a|\mathbf{a}_1\mathbf{a}_3) \\ P_k(a|\mathbf{a}_2\mathbf{a}_4) \end{pmatrix} + \sum_{i=1}^{r-1} \frac{r!}{i!\,(r-i)!} \begin{pmatrix} M_k^i(a|\mathbf{a}_1\mathbf{a}_3) \\ M_k^i(a|\mathbf{a}_2\mathbf{a}_4) \end{pmatrix} \tag{21}$$

with the boundary conditions:

$$M_0^r(a|\mathbf{a}_2\mathbf{a}_4)=0, \qquad M_M^r(a|\mathbf{a}_1\mathbf{a}_3)=0. \tag{22}$$

Solving Eqs. (17), (19) and (21) for $r=2$ by the methods of solution by elimination and undetermined coefficients (Appendix A), we have
the probability of a walk to be a loop $P_0 = \dfrac{M-1}{M+1}$,
the probability of a walk to be a tie $P_M = \dfrac{2}{M+1}$,

the expected length of a loop $L_0 = \frac{4}{3}M - \frac{1}{2(M+1)}$,
the expected length of a tie $L_M = \frac{1}{3}M^2 + \frac{2}{3}M - \frac{3}{4} - \frac{1}{2(M+1)}$,
and the expected length of a walk $= P_0L_0 + P_ML_M = 2(M-1)$.
The variance of the loop length

$$\sigma_0^2 = \frac{64M^5 + 128M^4 + 328M^3 + 648M^2 + 114M - 225}{180(M+1)^2},$$

the variance of the tie length

$$\sigma_M^2 = \frac{(M-1)(32M^5 + 224M^4 + 784M^3 + 2224M^2 + 3567M + 1845)}{720(M+1)^2},$$

and the variance of the walk length

$$\sigma^2 = P_0\sigma_0^2 + P_M\sigma_M^2 = \frac{32M^5 + 32M^4 + 160M^3 + 256M^2 - 201M - 279}{72(M+1)^2}.$$

At Chosen Temperatures. Semicrystalline polyethylene samples are often prepared at about 400K. The probabilities of a *trans*, *gauche*$^+$ and *gauche*$^-$ to occur at five different temperatures, calculated by taking $E_\sigma = (430+590)/2$ cal mol^{-1} and $E_\omega = (1700+2000)/2$ cal mol^{-1}, are given in Table II. In the analogy with the last section, Eqs. (8), (13) and (15) can be solved at different temperatures (Appendix B). The results are shown in Tables III, IV, V and VI.

Discussion

The amorphous region is filled with walks — ties joining the two crystal faces and loops from both sides. Therefore, the amount of carbon atoms contributed by an emerging polyethylene chain from the crystal on one side of the amorphous region and a chain from the crystal on the other side is: *two times the amount of carbon atoms contributed by a loop plus the amount contributed by a tie.* Table VII shows the average length of polyetylene chains in the amorphous region. It was pointed out that the density in the crystal region is $1g/cm^3$ and the density in the amorphous region is about $0.853g/cm^3$.[10] We therefore conclude that the lower bound on the adjacent reentry, at very high temperature, is

$$1 - \frac{0.853M(2\frac{M-1}{M+1} + \frac{2}{M+1})}{2\cdot\frac{M-1}{M+1}\cdot(\frac{4}{3}M - \frac{1}{2(M+1)}) + \frac{2}{M+1}\cdot(\frac{1}{3}M^2 + \frac{2}{3}M - \frac{3}{4} - \frac{1}{2(M+1)})},$$

which is about 49%. This can be compared to the the lower bound of 66% yielded by the gambler's ruin model.[1] Some other cubic lattice models, including Monte Carlo calculation [2] and mean-field lattice model,[3] predict high adjacent reentry also. However the results of Flory, Yoon and Dill's calculation [4] shows that the adjacent reentry is less than 20% (the density of the interphase was assumed to be the same as that of the crystal in their calculation and the result was later questioned by Marqusee and Dill [3],[5]). Our results also indicate at lower temperature less loops are formed and the average length of loops is longer, in contrast to more ties formed with shorter average length. As a result, the lower bound increases to about 55% at about 400K.

In principle, we could consider the random walk with three step memory using the transition matrix Eq. (2). The general idea would be the same, but the compexity appreciably greater.

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Table I

Possible vector representations of a rotational state in a random walk

step vector	successor	next successor		
		trans	$gauche^+$	$gauche^-$
$\mathbf{b}_1$	$\mathbf{b}_3$	$\mathbf{b}_1$	$\mathbf{b}_6$	$\mathbf{b}_8$
$\mathbf{b}_1$	$\mathbf{b}_5$	$\mathbf{b}_1$	$\mathbf{b}_2$	$\mathbf{b}_6$
$\mathbf{b}_1$	$\mathbf{b}_7$	$\mathbf{b}_1$	$\mathbf{b}_8$	$\mathbf{b}_2$
$\mathbf{b}_2$	$\mathbf{b}_4$	$\mathbf{b}_2$	$\mathbf{b}_8$	$\mathbf{b}_6$
$\mathbf{b}_2$	$\mathbf{b}_5$	$\mathbf{b}_2$	$\mathbf{b}_6$	$\mathbf{b}_1$
$\mathbf{b}_2$	$\mathbf{b}_7$	$\mathbf{b}_2$	$\mathbf{b}_1$	$\mathbf{b}_8$
$\mathbf{b}_3$	$\mathbf{b}_1$	$\mathbf{b}_3$	$\mathbf{b}_7$	$\mathbf{b}_5$
$\mathbf{b}_3$	$\mathbf{b}_6$	$\mathbf{b}_3$	$\mathbf{b}_5$	$\mathbf{b}_4$
$\mathbf{b}_3$	$\mathbf{b}_8$	$\mathbf{b}_3$	$\mathbf{b}_4$	$\mathbf{b}_7$
$\mathbf{b}_4$	$\mathbf{b}_2$	$\mathbf{b}_4$	$\mathbf{b}_5$	$\mathbf{b}_7$
$\mathbf{b}_4$	$\mathbf{b}_6$	$\mathbf{b}_4$	$\mathbf{b}_3$	$\mathbf{b}_5$
$\mathbf{b}_4$	$\mathbf{b}_8$	$\mathbf{b}_4$	$\mathbf{b}_7$	$\mathbf{b}_3$
$\mathbf{b}_5$	$\mathbf{b}_1$	$\mathbf{b}_5$	$\mathbf{b}_3$	$\mathbf{b}_7$
$\mathbf{b}_5$	$\mathbf{b}_2$	$\mathbf{b}_5$	$\mathbf{b}_7$	$\mathbf{b}_4$
$\mathbf{b}_5$	$\mathbf{b}_6$	$\mathbf{b}_5$	$\mathbf{b}_4$	$\mathbf{b}_3$
$\mathbf{b}_6$	$\mathbf{b}_3$	$\mathbf{b}_6$	$\mathbf{b}_8$	$\mathbf{b}_1$
$\mathbf{b}_6$	$\mathbf{b}_4$	$\mathbf{b}_6$	$\mathbf{b}_2$	$\mathbf{b}_8$
$\mathbf{b}_6$	$\mathbf{b}_5$	$\mathbf{b}_6$	$\mathbf{b}_1$	$\mathbf{b}_2$
$\mathbf{b}_7$	$\mathbf{b}_1$	$\mathbf{b}_7$	$\mathbf{b}_5$	$\mathbf{b}_3$
$\mathbf{b}_7$	$\mathbf{b}_2$	$\mathbf{b}_7$	$\mathbf{b}_4$	$\mathbf{b}_5$
$\mathbf{b}_7$	$\mathbf{b}_8$	$\mathbf{b}_7$	$\mathbf{b}_3$	$\mathbf{b}_4$
$\mathbf{b}_8$	$\mathbf{b}_3$	$\mathbf{b}_8$	$\mathbf{b}_1$	$\mathbf{b}_6$
$\mathbf{b}_8$	$\mathbf{b}_4$	$\mathbf{b}_8$	$\mathbf{b}_6$	$\mathbf{b}_2$
$\mathbf{b}_8$	$\mathbf{b}_7$	$\mathbf{b}_8$	$\mathbf{b}_2$	$\mathbf{b}_1$

Table II

Probabilities of *trans*, *gauche*$^+$ and *gauche*$^-$ to occur

temperature (K)	P_t	$P_{+/-}$
300	0.59993	0.20004
350	0.57305	0.21347
400	0.55174	0.22413
450	0.53424	0.23288
500	0.51952	0.24024
∞	0.33333	0.33333

Table III

Fractions of walks to be loops and ties

temperature (K)	fractions of loops	fractions of ties
300	$1-\frac{5.3698}{M}+\frac{21.0335}{M^2}+O(\frac{1}{M^3})$	$\frac{5.3698}{M}-\frac{21.0335}{M^2}+O(\frac{1}{M^3})$
350	$1-\frac{4.8377}{M}+\frac{16.7557}{M^2}+O(\frac{1}{M^3})$	$\frac{4.8377}{M}-\frac{16.7557}{M^2}+O(\frac{1}{M^3})$
400	$1-\frac{4.4611}{M}+\frac{14.0158}{M^2}+O(\frac{1}{M^3})$	$\frac{4.4611}{M}-\frac{14.0158}{M^2}+O(\frac{1}{M^3})$
450	$1-\frac{4.1779}{M}+\frac{12.1127}{M^2}+O(\frac{1}{M^3})$	$\frac{4.1779}{M}-\frac{12.1127}{M^2}+O(\frac{1}{M^3})$
500	$1-\frac{3.9557}{M}+\frac{10.7141}{M^2}+O(\frac{1}{M^3})$	$\frac{3.9557}{M}-\frac{10.7141}{M^2}+O(\frac{1}{M^3})$
∞	$1-\frac{2}{M}+\frac{2}{M^2}+O(\frac{1}{M^3})$	$\frac{2}{M}-\frac{2}{M^2}+O(\frac{1}{M^3})$

Table IV

Average lengths of loops

temperature (K)	expected loop length
300	$1.5346M + 1.6763 - \frac{4.4057}{M} + \frac{4.0565}{M^2} + O(\frac{1}{M^3})$
350	$1.5192M + 1.3774 - \frac{3.6909}{M} + \frac{3.4289}{M^2} + O(\frac{1}{M^3})$
400	$1.5063M + 1.1697 - \frac{3.2052}{M} + \frac{2.9699}{M^2} + O(\frac{1}{M^3})$
450	$1.4953M + 1.0161 - \frac{2.8513}{M} + \frac{2.6247}{M^2} + O(\frac{1}{M^3})$
500	$1.4857M + 0.8975 - \frac{2.5805}{M} + \frac{2.3573}{M^2} + O(\frac{1}{M^3})$
∞	$1.3333M - \frac{0.5}{M} + \frac{0.5}{M^2} + O(\frac{1}{M^3})$

Table V

Average lengths of ties

temperature (K)	expected tie length
300	$0.1429M^2 + 1.1194M - 1.3219 - \frac{1.9474}{M} + \frac{7.6278}{M^2} + O(\frac{1}{M^3})$
350	$0.1570M^2 + 1.0877M - 1.2378 - \frac{1.7572}{M} + \frac{6.0861}{M^2} + O(\frac{1}{M^3})$
400	$0.1688M^2 + 1.0608M - 1.1778 - \frac{1.6136}{M} + \frac{5.0697}{M^2} + O(\frac{1}{M^3})$
450	$0.1790M^2 + 1.0377M - 1.1324 - \frac{1.5009}{M} + \frac{4.3513}{M^2} + O(\frac{1}{M^3})$
500	$0.1878M^2 + 1.0173M - 1.0965 - \frac{1.4095}{M} + \frac{3.8176}{M^2} + O(\frac{1}{M^3})$
∞	$0.3333M^2 + 0.6667M - 0.75 - \frac{0.5}{M} + \frac{0.5}{M^2} + O(\frac{1}{M^3})$

Table VI

Average lengths of walks

temperature (K)	expected walk length
300	$2.3019M - 3.5587 - \frac{11.7728}{M} + \frac{80.3209}{M^2} + O(\frac{1}{M^3})$
350	$2.2788M - 3.3411 - \frac{9.1122}{M} + \frac{56.6040}{M^2} + O(\frac{1}{M^3})$
400	$2.2594M - 3.1838 - \frac{7.4341}{M} + \frac{42.9723}{M^2} + O(\frac{1}{M^3})$
450	$2.2429M - 3.0634 - \frac{6.2844}{M} + \frac{34.2907}{M^2} + O(\frac{1}{M^3})$
500	$2.2285M - 2.9673 - \frac{5.4497}{M} + \frac{28.3533}{M^2} + O(\frac{1}{M^3})$
∞	$2M - 2$

Table VII

Average length of polyethylene chains in the amorphous region

T (K)	average length of polyethylene chains in the amorphous region
300	$1.9183M + 0.0888 - \frac{16.3863}{M} + \frac{26.7168}{M^2} + O(\frac{1}{M^3})$
350	$1.8990M - 0.0631 - \frac{13.0675}{M} + \frac{19.4035}{M^2} + O(\frac{1}{M^3})$
400	$1.8828M - 0.1671 - \frac{10.9398}{M} + \frac{15.0869}{M^2} + O(\frac{1}{M^3})$
450	$1.8692M - 0.2428 - \frac{9.4624}{M} + \frac{12.2717}{M^2} + O(\frac{1}{M^3})$
500	$1.8571M - 0.3003 - \frac{8.3740}{M} + \frac{10.3134}{M^2} + O(\frac{1}{M^3})$
∞	$1.6666M - 0.6666 - \frac{1.5833}{M} + \frac{0.8333}{M^2} + O(\frac{1}{M^3})$