Role of the Crankshaft Motion in the Dynamics of Cubic Lattice Models of Polymer Chains

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ABSTRACT: The results of two computer simulation studies designed to investigate the role of the 90° crankshaft motion in the dynamics of cubic lattice models of polymer chains with excluded volume are reported. One of the studies shows that the simulation algorithm introduced by Crabb, Kovac, and co-workers does not introduce a bias into the chain dynamics. The second study shows that the effects of concentration on the chain dynamics observed by Crabb and Kovac are not due solely to the suppression of the crankshaft motion with increasing concentration.

Introduction

In a series of recent papers[1-3] Crabb, Kovac, and co-workers have developed a model for simulating the dynamics of cubic lattice models for polymer chains using a Monte Carlo technique. The feature of the Crabb–Kovac (CK) model that distinguishes it from most previous work on the cubic lattice model[4] is the use of a 90° crankshaft as one of the elementary motions. The CK model has been used to study the effect of both the intramolecular[1,3] and intermolecular[2] excluded volume on the dynamics of linear polymers, and a number of interesting results have been obtained. These studies have raised two questions concerning the role of the 90° crankshaft motion in the model. The purpose of this paper is to ask these question explicitly and to present the results of two simulation studies designed to provide answers.

The first question concerns the simulation algorithm itself. In the CK model the polymer is represented by a random or self-avoiding walk of $(N - 1)$ steps on a cubic lattice. The lattice vertices that are connected by the steps are called beads. The beads are moved according to a set of elementary motions. A bead movement cycle proceeds as follows in the presence of excluded volume. First, a bead is chosen at random. A check is then made to see if it is an end bead or an interior bead. If an end bead has been chosen, an end bead motion is attempted. If an interior bead has been chosen, a further check is made to see if that bead is part of a linear structure or a bent structure. If the bead is part of a linear structure, no movement is possible and the cycle is terminated. If the bead is part of a bent conformation, a normal bead motion is attempted. If that motion is blocked because the new position is occupied, then a check is made to see if the blocking bead is a second nearest neighbor along the chain contour of the original bead. If the blocking bead is a second nearest neighbor, then a crankshaft structure is present and a crankshaft motion is attempted. Each initial choice of a bead is called a bead cycle. Each bead cycle has the same time value no matter what the outcome. This means that a two-bead move is considered to happen in the same time as a one-bead move or no move if a linear structure is chosen. A more detailed description, including diagrams, is given in the original paper.[1]. In discussing the original results of Gurler, Crabb, Dahlin, and Kovac,[1] Romiszowski and Stockmayer[5] suggested that attempting two motions on the same bead cycle might distort the time scale, although the results did not support this criticism. Another objection that might be raised is that this coupling of the motions violates the detailed balance and microscopic reversibility conditions needed in a valid dynamic Monte Carlo scheme. In order to answer these questions we have modified our simulation algorithm to completely decouple the normal bead and crankshaft motions. The details will be presented below, but the basic conclusion is that the chain length dependences of the end-to-end vector relaxation time and the diffusion coefficient are essentially the same in both the original model and in the decoupled case.

A second question concerning the role of the crankshaft motion was raised by the results of Crabb and Kovac,[2] who studied the dynamics of multiple-chain systems. They found that at high concentrations the dynamic properties of the chain deviate strongly from the predictions of the Rouse model, tending toward the predictions of the reptation model. These deviations are clearly due to interchain interactions, but the precise origin of the effect could not be identified from the results of Crabb and Kovac. There is, however, a simple explanation for these results that must be investigated. As the concentration increases the number of successful crankshaft motions will decrease relative to the number of successful normal bead motions. In a mean field approximation the ratio of successful crankshafts to successful normal bead motions will be $(1 - c)$, where c is the concentration in beads per lattice site. The early simulation work of Verdier[6] and the analysis of Hilhorst and Deutch[7] have made it clear that a cubic lattice model that only uses the normal bead motion has a natural t^3 time scale. The obvious explanation for the results of Crabb and Kovac is that the deviations are due to the selective suppression of the crankshaft as the concentration increases. In order to test this hypothesis we have performed simulations of the dynamics of single chains in which the crankshaft motion is artifically suppressed. The suppression of the crankshaft does lead to deviations from Rouse-like behavior, but these deviations are much weaker than those observed by Crabb and Kovac. Although part of the deviations observed by Crabb and Kovac is due to crankshaft suppression, some must be due to longer range entanglement effects.

The details and the results of the two different simulation studies will be presented separately. The paper will conclude with a general discussion of the cubic lattice model.

Decoupling Study

In order to completely decouple the normal bead motion from the crankshaft motion a new decision statement was added to the simulation program in the following way. After an interior bead is chosen and found to be part of a bent conformation, a random choice is made between proceeding with the normal bead motion or moving directly to attempt a crankshaft motion. If the normal bead motion is chosen, then the crankshaft is *not* attempted, even if the normal bead motion is blocked. The decision

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Table I
Values of the End-to-End Vector Relaxation Times, τ_R, and Diffusion Constants, D, as a Function of the Chain Length, N, and the Probability of a Normal Bead Move, p_{NB}[a]

p_{NB}	N	τ_R	D
0.1	12	65.0	0.0055
	24	327	0.0025
	48	1900	0.0010
0.2	12	44.7	0.0086
	24	249	0.0040
	48	1230	0.0018
0.5	12	27.0	0.0154
	24	133	0.0076
	48	606	0.0033
0.8	12	21.5	0.0206
	24	102	0.0097
	48	480	0.0050
0.9	12	20.4	0.0219
	24	94.0	0.0103
	48	450	0.0047
b	12	38.5 (0.9)	0.0226 (0.0020)
	24	179 (8)	0.0117 (0.0020)
	48	874 (119)	0.0055 (0.0002)

[a] The final entries are the values obtained in ref 1 with the original algorithm. In parentheses are the stadard deviations for the ref 1 values. The relaxation times are in units of N bead cycles and the diffusion contents in lattice units squared per N bead cycles. [b] Original algorithm (ref 1).

is made by comparing a pseudorandom number with a preset probability, P_{NB}, which is the probability of a normal bead motion. The probability of a crankshaft motion is clearly $(1 - P_{NB})$. All other features of the simulation model remain the same.

The dynamics of isolated chains of lengths 12, 24, and 48 beads with excluded volume were simulated for a variety of choices of P_{NB}. The excluded-volume condition was rigorously observed in all simulations. Two dynamic properties were calculated: the end to end vector relaxation time, τ_R, and the self-diffusion constant, D. These properties were calculated in the same way as in previous papers.[1,2] The relaxation time is calculated by fitting a least-squares line to the linear long-time region of a semilogarithmic plot of the end-to-end vector autocorrelation function vs. time. This procedures requires some judgement since there is some freedom of choice in the region to be fit. The normal coordinate study of Dial et al.[3] shows that this procedure give a good estimate of the relaxation time of the first Rouse coordinate. The elementary time unit is N bead cycles.

The results for the relaxation times and the diffusion constants are given in Table I. Also shown in Table I are the values obtained by Gurler, Crabb, Dahlin, and Kovac using the original algorithm. The chain length dependence or scaling properties were investigated by plotting ln τ_R vs. ln $(N - 1)$ and ln D vs. ln $(N - 1)$. The slopes of the double-logarithmic plots give the scaling exponents, α and β, which are defined by the relationships

$$\tau_R \sim (N - 1)^{\alpha} \qquad (1)$$

$$D \sim (N - 1)^{-\beta} \qquad (2)$$

The values of α and β are given in Table II. Also given are the exponents obtained by Gurler, Crabb, Dahlin, and Kovac. It is clear that except for the smallest values of P_{NB} the scaling properties of the relaxation time are virtually independent of P_{NB} and essentially the same as those obtained with the original algorithm. The diffusion constant exponents have a similar behavior, but are slightly larger than the value obtained with the original algorithm. Considering the rather large statistical errors of these simulations, the differences are probably insignificant. The values of the relaxation times and diffusion constants are similar in absolute magnitude to those obtained with the original algorithm.

Table II
Values of Scaling Exponents α and β as a Function of the Probability of a Normal Bead Motion, p_{NB}

p_{NB}	α	β
0.1	2.32	1.16
0.2	2.28	1.07
0.5	2.14	1.06
0.8	2.14	0.97
0.9	2.13	1.06
a	2.13	1.00

[a] Values of exponents obtained with the original algorithm of ref 1.

The data given in Tables I and II strongly suggest that the CK model does not introduce any bias into the time scale or any other aspect of the dynamics as compared with a model in which one- and two-bead motions are selected independently. This is not to say that there is not a problem with the time scale that results merely from the existence of two kinds of motions. If any such problem exists it affects both models in the same way. The results presented here provide further justification for the validity of the CK model.

Crankshaft Motion Study

In order to study the effect of the selective suppression of the crankshaft motion at high concentrations, we modified the original CK algorithm for a single chain in the presence of excluded volume in the following way. An additional decision step was placed just before the execution of the crankshaft motion. A pseudorandom number was generated that was compared to a preset probability P_{CS}. If the random number was less than P_{CS} the motion was executed. If it was greater, no motion was allowed. This decision was made *after* it had been determined that both new sites for the crankshaft were unoccupied. We are therefore reducing the relative number of crankshaft motions. The idea was to crudely estimate the effect of the intermolecular excluded volume on the crankshaft motion. No other changes were made in the model.

The dynamics of isolated chains of lengths $N = 12$, 24, and 48 were simulated. The intramolecular excluded-volume condition was rigorously observed. Three dynamic properties were studied: the end-to-end vector relaxation time, τ_R, the center mass diffusion constant, D, and the central monomer diffusion. These properties were computed in the same way as in our previous papers.[1-3]

The values of the end-to-end vector relaxation time, τ_R, and the center of mass diffusion constant are listed in Table III as a function of the chain length, N, and the probability of a crankshaft execution, P_{CS}. Each of these values is an average of at least five simulation runs. In Table IV we have collected the values of the scaling exponents α and β, defined in eq 1 and 2, as a function of P_{CS}.

Table IV clearly shows that a very large fraction of the allowed crankshaft motions must be suppressed in order to cause a significant deviation from Rouse-like behavior. At $P_{CS} = 0.1$, which corresponds to a suppression of 90% of all allowed crankshafts, only a small deviation from the Rouse value of 2.2 is seen in α.

To make a rough mean field correspondence between a dense system and this crankshaft suppression model it is reasonable to equate the concentration c with $(1 - P_{CS})$. The physical idea behind this correspondence is the following. As the concentration increases the normal bead

Table III
Values of the End-to-End Vector Relaxation Time, τ_R, and Center of Mass Diffusion Constant, D, as a Function of Chain Length, N, and Probability of a Crankshaft Motion, p_{CS}[a]

p_{CS}	N	τ_R	D
0.00	12	75.9	0.00846
	24	654	0.00240
	48	5540	0.00059
0.01	12	70.9	0.00905
	24	542	0.00301
	48	2780	0.00114
0.05	12	65.8	0.0113
	24	386	0.0042
	48	2130	0.0019
0.10	12	58.1	0.0131
	24	317	0.0057
	48	1660	0.0029
0.20	12	44.4	0.0149
	24	272	0.0076
	48	1350	0.0033
0.50	12	44.4	0.0192
	24	212	0.0086
	48	967	0.0041

[a] The time unit is N bead cycles. The values of τ_R are bead units of (N bead cycles) and the diffusion constants in units of (lattice units)^2 per N bead cycles.

Table IV
Values of the Scaling Exponents α and β as a Function of the Crankshaft Probability, p_{CS}[a]

p_{CS}	α	β
0.00	2.95	1.84
0.01	2.53	1.43
0.05	2.39	1.24
0.10	2.31	1.05
0.20	2.22	1.04
0.50	2.12	1.06

[a] The exponents are defined in eq 1 and 2.

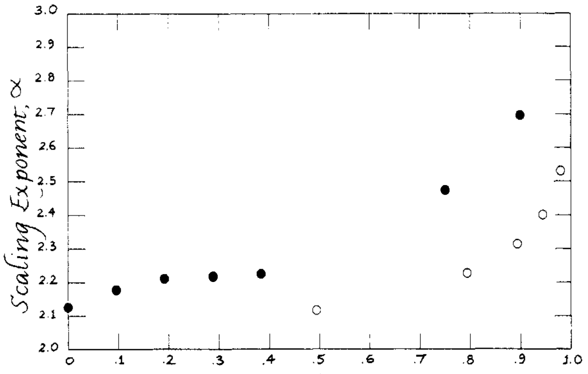

Figure 1. Plot of the scaling exponent α, defined in eq 1, as a function of concentration (●) and of $(1 - P_{CS})$ (○). The values of α at different concentrations are taken from ref 2. The values as a function of $(1 - P_{CS})$ are taken from Table IV.

motions will be suppressed by a factor of c and the crankshaft motions by a factor of c^2. In the crankshaft suppression study the normal bead motions is not altered so $(1 - P_{CS})$ must be identified with the relative rate of crankshaft suppression to normal bead suppression, which is just c.

In Figure 1 we have plotted the exponent α as a function of $(1 - P_{CS})$. On the same graph are plotted the values of α as a function of concentration as determined by Crabb and Kovac.[2] Figure 2 is a similar plot for the exponent β. In both cases the exponents calculated with the crankshaft suppression model lie well below the exponents calculated from the dynamics of multiple-chain systems.

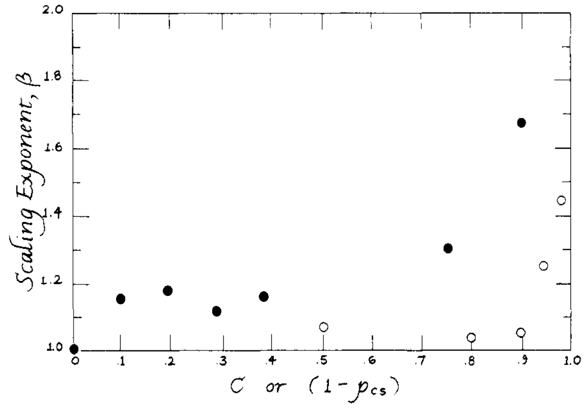

Figure 2. Plot of the scaling exponent β, defined in eq 1, as a function of concentration (●) and of $(1 - P_{CS})$ (○). The values of β at different concentrations are taken from ref 2. The values as a function of $(1 - P_{CS})$ are taken from table IV.

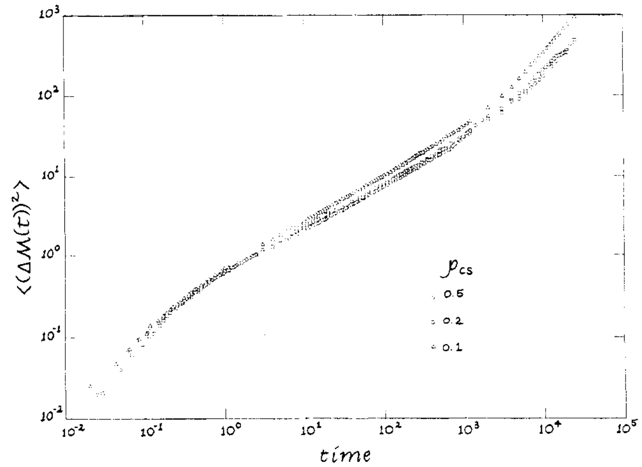

Figure 3. Double-logarithmic plot of the displacement of a central monomer $\langle(\Delta M(t))^2\rangle$ as a function of time for a chain of length $N = 48$ for different values of P_{CS}. Curves are shown for $P_{CS} = 0.5$, $P_{CS} = 0.2$, and $P_{CS} = 0.1$. $\langle(\Delta M(t))^2\rangle$ is measured in lattice units squared. The time is in units of N bead cycles.

It is clear from Figures 1 and 2 that although the suppression of the crankshaft does play a role in the change of the scaling exponent with concentation, it cannot explain the entire effect. Longer range entanglement effects must also be important. One way of examining the entanglement effects in more detail would be to study the dynamics of the normal modes as a function of concentration. This project is currently under way.

In Figure 3 we have plotted the mean square displacement of a central monomer, $\langle(\Delta M(t))^2\rangle$, of a chain of length 48 for 3 values of P_{CS}. All three plots exhibit basically Rouse-like behavior: an initial t region followed by a $t^{1/2}$ region, followed by a t region. There is no obvious hump or inflection in any of the curves as was seen at high concentrations in the multiple-chain study. The comparison of these curves with those in ref 2 provides further evidence that the crankshaft suppression accounts for only a part, maybe a minor part, of the deviation from Rouse-like behavior seen by Crabb and Kovac.

Discussion

It is clear from the results of the studies reported in this paper that the 90° crankshaft motion plays an important role in the dynamics of cubic lattice chains. It is also clear that the dynamic behavior is rather insensitive to the precise way in which the crankshaft is introduced. Only in extreme cases does one see significant deviations from the expected Rouse-like behavior.

The results reported here lend strong support to the original CK algorithm. The CK movement algorithm, which was designed for computational efficiency, does not seem to introduce any spurious effects.

Unfortunately, we are not able to answer the question of whether the mere existence of the two-bead motion somehow distorts the time scale. The question can perhaps be answered by comparing the cubic lattic results with the dynamics of chains on a face-centered cubic (FCC) lattice. One can construct an ergodic Monte Carlo algorithm for FCC chains using only one-bead moves. This work is currently in progress.[8]

We have also shown that the interchain entanglement effects observed by Crabb and Kovac are due to more than just the simple suppression of the crankshaft motion. We are currently investigating these enganglement effects in more detail.[9] By analyzing the dynamics in terms of the Rouse normal coordinates we hope to get a better understanding of the precise nature of the entanglements.

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Heterogeneous and Semiheterogeneous Photosensitization: Photochemical Processes Using Derivatives of Rose Bengal. 13

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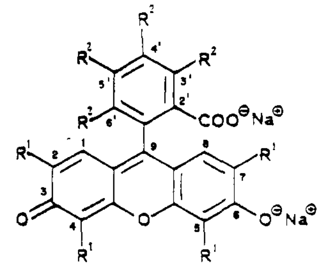
ABSTRACT: In this paper we outline the photochemical and spectroscopic properties of rose bengals immobilized to Merrifield resins and compare the properties of various heterogeneous photosensitizers with monomeric models as well as with soluble rose bengals.

Introduction

Heterogeneous photosensitizers that form singlet oxygen have proven most useful since the idea was introduced by Blossey, Neckers, Thayer, and Schaap.[1] The original idea derived from Merrifield's work[2] in which a polymer bead was used as a handle in a synthetic sequence—in the Merrifield case, the synthesis of a polypeptide. Essentially, the photosensitizer rationale was that if one could immobilize an energy-transfer donor to an insoluble bead and if the spectroscopic properties of the immobilized sensitizer were similar to those of the sensitizer in solution, one might effect heterogeneous energy transfer. At the time, heterogeneous energy transfer was unknown. Though a number of other dyes have been immobilized to polymer beads first by Blossey[5] and later by others[6,7] and some of these systems produced singlet oxygen, Ⓟ-RB[38] gave the highest quantum yield of singlet oxygen formation and was patented by Neckers, Blossey, and Schaap.[8] It has been commercially available for about a decade.

In retrospect, Ⓟ-RB—the first heterogeneous photosensitizer[9-11]—had at least three specific properties that made it unique: it was, by virtue of the polymer backbone, compatible with nonpolar solvents in contrast to the dye in solution; immobilized rose bengal was not bleached by the action of light and oxygen;[12] in contrast to the soluble dye, the excited states of the polymer-based dye were essentially isolated from one another by the polymer backbone.

It was on the basis of the acceptance of Ⓟ-RB that we began new studies on the dye rose bengal some three years ago.[13] Rose bengal, 3′,4′,5′,6′-tetrachloro-2,4,5,7-tetraiodouranine (4), was introduced as a singlet oxygen sensitizer by von Tappeiner[14] and used extensively by Schenck and Gollnick in their many mechanistic studies of dye-sensitized photooxidation.[15] It has been used as much as it has because of the high quantum yield of singlet oxygen that it produces ($\phi_{^1O_2} = 0.76$).[16,17]



The organic chemistry of rose bengal has been clarified by Lamberts and Neckers,[18-20] who synthesized a series of new derivatives of the dye. The rose bengal ammonium salts, for example, are soluble in nonpolar solvents like methylene chloride and even pentane in contrast to the parent dye, which is only soluble in water, low molecular weight alcohols, and polar solvents like DMF and Me_2SO. Since the ammonium salts are soluble in solvents of varying polarity, both the photochemistry and spectroscopy could be studied under varied conditions. This has allowed the first examples of nonpolar solvent photochemistry using rose bengal as the photosensitizer. Nonpolar derivatives and many others have been completely characterized in a full paper in *Free Radicals in Biology and Medicine*.[21] Lamberts and Neckers[17,18] also established

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