(21) Rajagopal, A. K.; Teitler, S.; Ngai, K. L. *J. Phys.* **1984**, *17*, 6611.

(22) Ngai, K. L.; Rajagopal, A. K.; Teitler, S., submitted for publication in *J. Chem. Phys.*

(23) Rendell, R. W.; Ngai, K. L., unpublished results. See pp 181–182 of second article of ref 14.

(24) Sudarshan, E. C. G.; Makunda, N. *Classical Dynamics: A Modern Perspective*: Wiley: New York, 1974.

(25) Anderson, J.; Ullman, R. *J. Chem. Phys.* **1967**, *47*, 2178. Ullman, R. *J. Chem. Phys.* **1968**, *49*, 831.

(26) We borrow the phrase "thermorheologically simple" and use it in a restricted meaning only, i.e., "rigidity" of relaxation spectrum for a *single* relaxation process. The conventional use of the phrase usually implies the successful reduction to a master curve of measurements made at different temperatures in an experimental time or frequency window and may involve more than one relaxation process, e.g., a local segmental relaxation and the terminal relaxation in a polymer liquid as studied in this work.

(27) Kohlrausch, R. *Prog. Ann. Phys.* **1847** *12*, 393; **1854**, *1*, 56, 179.

(28) Williams, G.; Watts, D. C. *Trans. Faraday Soc.* **1971**, *66*, 80.

(29) Ngai, K. L., Wright, G. B., Ed. *Relaxations in Complex Systems*; U.S. Government Printing Office: Washington, DC, 1985 (available from the National Technical Information Service, Springfield, VA 22161).

(30) Ngai, K. L.; Rajagopal, A. K.; Teitler, S. *Physics*, **1985**, *133A*, 213.

(31) Baur, M. E.; Stockmayer, W. H. *J. Chem. Phys.* **1965**, *43*, 4319.

(32) Cox, J. R.; Plazek, D. J., unpublished results.

(33) Fytas, G.; Dorfmuller, Th.; Chiu, B. *J. Polym. Sci., Polym. Phys. Ed.* **1984**, *22*, 1471.

# Loop Entanglement in a Constrained Liquid Region: Simulation Data, Simplified Models, and General Measurement Heuristics

**R. C. Lacher**

*Department of Computer Science, Florida State University, Tallahassee, Florida 32306.*

*Received April 13, 1987; Revised Manuscript Received July 10, 1987*

ABSTRACT: Complete entanglement measurement data from a computer simulation of the random walk model of a liquid region in a semicrystalline polymer is presented for plane separations out to 54 units. These data are compared with the same measures calculated analytically in a simplified model of the simulation. A case is presented for validation of the simplified model measurements as heuristics for the more complicated calculations used in the simulation. The model simplification process is general enough to apply to any model that contains loops and ties as chains between parallel planes. The heuristics may be applied directly from knowledge of single-chain statistics. As an example application, the heuristics are calculated for a model recently introduced by Marqusee and Dill, where it is found that both physical ties and loop entanglements are more likely than in the random case.

## Introduction

The extent and complexity of loop entanglement in long molecules, along with the significance of entanglement in determining chemical and physical properties, has been a subject of interest probably since long molecules were discovered.[1] In particular, there is considerable current research activity which directly or tangentially bears on such questions in the amorphous region of semicrystalline polymer. Various models of the intercrystalline region have been proposed, and most of these relate in some way to the entanglement question. The entanglement question is persistent, at least in part, because measures of entanglement are very difficult to calculate analytically[2] and very expensive to calculate numerically.[3]

The paper begins with a full report on the data from a computer simulation (announced in Lacher et al.[4]) calculating entanglement measures for the random walk/cubical lattice model. Three statistical measures are reported: link probability $P_{\text{link}}$ (the probability of a chain linking one from the opposing plane), link density $D_{\text{link}}$ (the expected number of opposing chains linked by a given chain), and total Gauss winding $W_1$ (the expected value of total winding of a chain about opposing chains). (Complete definitions are given in later sections.) These data cover plane separations out to 54 units and show that loop entanglements in the random walk model are significantly more prevalent than physical ties for separations greater than 20 units and, according $D_{\text{link}}$ and $W_1$, for separations greater than 14 units. This is a complex simulation that actually generates random walks from opposing planes in space, calculates Gauss linking numbers for opposing loops, and combines these calculations into measures of loop entanglement, all in sufficient quantity to assure stable statistical estimates.

Next the simplified model of Lacher, Bryant, and Howard[5] is considered. This is a general model in which counterparts of link probability and link density, $P^{s}_{\text{link}}$ and $D^{s}_{\text{link}}$, respectively, can be defined and calculated analytically. The simulation data are compared with the calculations in the simplified model. In the case of link density, where the asymptotics of $D^{s}_{\text{link}}$ are known,[5] the simulation data fit the asymptotic curve type with root-mean-square error on the order of 0.05 standard deviation in the data; the predicted limiting value of $D_{\text{link}}$ is the same as that of $D^{s}_{\text{link}}$ to within similar error. In the case of link probability, comparison of the $P_{\text{link}}$ data with the $P^{s}_{\text{link}}$ curve shows the two functions have the same discernible qualitative features and are in reasonable quantitative agreement.

The simplification process may be applied to any model whose basic components are loops and ties that are chains in the region between two parallel planes in space. The formulae derived for $D^{s}_{\text{link}}$ and $P^{s}_{\text{link}}$ are equally general, depending only on single-chain statistics (and not on interaction of two or more chains). Thus $P^{s}_{\text{link}}$ and $D^{s}_{\text{link}}$ can be calculated as entanglement measurement heuristics for any model in which these single-chain statistics are known. The paper concludes with calculations of these entanglement heuristics for the model recently introduced by Marqusee and Dill,[6] where it was found that introduction of a tendency to order near crystal faces significantly increases the likelihood of tie chains over that expected in the random walk model. These calculations show that in spite of a decrease in the number of loops, the likelihood of links connecting lamellar crystals is also higher than that for the random case, so that a tendency to order near

0024-9297/87/2220-3054$01.50/0

crystal faces increases the likelihood of both physical and topological connections between lamellae.

## Entanglement in Opposing Planes Models

An *opposing planes model* is any model whose objects of study are *chains* consisting of paths beginning and terminating on a parallel pair of planes in space.[4-12] In such a model, *loops* are chains that begin and end on the same plane, and *ties* are chains that traverse from one plane to the other. Free-ended chains might be considered for other purposes, but in the present context it is assumed that each end of each chain is on one of the boundary planes. Other useful terms in this setting are *reach* of a chain, defined to be its maximum travel away from its plane of origination, and *breadth* of a loop, a measure of lateral size. One generally accepted measure of structure in such a model is *tie probability*: $P_{\text{tie}}$ = the probability that a chain in the model is a tie.

Measures of loop entanglement may be defined in terms of the Gauss linking number of two opposing loops. The choice of the Gauss invariant as the atomic element in these measures deserves some scrutiny. As Wiegel[2] and Lacher et al.[4] point out, the Gauss number does not detect all linking. It does, however, detect the strongest form of linking, homological linking, and therefore will provide lower bounds for all other linking measures. It also is calculable numerically in a relatively straightforward manner (using the signed undercrossing method) that lends itself to the kind of mass processing of geometric information necessary for large-scale simulation.[3]

Linking of two closed curves is defined only when the curves do not intersect. And loops in an opposing planes model are not closed curves. Both these problems are overcome by defining an *offset linking number* of two opposing loops. First the two loops are closed by adding a straight segment from end to start of each loop. Then the resulting curve based on the right-hand plane is offset by a small perturbation so as to move off the curve based on the left-hand plane. The perturbation direction must be selected in some canonical way that may only depend on details of the particular model being studied, but exactly how this canonical choice is made is not important. (If the model has singly occupied sites, so that two chains cannot intersect, no perturbation is necessary.) For example, if the curves are smooth, the direction could be chosen with a framing of some sort. If the curves are constrained to a lattice, the direction can be any fixed direction not parallel to any lattice segment. For explicity in the unit cubical lattice case, perturb by subtracting $^1/_2$ from each coordinate. Then the *offset linking number* is defined to be the linking number of the two closed curves so constructed. It is said that two opposing loops *link* if their offset linking number is nonzero. By definition, the offset linking number of two chains is zero if either chain is not a loop or if they are loops based on the same plane. Several measures of entanglement are defined as follows: $P_{\text{link}}$ = the probability that a chain in the model is a loop that links some loop from the opposing plane; $D_{\text{link}}$ = the expected number of opposing loops that a given chain links; and $W_p$ = the expected $p$-norm of the total offset linking of a chain with all loops from the opposing plane. $P_{\text{link}}$, $D_{\text{link}}$, and $W_1$ are called *link probability, link density*, and *total (gauss) winding*, respectively. The *total offset linking* of a chain is defined as the vector whose components are the offset linking numbers of the chain with all chains from the opposing plane. Total offset linking is a vector with infinite length but finite support. Its 1-norm is the sum of the absolute values of its components and thus counts the total winding of the chain about chains from the opposing face. Total gauss winding $W_1$ is the expected value of this 1-norm. The 2-norm of total offset linking is the square root of the sum of the squares of its components; $W_2$ is the expected value of this 2-norm.

It may be worth noting that both link probability $P_{\text{link}}$ and link density $D_{\text{link}}$ can be defined by using any topologically invariant definition of "linking" and that in some models, all notions of "linking" are equivalent. In particular, all notions of "linking" are equivalent in the simplified models discussed later in this paper. On the other hand, total gauss winding $W_1$ requires a notion of linking that has numerical values. $W_1$ measures the expected total winding of a chain about opposing loops.

## The Random Walk Model

The random walk model, introduced in the setting of semicrystalline polymers by Guttman, DiMarzio, and Hoffman[7-9] (following Yoon and Flory[10]), considers random walk on a lattice (here the unit cubical lattice) between two parallel absorbing planes. With use of the gambler's ruin calculational model, single-chain statistics were obtained analytically and used to compare aspects of the model with experimental results and other theoretical calculations.[9] The model has defects, recognized by the introducers themselves, that have varying degrees of gravity depending on which properties one is studying and who is doing the study.[13] On the other hand, the model provides an ideal setting to begin a theoretical investigation of previously unstudied phenomena such as loop entanglement.

The specific setup chosen for the present discussion assumes two parallel vertical boundary planes at coordinates a distance $M$ units apart in space and considers paths of walks constrained to a unit cubical lattice in the slab between the planes. (The lattice is assumed to intersect each plane in a cubical sublattice.) Each walk begins ("exits") on one of the planes and takes an initial step in the direction normal to the plane and into the slab between boundary planes. Walk steps are chosen at random (probability $^1/_6$ for each direction) until the walk next encounters a boundary plane, at which point the walk is terminated.

To gather experimental data on entanglement measures in this model, one could proceed as follows: (1) choose a set of lattice points in the right-hand plane with density $d$ (i.e., $d$ is the expected number of points per unit area); (2) generate walks at each of these chosen points, saving any loops generated for use in the next step; (3a) generate walks from the origin of the left-hand plane one at a time, keeping up with frequencies and calculating offset linking numbers with each of the loops generated in the previous step; (3b) update counters for number of left loops with linking, number of right loops linked, and 1-norm of total offset linking; (4a) divide the counters of the previous step by the number of walks generated from the left; (4b) report these numbers as $P_{\text{link}}$, $D_{\text{link}}$, and $W_1$, respectively.

In practice, such a procedure is impossible only because it requires infinitely many walks to be generated in step (2). The CROSSWALK simulation follows the outline expressed by steps (1)–(4) precisely, except that in step (1) the set is chosen as a subset of a square centered at the origin of the right-hand plane, making the set finite. The side length of this "starting square" is maintained proportional to the plane separation $M$ in order to preserve geometric similarity among runs at various $M$; side length $2M$ was used to gather the data reported here, after preliminary investigations confirmed the conjecture that most linking for a loop occurs within $M$ lateral units of the point of beginning of the loop. The density $d$ is fixed at $^1/_6$ in

**Table I**
**CROSSWALK Data: Random Exit Pattern**

| $M$ | $P^r_{\text{link}}$ | std dev | $D^r_{\text{link}}$ | std dev | $W^r_1$ | std dev |
|---|---|---|---|---|---|---|
| 2 | 0.0262 | 0.0122 | 0.0270 | 0.0131 | 0.0272 | 0.0131 |
| 3 | 0.0380 | 0.0123 | 0.0394 | 0.0122 | 0.0403 | 0.0127 |
| 4 | 0.0385 | 0.0067 | 0.0421 | 0.0068 | 0.0445 | 0.0076 |
| 5 | 0.0412 | 0.0078 | 0.0464 | 0.0091 | 0.0497 | 0.0094 |
| 6 | 0.0432 | 0.0074 | 0.0504 | 0.0093 | 0.0549 | 0.0105 |
| 7 | 0.0479 | 0.0049 | 0.0576 | 0.0067 | 0.0640 | 0.0080 |
| 8 | 0.0463 | 0.0058 | 0.0589 | 0.0076 | 0.0658 | 0.0097 |
| 9 | 0.0485 | 0.0084 | 0.0628 | 0.0108 | 0.0718 | 0.0116 |
| 10 | 0.0503 | 0.0064 | 0.0676 | 0.0087 | 0.0789 | 0.0100 |
| 11 | 0.0492 | 0.0066 | 0.0687 | 0.0083 | 0.0806 | 0.0102 |
| 12 | 0.0501 | 0.0062 | 0.0726 | 0.0072 | 0.0873 | 0.0088 |
| 13 | 0.0472 | 0.0046 | 0.0705 | 0.0060 | 0.0853 | 0.0076 |
| 14 | 0.0487 | 0.0044 | 0.0746 | 0.0059 | 0.0917 | 0.0071 |
| 15 | 0.0514 | 0.0052 | 0.0812 | 0.0073 | 0.1012 | 0.0088 |
| 16 | 0.0479 | 0.0043 | 0.0783 | 0.0072 | 0.0984 | 0.0093 |
| 17 | 0.0476 | 0.0050 | 0.0796 | 0.0079 | 0.1015 | 0.0108 |
| 18 | 0.0490 | 0.0053 | 0.0822 | 0.0092 | 0.1063 | 0.0124 |
| 19 | 0.0479 | 0.0047 | 0.0856 | 0.0080 | 0.1126 | 0.0115 |
| 20 | 0.0470 | 0.0033 | 0.0862 | 0.0053 | 0.1135 | 0.0074 |
| 21 | 0.0452 | 0.0044 | 0.0840 | 0.0064 | 0.1123 | 0.0089 |
| 22 | 0.0453 | 0.0049 | 0.0863 | 0.0081 | 0.1164 | 0.0110 |
| 23 | 0.0464 | 0.0042 | 0.0908 | 0.0067 | 0.1237 | 0.0095 |
| 24 | 0.0458 | 0.0029 | 0.0919 | 0.0055 | 0.1269 | 0.0086 |

**Table II**
**CROSSWALK Data: Uniform Exit Pattern**

| $M$ | $P^u_{\text{link}}$ | std dev | $D^u_{\text{link}}$ | std dev | $W^u_1$ | std dev |
|---|---|---|---|---|---|---|
| 6 | 0.0479 | 0.0088 | 0.0575 | 0.0108 | 0.0627 | 0.0123 |
| 12 | 0.0501 | 0.0053 | 0.0742 | 0.0077 | 0.0874 | 0.0089 |
| 18 | 0.0495 | 0.0036 | 0.0874 | 0.0045 | 0.1125 | 0.0058 |
| 24 | 0.0463 | 0.0037 | 0.0964 | 0.0060 | 0.1318 | 0.0087 |
| 30 | 0.0433 | 0.0023 | 0.1020 | 0.0048 | 0.1471 | 0.0069 |
| 36 | 0.0422 | 0.0019 | 0.1076 | 0.0052 | 0.1627 | 0.0077 |
| 42 | 0.0390 | 0.0030 | 0.1108 | 0.0052 | 0.1740 | 0.0088 |
| 48 | 0.0370 | 0.0033 | 0.1135 | 0.0057 | 0.1856 | 0.0092 |
| 54 | 0.0350 | 0.0017 | 0.1167 | 0.0033 | 0.1980 | 0.0061 |

order to simulate a density of about one between the planes. The selection of starting (or exit) points in this square was made in two ways, random and uniform. Random exit data is available for plane separations 2 through 24 units. Uniform exit data is available for separations 6 through 54 units (in multiples of 6).[14]

To detail more precisely the statistical procedure, refer to one walk generated in step (3) as a "trial", one trip through steps (1)–(4) as a "game", and the running of several games as a "run". The statistics reported here are "run level", that is, the standard deviations were calculated over a number of runs. Thus the standard deviations are more a measure of accuracy of estimation of the mean than an intrinsic random walk model property.[15]

Another view of this simulation may be found in Lacher, Bryant, and Howard.[5] A complete description of the CROSSWALK algorithms, data structures, and random number generator, along with some runtime analysis, is given in Lacher and Braswell.[3] Actual source code is available on request.[16]

CROSSWALK reports computed estimates, broken down by reach of loop as well as summary data, for $P_{\text{tie}}$, $P_{\text{link}}$, $D_{\text{link}}$, $W_1$, and $W_2$ (the last available for uniform exit pattern only). Summary data for $P_{\text{link}}$, $D_{\text{link}}$, and $W_1$ using random exit (starting) pattern is given in Table I and for uniform exit pattern in Table II. A complete set of detailed data reports is available.[16] When a distinction should be made, a superscript r is used to denote CROSSWALK data generated by using random exit pattern and superscript u is used to denote uniform. For example, $D^u_{\text{link}}$ refers to link density data generated with uniform exit pattern.

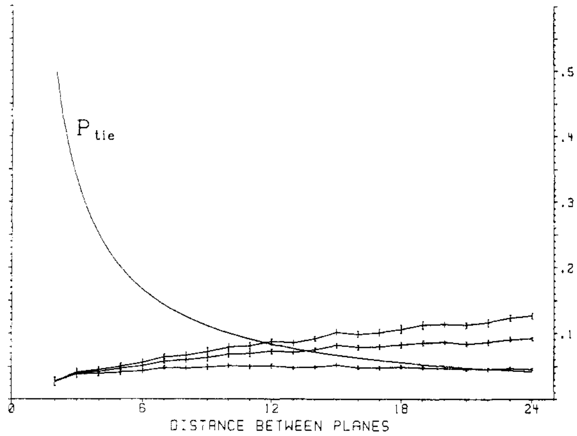

**Figure 1.** CROSSWALK data. Random exit pattern is shown with $^1/_2$ standard deviation from the mean indicated. Piecewise linear data curves for link probability (lower), link density (middle), and total gauss winding (upper) are compared with tie density.

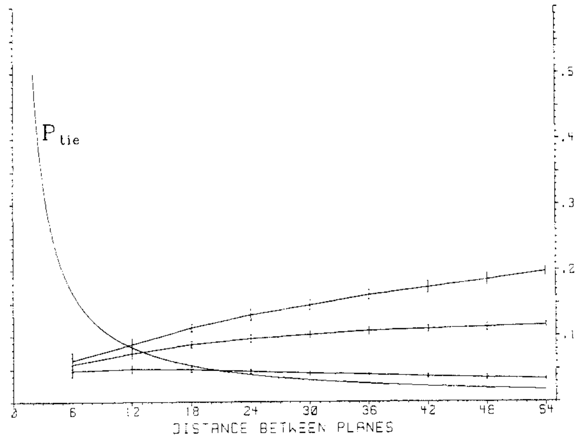

**Figure 2.** CROSSWALK data. Uniform exit pattern data is shown with one standard deviation from the mean indicated. Piecewise linear data curves for link probability (lower), link density (middle), and total gauss winding (upper) are compared with tie density.

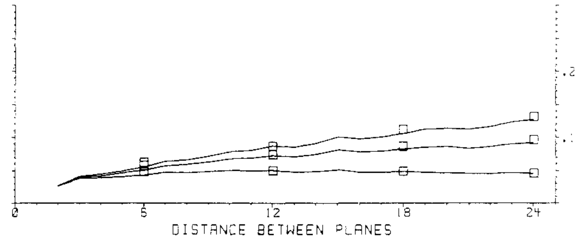

**Figure 3.** CROSSWALK data. Random exit pattern data (solid curves) is shown with uniform exit pattern data superimposed (squares).

Plots of the curves $P_{\text{link}}$, $D_{\text{link}}$, and $W_1$ as calculated by CROSSWALK are given in Figure 1 for random exit pattern and in Figure 2 for uniform exit pattern. The $P_{\text{tie}}$ curve, the probability of a walk ending as a tie, is shown for comparison. It is apparent from these graphs that entanglement effects begin to outweigh physical connections in this model at around $M = 14$. It is also apparent that $W_1$ seems to be increasing at a slowly decreasing rate, that $D_{\text{link}}$ appears to approach an asympotic value, and that $P_{\text{link}}$ attains an early maximum value whence it begins to decrease slowly. Further discussion of these qualitative features is made in following sections. Figure 3 compares the random and uniform exit data. The slight increase in uniform over random values is attributable to the fact that the density of walk starts in the uniform exiting case is effectively slightly more than $^1/_6$ as a density in the starting square (or, to look at it another way, the starting square is slightly larger in the uniform case).

## The Simplified Model

The simplified model of the random walk model (a model of a model) was introduced to study asymptotic properties of entanglement statistics.[5] This simplified model is an opposing planes model whose loops are formed by the legs of isosceles triangles whose bases lie in a boundary plane. These triangles are assumed to have a fixed height:base ratio. Loops (triangles) from the left are assumed to be subsets of horizontal planes, and loops from the right are subsets of vertical planes. Thus the altitude of each loop is perpendicular to a boundary plane and its length, the height of the triangle, is the *reach* of the loop. The *breadth* of a loop in this simplified model is defined to be $^1/_2$ the base of the loop. (See Figure 5 of Lacher et al.[5]) The overall density $d$ of walk starts as well as the relative density $d_k$ of walks of reach $k$ is defined to be the same in the simplified model as in the random walk model it emulates. (Note that $d_M = P_{\text{tie}}$.) Finally, the breadth:reach ratio $b$ for loops in the simplified model is *by* definition that expected for random walk loops. Thus

$$d = 1/6 \qquad \{\text{from CROSSWALK simulation}\} \tag{1}$$

$$d_k = 1/(k(k+1)) \text{ for } k = 1, ..., M-1 \qquad \{\text{eq 6 of Lacher et al.}^5\} \tag{2}$$

$$d_M = 1/M \qquad \{\text{eq 23 of Guttman et al.}^9\} \tag{3}$$

$$b = 1.19 \qquad \{\text{from CROSSWALK data}^{17}\} \tag{4}$$

In this simplified setting, formulae for both link probability and link density can be derived. The basic ingredient for these derivations is the probability that a given loop of reach $i$ links an opposing loop of reach $j$, derived to be

$$L_{i,j} = 2b^2d(i + j + \tfrac{1}{2} - M)^2d_j$$

when $i + j \leq M$ and zero otherwise by Lacher et al.[5] (This assumes that densities are small enough so that the formula has value less than one. The $^1/_2$ in the formula comes from the canonical perturbation that is part of the definition of offset linking number for unit cubical lattice models.)

The probability that a given loop of reach $i$ does not link an opposing loop of reach $j$ is $1 - L_{i,j}$, so the probability that a loop of reach $i$ links no opposing loop is the product

$$\tilde{L}_i = \prod_{j=M-i}^{M-1} (1 - L_{i,j})$$

The probability of a loop of each $i$ linking some opposing loop is thus $L_i = 1 - \tilde{L}_i$. Taking a weighted sum as the probability that a random loop links some opposing loop yields

$$\sum_{i=1}^{M-1} L_i d_i = \sum_{i=1}^{M-1} d_i - \sum_{i=1}^{M-1} \tilde{L}_i d_i = 1 - d_M - \sum_{i=1}^{M-1} d_i \prod_{j=M-i}^{M-1} [1 - L_{i,j}]$$

Therefore the link probability is

$$P^{\text{s}}_{\text{link}}(M) = 1 - d_M - \sum_{i=1}^{M-1} d_i \prod_{j=M-i}^{M-1} [1 - 2b^2d(i + j + \tfrac{1}{2} - M)^2d_j] \tag{5}$$

A similar argument yields the formula for link density:[5]

$$D^{\text{s}}_{\text{link}}(M) = 2b^2d \sum_{i=1}^{M-1} \sum_{j=M-i}^{M-1} (i + j + \tfrac{1}{2} - M)^2 d_i d_j \tag{6}$$

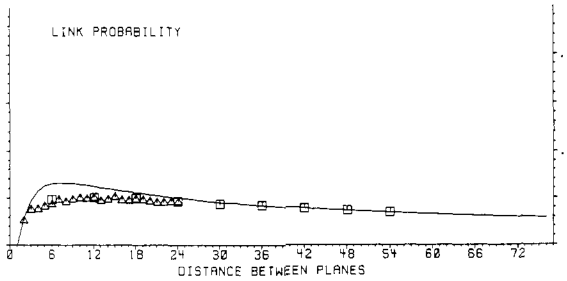

**Figure 4.** Link probability. The graph of $P^{\text{s}}_{\text{link}}$ for the random walk model, given by eq 5 and 1–4, is shown with CROSSWALK data superimposed. Triangles denote random exit pattern data and squares denote uniform exit pattern data.

**Table III**
**Selected Values of $P^{\text{s}}_{\text{link}}$ and $P^{\text{s}}_{\text{link}}/P^{\text{s}}_{\text{tie}}$**
**(Pure Random Walk)**

| $M$ | $P^{\text{s}}_{\text{link}}$ | $P^{\text{s}}_{\text{link}}/P^{\text{s}}_{\text{tie}}$ | $M$ | $P^{\text{s}}_{\text{link}}$ | $P^{\text{s}}_{\text{link}}/P^{\text{s}}_{\text{tie}}$ |
|---|---|---|---|---|---|
| 1 | 0 | 0 | 36 | 0.0419 | 1.5098 |
| 2 | 0.0295 | 0.0590 | 42 | 0.0391 | 1.6403 |
| 3 | 0.0474 | 0.1423 | 48 | 0.0366 | 1.7586 |
| 4 | 0.0573 | 0.2292 | 54 | 0.0346 | 1.8673 |
| 5 | 0.0624 | 0.3122 | 100 | 0.0251 | 2.5082 |
| 6 | 0.0649 | 0.3891 | 200 | 0.0170 | 3.4005 |
| 7 | 0.0657 | 0.4600 | 300 | 0.0134 | 4.0243 |
| 8 | 0.0657 | 0.5253 | 400 | 0.0113 | 4.5201 |
| 9 | 0.0651 | 0.5859 | 500 | 0.0099 | 4.9384 |
| 10 | 0.0642 | 0.6423 | 1000 | 0.0065 | 6.4528 |
| 11 | 0.0632 | 0.6951 | 2000 | 0.0042 | 8.3576 |
| 12 | 0.0621 | 0.7449 | 3000 | 0.0032 | 9.6933 |
| 18 | 0.0554 | 0.9964 | 4000 | 0.0027 | 10.7559 |
| 24 | 0.0498 | 1.1958 | 5000 | 0.0023 | 11.6531 |
| 30 | 0.0455 | 1.3636 | | | |

(The superscript s indicates the derivation is from the simplified model.) These formulae have the obvious virtue of ease of calculation. It remains to be argued how well they reflect the statistics of the original model.

**Link Probability.** The asymptotic form of $P^{\text{s}}_{\text{link}}$ (as determined by (5) and (1)–(4)) is not presently known, but numerical study indicates the graph of $P^{\text{s}}_{\text{link}}$ has the same qualitative features noticed in the $P_{\text{link}}$ data from CROSSWALK: a maximum value attained at $M = 8$ followed by slow decrease toward 0 as $M$ increases. Table III gives selected values of $P^{\text{s}}_{\text{link}}$. Figure 4 offers quantitative comparison of $P^{\text{s}}_{\text{link}}$ with CROSSWALK data.

Note that the early $P_{\text{link}}$ values computed by CROSSWALK are smaller than those predicted by $P^{\text{s}}_{\text{link}}$. This discrepancy is mostly attributable to the courseness of the lattice (relative to plane separation) for small $M$. Walks in the random walk model must begin at points of the lattice in the boundary planes, whereas "walks" in the simplified model are allowed to exit at any point in the boundary planes. For small $M$, this increases the likelihood of linking in the simplified model.

**Link Density.** The asymptotic form of $D^{\text{s}}_{\text{link}}(M)$ is known in the case of the random walk model,[5] where $D^{\text{s}}_{\text{link}}(M)$ is specified by (6) and (1)–(4). This is expressed by

$$D^{\text{s}}_{\text{link}}(M) \sim 2b^2d\left[\frac{\pi^2}{3} - 3 - \frac{1}{M} + \frac{\gamma + \ln(M)}{M(M+1)}\right] + 0\left(\frac{1}{M^2}\right) \tag{7}$$

where $\gamma$ is Euler's constant. Inspection shows that $D^{\text{s}}_{\text{link}}(M)$ approaches a positive asymptotic value $D^{\text{s}}_{\text{link}}(\infty)$

Table IV
Coefficients and Error from Best Fit Calculation Using $D^{u}_{\text{link}}$ Data and Minimizing Square Error

| curve type | A | B | C | SQERR | RMSERR |
|---|---|---|---|---|---|
| $Y = A + B/X$ | 0.1171 | −0.3974 | | 0.0003 | 0.0058 |
| $Y = A + B/X + C/X^2$ | 0.1323 | −0.9762 | 3.1703 | 0.0000 | 0.0008 |
| $Y = A + B/X + C \ln (X)/X^2$ | 0.1380 | −1.4113 | 3.1100 | 0.0000 | 0.0003 |

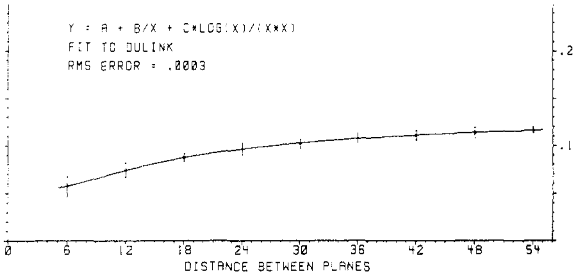

**Figure 5.** Link density. The least-squares best fit curve of the form (8) for uniform exit pattern CROSSWALK data is shown with data superimposed. One standard deviation from the mean in the data is indicated. Minimum square error is less than 0.000 05. RMS error is 0.0003 or approximately 0.05 mean standard deviations in the data.

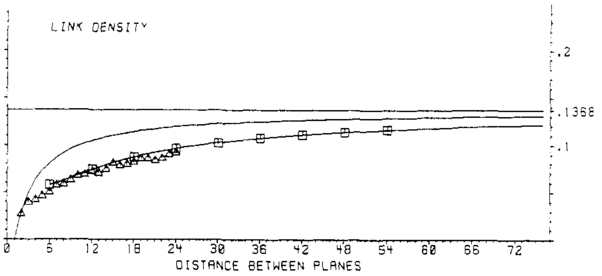

**Figure 6.** Link density. The graph of $D^{s}_{\text{link}}$ for the random walk model, as given by eq 6 and 1–4, is compared with CROSSWALK data. Triangles denote random exit pattern data, and squares denote uniform exit pattern data. The best fit curve from Figure 5 is also shown as the lower curve, along with the asymptote of $D^{s}_{\text{link}}$. The best fit curve approaches an asymptotic value of 0.1380, or approximately 0.2 mean standard deviations in the data above that of $D^{s}_{\text{link}}$.

as $M$ increases. To four decimal places, $D^{s}_{\text{link}}(\infty) = 0.1368$.

The asymptotic type of $D^{s}_{\text{link}}(M)$ to order 2 is

$$A + \frac{B}{M} + C\left(\frac{\ln (M)}{M^2}\right) \tag{8}$$

which can be used as a class of curves to fit $D_{\text{link}}$ data. Results of such a fit, using minimum square error as a fit criterion, produce the coefficients shown in Table IV. Note that the predicted limiting value for $D^{u}_{\text{link}}$ is $A = 0.1380$, differing with $D^{s}_{\text{link}}(\infty)$ on the order of 0.2 standard deviations in the data. Figure 5 shows this best fit curve with $D^{u}_{\text{link}}$ data superimposed. Figure 6 compares this curve with the graph of $D^{s}_{\text{link}}(M)$ and the asymptote at $D^{s}_{\text{link}}(\infty)$.

The $D^{u}_{\text{link}}$ values computed by CROSSWALK are smaller than predicted by $D^{s}_{\text{link}}$. This difference appears to decrease as $M$ increases, and curve fitting predicts virtual elimination of the shortfall for large $M$. A minor contribution to the shortfall is made by the limited size of the starting square in CROSSWALK, resulting in slight underestimates of entanglement statistics for the random walk model. The early shortfall is due largely to the lattice effect mentioned above in connection with link probability.

**Link–Tie Ratio.** Given the asymptotic form for $D^{s}_{\text{link}}$ and the relatively good fit of $D_{\text{link}}$ data to that form, a strong case is made for the conjecture that $D_{\text{link}}$ approaches a positive value asymptotically. The lack of a known asymptotic form for $P^{S}_{\text{link}}$, together with its subtle behavior as observed numerically, makes conjectures risky, but one might believe that $P_{\text{link}}$ approaches zero very slowly as $M$ increases. Certainly this behavior holds through $M = 5000$. This tendency toward zero makes interpretation in terms of physical characteristics difficult.

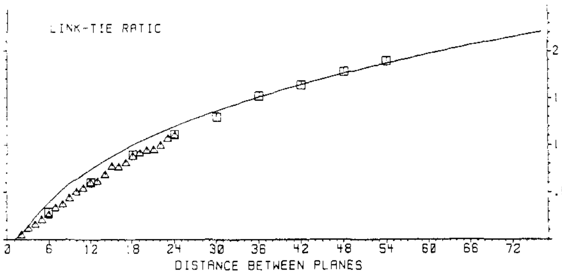

**Figure 7.** Link–tie ratio. The link–tie heuristic for the random walk model, as given by eq 9 and 1–4, is compared with CROSSWALK data. Triangles denote random exit pattern data, and squares denote uniform exit pattern data.

The ratio of links to ties gives a measure of the relative importance of links (topological connections) to ties (physical connections) in material strength in substances idealized by the model. (The ratio of loops to ties has been computed by other authors as another interesting structural indicator.[6]) In the simplified model this ratio is given by

$$\frac{P^{s}_{\text{link}}}{P^{s}_{\text{tie}}} = \frac{P^{s}_{\text{link}}}{d_M} \tag{9}$$

This ratio may be readily computed for both the random walk model and its simplification. Both investigations yield the same conclusions: The ratio is an increasing function throughout the range for which data are available ($2 \leq M \leq 54$ for the complex model and $2 \leq M \leq 5000$ for the simplification), and the ratio overtakes and excedes unity at around $M = 20$. See Table III and Figure 7.

## General Simplified Models

A simplified model is any model in the class of opposing planes models whose ties are simple line segments from plane to plane and whose loops belong to a similarity class of isosceles triangles oriented horizontally for loops based on the left-hand plane and vertically for opposite loops. If the original model is based on walks, chains in the simplified model may be called "walks" by analogy. A simplified model is called *discrete* or *continuous* depending on whether loop reach is restricted to integer values or allowed to have any real value between 0 and $M$, where $M$ is the distance between planes.

The three formulae (5), (6), and (9) are valid calculations of link probability, link density, and link-tie ratio in any discrete simplified model. The simplified model is made to emulate a more complex model by setting the values of the parameters $d$, $b$, and $d_1$, ..., $d_M$ to be those values calculated for the complex model, where

$d$ = density of chain starts (10)

$d_1$, ..., $d_M$ = distribution of chain frequencies by reach (11)

$b$ = mean breadth/reach of chains in the model (12)

The reader is reminded that the distribution of chains by reach may well depend on $M$, even though in the interest of readability the notation does not reflect this dependence. These formulae provide *heuristics* for comparing the

**Table V**
**Comparing Chain Statistics of Marqusee-Dill with Random Walk**

| | link probability | | link density | | links/ties | | loops/ties/($M$ - 1) | |
|---|---|---|---|---|---|---|---|---|
| $M$ | MD | RW | MD | RW | MD | RW | MD | RW |
| 12 | 0.0818 | 0.0621 | 0.1423 | 0.1046 | 0.7879 | 0.7449 | 0.7851 | 1.0 |
| 20 | 0.0696 | 0.0534 | 0.1557 | 0.1161 | 1.0982 | 1.0673 | 0.7773 | 1.0 |
| 45 | 0.0492 | 0.0378 | 0.1680 | 0.1270 | 1.7190 | 1.7008 | 0.7713 | 1.0 |

propensity for entanglement and the importance of topological connections among lattice-bound models.[18,19]

**Simplifying the Marqusee–Dill Model.** The model recently proposed by Marqusee and Dill[6] is an opposing planes model whose chains are walks on the unit cubical lattice. The walks in this model are not random but rather are based on step probabilities that are calculated by using an entropy maximization technique. The motivation for these calculations was better understanding of the interphase region near the planes (crystal faces). Marqusee and Dill found that more than three steps away from these faces step probabilities are in fact as in the random case, but near the faces the probabilities reflect a tendency to order in the chain segments.

This tendency to order near the faces has some interesting consequences for the liquid region, reflected by qualitative changes in the single-chain statistics of the model. For a Marqusee–Dill model of size $M$, for example, the ratio loops/ties/($M$ - 1) is found by the authors to be around 0.8 as compared to 1.0 expected for pure random walk, and the mean length of walks is found to be somewhat longer than expected for the random case.[20] Thus, in particular, there is evidence that ordering near the crystal faces may increase the number of physical connections between lamellae. The relative decrease in the number of loops might at first suggest a decrease in importance in the topological connections possible through topological links, but we argue below that the opposite is the case.

In fact, one can compute the heuristics for link probability, link density, and link–tie ratio for the Marqusee–Dill models. As input, one needs estimates for the single–chain statistics of equations 10, 11, and 12. The density of chain starts is a parameter that affects the chain-interaction statistics and must be chosen judiciously. For the random walk case, this parameter was set at $d = {}^1/_6$ in order to simulate a density of unity in the liquid region. Using this same criterion, one can set $d$ to be the reciprocal of twice the expected length of a walk in the Marqusee–Dill model. Conveniently, these values are already calculated for $M$ = 12, 20, and 45.[6] The distribution $d_1, ..., d_M$ of walks by reach can be calculated numerically by solving difference equations similar to the ones determining loop and tie probability in the model. The ratio $b$ = breadth/reach can be expected to be very close to that for pure random walk, at least for long walks, since most steps of most long walks in the Marqusee–Dill model are determined by uniform step probabilities as in the random case. (I.e., most steps of long walks are in the isotropic region.)

Results of these computations for $M$ = 12, 20, and 45 are shown for the one-segment approximation in Table V. The heuristic values for the Marqusee–Dill model (MD) are compared with those for the random walk model (RW), where exit density is computed to yield mean density one in each case. The results show a qualitative increase in physical connections for MD, as found by Marqusee and Dill and reflected in the lower value for loops/ties/($M$ - 1). The results also show an increase in topological connections for MD, reflected in increases in link probability, link density, and link–tie ratio. These topological connections are favored even though both the overall number of chains is decreased (due to density effects) and the relative number of loops is decreased. These results suggest that the tendency to order near crystal faces may imply an increase in both physical connections in the form of tie chains and topological connections in the form of linked loops.

**Acknowledgment.** The author thanks Leo Mandelkern and Kevin McLaughlin for valuable discussion, Lou Howard for his communication of an estimate for $b$, and Doug Klein for suggesting the use of curve fitting as validation of the simplified model. The investigator was supported by the Office of Naval Research under Grant N00014-84-K-0761 and received technical support from the Florida State University Supercomputer Computations Research Institute which is partially funded by the U.S. Department of Energy through Contract DE-FC05-85ER250000.

## References and Notes

(1) Flory, P. J.; Yoon, D. Y. *Nature (London)* **1978**, *272*, 226.

(2) Wiegel, F. W. *Introduction to Path Integral Methods in Physics and Polymer Science*; World Scientific Publishing: Philadelphia, 1986.

(3) Lacher, R. C.; Braswell, C. R. *Mass processing of randomly generated geometric information, Proceedings Supercomputing '87*; International Supercomputing Institute, Inc.: St. Petersburg, 1987; Vol. II, p 229.

(4) Lacher, R. C.; Bryant, J. L.; Howard, L. N.; Sumners, D. W. *Macromolecules* **1986**, *19*, 2639.

(5) Lacher, R. C.; Bryant, J. L.; Howard, L. N. *J. Chem. Phys.* **1986**, *85*, 6147.

(6) Marqusee, J. A.; Dill, K. A. *Macromolecules* **1986**, *19*, 2420.

(7) DiMarzio, E. A.; Guttman, C. M. *Polymer* **1980**, *21*, 733.

(8) DiMarzio, E. A.; Guttman, C. M.; Hoffman, J. D. *Polymer* **1980**, *21*, 1379.

(9) Guttman, C. M.; DiMarzio, E. A.; Hoffman, J. D. *Polymer* **1981**, *22*, 1466.

(10) Yoon, Y. D.; Flory, P. J. *Polymer* **1976**, *18*, 509.

(11) Mansfield, M. L. *Macromolecules* **1983**, *16*, 914.

(12) Flory, P. J.; Yoon, D. Y.; Dill, K. A. *Macromolecules* **1984**, *17*, 862.

(13) *Faraday Discuss. Chem. Soc.* **1979**, 68.

(14) The original terminology for these data, left link density, right link density, and total linking density, was an artifact of the design of the CROSSWALK simulation and has been changed to link probability, link density, and total gauss winding, respectively.

(15) The data reported here was generated with one important change in the technique used to collect the data announced previously.[4] The number of trials in a game, previously set to the fixed number 200, was changed to $M^2$. Since the expected number of loops of reach $M$ - 1 is $1/((M - 1)M)$, this new setting of the number of trials to be proportional to $M^2$ allows the expectation of some long loops for large $M$. There is no significant difference in the previous data (computed for $M \leq$ 24 only) and the current data.

(16) Lacher, R. C. *The CROSSWALK Simulation*; Technical Report, Florida State University, 1987.

(17) Howard, L. N., personal communication.

(18) Similar heuristics for continuous simplified models can be defined. These are currently under investigation.

(19) Of the statistics described in ref 10–12, $b$ seems to be the most problematical for many models. For the random walk model, Howard[17] has produced an estimate of 1.19 for $b$ using the "sup-norm" definition of breadth, i.e., defining breadth of a walk to be its maximum travel in either coordinate direction parallel to the boundary planes, but even that estimate is subject to revision, and it is not clear that other definitions of breadth, such as the "2-norm" definition, might not be more appropriate. This problem is currently under investigation.

(20) The parameter $M$ denotes one less than the distance between planes in ref 6 while it denotes the actual distance between planes in the present work.