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Exact and Monte Carlo Computations on a Lattice Model for Change of Conformation of a Polymer

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Conformational changes of linear polymers are studied by means of dynamic lattice models. The relaxation rates for the following four parameters describing the conformation of the polymer are studied for various polymer lengths: the square of the end-to-end distance, the square of the radius of gyration, the x component of the end-to-end vector, and the number of windings.

In the most realistic models the relaxation rates for the first three of the above-mentioned properties decrease approximately proportional to the square of the number of monomers in agreement with the well-known Rouse model, while the relaxation of the winding number appears to be independent of the polymer length. The long-range interactions due to excluded volume restrictions are found to be of only minor importance compared to the rules presented for the local movements of the polymer segments.

The results are obtained by diagonalizing the Markov matrix for $n = 3, 4, 5$, and 6 and by Monte Carlo simulation for $n = 8, 16, 32, 64$, and 128, where n is the number of monomers.

KEY WORDS: Polymer conformation; dynamic lattice model; Monte Carlo method.

1. INTRODUCTION

In lattice models for polymer conformations the monomer units of the polymer are situated on the vertices of a regular lattice with consecutive monomers placed on neighboring vertices of the lattice. Such models are particularly well suited for investigations by means of high-speed digital computers; the first major contribution in this field is the Monte Carlo computations by Wall and his co-workers,(1) which primarily deal with the

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influence of the excluded volume on the dimensions of the polymer at equilibrium.

The extension of the computations to study certain dynamical properties of changes of conformation in polymers was introduced by Verdier and Stockmayer(2); this work was followed by a series of papers by Verdier(3–5) and Kranbuehl and Verdier(6–11) in all cases using the simple cubic lattice. Monnerie and Geny(12–19) made similar computations for the diamond lattice. The papers by Birshtein *et al.*(20) and Lax and Bender,(21) both of which deal with the simple cubic lattice, should also be mentioned in this connection.

The present work is a continuation of an earlier work by Heilmann(22) (hereafter denoted I); a brief account of the results has been given earlier.(23) The computer calculations were finished as early as the beginning of 1976. In view of some of the more recent publications we might wish that we had done some additional computations; however, we feel that the results are of sufficient substance to still make them worthy of complete publication.

The present work is primarily concerned with the influence of the long-range interaction imposed by the excluded volume restriction as contrasted by the short-ranged effect obtained by merely excluding "backfolding" and with the effect of including the "crankshaft" motion. Both problems were first considered in I. The crankshaft movement has also been included in the computations by Monnerie and Geny.(12–19) Hilhorst and Deutch(24) recognized independently the same two problems when they tried to give a theoretical explanation of the results obtained by Verdier(3–7) which did not include any crankshaft movement. Later the crankshaft movement was included in the computations by Birshtein *et al.*(20) and Lax and Bender(21) and Kranbuehl and Verdier.(11) A model by Verdier and Kranbuehl(9) which included the crankshaft movement but excluded the "one-bead move" is not relevant in this connection as pointed out by Boots and Deutch.(25)

The present calculations are mainly Monte Carlo simulations done by starting the polymer many times in the same conformation and monitoring the relaxation of a few properties towards their equilibrium values; we have used the simple cubic lattice in all computations. The Monte Carlo simulations have been supplemented with exact calculations for very short polymers. The details of the models and the computations are given in Sections 2 and 3. The results for the relaxation of the end-to-end vector and the radius of gyration are given in Section 4.

In Section 5 we introduce a new property called the "winding number" defined as (four times) the difference between the number of left turns and the number of right turns (for details see Section 5); this property, although not directly related to the helix content, might be expected to relax similarly. The results (also given in Section 5) show that the relaxation rates depend only weakly on the polymer length; but the effect of the excluded volume restriction is stronger than for the other properties.

We conclude with a discussion of the relation of the present work to other investigations, primarily the simulations by Kranbuehl and Verdier,(11) the predictions by Hilhorst and Deutch(24) and the scaling predictions of the Gennes(26) and of Jasnow and Moore.(27)

2. THE MODELS

We first define the allowed conformations of the polymers. A polymer is supposed to consist of n atoms numbered from 1 to n. The restriction to the cubic lattice is imposed by requiring that the x, y, and z coordinates of the position of each atom should be integers and that the distance between atom number j and atom number $j + 1$ should be one (for $j = 1, 2, \ldots, n - 1$). The line from atom number j to atom number $j + 1$ is called the jth bond; the direction of the jth bond will always mean the direction from the jth to $(j + 1)$th atom.

In models with excluded volume no two atoms of the polymer are allowed to simultaneously occupy the same position. In models without excluded volume this restriction is relaxed to only forbidding atom number j and atom number $j + 2$ to occupy the same position (for $j = 1, 2, \ldots, n - 2$), i.e., no "backfolding."

In this paper we present the results for six different models: models numbered 1, 2, and 3 are with excluded volume, while models numbered 4, 5, and 6 are the corresponding models without excluded volume.

The kinetic rules of the models are as follows. At times $t = 1, 2, 3, \ldots$ one of the n atoms is chosen at random with equal probability. The chosen atom is then moved according to the kinetic rules of the model provided the movement does not result in a conformation which violates the overlap conditions of the model. If the atom chosen is an end atom (i.e., number 1 or number n), then in all six models a random choice with equal probability is made between the four positions of the end atom which would alter the direction of the first [respectively, $(n - 1)$th] bond to be perpendicular to its current direction.

If the chosen atom is not an end atom ($2 \leqslant j \leqslant n - 1$) and the two bonds from the atom to its neighbors are in the same direction, then the atom is not moved in any of the models. Otherwise the directions of the two neighboring bonds are perpendicular to each other and a movement is attempted. In models 1 and 4 one only tries one possibility: to interchange

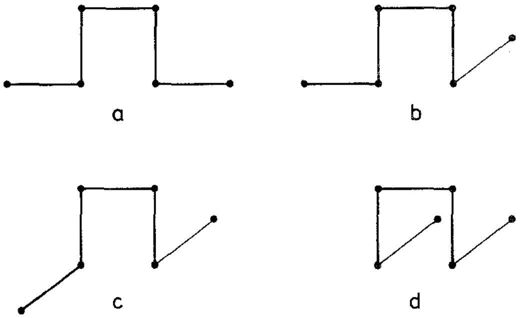

Fig. 1. Four examples of the crankshaft conformation. In versions (b) and (d) the crankshaft is only turned with 50% probability in models 2 and 5, and in version (c) the crankshaft is not turned. It is also possible to construct crankshaft conformations where the crankshaft is not turned using models 3 and 6.

the directions of the two bonds; this means that model 1 is identical to the model considered by Verdier,(2–8,10,11) while model 4 is identical to model 3 of I. In the remaining models one also tries first to interchange the directions of the neighboring bonds, but if this fails because it results in an overlap between the jth atom and either the $(j-2)$th atom or the $(j+2)$th atom, then it is recognized that one has a crankshaft conformation (see Fig. 1), and it is attempted to turn the crankshaft. Assuming that the overlap occurs between the jth and the $(j+2)$th atom then the two atoms to be moved are number j and number $j+1$, and the bonds to be changed are the $(j-1)$th and $(j+1)$th. In models 2 and 5 one changes their directions to one of the two possible perpendicular directions (making a random choice with equal probability); these two models are identical to model 2 or model 4, respectively, of I. Finally, in models 3 and 6 the directions of the $(j-1)$th and $(j+1)$th bonds are changed to their opposites (which means an interchange of the directions of the two bonds).

The rules imply that the chance of moving a particular atom in one unit of time is proportional to $1/n$. In order to compare with real systems all times should be divided by n. This will be done without mentioning when relaxation times are presented in the following sections.

Note that in the present class of models the internal forces in a polymer molecule do not obey Newton's third law. Rather they are divided into constraining forces which ensure that the polymer stay connected and that the excluded volume restrictions are satisfied, and random forces which allow one to neglect the fact that the presence of one part of the polymer might screen another part from the random force of the surrounding solvent.

3. THE COMPUTATIONS

The main attention has been given to the computations of the longest relaxation time for the following three properties of the polymer conformation: the (signed) x coordinate of the end-to-end vector (denoted x), the square of the length of the end-to-end vector (denoted x^2) and the square of the radius of gyration (denoted h^2). This has been attempted by Monte Carlo simulation for $n = 8$, 16, 32, 64, and 128 and by exact computations for $n = 3$, 4, 5, and 6.

In the Monte Carlo calculations the polymer is started many times for each model from a given initial conformation and allowed to move according to the rules of the model for a fixed length of time. For each unit of time the random selection of an atom is done by a linear congruential random number generator (see Knuth$^{(28)}$)

$$X_{k+1} = \left(X_k * 5^{15} + 1\right) \text{modulo}\, 2^{35} \tag{1}$$

where X_k is the kth random number.

At fixed time intervals the conformation is analyzed and the values of the desired physical properties are computed and stored. In the present case we have chosen to let each start run until we had a set of 32 values obtained at equally spaced time intervals for each property. These sets of 32 data points are averaged over the repeated starts; also, we extract from the repeated starts an estimate of the covariance matrix for a set of data points according to formula (I.4) of the appendix of I. The estimation of the relaxation times is then carried out according to the least-squares method discussed in the appendix of I. We have fitted to an expression either of the form

$$a_0 + a_1 \exp(-\gamma_1 t) \tag{2}$$

or

$$a_0 + a_1 \exp(-\gamma_1 t) + a_2 \exp(-\gamma_2 t) \tag{3}$$

We have generally preferred the form (3) with two relaxation times over the form (2) if was possible to distinguish two relaxation times. When the value of a_0 was known we made the estimation both with a_0 fixed at its known value and as a free parameter, to obtain a check on the goodness of the fit. For estimating the relaxation times of x, x^2, and h^2 we have used an initial conformation with bond directions $+x, +y, +z, +x, +y, +z, +x, \ldots$; i.e., the same very stretched initial conformation as was used in I. This conformation is denoted A. In order to check the influence of the initial conformation on the computed results we also tried a very compact initial conformation, but only for $n = 64$; this conformation is denoted B and is shown in Fig. 2. Since x has the equilibrium value, zero, in this

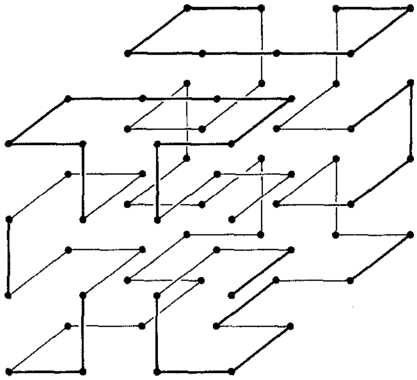

Fig. 2. The very compact initial conformation B used in testing the relaxation rates unfolding a 64-mer.

conformation, only the relaxation of x^2 and h^2 can be monitored successfully.

The computations were done in part on a RC4000 computer and in part on a Texas Instruments model 980A computer. All the Monte Carlo simulations were written in assembly language.

The number of movements per single start have ranged between 128 and 32×10^6, and the number of starts have been between 160 and 16000; in the worst possible case we used 5×10^9 random numbers to generate necessary data for a given polymer length and a given model [this is probably about as high as one can go when the period of the generator is 2^{35} ($\sim 3 \times 10^{10}$)].

In all we have effectively used between $\frac{1}{2}$ year and 1 year of c.p.u. time (both computers have a cycle-time of the order 0.1 μsec).

In exact computations we write down the stochastic matrices for the models explicitly and compute the largest eigenvalue (less than one) by a standard numerical procedure; the corresponding relaxation time is then obtained as (minus) the logarithm of the eigenvalue. The only problem is (as mentioned in I) that the spatial symmetry of the cubic lattice should be taken into consideration. However, this has the advantage of reducing the size of the individual matrices enormously.

4. THE RESULTS FOR x^2, h^2, AND x

The computed relaxation times for x^2, h^2, and x for the six models are given in Tables I, II, and III, respectively. We have divided the relaxation times for models 1 and 4 by $(n-1)^3$ and the relaxation times for models 2, 3, 5, and 6 by $(n-1)^2$ in order to exhibit the n dependence more clearly.

Table I. Relaxation Rates for the Squared Length of the End-to-End Vector x^2[a]

n	Model 1	Model 2	Model 3	Model 4	Model 5	Model 6
3	43.0	21.5	21.5	43.0	21.5	21.5
4	44.9	15.0	15.0	44.9	15.0	15.0
5	54.9	13.8	13.7	49.2	12.3	12.3
6	62.8	13.9	12.8	52.4	11.5	10.9
8	74 ± 12	14.3 ± 2	15.4 ± 3	53 ± 3	12.8 ± 0.6	9.5 ± 2
16	62 ± 30	14.0 ± 0.8	13.8 ± 1.2	61 ± 4	12.7 ± 0.8	15.0 ± 1
32	49 ± 25	12.8 ± 0.5	14.6 ± 0.4	46 ± 6	11.9 ± 1	15.9 ± 1.5
64A	51 ± 10	11.7 ± 0.8	11.5 ± 0.6	36 ± 5	13.1 ± 0.8	14.8 ± 1.5
64B	—	13 ± 4	10.4 ± 0.8	25 ± 2	9 ± 6	12 ± 3
128	21 ± 5	9.8 ± 0.4	11.5 ± 0.3	39 ± 2	14.1 ± 0.8	17.6 ± 0.5

[a] The results have been multiplied by $(n-1)^3$ in case of models 1 and 4, and by $(n-1)^2$ elsewhere.

For model 1 with initial conformation B (and $n = 64$) we did not get anywhere near equilibrium within the time range chosen for the computation which indicates that the relaxation time is much longer than the relaxation time we have computed from the initial conformation A. It should be noted that it is possible within model 1 to move from conformation B to conformation A; i.e., the two initial conformations belong to the same ergodic class. However, it is also obvious that the path away from B is a very narrow one within model 1.

For the other 5 models, the agreement between the relaxation times for the two initial conformations is fair. Also, the agreement between the relaxation times for x^2 and h^2 is very good and continuation from the exact computations to the Monte Carlo estimates is reasonably smooth. In all, we conclude the results do have a high degree of internal consistency, although the standard deviations probably have a tendency to come out on the small side.

Table II. Relaxation Rates for the Squared Length of Gyration[a]

n	Model 1	Model 2	Model 3
3	43.0	21.5	21.5
4	44.9	15.0	15.0
5	54.9	13.8	13.7
6	62.8	13.9	12.8
8	57 ± 3	13.0 ± 1.2	14.8 ± 1
16	85 ± 2	14.0 ± 1	9 ± 4
32	89 ± 10	12.2 ± 1.2	11.6 ± 1.2
64A	37 ± 10	10.1 ± 3	11.2 ± 0.6
64B		9 ± 5	10.8 ± 1
128	20 ± 10	7.7 ± 1.2	11.5 ± 0.3

n	Model 4	Model 5	Model 6
3	43.0	21.5	21.5
4	44.9	15.0	15.0
5	49.2	12.3	12.3
6	52.4	11.5	10.9
8	47 ± 2	12.6 ± 2	11.2 ± 0.5
16	60 ± 6	14 ± 10	15.0 ± 0.5
32	46 ± 6	14.9 ± 0.3	18.5 ± 2
64A	30 ± 8	12.9 ± 1.5	16.7 ± 0.3
64B	24 ± 2	17 ± 2	12 ± 4
128	37 ± 2	13.5 ± 0.8	16.7 ± 0.6

[a] The results have been multiplied by $(n-1)^3$ in case of models 1 and 4, and by $(n-1)^2$ elsewhere.

The most surprising result is that the relaxation of x^2 and h^2 is slowed down when the excluded volume restriction is lifted, at least for short polymers. For the models with the crankshaft movement (2–5 and 3–6) the crossover to the expected behavior occurs around $n = 25$; for the models without the crankshaft movement no crossover appears below $n = 100$. This behavior is in fact so surprising that if it had not been supported by the exact results for $n = 5$ and 6 then we would have dismissed it as some strange artefact of the Monte Carlo method.

The relaxation of x behaves more normally; i.e., it relaxes faster when the excluded volume restriction is lifted. For the models without the excluded volume restriction the relaxation time for x appears to be twice as large as the corresponding relaxation time for x^2 and h^2; this is in agreement with the intuitive expectation. For the models with excluded volume the relaxation of x is slower by a factor somewhere between 3 and

Table III. Relaxation Rates for the Signed x Coordinate of the End-to-End Vector[a]

n	Model 1	Model 2	Model 3
3	5.7	2.9	2.9
4	8.8	2.9	2.9
5	11.7	3.2	3.3
8	15.4 ± 0.4	3.5 ± 0.1	3.6 ± 0.1
16	18.6 ± 0.8	3.5 ± 0.2	3.7 ± 0.2
32	16.9 ± 0.6	2.7 ± 0.3	3.2 ± 0.4
64A	18.8 ± 1.5	2.8 ± 0.6	3.5 ± 0.3
64B		1.9 ± 1.2	
128	13 ± 4	2.8 ± 0.4	2.7 ± 0.4
n	Model 4	Model 5	Model 6
3	5.7	2.9	2.9
4	8.8	2.9	2.9
5	11.6	3.5	3.7
8	18.6 ± 0.4	4.5 ± 0.1	4.7 ± 0.1
16	27 ± 1	5.9 ± 0.2	5.7 ± 0.4
32	28 ± 2	5.9 ± 0.3	7.2 ± 0.5
64A	22 ± 6	6.3 ± 0.5	6.8 ± 0.8
128	24 ± 2	5.9 ± 1.5	8.5 ± 0.6

[a] The results have been multiplied by $(n-1)^3$ in case of models 1 and 4 and by $(n-1)^2$ elsewhere.

5; i.e., definitely more than a factor 2 for the values of n used in the computations.

The dependence of the relaxation times on n is of the same order of magnitude for x and x^2 and h^2; but the increase appears to be slower for x than for x^2 and h^2. For models 5 and 6 which have crankshaft movement and no excluded volume restriction one finds, as expected, that the relaxation times increase with the second power of $n-1$. For models 1 and 4 which have no crankshaft movement the relaxation times increase at least as fast as $(n-1)^3$; there is no discernible effect of the excluded volume on the dependence on $n-1$. For the two models with the crankshaft movement and the excluded volume restriction included (models 2 and 3) the increase is at least as $(n-1)^2$ and definitely not as fast as $(n-1)^3$; in fact, a very good fit is obtained with scaling prediction (de Gennes,(26) Jasnow and Moore(27)) $(n-1)^{2.2}$ when applied to the relaxation of x^2 and h^2. However, in view of the fact that this partly is obtained by having rather small values of the relaxation time for small values of n (as compared to the models without the excluded volume restriction), one should not attach too much importance to this accordance.

5. RELAXATION OF THE WINDING NUMBER

The original aim of introducing a measure for the number of windings in a polymer conformation was to get a measure of the helix content of the conformation to be used in connection with studies of the helix-coil transition. This property might (at least in principle) be measurable by circular dichroism.

The property which we decided to use is defined as follows: We consider the bond directions as forming an ordered sequence (taking the bonds in their natural order) of symbols which can be either $+x$, $-x$, $+y$, $-y$, $+z$, or $-z$. From this sequence we delete all $+x$ or $-x$, leaving a sequence which contains only $+y$, $-y$, $+z$, and $-z$. In this we count $+1$ each time we have one of the following ordered neighboring pairs:

$$(+y, +z), \qquad (+z, -y), \qquad (-y, -z), \qquad (-z, +y)$$

We count -1 when the ordered neighbors are

$$(+z, +y), \qquad (-y, +z), \qquad (-z, -y), \qquad (+y, -z)$$

while we count zero if we have two y's (+ or −) or two z's next to each other.

As an example we take the following conformation (defined by the sequence of bond directions) of a 16-mer:

$$(+x, +y, +y, +z, -x, -z, +y, +z, +z, +x, -y, +z, -y, -z, -z)$$

Deleting the x's we get

$$(+y, +y, +z, -z, +y, +z, +z, -y, +z, -y, -z, -z)$$

which contains 11 neighbor pairs. In order they contribute

$$0+1+0+1+1+0+1-1+1+1+0$$

In all we find that the winding number is 5 for this configuration.[2]

To be sure, the winding number defined above is not related to the circular dichroism of the polymer, neither do we expect to convince anybody that the winding number measures the helix content. However, we do think that our "winding number" is sufficiently similar to these more physical quantities to allow us to draw relevant conclusions from our calculations.

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[2] The "winding number" as defined here can be considered as a generalization of the "winding number" (also called the "index") defined in complex analysis for a closed curve in a plane with respect to a point in the plane.

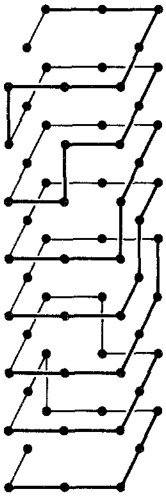

Fig. 3. The tightly wound spiral conformation C used in testing the relaxation of the winding number.

The initial conformations A and B are of course not particularly useful in the study of the relaxation of the winding number. Instead, we have created two new initial conformations which both have a high value of the winding number. The first one, a rather tightly wound spiral, is shown for $n = 64$ in Fig. 3; it is denoted C. Again to test the significance of the excluded volume we also tried a more open spiral, which is shown in Fig. 4 for $n = 64$; this conformation is denoted D. The continuation of C and D to higher values of n should be obvious.

Several of the models showed a marked influence of the choice of start configurations on the relaxation times; for these models (model 1, 2, 3, and 4) we have used both start configurations for almost all values of n, while we for models 5 and 6 and start configuration D only have tried $n = 256$.

We have no exact results on the relaxation of the winding number since this property appears to be meaningless for small values of n. The relaxation times for $n = 32$, 64, 128, 256, and 512 have been estimated by the Monte Carlo method for all six models and initial configuration C and D. The results are shown in Tables IV and V. For models 5 and 6 the relaxation rate is clearly independent of n. For the other models the relaxation times show a weak increase with n, and some dependence on the initial configuration. However, we think it is fair to conclude that the winding number relaxes primarily through local changes in the conformation and not through diffusion of disorder along the polymer chain. This

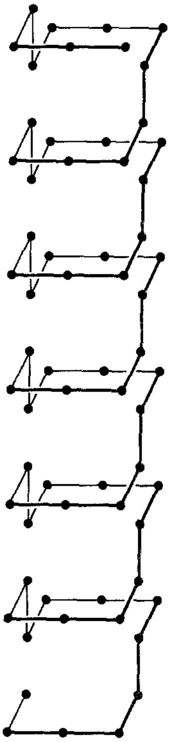

Fig. 4. The open spiral conformation D used in testing the relaxation of the winding number.

Table IV. Relaxation Rates for the Winding Number Using Initial Configuration C^a

n	Model 1	Model 2	Model 3
32	30.2 ± 0.3	149 ± 2	126 ± 1
64	12.3 ± 0.1	134 ± 10	75 ± 0.4
128	6.1 ± 0.5	128 ± 10	39 ± 4
256	2.6 ± 0.2	74 ± 5	32 ± 4
512	1.0 ± 0.1	64 ± 5	29 ± 3
1024		61 ± 5	
n	Model 4	Model 5	Model 6
32	28.3 ± 0.6	490 ± 20	710 ± 50
64	13.4 ± 0.6	510 ± 500	730 ± 70
128	5.3 ± 0.6	520 ± 50	700 ± 30
256	5.8 ± 0.7	490 ± 30	640 ± 10
512	4.1 ± 0.4	510 ± 80	645 ± 12

[a] All results have been multiplied by a factor of 10^3.

Table V. Relaxation Rates for the Winding Number Using Initial Configuration D^a

n	Model 1	Model 2	Model 3
32	38.2 ± 1.5	124 ± 1	202 ± 5
64	17 ± 6	151 ± 5	186 ± 10
128	16.5 ± 1	118 ± 8	168 ± 12
256	11.7 ± 2	131 ± 15	135 ± 25
512	12.0 ± 1	106 ± 7	197 ± 5

n	Model 4	Model 5	Model 6
32	33.5 ± 1.5	438 ± 3	490 ± 50
64	17.7 ± 1.2	404 ± 8	850 ± 100
128	14.8 ± 2	408 ± 3	770 ± 120
256	12.7 ± 1.2	460 ± 400	690 ± 12
512	9.8 ± 0.8	420 ± 50	840 ± 100

[a] All results have been multiplied by a factor 10^3.

would mean that the relaxation times should be essentially independent of the polymer length.

6. DISCUSSION

The main result one can obtain from these computations is the dependence of the relaxation times on the polymer length. It may be compared with the predictions of the scaling theory(26,27) and the theory of Hilhorst and Deutch.(24) The scaling theory, in principle, applies only to the Rouse model,(29) but the present models should be expected to behave similarly unless some special feature of the model plays a role. Hilhorst and Deutch(24) showed that the models without the crankshaft movement (models 1 and 4) do have such a special feature and that the relaxation times in these models should increase at least as n^3 as contrasted with an increase as n^2 in the other models. The scaling prediction is an increase as n^2 in models without the excluded volume restriction and as $n^{2.2}$ in models with the excluded volume restriction.

As mentioned already in Section 4 our results for the relaxation of x^2 and n^2 in models 2, 3, 5, and 6 do agree with the scaling prediction. However, the effect of introducing the excluded volume restriction is at low values of n in clear disagreement with assumptions of the scaling theory. Also, the relaxation of x shows an n^2 dependence in all four models; since it is impossible for the relaxation time of x to be smaller than the relaxation time of x^2 (at least in the present class of models) we can only confirm the statement by Boots and Deutch(25) that one needs much larger values of n in order to see scaling behavior.

Table VI. Relaxation Rates for Model 3, Multiplied by $(n-1)^2$, Found in Present Work and Results by Birshtein *et al.*(20) (Bi), Recalculated for Comparison

n	x	x^2	h^2
16Bi	4.2	16	15
16	3.7	14	9
32Bi	3.5	18	15
32	3.2	15	12

The paper by Hilhorst and Deutch(24) does not really consider the effect of the excluded volume restriction. Therefore, their predictions should be compared primarily to models 4, 5, and 6 for which the agreement is perfect. They also conjecture that the effect of the excluded volume should be weak; this is confirmed by the present calculations.

Our results can of course also be compared to the other Monte Carlo simulations. Lax and Bender(21) made simulations for $n = 16$, 32, and 64 on the model which is denoted model 1 in the present paper. They found relaxation times for x^2 only; their values are so much smaller than ours that we can only conclude that their way of determining the relaxation time is not compatible with the method we have used.

Birshtein *et al.*(20) made simulations on the model we call model 3. They record values for the relaxation times for x, x^2, and h^2 (as well as many other properties), but only for $n = 16$ and $n = 32$. Their results are listed in Table VI together with the corresponding results from our Table III. It is seen that the agreement is fairly good.

The simulations by Kranbuehl and Verdier(11) include both models with and without the crankshaft movement. They have only monitored the end-to-end vector obtaining a relaxation time which should be compared with our results for the relaxation of x. Their model without the crankshaft movement is almost identical to our model 1; they are compared in Table VII. The agreement is very good except for $n = 64$ (63); we do not think that the difference is significantly larger than the uncertainty connected with the methods. The comparison of our model 3 with their models with the crankshaft movement is complicated by the fact that the rules are somewhat different, since they include other two-bead movements than the crankshaft movement. If one counts these other two-bead movements as the two "one-bead movements" of which they are composed and one ignores the excluded volume except for backfolding then Table VIII obtains. Clearly, our model 3 has a much larger proportion of crankshaft

Table VII. Relaxation Rates for x in Model 1, Multiplied by $(n-1)^3$; Left Side Recalculated Results by Kranbuehl and Verdier,[(11)] Right Side Present Results

n	x	x	n
9	17.3	15.4	8
15	18.4	18.6	16
33	16.7	16.9	32
63	12.5	18.8	64A
		13	128

Table VIII. The Average Number of "One-Bead Moves" and "Crankshaft Moves" Per Cycle in the Three Models of Ref. 11 and in Our Model 6 (and Model 3 if the Excluded Volume is Ignored)

	$p = 0.1$	$p = 0.5$	$p = 0.9$	Model 6 (3)
One bead	0.56	0.68	0.79	0.53
Crankshaft	0.009	0.045	0.08	0.15

Table IX. Relaxation Rates for x Multiplied by $(n-1)^2$; Left Side Recalculated Results of Ref. 11 with $p = 0,9$, Right Side Present Results Using Model 3

n	x	x	n
9	5.8	3.6	8
15	5.7	3.7	16
33	4.2	3.2	32
63	1.8	3.5	64A
		2.7	128

movements than any of the three mixed models used by Kranbuehl and Verdier. In Table IX we have compared their result for $p = 0.9$ with model 3; the fact that Kranbuehl and Verdier find a faster relaxation at the lower values of n might be attributed to the higher mobility at the ends in their model.

In conclusion, we do not see any obvious discrepancies between our results and the results obtained by using autocorrelation functions (Birshtein *et al.*[(20)] and Kranbuehl and Verdier[(11)]). The difference in the conclusion reached by us and the conclusion reached by Kranbuehl and

Verdier concerning the importance of the excluded volume might be attributed to the fact the computations only consider rather low values in n.

The monitoring of the relaxation from an extreme conformation seems thus to be justified both by the agreement with the results obtained from autocorrelation functions and by the internal consistency of our own computations (consistent relaxation times for the two initial conformations for $n = 64$, consistent relaxation times for x^2 and h^2, and consistent relaxation times whether knowledge of the equilibrium value was used in the estimation or not).

In this connection we want to stress that we also think that the possibility that part of the polymer chain might be in a locked or an almost locked conformation does constitute a serious problem. It was already pointed out in I and by Verdier$^{(4)}$ that the models with excluded volume are not ergodic for n larger than 20. For moderate values of n it is only a small fraction of the conformations which is separated from the main ergodic class and placed in a separate ergodic class each of which is very small. But as n increases the probability of having a locked conformation in part of the chain increases (to one in the limit $n = \infty$) and the fraction of the conformations which belong to the main ergodic class (the class with all the open conformations) will decrease (to zero in the limit $n = \infty$); however, the main ergodic class will still be much larger than any of the other classes and the averages of equilibrium properties taken over this class will generally not deviate much from the averages taken over the whole ensemble. Consequently, one might hope that the problem posed by the lack of ergodicity is not a serious obstacle.

A related problem is the existence of conformations which, although they do belong to the main ergodic class, have only a very thin connection to the rest of the conformations in the class. An example is, as mentioned earlier, conformation B in model 1. One might picture the main ergodic class as consisting of a body of conformations which have a rather high mobility and are well connected to each other by legal movements and some long, narrow dendrites of conformations with low mobility (the mobility decreasing towards the tip of the dendrite) and connections which make it essentially one dimensional. The relaxation times for the body will be the ones normally observed; the relaxation times corresponding to movements along one of the dendrites will be much larger, but they will have a low weight and only be observable if one explicitly starts near the tip of the dendrite.

REFERENCES

1. F. T. Wall, S. Windwer, and P. J. Glans, in *Methods of Computational Physics*, Vol. 1 (Academic Press, New York, 1963).

2. P. H. Verdier and W. H. Stockmayer, *J. Chem. Phys.* **36**:227 (1962).
3. P. H. Verdier, *J. Chem. Phys.* **45**:2122 (1966).
4. P. H. Verdier, *J. Comp. Phys.* **4**:204 (1969).
5. P. H. Verdier, *J. Chem. Phys.* **59**:6119 (1973).
6. D. E. Kranbuehl and P. H. Verdier, *J. Chem. Phys.* **56**:3145 (1972).
7. D. E. Kranbuehl, P. H. Verdier, and J. M. Spencer, *J. Chem. Phys.* **59**:3861 (1973).
8. D. E. Kranbuehl and P. H. Verdier. *Polym. Prepr. Am. Chem. Soc. Div. Polym. Chem.* **17-2**:144 (1976).
9. D. E. Kranbuehl and P. H. Verdier, *Polym. Prepr. Am. Soc. Div. Polym. Chem.* **17-2**:148 (1976).
10. D. E. Kranbuehl and P. H. Verdier, *J. Chem. Phys.* **67**:361 (1977).
11. D. E. Kranbuehl and P. H. Verdier, *J. Chem. Phys.* **71**:2662 (1979).
12. L. Monnerie and F. Geny, *J. Chim. Phys.* **66**:1691 (1969).
13. L. Monnerie, F. Geny, and J. Fouquet, *J. Chim. Phys.* **66**:1698 (1969).
14. F. Geny and L. Monnerie, *J. Chim. Phys.* **66**:1708 (1969).
15. F. Geny and L. Monnerie, *J. Chim. Phys.* **66**:1872 (1969).
16. L. Monnerie and F. Geny, *J. Polym. Sci.* **C30**:93 (1970).
17. F. Geny and L. Monnerie, *J. Polym. Sci., Polym. Phys. Ed.* **17**:131 (1979).
18. F. Geny and L. Monnerie, *J. Polym. Sci., Polym. Phys. Ed.* **17**:147 (1979).
19. F. Geny and L. Monnerie, *J. Polym. Sci., Polym. Phys. Ed.* **17**:173 (1979).
20. T. M. Birshtein, V. N. Gridnev, Yu. Ya. Gotlib, and A. M. Skvortsov, *Vysokomol. Soyed.* **A19**:1398 (1977).
21. M. Lax and C. Brenner, *J. Chem. Phys.* **67**:1785 (1977).
22. O. J. Heilmann, *Kgl. Danske Vid. Selsk. Mat. Fys. Medd.* **37.2** (1968).
23. J. Rotne and O. J. Heilmann, Proc. VIIth Int. Congress on Rheology Gothenburg, p. 510 (1976).
24. H. J. Hilhorst and J. M. Deutch, *J. Chem. Phys.* **63**:5153 (1975).
25. H. Boots and J. M. Deutch, *J. Chem. Phys.* **67**:4608 (1977).
26. P. G. De Gennes, *Macromolecules* **9**:587 (1976).
27. D. Jasnow and M. A. Moore, *J. Phys. (Paris)* **38**:L467 (1977).
28. D. E. Knuth, *The Art of Computer Programming*, Vol. 2. *Seminumerical Algorithms* (Addison-Wesley, Reading, Massachusetts, 1969).
29. P. E. Rouse, *J. Chem. Phys.* **21**:1272 (1953).