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Static and Dynamic Scaling Properties of Single, Self-Avoiding Polymer Chains in Two Dimensions via the Bond Fluctuation Method of Monte Carlo Simulation

James Patton Downey

ES74, Marshall Space Flight Center, Alabama 35812

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ABSTRACT: Monte Carlo simulations utilizing the bond fluctuation method for a square lattice were performed to simulate the dynamics of two-dimensional polymer chains. Relaxation times of the modes were determined as were average intrachain distances. Scaling exponents were found relating the relaxation times with mode number and the total number of chain segments. Scaling exponents relating intrachain distance with mode number and the total number of chain segments were also found. Scaling behavior indicated that internal fragments of the chains were more expanded than would be the case of a self-similar chain but that the higher order modes relaxed more quickly relative to the lower order modes than would be the case for a Rouse chain. Small but noticeable cross-correlations between the modes were observed.

Introduction

The bond fluctuation method for simulating the dynamic behavior of polymer chains was introduced by Carmesin and Kramer[1] and has been utilized in several studies.[2–4] The method is particularly useful in describing the dynamics of dense melts since the variable bond lengths used in this model avoid problems with nonergodic behavior. That is to say that for this model all energetically allowed states are dynamically accessed with the correct probabilities. Another advantage of this model is that in a two-dimensional simulation, internal structures within the chain may relax without having to diffuse out the chain ends. The ability to undergo such an intrastructural relaxation avoids a common feature which has been found within other simulations.[5] The chain movement rules of the bond fluctuation model seem to give Rouse-like dynamics in two dimensions where other models do not.

The bond fluctuation method has not been previously used to examine the internal dynamic scaling properties for the modes of a single, two-dimensional chain. This has not been done previously by any Monte Carlo method, and the bond fluctuation method would seem ideal for such a study. The most likely reason that this method has not been applied in such a study is that it is widely assumed that the motions of the vibrational modes of self-avoiding chains would have large cross-correlations and, therefore, not be well approximated by eigenmode analysis. Perhaps it is assumed that cross-correlated modes would give a poor description of the dynamic scaling properties within a chain, but this is not necessarily the case. Cross-correlations would arise if there are large deviations from circular symmetry. They might also occur if chain movement rules favor correlated motions. This should be the case if solvent backflow interactions with the chain are taken into account.[6] However, a real two-dimensional chain on a surface has minimal interaction with a solvent, and, therefore, solvent backflow effects may be ignored. In any case, the bond fluctuation method does not attempt to include such effects. The only solvent interaction included in this model is Brownian forces on individual chain segments. A previous study utilizing this method found the cross-correlations of these modes to be insignificant for a moderately concentrated, two-dimensional system, where the lattice occupation density was 40%.[4] Similarly, three-dimensional studies with fixed bonds by Kovac and co-workers have shown no cross-correlations between the modes.[7] A Monte Carlo study by Verdier[8] indicated cross-correlations between modes, but the dynamics of this model required internal chain structures to relax via diffusion out the chain ends.[5] This restriction probably results in a requirement that higher order modes can relax only in conjunction with the first mode.

In this study, the bond fluctuation model is used to simulate the dynamics of two-dimensional isolated polymer chains. Chains of varying length, are used to ascertain scaling properties, whether the chains are sufficiently long to attain asymptotic values and whether Rouse-like behavior is observed. Static properties of the chains are also determined to examine the relationships to the dynamic properties, and it is verified that this model obeys the dynamic scaling hypothesis. Finally, a dynamic scaling exponent relating the relaxation times of the modes of a chain with mode number is determined. To the best of the author's knowledge, this scaling exponent has not been previously obtained in two dimensions by any Monte Carlo model with self-avoiding properties.

The Model

The bond fluctuation model has been described in detail elsewhere[1] and will be covered only briefly here. A polymer chain is modeled as a series of bonded segments lying on a square lattice. Each segment occupies four lattice sites which together form a square. The distance between the centers of bonded segments must be between 2 and $\sqrt{13}$ (inclusive) lattice units. A segment may move a distance of one lattice unit up, down, left, or right at a time. None of the four lattice sites which make up a segment may occupy the same lattice site as another segment (also referred to as the excluded volume condition). This ensures that the chain will behave as a self-avoiding walk and distinguishes this chain from a true Rouse chain, which is a random walk.[9] The chains modeled in this paper do not have temperature-dependent properties, meaning that all allowed chain configurations are of equal energy.

The dynamics are achieved by selecting a segment at random and attempting to move that segment one lattice unit in one of the four allowed directions which is also chosen at random. If this attempt results in the double

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occupancy of a lattice site or an impermissible bond length, the attempted motion is abandoned. Otherwise, the segment is placed in the new location. Throughout this paper, the basic time unit for a chain consisting of N segments will be N attempted segment motions.

Calculations

The dynamics are analyzed in terms of the normal coordinates $\vec{U}_k(t)$, which are defined by[8]

$$\vec{U}_k(t) = \sum_{j=1}^{N} [(2 - \sigma_{k0})/N]^{1/2} \cos[(j - 1/2)\pi k/N]\vec{R}_j(t) \tag{1}$$

where $\vec{R}_j$ is the center of the jth segment with respect to the origin, k is the mode number, and N is the total number of segments. Using the above definition, the autocorrelation functions of the normal coordinates are given by the equation

$$\rho(t) = \langle \vec{U}_k(t)\cdot\vec{U}_k(0)\rangle/\langle U_k^{\,2}\rangle \tag{2}$$

where the brackets indicate average values. The autocorrelation functions of normal coordinates decay exponentially with time (the number of bead cycles). We, therefore, define the relaxation time of the mode as the negative of the slope of $\ln \rho$ versus time. This slope is calculated for the values of $\ln \rho$ between 0 and -1.

Simulations

The simulations were carried out for chains of 13, 25, 37, 49, 61, and 73 segments. During each run, samples of the coordinates of the chains were recorded at regular intervals. It was attempted to space these intervals far enough apart so that the autocorrelation function of the first normal coordinate would drop on average approximately 0.6% between samplings. The last chain configuration for a given run was used as the starting configuration for the next run.

For the chains of 13 and 25 segments, 4 runs were performed with 60 000 samples collected per run. For the chains of 37 segments, 6 runs were performed with 45 000 samples collected per run. For the chains of 49, 61, and 73 segments, 8 runs were performed and 30 000 samples were collected per run. A run for the 73-segment chain took about 4500 CPU seconds on a CRAY XMP.

Results and Discussion

For chains of length 61 beads and less, the cross-correlations $\langle \vec{U}_i(0)\cdot\vec{U}_j(0)\rangle$ between modes 1, 2, and 3 were calculated. For the chain of 61 beads, the cross-correlations between modes 4, 5, and 6 were also calculated. It was found that the average cross-correlation between an even and an odd mode was indistinguishable from zero given the statistical uncertainties of the analysis. However, the cross-correlation between mode pairs which were both even or odd was significant. It was found that for chains of 49 beads and less, the value of the normalized cross-correlation given by

$$Q_{ij} = \langle\langle \vec{U}_i(0)\cdot\vec{U}_j(0)\rangle\rangle/(\langle U_i^{2}(0)\rangle\langle U_j^{2}(0)\rangle)^{1/2} \tag{3}$$

was consistently equal to a value of approximately $0.04 < Q_{13} < 0.05$ when averaged over several runs for ($i = 1$, $j = 3$). For the chain of 61 beads, values of Q_{ij} are given in Table 1 for several pairs of (i,j). The value of $Q_{13} = 0.08$ was found for this chain length, but within the large experimental error for this point, this was not significantly different from the value found for the shorter chains. Looking at Table 1, it appears that there are significant normalized cross-correlations between the other mode pairs of $(i, i + 2)$ of about 10%. There are also significant cross-correlations for the $(i, i + 4)$ pairs, but these are significantly smaller. There was no computational time available to study longer chains, but presumably the cross-correlations between mode pairs (i, j) where $i > j + 2$ get progressively smaller with increasing i. The observed cross-correlations are due to deviations from circular symmetry arising from excluded volume effects. The fact that no significant cross-correlations were found in three-dimensional studies,[7] but are found here, is due to the fact that excluded volume effects are greater in two dimensions. The cross-correlations are not large, and therefore the use of normal mode analysis may give a fair description of the chain dynamics.

Table 1. Normalized Cross-Correlations for the Mode Pairs (i,j)

	Q_{ij}				
i	$j = 1$	$j = 2$	$j = 3$	$j = 4$	$j = 5$
2	0.00	0.08	0.00	0.03	0.00
3		0.00	0.12	−0.01	0.05
4			0.00	0.11	0.00
5				0.00	0.10
6					0.00

Table 2. Relaxation Times $\tau(k,N)$ as a Function of Chain Length N and Mode Number k

	$\tau(k,N)$		
N	$k = 1$	$k = 2$	$k = 3$
13	3370(20)	601(38)	192(6)
25	17700(200)	3320(240)	1100(30)
37	47900(3600)	9310(440)	3120(110)
49	104000(11000)	18200(1100)	6420(250)
61	171000(19000)	34200(2800)	11100(500)
73	273000(28000)	49800(4000)	17600(1200)

The average relaxation times, $\tau(k,N)$, for the first three modes of the chains are shown in Table 2 as functions of N and k. The values within the parentheses are the standard deviations for the runs. This seems a reasonable measure of reproducibility since the runs are so long as to be nearly independent of one another. The relaxation times $\tau(k,N)$ are fit by multiple linear regression to the scaling relation

$$\ln[\tau(k,N)] = \alpha \ln(N - 1) - \gamma \ln k + c \tag{4}$$

where α is the scaling exponent expressing the relaxation times as a function of the chain length N and γ is the scaling exponent expressing the relaxation times as a function of the mode number k. c is the intercept. A typical plot of the autocorrelation functions for the first 3 modes of a chain of 61 beads is shown by a semilogarithmic plot in Figure 1. The autocorrelation functions given by the plot are not linear, thereby showing the effects of cross-correlations between the modes.

The values of the exponents obtained are $\alpha = 2.49$, $\gamma = 2.51$, and $c = 1.90$. The fit predicts the values of each of the data points well. The worst fit is found for $\tau(3,13)$, where the predicted fit value is 206 and the simulation value is 192. The relative difference between these values is less than 7%. Given the uncertainties in the data, the values of α and γ are indistinguishable from 2.5.

$\alpha = 2.5$ is the value expected for a Rouse-like chain once excluded volume effects are added to the original Rouse

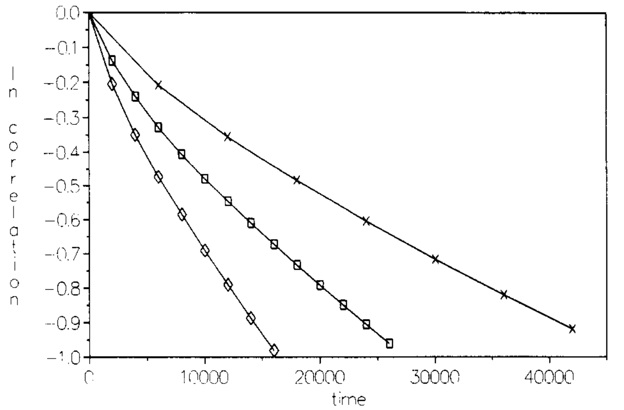

Figure 1. Autocorrelation functions: (◇) mode 1; (□) mode 2; (×) mode 3.

Table 3. Mean Fragment End-to-End Lengths $\langle R_k(N)^2\rangle$ as a Function of Chain Length N and Fragment Length k

	$\langle R_k(N)^2\rangle$		
N	$k = 1$	$k = 2$	$k = 3$
13	268(3)	111(0.3)	61.7(0.1)
25	741(15)	315(3)	175(1)
37	1350(30)	582(5)	324(1)
49	2090(50)	897(10)	500(3)
61	2920(60)	1260(10)	703(4)
73	3850(80)	1670(10)	928(5)

model.[10] This scaling behavior is predicted by the well-known dynamic scaling hypothesis:

$$\tau(1,N) \sim \langle R^2\rangle(N-1) \sim (N-1)^{2\nu+1} \qquad (5)$$

where $\langle R^2\rangle$ is the mean-square end-to-end distance separating the two end segments of the chain. The value of 2ν is known to be 1.5 for two dimensions.[6]

To verify that these chains do indeed obey the dynamic scaling hypothesis and to investigate the static conformations of the chains, the following quantities are calculated:

$$\langle R_k(N)^2\rangle = \langle(\vec{R}_i - \vec{R}_j)^2\rangle \qquad (6)$$

where the brackets indicate an average determined over all the chain segments i and j which are separated by $(N-1)/k$ bonds. The subscript k is used here since the nodes of the kth mode are separated by a length scale of $(N-1)/k$ bonds. $\langle R_k(N)^2\rangle$ will be referred to as the mean squared fragment end-to-end length of a chain and is written as a function of k and N. The values of $\langle R_k(N)^2\rangle$ obtained for each run were averaged together, and the results are in Table 3 along with the standard deviations for each run. These values are then fit by multiple linear regression to the scaling law

$$\ln\langle R_k(N)^2\rangle = 2\nu \ln(N-1) - 2\omega \ln k + c \qquad (7)$$

The values obtained are $2\nu = 1.50$, $2\omega = 1.30$, and $c = 1.84$. All points were fit well by the equation. The worst relative difference between fit and simulation values was for $\langle R_2(73)^2\rangle$, where the value for the fit was 1590 and the value from the simulation was 1670. The above results show that relaxation times scale with length as

$$\tau(k_1,N) \sim \langle R_j(N)^2\rangle(N-1) \sim (N-1)^{2\nu+1} \qquad (8)$$

where j is not necessarily the same mode number as k, but may be any mode. Thus the N dependence of $\tau(k,N)/\langle R_j(N)^2\rangle$ is found to be in excellent agreement with the dynamic scaling hypothesis.

Table 4. Summary of Scaling Exponents from the 2D Rouse Model and Those Observed for the 2D Bond Fluctuation Simulations with Excluded Volume

	Rouse value	bond fluctuation simulation
2ν	1.0	1.5
2ω	1.0	1.3
α	2.0	2.5
γ	2.0	2.5

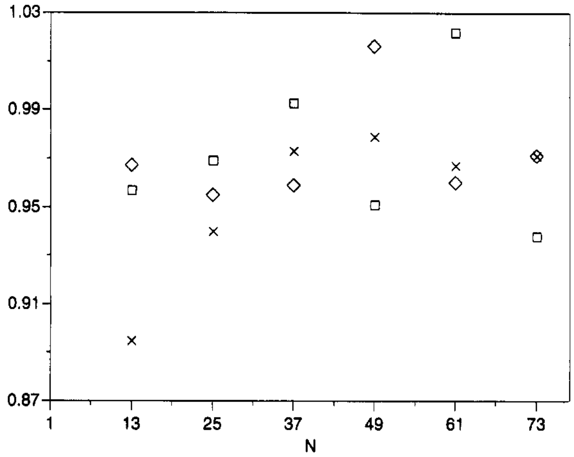

Figure 2. Plot of C as a function of the total number of chain segments, N: (◇) mode 1; (□) mode 2; (×) mode 3.

The above discussions are mainly concerned with the scaling properties of a chain as a function of length. For the most part these results are well-known and are to be expected if this model is valid. The dynamic scaling properties within a chain are not nearly as well understood.

The value of $\gamma = 2.5$ is somewhat higher than the Rouse value of 2.0, indicating that the effect of excluded volume is quite large. This value is also much greater than the value of about 2.1 which Carmesin and Kremer[4] found for a multiple-chain system at 40% density using this model. The three-dimensional value for this exponent is reported by Kovac and co-workers to be around 2.13 for single chains using fixed bond length models.[7,11,12] A similar study showed that γ drops toward the Rouse value of 2.0 as concentration is increased.[13] A three-dimensional, temperature-dependent model simulation revealed that γ drops to 2.0 as the Θ point is reached.[14]

The values for 2ω are essentially 1.3, which is far less than the value of 1.5 which a self-similar chain would have. The value of this exponent implies that on average the internal chain fragments are more extended than an isolated chain of the same number of segments. This expansion is the opposite of that predicted by some applications of the blob model. These blob model applications assume that over some short range (a blob) excluded volume effects are unimportant and the chain is nearly ideal and that expansion due to excluded volume only occurs at long range. Nonblob behavior was reported some time ago by Curro and Schaefer in a study using fixed bond length models.[15] These authors also gave a plausible explanation for the observed short-range chain expansion, and the reader may refer to ref 15 for details. Internal chain expansion has also been studied by Kremer et al. using renormalization techniques for two- through five-dimensional systems.[16]

This paper is the first describing internal expansion in terms of a scaling exponent, although other papers also contain data which can be well fit by the scaling exponent 2ω. It appears that for a three-dimensional fixed bond length simulation, $2\omega = 1.1$.[17] That the difference in 2ω from the Rouse value of 1.0 is greater in two dimensions

Table 5. Mode Amplitudes for Chain Lengths *N* and Modes *k*

	$\langle U_{k,N}^2(0) \rangle$					
N	$k = 1$	$k = 2$	$k = 3$	$k = 4$	$k = 5$	$k = 6$
13	2613(67)	375(14)	126.6(0.7)	61.85(0.06)		
25	25796(99)	3894(22)	1238(22)	569.4(7.3)		
37	103000(1700)	15220(270)	4975(61)	2269(19)		
49	274340(350)	41820(370)	13420(140)	6122(15)		
61	602000(11000)	89200(1900)	289200(360)	13216(8)	7319(69)	4523(19)

than three dimensions should not be a surprise since the excluded volume effect should be greater for fewer dimensions; however, the flexibility of the bonds may account for some of this difference.

The values of the exponents found for the simulations are summarized in Table 4 along with the values given by the Rouse model. The quality with which the scaling exponents observed agree with the data may be seen in a graph of C, where C is given by

$$C = \frac{\tau(k,N)}{\langle R_k(N)^2 \rangle} \frac{k^{\gamma-2\omega}}{(N-1)^{\alpha-2\nu}} \qquad (9)$$

and is shown in Figure 2. The values of the data on the right-hand side of eq 9 are taken from Tables 3 and 4. From the figure it can be seen that the data from the 2D bond fluctuation simulations with excluded volume are well described by the scaling exponents. It should be noted that $\gamma - 2\omega$ is found to be 1.2 for the bond fluctuation model as opposed to the value of 1.0 given by the Rouse model. The k dependence of $\tau(k,N)/\langle R_k(N)^2 \rangle$ is therefore different from what is expected from the standard dynamic scaling argument.

The value of the dynamic scaling exponent, γ, observed for the bond fluctuation model is surprisingly high considering the value for its associated static scaling exponent 2ω. From the table it can be seen that the effect of excluded volume is greater for γ than for 2ω. Intuitively, it seems the excluded volume effects which result in short-range expansions that are greater than that expected for a self-similar chain would cause short chain fragments to be particularly stiff and slow to relax, but this would imply that $\gamma < 2.3$. The value found for γ shows the opposite behavior.

At the suggestion of a referee, the scaling behavior of the amplitude of the modes was investigated as a function of chain length and mode number. The amplitudes were fit to the equation

$$\langle U_{k,N}^2(0) \rangle = \beta \ln N - \delta \ln k + c \qquad (10)$$

where all terms have been previously defined and the dependence of the mode on N is now included. The amplitudes of the modes were found for chains from 13 to 61 beads in length. The values obtained are given in Table 5. These data were fit by multiple linear regression and found to give a good fit. The values obtained were $\beta = 3.52$, $\delta = 2.74$, and $c = -1.17$. The values obtained for β and δ were quite different from the values predicted for a Rouse chain of 1.0 and 2.0, respectively.

Conclusion

The relationship between dynamic and static properties shows that this model obeys the dynamic scaling hypothesis well and also that the relaxations of the modes are a good probe of internal chain dynamics. The internal fragments of the chain are more expanded than would be the case for a self-similar chain. The degree of this internal expansion can be expressed well by a scaling law. A dynamic scaling exponent indicates that the higher order modes relax more quickly in comparison to the lower modes than would be expected for a Rouse chain.

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