Simulation Studies of Excluded Volume Effects on Polymer Chain Dynamics in Several Nonlattice Models

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ABSTRACT: Computer simulations of off-lattice bead–stick models of polymer chains with a variety of move rules have been carried out to gauge the effect of these move rules on the dynamical behavior of the chains. We report long relaxation times, translational diffusion constants, and mean-square end-to-end length for chains of from 9 to 99 beads, both with and without excluded volume. For several move rules the excluded volume constraints increase the chain-length dependence of the long relaxation times by about the square root of chain length, roughly twice the exponent expected from simple scaling arguments based on the expansion of equilibrium dimensions by excluded volume. Move rules analogous to some of those used in the present study have been employed by others in previous lattice-model studies. Those earlier lattice-model results appeared to suggest that relaxation times scale like mean-square chain dimensions. Our present results suggest, however, that the earlier result is an artifact resulting from the combination of lattice constraints with the use of move rules explicitly dependent upon local chain conformation.

Introduction

The use of lattice-model chains and Monte Carlo techniques has been the basis of numerous studies of the dynamics of random-coil polymer chains. Computer models of polymer chain dynamics have been developed over the past 30 years by Verdier, Stockmayer, and Kranbuehl[1–24] and others.[25–39] In these models, a number of monomer units sufficient to constitute a statistical segment in a random-coil chain is represented by a "bead", a structureless unit connected to its neighboring beads along the chain by "sticks" of fixed length. The lattice chain model has been especially useful because it is readily amenable to the introduction of hard-core excluded volume interactions. These repulsive forces between segments of the polymer chain give rise to the expansion of chain dimensions, lengthening of relaxation times, and ultimately chain entanglement for sufficiently long chains and high segment densities. The effect of excluded volume interactions on the dynamic properties of polymer chains is particularly difficult to treat analytically. While significant progress has been made over the years using a variety of theoretical techniques,[40–47] there is still no single analytical excluded volume model that treats chain length and segment density continuously.

Monte Carlo simulations of lattice models with and without excluded volume, on the other hand, have been particularly effective for studying excluded volume effects upon chain dynamics. Most simulation studies to date have focused on the effects of excluded volume and the associated effects of chain connectivity and entanglement on the dynamic properties of polymer chains as functions of chain length[1–15,17–21,24–30,32,34,36–38] and segment density.[16,22,23,31,33,35,39] At the same time, the increasing use of lattice models and the discussions generated by their predictions have heightened concern about the possibility of anomalous effects due to the lattice constraints and the choices of bead movement rules. This question is particularly important given the strong chain-length dependence of the long relaxation times found in these simulations when excluded volume constraints are present. Initially questions about the possibility of artifacts in the model were raised by Deutch and co-workers,[48,49] who suggested that this strong chain-length dependence was due to geometric constraints imposed by the use of a particular kind of local bead movement rule on the simple cubic lattice. Subsequent work,[18,19] in which bead movement rules and lattice constraints were varied, showed that the apparent excluded volume effects were indeed somewhat dependent upon the details of the models and simulations, but the simulation results never came close to simple scaling predictions. In the following years Kovac and co-workers raised further questions about the dependence of simulation results on both the lattice and the bead movement rules.[32,36] Recent summaries[24,39] of their work and ours show that dynamical behavior depends upon the bead movement rules chosen for a given lattice and upon the presence or absence of a lattice but is essentially independent of lattice coordination number. In order to study the effects of these various constraints on the chain dynamics and to remove the possibility of effects due to the lattice, we have carried out simulations in which no lattice constraints are present and where several types of movement rules are employed.

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Model

A random-coil polymer chain $N-1$ units long is modeled by a string of N beads. The vectors connecting each bead along the chain with the next are all the same length. In contrast to the lattice models employed in most of the earlier work, there is no restriction on the angle between successive vectors. In the work reported here, the bead diameter is taken to be equal to the length of the vectors connecting the centers of adjacent beads along the chain. Brownian motion of the chain is simulated by sequences of moves, which we shall call move cycles, each of which consists of selecting a piece of the chain at random and attempting a local move of just the selected piece. A chosen piece may be either a single bead or an adjacent pair of beads; we shall refer to the resulting moves as one-bead

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and two-bead moves, respectively. An attempted move can be described as a rotation of the selected piece of chain by an angle $\Delta\phi$ about a line between the two neighbor beads to which the chosen piece is connected. If we number the beads along the chain from 1 to N, selection of bead j results in a rotation of bead j about a line between beads $j-1$ and $j+1$; selection of the bead pair j and $j+1$ results in an attempted rotation of both beads about a line between beads $j-1$ and $j+2$. In general, $\Delta\phi$ is chosen at random from a specified set of possible values. When beads are selected at the ends of the chain, "phantom" beads -1, 0, $N+1$, and $N+2$ are temporarily created at random as needed to serve as neighbor beads for the move algorithm. Simulations can be carried out both with and without excluded volume constraints. For simulations of chains with excluded volume, after a proposed move has been calculated, the new chain configuration is tested for overlap between (nonphantom) beads. If the proposed move would result in overlap, the current move cycle ends with no move; otherwise, the proposed move is carried out. In either case, the move cycle is taken to represent N^{-1} units of simulated time. It should be noted that there are no hydrodynamic or other velocity-dependent forces in these models.

In general, a move cycle begins with the random selection of a one-bead or a two-bead move, with a preset probability p of choosing a two-bead move. For the models employed in the present work, either $p = 0$ (one-bead moves only) or $p = 0.5$ (equal probability of a one-bead move or a two-bead move each cycle). The models are also characterized by the set of possible allowed values of the rotation angle $\Delta\phi$. In these terms, the five models for which we report results here may be characterized as follows:

Model 1: $p = 0.0$, $\Delta\phi$ = all (i.e., a continuous distribution of allowed values of $\Delta\phi$).[50]

Model 2: $p = 0.5$, $\Delta\phi$ = all (some preliminary results obtained for this model have previously been reported.[51,52]

Model 3: $p = 0.0$, $\Delta\phi = \pm\pi/2, \pi$.

Model 4: $p = 0.0$, $\Delta\phi = \pm\pi/2$.

Model 5: $p = 0.0$, $\Delta\phi = \pi$. In this special case, the resulting move may be described either as a rotation or as an exchange of the vectors connecting the chosen bead with its two neighbors along the chain.

A similar model with which we shall compare our present results is one previously reported by Verdier and Kranbuehl.[24] The moves in this model consist of a random mixture, with equal probabilities, of one-bead and two-bead moves ($p = 0.5$), but instead of rotations, the moves consist of interchanging the vectors connecting the chosen bead or bead pair with its neighbors along the chain. For a one-bead move, such an exchange is equivalent to a rotation with $\Delta\phi = \pi$, i.e., a model 5 move. For a two-bead move, the exchange is in general not describable as a simple rotation. We shall refer to these moves as "exchange" moves:

Model 6: $p = 0.5$, "exchange" moves.

After the random choice (for models 2 and 6) between a one-bead and a two-bead move, the random selection of a bead or bead pair, and the random choice (for models 1–4) of $\Delta\phi$, the proposed new position of the selected bead or bead pair is calculated. The proposed move is then made, unless the simulation is being carried out with excluded volume constraints and the proposed move would result in bead overlap, in which case no move at all is made. In either case, the move cycle is complete at this point, and the next move cycle may be begun.

The work reported here is primarily directed at the study of the dynamical behavior of chains in thermal equilibrium with their surroundings. Each chain is started from one or more randomly chosen starting configurations and allowed to move in the manner previously described. As the simulation proceeds, the chain position and configuration are sampled and stored at intervals, and the stored values are then used to generate sampled values of quantities of interest. For example, we obtain time-correlation functions $\rho(\mathbf{q},\mathbf{q},t) = \langle \mathbf{q}(0)\cdot\mathbf{q}(t)\rangle/\langle q^2\rangle$ from sampled values of vector quantities $\mathbf{q}$, which are functions of the chain configuration, for values of simulated time differences t in the region of interest.[53] In particular, by letting $\mathbf{q}$ be the end-to-end vector $\mathbf{l}$, we obtain the autocorrelation function $\rho(\mathbf{l},\mathbf{l},t)$. Since the long-time behavior of $\rho(\mathbf{l},\mathbf{l},t)$ is governed primarily by the longest internal relaxation time τ_1 of the chain, we can estimate τ_1 from the behavior of $\rho(\mathbf{l},\mathbf{l},t)$ as t becomes large. We also obtain estimates of translational diffusion constants D of the center of mass of a chain as $D = (1/6)\langle d^2\rangle/T_D$, where $\langle d^2\rangle$ is the mean-square displacement of the center of mass of the chain in a suitably long time interval T_D. Finally, in the course of sampling dynamical behavior we obtain equilibrium averages such as $\langle l^2\rangle$.

Results

Relaxation Times. Simulations were carried out for the types of bead movement rule listed in the preceding section as models 1 and 2 for chains of from 9 to 99 beads, both with and without excluded volume constraints. In addition, simulations were carried out for chains of models 3, 4, and 5, of from 9 to 63 beads, with excluded volume constraints and for chains of models 3 and 4, of from 9 to 63 beads, without excluded volume constraints. (Simulations were not carried out for model 5 chains without excluded volume constraints because the relaxation behavior of this model without excluded volume can be obtained analytically.) Representative semilogarithmic plots of the autocorrelation functions $\rho(\mathbf{l},\mathbf{l},t)$ for the end-to-end vector $\mathbf{l}$ for models 1–4 are shown in Figure 1. As in previous simulations both on[8,10,18,19,22,24] and off[24] lattices, these plots appear to exhibit limiting linear behavior at sufficiently long times, suggesting the existence of unique longest internal relaxation times τ_1. As in earlier work, we have therefore *assumed* that the relaxation eventually becomes exponential. Accordingly, we have extracted values of τ_1 by fitting the functions $\rho(\mathbf{l},\mathbf{l},t)$ to the form $a\exp(-t/\tau_1)$ by unweighted nonlinear least squares at times longer than the times required for ρ to drop below 0.6, a range in t that appears to be safely within the limiting long-time region. Values of a and τ_1 so obtained are shown in Table I for chains with excluded volume, and in Table II for chains without excluded volume.

For each model and chain length, the simulation employed one starting configuration, which was obtained as the result of simulating the relaxation of the chain from a known (usually extended) configuration for a very long time. In order to obtain estimates of the uncertainties in the values of autocorrelation functions and relaxation times obtained from the simulations, each simulation was divided into a number n_s (between 6 and 24) of subintervals, each much longer than τ_1. Thus the data obtained from different subintervals may be taken as independent samples, and sample standard deviations may be calculated from the subinterval means in the usual way. This technique was used to obtain the uncertainties in the sampled values of $\rho(\mathbf{l},\mathbf{l},t)$ shown as error bars in the plots of Figure 1. The uncertainties in a and τ_1 given in Table

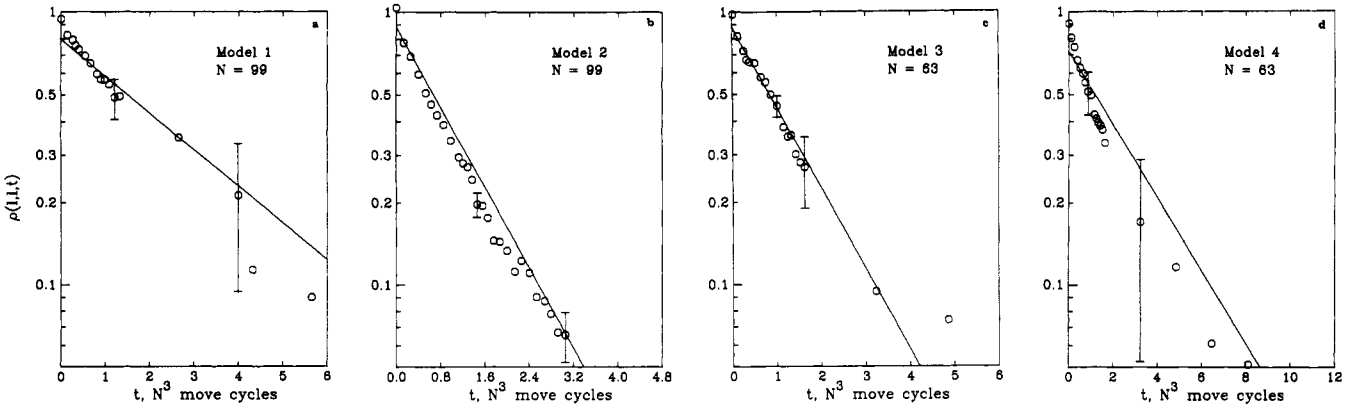

Figure 1. Semilogarithmic plots of autocorrelation functions $\rho(\mathbf{l},\mathbf{l},t)$ for the end-to-end vector $\mathbf{l}$ for chains of N beads with excluded volume not constrained to lie on space lattices. The move rules for models 1–4 are described in the text. The time t is in units of N^3 move cycles. The error bars extend upward and downward one standard deviation of the mean values of ρ shown. The solid lines are plots of $a \exp(-t/\tau_1)$ for values of a and τ_1 determined by least squares as described in the text and given in Table I. For clarity, only a fraction of the sampled values of ρ are shown, and the plots stop as soon as a value of ρ less than 0.05 occurs.

Table I
Long Relaxation Times τ_1 for Nonlattice Chains with Excluded Volume[a]

move rules	N	a	τ_1	n_s	T/τ_1
model 1	9	0.855 (0.004)	1.06 (0.09)	7	693
$p = 0$	15	0.716 (0.021)	1.80 (0.15)	7	431
$\Delta\phi$ = all	33	0.822 (0.043)	1.85 (0.18)	7	407
	45	0.731 (0.019)	2.86 (0.45)	7	260
	63	0.787 (0.040)	3.02 (0.39)	7	240
	99	0.799 (0.058)	3.21 (0.48)	8	106
model 2	9	1.100 (0.104)	0.439 (0.054)	12	1312
$p = 0.5$	15	0.939 (0.087)	0.729 (0.114)	12	790
$\Delta\phi$ = all	33	0.822 (0.089)	1.212 (0.222)	12	952
	45	0.844 (0.056)	1.019 (0.100)	12	1281
	63	0.810 (0.041)	1.078 (0.087)	12	1306
	99	0.887 (0.041)	1.178 (0.118)	24	1304
model 3	9	0.904 (0.034)	0.754 (0.071)	6	835
$p = 0$	15	0.817 (0.057)	1.04 (0.11)	6	639
$\Delta\phi = \pm\pi/2,\pi$	33	0.794 (0.033)	1.67 (0.19)	6	386
	45	0.867 (0.082)	1.51 (0.16)	6	422
	63	0.881 (0.022)	1.47 (0.15)	6	423
model 4	9	0.906 (0.049)	0.92 (0.12)	6	334
$p = 0$	15	0.879 (0.062)	1.50 (0.28)	6	443
$\Delta\phi = \pm\pi/2$	33	0.792 (0.031)	2.12 (0.27)	6	304
	45	0.821 (0.033)	1.84 (0.17)	6	346
	63	0.721 (0.033)	3.24 (0.58)	6	192
model 5	9	0.885 (0.030)	0.627 (0.039)	12	975
$p = 0$	15	0.776 (0.033)	1.51 (0.12)	12	1024
$\Delta\phi = \pi$	33	0.653 (0.014)	11.93 (0.61)	12	387
model 6[b]	9	0.98[c] (0.11)	0.301 (0.036)	12	382
$p = 0.5$	15	0.804 (0.054)	0.466 (0.044)	12	330
exchange moves	33	0.787 (0.038)	1.01 (0.13)[d]	12	304
	63	0.697 (0.035)	2.55 (0.33)	9	432

[a] Values of a and τ_1 for nonlattice chains of N beads with excluded volume. The models employ various local bead-move rules as described in the text. The values of a and τ_1 are obtained by fitting the limiting long-time behavior of autocorrelation functions $\rho(\mathbf{l},\mathbf{l},t)$ for the end-to-end vector $\mathbf{l}$ to the form $\rho(\mathbf{l},\mathbf{l},t) = a \exp(-t/\tau_1)$ by least squares. The values of τ_1 are in units of N^3 move cycles. Values in parentheses are sample standard deviations of the mean. Also shown are the numbers n_s of subintervals into which the simulations were divided for estimating sample standard deviations of the mean and ratios T/τ_1 of the total lengths T of the simulations to the long relaxation times τ_1. [b] Values obtained from ref 24. [c] This value was erroneously given as 0.098 in ref 24. [d] This value was erroneously given as (0.013) in ref 24.

Table II
Long Relaxation Times ${}^0\tau_1$ for Nonlattice Chains with No Excluded Volume[a]

move rules	N	a	${}^0\tau_1$	n_s	$T/{}^0\tau_1$
model 1	9	0.961 (0.098)	0.232 (0.029)	12	1653
$p = 0$	15	0.922 (0.094)	0.244 (0.032)	16	839
$\Delta\phi$ = all	33	0.808 (0.054)	0.213 (0.021)	12	1803
	45	0.802 (0.057)	0.237 (0.035)	16	864
	63	0.878 (0.051)	0.198 (0.020)	12	1939
	99	0.861 (0.068)	0.234 (0.026)	16	875
model 2	9	0.808 (0.060)	0.163 (0.029)	12	707
$p = 0.5$	15	0.847 (0.051)	0.124 (0.017)	12	929
$\Delta\phi$ = all	33	0.707 (0.027)	0.133 (0.011)	12	866
	45	0.845 (0.064)	0.106 (0.012)	12	1087
	63	0.812 (0.057)	0.116 (0.013)	12	993
	99	0.798 (0.052)	0.122 (0.017)	12	944
model 3	9	0.911 (0.076)	0.200 (0.032)	16	1024
$p = 0$	15	0.936 (0.091)	0.157 (0.017)	16	1304
$\Delta\phi = \pm\pi/2,\pi$	33	0.895 (0.065)	0.151 (0.014)	16	1356
	45	0.83 (0.12)	0.201 (0.029)	16	1019
	63	0.811 (0.049)	0.161 (0.017)	16	1272
model 4	9	1.05 (0.13)	0.251 (0.038)	16	1224
$p = 0$	15	0.780 (0.045)	0.254 (0.027)	16	1209
$\Delta\phi = \pm\pi/2$	33	0.756 (0.046)	0.273 (0.037)	16	1125
	45	0.754 (0.039)	0.252 (0.024)	16	1219
	63	1.02 (0.12)	0.184 (0.015)	16	1670
model 5[b]	9		0.1017		
$p = 0$	15		0.1015		
$\Delta\phi = \pi$	33		0.1014		
model 6[b]	9		0.0504		
$p = 0.5$	15		0.0462		
exchange moves	33		0.0430		
	63		0.0418		

[a] Values of a and ${}^0\tau_1$ for nonlattice chains of N beads without excluded volume constraints. The models employ various local bead-move rules as described in the text. The values of a and ${}^0\tau_1$ are obtained by fitting the limiting long-time behavior of autocorrelation functions $\rho(\mathbf{l},\mathbf{l},t)$ for the end-to-end vector $\mathbf{l}$ to the form $\rho(\mathbf{l},\mathbf{l},t) = a \exp(-t/{}^0\tau_1)$ by least squares. The values of ${}^0\tau_1$ are in units of N^3 move cycles. Values in parenthese are sample standard deviations of the mean. Also shown are the numbers n_s of subintervals into which the simulations were divided for estimating sample standard deviations of the mean and ratios $T/{}^0\tau_1$ of the total lengths T of the simulations to the long relaxation times ${}^0\tau_1$. [b] Calculated values obtained from ref 18.

I were calculated by fitting the ρ's sampled in each subinterval separately to obtain sets of n_s values of a and τ_1. The means and sample standard deviations of the mean of these sets are given in Table I.

Simulations carried out with model 5 yielded autocorrelation functions and relaxation times for the shorter chains that were generally similar to those obtained for the other models. However, for the 63-bead chain, the longest studied for this model, the relaxation of the au-

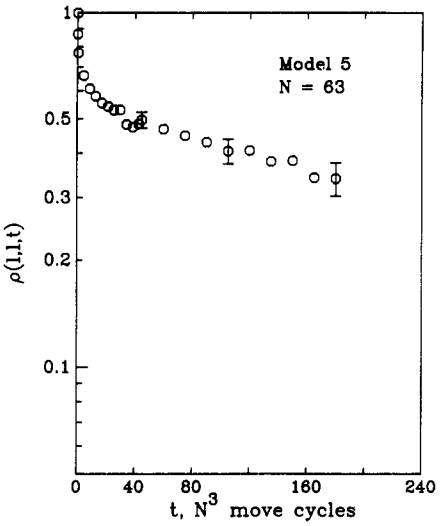

Figure 2. Semilogarithmic plot of the autocorrelation function $\rho(\mathbf{l},\mathbf{l},t)$ for the end-to-end vector $\mathbf{l}$ for a 63-bead chain with excluded volume not constrained to lie on a lattice, using the move rules for model 5 described in the text. The time t is in units of N^3 move cycles.

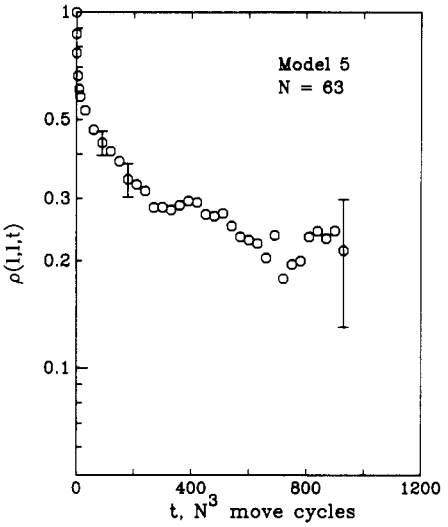

Figure 3. Autocorrelation function of Figure 2 plotted out to very long times.

tocorrelation function was found to be qualitatively different from that found for other models. This autocorrelation function, shown in Figure 2, does *not* appear to exhibit limiting simple-exponential behavior after ρ has dropped below 0.6. The region after ρ has dropped below 0.5 does appear linear on this semilogarithmic plot, which extends out to time intervals of nearly $200N^3$ move cycles and exhibits an apparent limiting slope correponding to a relaxation time of about $450N^3$ move cycles. However, as shown in Figure 3, the behavior of ρ at much longer time intervals, up to nearly $1000N^3$ move cycles, makes it clear that the apparent limiting slope in Figure 2 is a delusion. Indeed, from Figure 3 it is not even clear that the 63-bead chain *ever* relaxes completely. We are therefore unable to report a meaningful relaxation time for model 5 at this chain length. The remarkable behavior of the longer model 5 chains is the subject of continuing investigation, the results of which will be reported elsewhere.

A measure of the number of independent samples in each of the simulations is given by the ratio T/τ_1 of the total length T of each simulation divided by the value found for τ_1 for that simulation. Values of T/τ_1 for the simulations reported in this paper are given in Tables I and II; they range from slightly more than 100 to nearly 2000. (The simulation of a model 5 chain with 63 beads with excluded volume, for which τ_1 could not be obtained, was run for a total of about 2.6×10^9 move cycles, about 10 times as many as were needed for the simulations of 63-bead chains with excluded volume of the other models.)

Table III
Ratios of Properties with and without Excluded Volume for Nonlattice Chains[a]

model	N	$R_\tau = \tau_1/{}^0\tau_1$	$R_D^{-1} = {}^0D/D$	$\langle l^2\rangle/(N-1)$
1	9	4.57 (0.69)	2.16 (0.12)	1.995 (0.038)
1	15	7.4 (1.1)	2.27 (0.06)	2.295 (0.030)
1	33	8.7 (1.2)	2.85 (0.25)	2.888 (0.013)
1	45	12.1 (2.6)	2.31 (0.22)	3.089 (0.064)
1	63	15.3 (2.5)	2.93 (0.23)	3.379 (0.069)
1	99	13.7 (2.6)	2.56 (0.25)	3.807 (0.097)
2	9	2.69 (0.58)	1.78 (0.13)	1.999 (0.024)
2	15	5.9 (1.2)	1.84 (0.14)	2.331 (0.016)
2	33	9.1 (1.8)	2.59 (0.18)	2.869 (0.031)
2	45	9.6 (1.4)	2.56 (0.17)	3.132 (0.030)
2	63	9.3 (1.3)	2.12 (0.14)	3.295 (0.023)
2	99	9.7 (1.7)	2.37 (0.25)	3.679 (0.032)
3	9	3.77 (0.70)	2.21 (0.14)	2.035 (0.023)
3	15	6.6 (1.0)	2.65 (0.19)	2.261 (0.033)
3	33	11.1 (1.6)	2.80 (0.18)	2.931 (0.026)
3	45	7.5 (1.3)	2.44 (0.20)	3.041 (0.070)
3	63	9.1 (1.3)	2.43 (0.24)	3.252 (0.045)
4	9	3.71 (0.74)	1.83 (0.20)	1.978 (0.023)
4	15	5.9 (1.3)	2.00 (0.22)	2.370 (0.029)
4	33	7.8 (1.4)	2.37 (0.32)	2.900 (0.047)
4	45	7.30 (0.97)	2.31 (0.24)	3.132 (0.061)
4	63	17.6 (3.5)	2.50 (0.23)	3.229 (0.026)
5	9	6.17 (0.38)	4.22 (0.18)	1.980 (0.018)
5	15	14.9 (1.2)	7.37 (0.35)	2.320 (0.021)
5	33	117.7 (6.0)	47.2 (3.6)	2.891 (0.031)
6[b]	9	5.97 (0.71)	3.62 (0.37)	1.908 (0.021)
6	15	10.09 (0.95)	3.70 (0.49)	2.316 (0.041)
6	33	23.49 (0.30)	8.7 (1.0)	2.844 (0.028)
6	63	61.0 (7.9)	10.67 (0.68)	3.389 (0.039)

[a] The move rules for models 1–6 are explained in the text. In the table headings, N is the number of beads in a chain, τ_1 and ${}^0\tau_1$ are long relaxation times with and without excluded volume, respectively, D and ${}^0D$ are the corresponding translational diffusion constants of the chain center of mass, and $\langle l^2\rangle$ is the mean-square end-to-end length for chains with excluded volume. Values of ${}^0D$ used to calculate the ratios ${}^0D/D$ are not obtained from the simulations but are calculated as described in the text. Numbers in parentheses are sample standard deviations inferred from the sample standard deviations in the values of τ_1 and ${}^0\tau_1$ in the case of R_τ and from the sample standard deviations in the values of D and $\langle l^2\rangle$ for the other ratios. [b] Values of R_τ, R_D^{-1}, and $\langle l^2\rangle$ obtained from ref 24.

The effects of excluded volume upon chain dynamics are exhibited directly by the ratios $R_\tau = \tau_1/{}^0\tau_1$ of values of τ_1 for chains with excluded volume to the corresponding values ${}^0\tau_1$ for chains of the same length and the same move rules except for the absence of excluded volume constraints. Values of R_τ are given in Table III for models 1–6. For models 1–5, R_τ is calculated from values of τ_1 and ${}^0\tau_1$ in Tables I and II, respectively. For model 6, values of R_τ are taken from ref 24.

Scaled log–log plots of R_τ vs N are shown in Figure 4. The values of R_τ from Table III have been multiplied by the model numbers for plotting in Figure 4 to separate the different plots and exhibit their chain-length dependence. The slopes of these plots are a measure of the "extra" power-law dependence of long relaxation time upon chain length introduced by the excluded volume constraints. For each model, an effective exponent γ_τ for chain-length dependence was determined by fitting the values of R_τ in

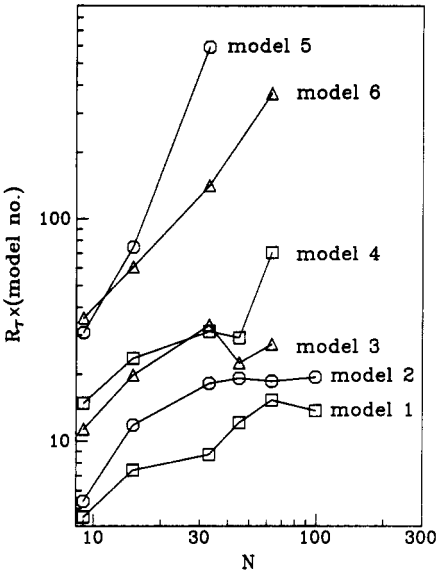

Figure 4. log–log plots of $R_\tau \times$ (model no.) vs N, where the R_τ are the ratios $\tau_1/{}^0\tau_1$ of long relaxation times τ_1 for chains of N beads with excluded volume to the corresponding values ${}^0\tau_1$ for chains of the same length and the same move rules except for the absence of excluded volume constraints. The move rules for models 1–6 are described in the text.

Table IV
Power-Law Exponents for Ratios of Dynamical and Equilibrium Properties of Nonlattice Chains[a]

model	γ_τ	γ_D	γ_l
1	0.48 (0.08)	0.09 (0.05)	0.258 (0.003)
2	0.50 (0.14)	0.13 (0.06)	0.243 (0.007)
3	0.42 (0.17)	0.03 (0.06)	0.240 (0.016)
4	0.63 (0.18)	0.16 (0.02)	0.244 (0.018)
5	>2.3	>1.9	0.273 (0.005)
6	1.18 (0.07)	0.63 (0.13)	0.276 (0.013)

[a] Power-law dependence of ratios of dynamical and equilibrium quantities with and without excluded volume. The exponents γ_τ for long relaxation time τ_1 are obtained by fitting $\ln(\tau_1/{}^0\tau_1)$ vs the number N of beads in a chain to the form $A_\tau + \gamma_\tau \ln(N)$, where the left superscript zero denotes the absence of excluded volume constraints. In a similar way, the exponents γ_D for translational diffusion constant D are obtained by fitting $\ln({}^0D/D)$ vs N to the form $A_D + \gamma_D \ln(N)$, and the exponents γ_l for mean-square end-to-end length $\langle l^2\rangle$ are obtained by fitting $\ln[\langle l^2\rangle/(N-1)]$ vs $N-1$ to the form $A_l + \gamma_l \ln(N-1)$. All fits were carried out by using unweighted linear least squares. Numbers in parentheses are standard deviations inferred from the least-squares fits, without regard to the estimated standard deviations in the individual values of the ratios $\tau_1/{}^0\tau_1$, ${}^0D/D$, and $\langle l^2\rangle/(N-1)$.

Table III to the form $\ln(R_\tau) = A_\tau + \gamma_\tau \ln(N)$ by unweighted linear least squares. The values of γ_τ so obtained are shown in Table IV, together with standard deviations inferred from the least-squares analyses, except for model 5. The apparent value of γ_τ obtained for model 5 from chains of 9, 15, and 33 beads is 2.3, but the results obtained for 63-bead chains, previously discussed, appear to preclude any possibility of a power-law dependence of R_τ upon N for this model. We have therefore listed the value of γ_τ for model 5 as ">2.3", and have omitted an estimate of standard deviation, which would be meaningless in this case.

Translational Diffusion and Equilibrium Dimensions. Values of the mean-square end-to-end length $\langle l^2\rangle$ and the translational diffusion constant D obtained from the simulations of chains with excluded volume are shown in Table V. As previously described, values of D are obtained by sampling mean-square displacements of the chains over time intervals T_D. The values of T_D chosen

Table V
Diffusion Constants and Mean-Square End-to-End Lengths for Nonlattice Chains[a]

model	N	D	T_D/τ_1	${}^0D$	${}^0T_D/{}^0\tau_1$	$\langle l^2\rangle$
1	9	0.694 (0.038)	6.2	1.43 (0.10)	8.6	15.96 (0.30)
1	15	1.10 (0.03)	3.8	2.61 (0.16)	6.6	32.13 (0.42)
1	33	1.93 (0.17)	3.6	5.30 (0.50)	9.4	92.40 (0.41)
1	45	3.24 (0.31)	2.3	6.42 (0.44)	6.8	135.9 (2.8)
1	63	3.58 (0.28)	2.1	10.11 (0.81)	10.1	209.5 (4.3)
1	99	6.44 (0.62)	1.7	16.9 (1.2)	6.8	373.1 (9.5)
2	9	1.54 (0.11)	13.7	2.65 (0.19)	7.4	15.99 (0.19)
2	15	2.59 (0.20)	8.2	3.99 (0.26)	9.7	32.64 (0.23)
2	33	4.21 (0.30)	9.9	12.04 (0.78)	9.0	91.8 (1.0)
2	45	5.85 (0.38)	13.3	15.51 (0.95)	11.3	137.8 (1.3)
2	63	9.94 (0.65)	12.6	20.2 (1.6)	10.3	204.3 (1.4)
2	99	14.0 (1.5)	13.6	34.0 (2.1)	9.8	360.5 (3.1)
3	9	0.905 (0.056)	8.7	2.08 (0.19)	8.0	16.28 (0.18)
3	15	1.26 (0.09)	6.7	3.48 (0.28)	10.2	31.66 (0.46)
3	33	2.62 (0.17)	4.0	7.71 (0.51)	10.6	93.80 (0.84)
3	45	4.10 (0.33)	4.4	10.02 (0.78)	8.0	133.8 (3.1)
3	63	5.76 (0.56)	4.4	14.5 (1.1)	9.9	201.6 (2.8)
4	9	0.820 (0.088)	3.5	1.79 (0.15)	9.6	15.82 (0.18)
4	15	1.25 (0.14)	4.6	2.35 (0.23)	9.4	33.18 (0.41)
4	33	2.32 (0.31)	3.2	4.63 (0.44)	8.8	92.8 (1.5)
4	45	3.24 (0.33)	3.6	8.03 (0.84)	9.5	137.8 (2.7)
4	63	4.20 (0.39)	2.0	10.40 (0.58)	13.0	200.2 (1.6)
5	9	0.711 (0.030)	5.1			15.84 (0.14)
5	15	0.678 (0.032)	5.3			32.48 (0.30)
5	33	0.233 (0.018)	2.0			92.5 (1.0)
6[b]	9	1.83 (0.19)	8.5			15.26 (0.17)
6	15	3.13 (0.41)	7.4			32.43 (0.57)
6	33	3.04 (0.35)	6.8			91.00 (0.90)
6	63	4.83 (0.31)	3.4			210.1 (2.4)

[a] Translational diffusion constants D and ${}^0D$ for nonlattice chains of N beads with and without excluded volume constraints, respectively, in units of $b^2/(N^3$ move cycles), where b is the distance from one bead to the next along the chain, for models employing various local bead-move rules as described in the text. Also shown are ratios T_D/τ_1 and ${}^0T_D/{}^0\tau_1$ of the times T_D and ${}^0T_D$ over which displacements of the centers of mass of the chains were sampled to estimate the diffusion constants to the long relaxation times, τ_1 and ${}^0\tau_1$, and mean-square end-to-end lengths, $\langle l^2\rangle$, in units of b^2, for chains with excluded volume. Numbers in parentheses are sample standard deviations of the mean. [b] Values obtained from ref 24.

for this purpose are shown in Table V, expressed as multiples of the long relaxation times τ_1 in Table I. It will be seen that the ratios T_D/τ_1 are always at least 2, except for the 99-bead chains of model 1.

Also shown in Table V are values of ${}^0D$ and ${}^0T_D/{}^0\tau_1$ obtained from simulations of chains without excluded volume. The values of ${}^0D$ may be calculated from the geometry of the local bead moves. In the units of (stick length)$^2/(N^3$ move cycles) employed here, the calculated values of ${}^0D$ are $(1/6)N$, $0.31[1-1.02/(N+1)]N$, $(2/9)N$, and $(1/6)N$ for models 1, 2, 3, and 4, respectively. It will be seen that the values of ${}^0D$ in Table V are in satisfactory agreement with the calculated values. Values of $\langle l^2\rangle$ are not tabulated for chains without excluded volume; they were all consistent with the random-walk value $N-1$.

Ratios $R_D = D/{}^0D$ of diffusion constants of chains with and without excluded volume, analogous to the ratios $\tau_1/{}^0\tau_1$ previously discussed and exhibited, may also be obtained. For models 5 and 6, ${}^0D$ is given by eq 6 of ref 18 as $(1/3)N$ and $[(5/6)-1/(N+1)]N$, respectively. Values of R_D^{-1}, calculated from the values of D in Table V and the calculated values of ${}^0D$, are given in Table III and shown as log–log plots vs N in Figure 5. (The scaling by model number employed in Figure 4 to provide vertical separation between plots is not used in Figure 5.) As with the values of R_τ previously discussed, the power-law dependence of R_D^{-1} upon chain length was estimated by

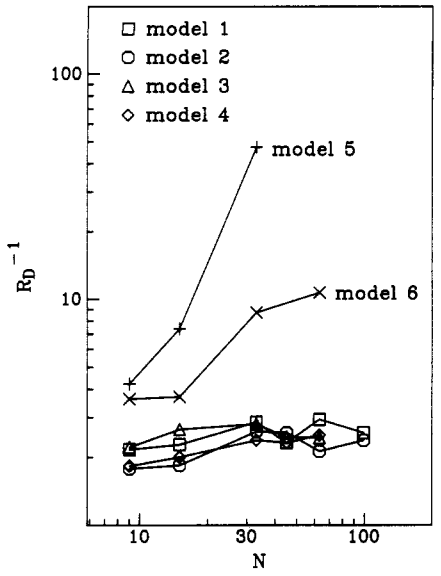

Figure 5. log–log plots of R_D^{-1} vs N, where the R_D are the ratios $D/^0D$ of translational diffusion constants D of chains of N beads with excluded volume to the corresponding values ^0D for chains of the same chain length and the same move rules but without excluded volume constraints. The move rules for models 1–6 are described in the text.

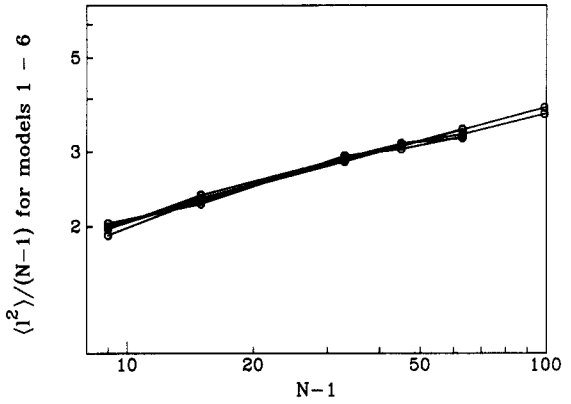

Figure 6. log–log plots of $\langle l^2\rangle/(N-1)$ vs $N-1$, where $\langle l^2\rangle$ is the mean-square end-to-end length of chains of N beads with excluded volume. The move rules are described in the text.

fitting the values of R_D^{-1} in Table III to the form $\ln(R_D^{-1}) = A_D + \gamma_D \ln(N)$ by unweighted linear least squares. The values of γ_D so obtained are given in Table IV. As with the values of R_τ, it is clear that a power-law fit is meaningless for model 5.

Values of $\langle l^2\rangle/(N-1)$, calculated from the values of $\langle l^2\rangle$ in Table V, are shown in Figure 6 as log–log plots vs $N-1$. As expected, all the models exhibit the same equilibrium dimensions. Values of the power-law exponent γ_l, obtained by fitting $\ln[\langle l^2\rangle/(N-1)]$ to the form $\ln[\langle l^2\rangle/(N-1)] = A_l + \gamma_l \ln(N-1)$ by unweighted linear least squares, are given in Table IV.

Conclusions

Relaxation Times. The primary purpose of this paper is to investigate the extent to which the exponent γ_τ, which reflects the extra chain-length dependence of the long relaxation times produced by excluded volume constraints, depends upon the details of chain move rules. In order to compare the results reported here with each other and with earlier results of Verdier and Kranbuehl,[24] let us define two additional models, both on lattices:

Model 7: $p = 0.5$, "exchange" moves (i.e., like model 6 but on lattices; see ref 24).

Table VI
Rough Values of γ_τ for Various Models[a]

lattice?	type of move? (rotation or exchange)	both one- and two-bead moves?	rough value of γ_τ	model(s)
no	rotation	yes	$^1/_2$	2
no	rotation	no	$^1/_2$	1, 3, 4
no	exchange	yes	1	6
no	exchange	no	>2.3	5
yes	rotation	yes		
yes	rotation	no		
yes	exchange	yes	$^1/_2$	7
yes	exchange	no	1	8

[a] The quantity γ_τ is defined as $d[\ln(\tau_1/^0\tau_1)]/d(\ln N)$, the slope of a log–log plot of $\tau_1/^0\tau_1$ vs N, where τ_1 is the long relaxation time for chains of N beads with excluded volume and $^0\tau_1$ is the corresponding relaxation time for chains without excluded volume. For simplicity we represent values of γ_τ in the range 0.4–0.6 as "$^1/_2$" and values in the range 1.0–1.2 as "1".

Model 8: $p = 0.0$, "exchange" moves (i.e., like model 5 but on lattices; see ref 24). Our bead-stick models may then be categorized in three ways: Chains constrained to lie on lattices vs chains not so constrained; "exchange" moves vs "rotation" moves; only one kind of bead-move rule ($p = 0.0$) vs a random mixture of two kinds ($p = 0.5$). Of the eight kinds of model implied by this categorization, three have previously been studied and reported;[24] three others are reported here. (The remaining categories are chains that are constrained to lie on lattices but that permit rotation-like moves.[32,37,38] Such moves on a lattice are strongly dependent upon both the type of lattice and the local chain conformation. We shall not consider them further here.) In Table VI, we show *rough* values of γ_τ from Table IV of this paper and from ref 24.

The effects of model variations upon γ_τ exhibited in Tables IV and VI may be summarized as follows:

1. The use of *exchange* moves, rather than rotation moves, increases the value of γ_τ (cf. model 6 vs model 2, and model 5 vs models 1, 3, and 4).

2. For exchange-move models only, the use of *one kind of bead move* ($p = 0$) increases the value of γ_τ (cf. model 5 vs model 6). For rotation-move models, the number of kinds of bead move does not affect γ_τ (cf. models 1, 3, and 4 vs model 2).

3. *Lattice* constraints (for exchange-move models only) *decrease* the value of γ_τ (cf. model 7 vs model 6, and model 8 vs model 5).

4. For rotation-move models with one kind of bead move, the number of values of the rotation angle $\Delta\phi$ does not affect γ_τ, as long as there are at least 2 such values (cf. models 1, 3, and 4).

5. For all the variations in move rules studied and reported here, the value of γ_τ never drops below about $^1/_2$.

These results appear to suggest that a (nominal) value of $^1/_2$ for γ_τ represents the effect of excluded volume constraints upon chain motion, at least for bead–stick models, while the larger values found for models 5, 6, and 8 are the result of constraints in the local move rules. Specifically, it appears that at least for chains not constrained to lie on lattices, the use of exchange move rules rather than rotation move rules results in an appreciable increase in the value of γ_τ which must be regarded as an artifact. Curiously, for models with two kinds of exchange move, constraining the chains to move on a lattice "recovers" the value $^1/_2$ for γ_τ. However, since the presence of a lattice constraint is clearly more artificial than its absence, this value must be regarded as the result of a fortuitous interaction between the artificial constraints of the lattice and those of the move rules. In this connection, the

argument of Deutch et al.[48,49] that the use of only one kind of exchange move results in an artificially large value of γ_τ might at first appear to depend upon the presence of a lattice. That argument can be recast to show that the cause of the additional, artificial hindrance to chain motion in this case is simply the prohibition of self-reversal in the set of allowed configurations of chains with excluded volume. However, self-reversal and near self-reversal are just as prohibited in chains that are not on lattices as in chains that are. Therefore, this same effect should also occur in chains not on lattices. Indeed, this effect is seen in the comparison of models 5 and 6 as previously discussed.

Arguments that assume that the only effects of excluded volume on dynamical properties are those due to the expansion of equilibrium chain dimensions have been used[42] to predict $\gamma_\tau = 0.2$. It seems reasonable to attribute the difference between this predicted value and the nominal $^1/_2$ found as a minimum in this work to the direct slowdown of chain relaxation by the prohibition of moves resulting from the excluded volume constraint. Put another way, this "quasi-dynamical" theory predicts that a chain with excluded volume constraints takes longer to relax than one without *only* because the chain with excluded volume is larger and therefore must move farther to relax. However, in addition to this size effect, which surely exists, relaxation of a chain with excluded volume is *additionally* slowed down by the prohibition of bead overlap, blocking some moves that would otherwise take place and thereby reducing chain mobility.

Several simulation studies by Kovac et al.[32,37,38] of bead–stick chains on lattices have reported values of γ_τ in the range 0.13–0.29, bracketing the equilibrium expansion value of 0.2 and distinctly less than the values we find both on and off lattices. Indeed, one of the reasons for undertaking the work reported here was to see whether we could find seemingly reasonable local bead move rules that would produce smaller values of γ_τ than those found in our previous work. The principal difference between the move rules used in the Kovac studies and those reported here is that in the Kovac models, the kind of move attempted at each step depends explicitly upon the local chain conformation, whereas in our models the attempted moves are described by equations that do not depend upon local chain conformation. In particular, the rules used by Kovac et al. for chains on a simple cubic lattice[32] are contingent in nature: Two kinds of elementary moves are allowed, but one of them (a two-bead motion) is only attempted if the local chain conformation is such that the other (a single-bead motion) would have been prohibited by the excluded volume constraint. In effect, this amounts to stopping the clock whenever certain moves are attempted that would have been blocked by the excluded volume constraint. As pointed out by Romiszowski and Stockmayer,[21] who obtained larger values of γ_τ consistent with those reported by Verdier and Kranbuehl,[24] such contingent move rules can distort the time scale. It is hardly surprising that the effects of excluded volume upon relaxation time are smaller in models that do not count some of the blocked moves than in models that do. For models on face-centered[37] and body-centered[38] cubic lattices, the moves employed by Kovac et al. do not contain the explicit contingency of the simple cubic lattice rules, but the choice of move rule again depends directly upon the local chain conformation, and this implicit contingency may affect chain motion in a way similar to that of the contingent rules of the simple cubic lattice study.

A more extreme example of contingent bead move rules is to be found in a study by Meirovitch.[54] Here each local move is chosen from a set of possible moves that would not be blocked by excluded volume if they were to be attempted. By definition, in this model no move is ever blocked by excluded volume, because no move that would be so blocked is ever attempted. This work produced values of γ_τ in the range 0.2–0.4, which is stated[54] to be "close to de Gennes' prediction of 0.2". Again, with move rules of this sort one might reasonably expect minimal effect of excluded volume upon chain motion beyond the inescapable equilibrium size-expansion effect.

In comparing the results given here with those obtained in other simulations and with theoretical predictions, we need to consider both the precision of the results and the adequacy of the ranges of chain lengths employed. The standard deviations shown in Table IV for the exponents γ_τ for modesl 1–4 range from 0.08 to 0.18. We believe the results of other workers show comparable or larger imprecision. The estimates we obtain for γ_τ itself, ranging from 0.42 to 0.63, suggest a value of γ_τ of about $^1/_2$. However, these estimates, taken together with their standard deviations, certainly cannot rule out a value of 0.2. All that can be said definitely from these results is that the likeliest value of γ_τ is something like $^1/_2$ and appreciably larger than 0.2.

The chains studied in this work range from 9 to 99 beads for models 1 and 2 and from 9 to 63 beads for models 3 and 4. Again, this range is comparable to or exceeds the range of most other simulations. The values of R_τ shown in Table III and Figure 4 for models 1–4 show too much scatter to test whether a simple power-law fit in this range of chain length is justified (though the data for model 6 appear to support such an assumption). It is, of course, never possible to be certain that limiting long-chain behavior, if it exists, has been reached in *any* simulation. On the other hand, one might arbitrarily decide that chains of only 9 beads are too short to be utilized in forming estimates of chain-length dependence (though the results obtained for model 6, and for lattice models in earlier work, suggest otherwise). If we remove the data for 9-bead chains and redetermine γ_τ using only the values of R_τ for chains of 15 or more beads, we obtain values of γ_τ and their associated standard deviations (in parentheses) of 0.39 (0.11), 0.26 (0.09), 0.18 (0.23), and 0.63 (0.33) for models 1–4, respectively. It will be seen that the estimates have decreased for three of the four models and are less incompatible with a value of 0.2 than are the values obtained by including the $N = 9$ data. Nevertheless, they still suggest a value of γ_τ in the region of 0.3–0.4, again appreciably larger than the exponent for the expansion of mean-square chain dimensions.

In summary, it appears that expansion of the equilibrium chain dimensions contributes something like 0.2 or so to γ_τ, and the direct slowing of chain dynamics by entanglement and other excluded volume produced restrictions on chain mobility contributes an additional roughly similar amount, except when move rules are employed that suppress this effect by distorting the time scale. In addition, as detailed in the foregoing discussion, overly constrained local move rules can lead to further increases in γ_τ, which must be regarded as artifacts of the models.

Equilibrium Dimensions. The values of $\langle l^2 \rangle / (N-1)$ listed in Table III and plotted vs $N-1$ in Figure 6 appear to be independent of the model move rules (as, of course, they should). The values of γ_l in Table IV have a mean of 0.256, a standard deviation of 0.016, and a standard

Table VII
Dimensionless Scaling Ratios for Nonlattice Chains[a]

model	N	$F = D\tau_1/\langle l^2\rangle$	${}^0F = {}^0D{}^0\tau_1/(N-1)$	$F/{}^0F$
1	9	0.046 (0.007)	0.0435 (0.0054)	1.06 (0.21)
1	15	0.062 (0.015)	0.0436 (0.0057)	1.42 (0.39)
1	33	0.040 (0.012)	0.0366 (0.0036)	1.09 (0.35)
1	45	0.065 (0.022)	0.0404 (0.0060)	1.61 (0.59)
1	63	0.047 (0.021)	0.0335 (0.0034)	1.40 (0.64)
1	99	0.054 (0.021)	0.0394 (0.0044)	1.37 (0.55)
2	9	0.0424 (0.0068)	0.0451 (0.0100)	0.94 (0.26)
2	15	0.0560 (0.0101)	0.0423 (0.0058)	1.32 (0.30)
2	33	0.0557 (0.0095)	0.0453 (0.0037)	1.23 (0.23)
2	45	0.0426 (0.0049)	0.0361 (0.0041)	1.18 (0.19)
2	63	0.0527 (0.0058)	0.0394 (0.0044)	1.34 (0.21)
2	99	0.0466 (0.0073)	0.0415 (0.0058)	1.12 (0.24)
3	9	0.042 (0.008)	0.0500 (0.0080)	0.84 (0.21)
3	15	0.041 (0.008)	0.0374 (0.0040)	1.10 (0.24)
3	33	0.046 (0.010)	0.0346 (0.0032)	1.33 (0.31)
3	45	0.051 (0.021)	0.0457 (0.0066)	1.12 (0.49)
3	63	0.042 (0.012)	0.0364 (0.0038)	1.15 (0.35)
4	9	0.050 (0.027)	0.0471 (0.0071)	1.06 (0.60)
4	15	0.055 (0.020)	0.0454 (0.0048)	1.21 (0.46)
4	33	0.052 (0.015)	0.0469 (0.0064)	1.11 (0.35)
4	45	0.042 (0.006)	0.0430 (0.0041)	0.98 (0.17)
4	63	0.068 (0.031)	0.0312 (0.0025)	2.18 (1.01)
5	9	0.0279 (0.0017)	0.0381 (0.0)[b]	0.73 (0.04)
5	15	0.0309 (0.0022)	0.0362 (0.0)	0.85 (0.06)
5	33	0.0297 (0.0024)	0.0349 (0.0)	0.85 (0.07)
6	9	0.0360 (—)[c]	0.0416 (0.0)[b]	0.87 (—)
6	15	0.0450 (—)	0.0382 (0.0)	1.18 (—)
6	33	0.0340 (—)	0.0356 (0.0)	0.96 (—)
6	63	0.0540 (—)	0.0347 (0.0)	1.56 (—)

[a] Ratios F of translational diffusion constant D, long relaxation time τ_1, and mean-square end-to-end length $\langle l^2\rangle$ for nonlattice chains of N beads with excluded volume, ratios ${}^0F$ of the corresponding quantities ${}^0D$, ${}^0\tau_1$, and $N-1$ for nonlattice chains without excluded volume, and values of $F/{}^0F$. The local bead-move rules employed by the various models are described in the text. Values in parentheses are sample standard deviations of the mean. [b] Values of ${}^0F$ for models 5 and 6 were calculated, rather than being obtained from simulations. [c] Values of F for model 6 are taken from ref 24; standard deviations in F are not available.

deviation of the mean of 0.006. The difference between this value and the value 0.2 found for chains on lattices and predicted by mean-field theory[45] is statistically highly significant. It may be compared with values of 1.29 and 1.21–1.24 reported by Windwer[55] and by Loftus and Gans,[56] respectively, for nonlattice bead-stick models with various constraints on the angles between successive sticks.

Diffusion and Scaling Ratios. The power-law exponents γ_D shown in Table IV more or less track the values of γ_τ, at least for models 1–4: They are all about 0.1, and the differences $\gamma_\tau - \gamma_D$ are all in the range 0.37–0.47.

The dimensionless scaling ratio $F = D\tau_1/\langle l^2\rangle$ and its no-excluded-volume counterpart ${}^0F = {}^0D{}^0\tau_1/(N-1)$ are shown in Table VII, together with ratios $F/{}^0F$. Table VIII shows the power-law exponents γ_F obtained by fitting the values of $F/{}^0F$ for each model to the form $\ln(F/{}^0F) = A_F + \gamma_F \ln(N)$ by unweighted least squares and the mean values m_F, which amount to fitting $F/{}^0F$ to the form $F/{}^0F = m_F$. The values obtained for model 5 are omitted from this fitting, since meaningful relaxation times and diffusion constants were not obtained for this model at the longer chain lengths.

The ratios $F/{}^0F$ may be examined in two ways. First, we may look at the exponents γ_F, which would be zero according to simple scaling theory. Second, we may examine the mean values m_F, whose deviation from unity is a direct measure of the effect of excluded volume upon

Table VIII
Chain-Length Dependence of $F/{}^0F$ for Nonlattice Chains[a]

model	exponents γ_F	mean values $m_F = F/{}^0F$
1	0.092 (0.079)	1.326 (0.086)
2	0.057 (0.067)	1.189 (0.060)
3	0.149 (0.084)	1.107 (0.078)
4	0.20 (0.20)	1.31 (0.22)
6	0.22 (0.14)	1.14 (0.15)
mean[b]	0.144 (0.031)	1.214 (0.044)

[a] Values of the exponent γ_F obtained from least-squares fits of $\ln(F/{}^0F)$ to the form $A_F + \gamma_F \ln(N)$, where $F = D\tau_1/\langle l^2\rangle$ for chains of N beads with excluded volume and ${}^0F$ is the corresponding quantity for chains without excluded volume. For each model, m_F is the mean value of $F/{}^0F$ over all the chain lengths studied, ignoring chain-length dependence. Values in parentheses are sample standard deviations in γ_F and m_F, and sample standard deviations of the mean for the mean values of γ_F and m_F in the last line. [b] Mean values for models 1–4 and model 6.

F. Table VIII shows the mean values obtained by averaging γ_F and m_F over models 1–4 and model 6. The mean value obtained for γ_F is 0.144, with a sample standard deviation of the mean of 0.031. The mean value obtained for m_F is 1.214, with a sample standard deviation of the mean of 0.044. For three degrees of freedom, the deviations of γ_F and m_F from zero and unity, respectively, are both significant at confidence limits between 1 and 5%. Thus it appears that F does depend, though only slightly, upon the presence or absence of excluded volume constraints and that it also depends, though again rather weakly, upon chain length.

Summary

First, excluded volume has a considerably larger effect on the relaxation time of the end-to-end vector than on its mean-square value, which shows that the chain-length dependence of dynamical properties such as the long relaxation times cannot be inferred from that of equilibrium dimensions. In other words, *equilibrium* scaling exponents cannot necessarily be used for *dynamical* scaling. For a variety of bead–stick models not constrained to lie on lattices, excluded volume interactions increase the power-law dependence of the longest internal relaxation time upon chain length by an exponent γ_τ of about $^1/_2$. About half this value would be predicted by a size-based equilibrium expansion argument; the remainder presumably reflects additional dynamic effects of excluded volume interactions in slowing down chain motion. Second, this work confirms the finding of others that, for walks not on lattices, the exponent γ_l for the expansion of mean-square end-to-end length is distinctly greater than the lattice value of 0.2. Third, the dimensionless ratio $D\tau_1/\langle l^2\rangle$ appears to depend, though weakly, both upon chain length and upon the presence or absence of excluded volume interactions.

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