

# Analysis of the model dependence of Monte Carlo results for the relaxation of the end-to-end distance of polymer chains<sup>a)</sup>

Henk Boots and J. M. Deutch

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139  
(Received 19 May 1977)

Recently, Verdier and Kranbuehl (VK) have examined by Monte Carlo simulation the relaxation times for the end-to-end vector of a polymer, with excluded volume, on a lattice. The kinetic model employed by VK includes two-bead crankshaft motions in contrast to earlier kinetic models that included only single-bead motions. It is shown that the new VK model contains constraints similar to those discussed by Hilhorst and Deutch for the single-bead model. These constraints lead to artificially long relaxation times not due to the long-range excluded-volume effect.

## I. INTRODUCTION

In recent years Verdier and co-workers<sup>1-4</sup> have employed Monte Carlo simulations to study the configurational dynamics of a polymer in solution under the random forces of the solvent. Their various models, in which a polymer chain is inscribed in a cubic lattice, differ by the way of introducing the random bead motions (consistent with the connectivity of the chain).

In their original model the dynamics was simulated by randomly choosing one bead every interval of unit time and interchanging the two neighboring links of that bead (see Fig. 1, where only a part of the chain around the chosen bead is drawn). By repeating this process, called a *bead cycle*, one simulates the dynamics of the chain. The surprising result of this "single-bead cycle" (SBC) model, in which not more than *one bead* is affected per bead cycle, was that the introduction of the excluded-volume effect caused a strong slowing down on the relaxation times of the correlation functions

$$C_N^{(2)}(t) = \langle \mathbf{R}_N^2(t) \mathbf{R}_N^2(0) \rangle / \langle \mathbf{R}_N^4(0) \rangle \quad (1.1)$$

and

$$C_N^{(1)}(t) = \langle \mathbf{R}_N(t) \cdot \mathbf{R}_N(0) \rangle / \langle \mathbf{R}_N^2(0) \rangle. \quad (1.2)$$

(Here  $\mathbf{R}_N$  is the end-to-end vector). In the absence of excluded-volume effects these correlation functions decay, while not exponentially, with a characteristic correlation time that behaves as

$$\tau_0 = \text{const } N^2, \quad (1.3)$$

where  $N$  is the number of beads of the chain. When excluded-volume effects are included, the simulations lead to

$$\tau_E(\text{SBC}) = \text{const } N^3. \quad (1.4)$$

This effect of excluded volume is much more pronounced than one expects from physical considerations and the results for frequency dependent relaxation properties of dilute polymer solutions. The conven-

tional conjecture is that the relaxation time for a chain should behave as

$$\tau = \text{const } N^{2+\epsilon(d)} \quad (1.5)$$

for large  $N$ . For random chains with no excluded volume  $\epsilon = 0$ ; when excluded volume is present  $\epsilon$  is a small positive constant which depends upon the dimensionality  $d$ .

Hilhorst and Deutch<sup>5</sup> (HD) in an effort to explain the discrepancy between the SBC model, Eqs. (1.3) and (1.4) and the conventional expectation Eq. (1.5), demonstrated that the SBC model with excluded volume gave the result Eq. (1.4) as a consequence of a special constraint, not present in more realistic dynamical models. The special constraint consists of the inability for single-bead cycles to permit local extrema in chain conformations to pass each other or to disappear without passage of these extrema all the way to one of the ends of the chain. A model was constructed by HD to show that this constraint led to the result Eq. (1.4). It was argued that a more realistic model, which included the possibility of bead cycles with simultaneous two-bead jumps, would remove the special constraint and presumably lead to the result Eq. (1.5). The simultaneous two-bead jumps would permit local conformational changes that removed the

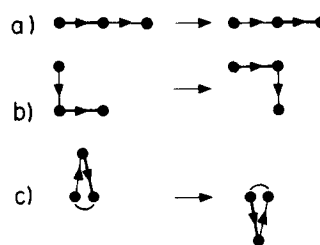


FIG. 1. The three types of bead cycles for the SBC model, drawn for the two-dimensional case. Only the part of the chain that is affected in the cycle is shown. Beads occupying the same lattice site have been drawn as distinct dots for clarity; a "tagged" lattice vector is indicated by a thinner line. Fig. 2(c) shows a cycle that interchanges "upward" and "downward" vectors. This cycle does not occur if excluded-volume effects are taken into account, because the configuration of the chain before (and after) the move is forbidden in that case.

<sup>a)</sup>Supported in part by the National Science Foundation.

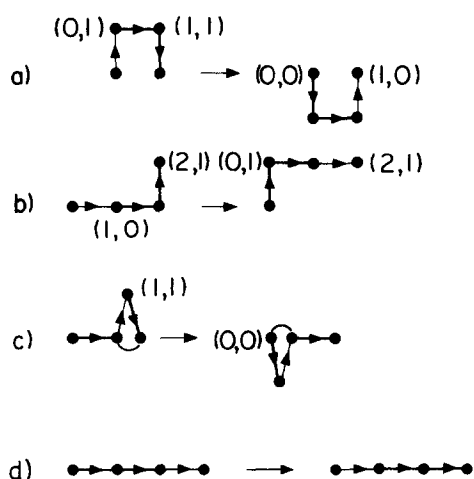


FIG. 2. Four typical cycles for the VK model, drawn for the two-dimensional case. In Fig. 2(a) the crankshaft move is shown. Fig. 2(c) shows a cycle in which “upward” and “downward” vectors of the same type (maximum  $y$  coordinate at even sum of coordinates) are interchanged. This cycle does not occur if the excluded-volume effect is accounted for.

constraint and allowed neighboring extrema to pass each other; an example is the well-known local “crankshaft” motion [Fig. 2(a)]. Of course, not all two-bead jump rules introduce the dynamical flexibility to avoid constraints. HD conjectured that the SBC model plus crankshaft motions would be adequate to remove constraints and lead to the result Eq. (1.5) for the excluded volume case.

Recently Verdier and Kranbuehl<sup>6</sup> (VK) motivated by the HD analysis, have undertaken Monte Carlo simulations of a model which includes two-bead jump rules. While these authors refer to their model as “the crankshaft model”, we prefer to term it the VK model, in order to distinguish it from a model where both SBC and crankshaft motions are simultaneously possible.

The results obtained by VK for the VK model are the same as the earlier results of the SBC model, namely Eqs. (1.3) and (1.4).

The purpose of this note is to point out that the VK model still contains a constraint that leads to the artificially strong slowing down effect of excluded volume.

## II. ANALYSIS OF THE VK MODEL

The introduction of the excluded volume into a lattice model of a polymer chain means that two beads cannot occupy the same lattice point. This has two qualitatively different effects. One of these is the occurrence of “repulsion” of beads that are at a short distance from each other in space but far apart if one measures along the chain. It is this effect which should be associated with the concept of “excluded volume”; it is a long-range effect.

The second effect is of a strictly local nature: If multiple occupancy of a lattice site is forbidden, zero valence angles [as in Figs. 1(c) and 2(c)] do not occur, whereas in the absence of the excluded-volume

condition the models of Verdier and co-workers do allow for zero valence angles. Here we will show that the latter effect is the reason for the strong slowing down in the SBC and VK models.

We follow a line of reasoning very similar to the HD analysis of the SBC model. Let us first rephrase the HD argument in a way which facilitates understanding what happens in the VK model. For this purpose we assign an orientation to all polymer lattice vectors according to the way one passes them going through the chain from the beginning to the end [see Fig. 3(a)]. In the SBC model one can only interchange links of the chain which have a bead in common. So one can only interchange vectors in the  $+\alpha$  (“upward”) and  $-\alpha$  (“downward”) directions ( $\alpha = x, y, z$ ), if these vectors have a bead in common [see Fig. 1(c)]. But this implies a zero valence angle, which is forbidden in the excluded-volume case. If angles of zero degrees are not allowed, there is no mechanism to interchange “upward” and “downward” vectors and hence there are *barriers* between groups of “upward” and “downward” vectors. [In Fig. 3(a) a polymer configuration is shown; in Fig. 3(b) only the vertical vectors are drawn for the same polymer configuration; one sees that the barriers are the local extrema of the configuration.] The barriers cannot pass each other and can only be created or destroyed at the chain ends (i. e., by bead cycles in which one of the end beads is chosen). HD describe this situation as a collective random walk of the barriers and deduce from it Eq. (1.4). They observe, that this relaxation behavior would probably not occur if one would add the possibility of a crankshaft move [Fig. 2(a)] to the SBC model, because the crankshaft move would provide for a mechanism to interchange “upward” and “downward” vectors.

In the VK model the crankshaft move is included. However, the VK model is not equivalent to SBC plus crankshaft. In the VK model a cycle consists of choos-

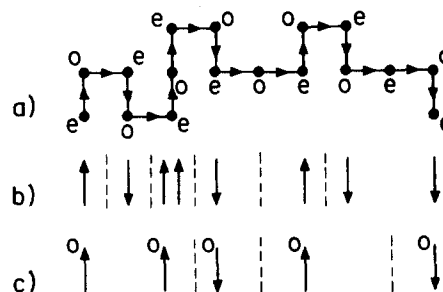


FIG. 3. An oriented chain on a lattice as an illustration of the barriers in the SBC and VK models;  $e$  stands for a bead with even sum of coordinates,  $o$  for a bead with odd sum of coordinates. In Fig. 3(b) only the vertical vectors of this chain are drawn and the corresponding SBC barriers between upward and downward vectors are indicated by broken lines; obviously, these barriers are local extrema of the chain. In Fig. 3(c) only the vertical vectors of type  $I_1$  (with maximum  $y$  coordinate at a bead with odd sum of coordinates) are drawn and the VK barriers between upward and downward vectors of type  $I_1$  are indicated.

ing a vector of the chain in a random way and, if possible, interchanging the two neighboring vectors. (In Fig. 2 some typical cycles are shown). Let us divide the  $\pm \alpha$  ("vertical") vectors in two subsets, vectors of the type  $I_\alpha$  with maximum  $\alpha$  coordinate at a lattice point of odd sum of coordinates, and vectors of type  $II_\alpha$ , for which the sum is even. It is easy to see, that a vector of type  $I_\alpha$  ( $II_\alpha$ ) transforms into a vector of the same type under the VK rule. Furthermore, an "upward" vector and a "downward" vector of the same type cannot be interchanged unless they form a zero valence angle [see Fig. 2(c)]. If angles zero are forbidden there are barriers between groups of "upward" and "downward" vectors of the same type. [In Fig. 3(c) only the vertical vectors of one type are drawn and the corresponding barriers are indicated]. For these barriers the argument of HD holds and one therefore arrives again at Eq. (1.4).

Of course, for the preceding analysis to apply, there must be two or more barriers. On the average for the SBC model without zero valence angles, a given vector (for example,  $up$ ) will be separated six vectors from the first vector down. In the VK model the separation between an upward vector and the nearest downward vector will be twelve vectors, on the average. These estimates are of course very crude; a long-range excluded-volume effect, e.g., is not taken into account. The chain lengths used in the VK model simulations are  $N=15$  (marginally insufficient) and  $N=63$  (sufficient for our analysis to apply).

### III. CONCLUDING REMARKS

In related work, the computer results of Heilmann<sup>7</sup> for the SBC model and variations of the SBC model agree with the ideas presented in Ref. 5 and here. For the SBC model Heilmann reproduced the result of Verdier and co-workers: He found Eq. (1.4) for the relaxation time. For the SBC model with a 90° crankshaft (i. e., the crank is turned to a position which is perpendicular to its original position) he found in the excluded-volume case the result

$$\tau^{-1} \sim N^{-2} [1 + O(N^{-1})] . \quad (3.1)$$

The coefficients of  $N^{-2}$  and  $N^{-3}$  in the expansion were not dramatically changed if only zero valence angles were forbidden but no other excluded-volume effect was taken into account. Heilmann concludes that the local structure of the chain rather than the long-range effect of the excluded volume is of importance for understanding the movements of chains, which is true at least for the chain lengths used in his computer experiment ( $N \leq 128$ ).

The mean field<sup>8</sup> and scaling results for the long-range excluded-volume effect, as derived by De Gennes,<sup>9</sup> are

$$\tau \sim N^2 \quad (\text{mean field}) \quad (3.2)$$

$$\tau \sim N^{2.2} . \quad (\text{scaling in three dimensions}) \quad (3.3)$$

In this derivation the chain dynamics is introduced with the use of a Rouse model. The problem of special constraints due to local effects does not arise in this theory.

The chain lengths in Heilmann's computer simulations are much too small to discern between the relaxation behaviors of Eqs. (3.2) and (3.3), if one does not know the proportionality constants in these equations. The proportionality constants depend not only on the type of lattice, but also on the rules for the chain motion. The chains are much too short to find the correct power law because of an appreciable contribution of the higher order in  $1/N$ . Eqs. (3.2) and (3.3) are, however, consistent with Heilmann's computer results in that the excluded-volume condition has a much smaller effect on the relaxation behavior than the SBC and VK models suggest.

The conclusion of this analysis is that the new model of Verdier and Kranbuehl, like the SBC model, does not show a relaxation behavior which is representative for models of chain dynamics with excluded volume, because of the occurrence of a special constraint. In the SBC model, the special constraint was the inability for adjacent local extrema of the chain to pass each other. In the more recent VK model, the particular two-bead jump rule does not permit certain adjacent local conformations of the same class to pass each other. In both models, the barriers must diffuse to the chain ends before relaxation occurs. This explains the observed long relaxation time in the excluded-volume case found by VK. Other jump rules, such as SBC plus crankshaft, we conjecture will not contain constraints of this type and should exhibit the weaker slowing down expected for the excluded-volume case. This conjecture is supported by the numerical work of Heilmann and the dynamic scaling argument of De Gennes. Clearly it would be useful to have additional simulations undertaken to resolve this important question about polymer dynamics.

*Note added in proof:* Lax and Brender<sup>10</sup> have recently reported computer experiments consistent with the conclusions of Hilhorst and Deutch. In a new publication<sup>11</sup> Kranbuehl and Verdier use the SBC model to study the relaxation of aspherical polymer shapes. We expect here also a strong effect of the SBC constraint on the relaxation time scales.

<sup>1</sup>P. H. Verdier and W. H. Stockmayer, *J. Chem. Phys.* **36**, 227 (1962).

<sup>2</sup>P. H. Verdier, *J. Chem. Phys.* **45**, 2122 (1966).

<sup>3</sup>D. E. Kranbuehl and P. H. Verdier, *J. Chem. Phys.* **56**, 3145 (1972).

<sup>4</sup>P. H. Verdier, *J. Chem. Phys.* **59**, 6119 (1973).

<sup>5</sup>H. J. Hilhorst and J. M. Deutch, *J. Chem. Phys.* **63**, 5153 (1975).

<sup>6</sup>P. H. Verdier and D. E. Kranguehl, *Polym. Prepr. Am. Chem. Soc. Div. Polym. Chem.* **17-2**, 148 (1976).

<sup>7</sup>O. Heilmann, *Mater. Fys. Medd. Dan. Vid. Selsk.* **37-2**, (1968). We thank Prof. Heilmann for drawing our attention to this work.

<sup>8</sup>P. Flory, *Principles of Polymer Chemistry* (Cornell University, Ithaca, 1967).

<sup>9</sup>P. G. de Gennes, *Macromolecules* **9**, 587 (1976).

<sup>10</sup>M. Lax and C. Brender, *J. Chem. Phys.* **67**, 1785 (1977).

<sup>11</sup>D. E. Kranbuehl and P. H. Verdier, *J. Chem. Phys.* **67**, 361 (1977).