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A Simulation Model for the Study of the Motion of Random-Coil Polymer Chains

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ABSTRACT

A lattice model of the dynamical behavior of a random-coil polymer chain in solution is described. Simulation of the model by a high-speed digital computer is discussed. The model appears especially suitable for the study of the effects of excluded volume interactions upon the motions of random-coil polymer chains.

Lattice models of random-coil polymer chains have seen extensive use in the study of the equilibrium properties of such chains [1]. In particular, they have proven useful for Monte Carlo studies of the effects of interference between different parts of a chain (the so-called excluded volume effects), which have thus far not yielded to analytical treatment. Not surprisingly, less attention has been paid to the effects of excluded volume interactions upon the dynamical behavior of random-coil chains, although the majority of the interesting physical properties of these chains are dynamical rather than equilibrium properties. In this paper, we describe a model of randomly moving lattice-model polymer chains in solution. The model has been simulated on digital computers in order to study both dynamical and equilibrium properties of random-coil chains [2–5]. A variation of the model has also been used by Bluestone and Vold [6], and by Bluestone and Cronan [7].

DESCRIPTION OF THE MODEL

Although the model used has previously been described elsewhere [2, 4], for convenience we shall briefly restate its definition. The configuration of a random-coil chain in solution at a given time is represented by a string of connected points on a simple cubic lattice in three dimensions, the points (which we shall refer to as beads) lying on cube vertices, and the connections lying along cube sides. Motion

of the chain resulting from random collision with solvent is simulated by choosing one bead at random and moving it in a way to be described, then again choosing a bead at random and moving it, and so forth. Since the unit event is a motion of at most one bead, cooperative motions of large segments of the chain occur only as the result of individual bead motions.

Chains may be studied either with or without an excluded volume restriction. The rules for moving a selected bead depend upon the presence or absence of excluded volume. For convenience, we first describe their operation without excluded volume. Let the beads be numbered along the chain, from bead 1 at one end to bead N at the other, and let $\mathbf{r}_j$ be the vector from some arbitrary origin to the j-th bead. Then if j is not 1 or N, selection of the j-th bead results in its moving from $\mathbf{r}_j$ to $\mathbf{r}_{j+1} + \mathbf{r}_{j-1} - \mathbf{r}_j$. The possible moves are shown schematically in Fig. 1. We may note that chain connectivity is not violated by moves of this type, and that the new position of a bead is always a lattice point.

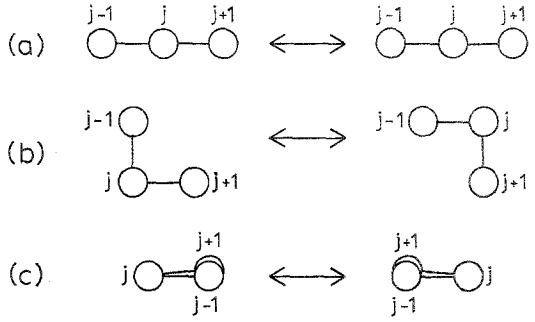

FIG. 1. Possible moves of a non-end bead. Beads $j-1$, j, and $j+1$ are shown in each case.
(a): Angle between successive bead connections is 180°; no move is made.
(b): Angle between successive bead connections is 90°.
(c): Angle between successive bead connections is 0°, i.e., beads $j-1$ and $j+1$ occupy the same lattice site.

When the first or last bead is selected, it is moved to one of the four positions, chosen at random, which correspond to changing the direction of the line connecting it with the next bead by 90 degrees.

In this model, the excluded volume restriction is introduced by requiring that no two beads occupy the same lattice site. Thus, the configuration shown in Fig. 1(c) cannot arise for a chain with excluded volume. For such a chain, after a bead has been selected, a possible new position for it is computed as described above for chains without excluded volume. The computed new site is then checked to see whether there is already another bead at that position. If there is not, the move is made; if there is, no move is made.

Several properties of the model may be noted. First, chain motion is always reversible. The change in configuration produced by selecting a particular bead may be undone by reselecting the same bead. A more complex change produced by selecting beads in some sequence may be reversed by choosing the same bead sequence in reverse order.

Next, we consider the ergodic properties of the model. We note first that under the rules given for chain motion, the parity of the sum of the x-, y-, and z-coordinates of each bead remains constant, being even and odd alternately for the beads along the chain. In a sense, therefore, half the possible positions are not accessible to a given chain. Of the half which are accessible, however, any may be reached from any other in a finite number of steps in the absence of the excluded volume restriction, provided the two positions are a finite distance apart. It follows [8] that the equilibrium dimensions of the model without excluded volume will just be those of an unrestricted random walk on a simple cubic lattice.

For the model with excluded volume the situation is more complicated. It is no longer true that any configuration can be reached from any other. Even for relatively short chains, there are configurations for which no move at all is possible. An example for a chain of 22 beads is shown in Fig. 2. Clearly, any configuration

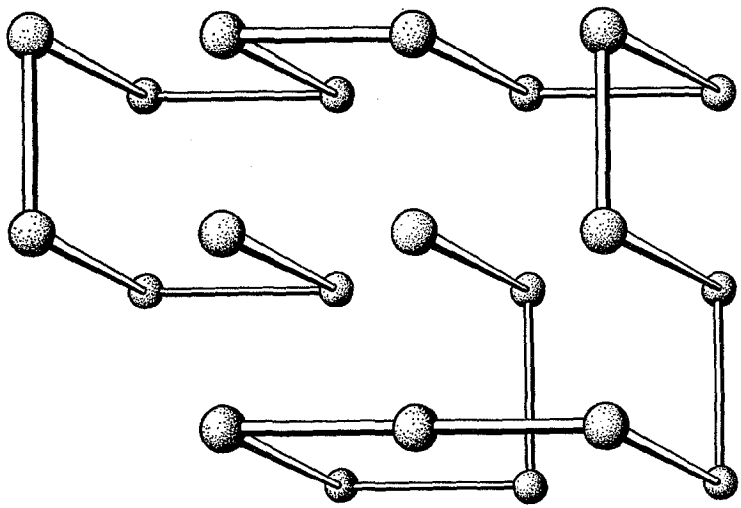

FIG. 2. A completely immobile configuration of a chain of 22 beads with excluded volume.

formed by adding steps to either end of the configuration shown in Fig. 2 will be permanently immobilized in the sense that the part shown in Fig. 2 can never move, no matter what the rest of the chain does. It seems reasonable to guess that all posi-

tions in which no moves are forbidden by the excluded volume condition are accessible to each other, but this is only conjecture at present. In any event, the set of possible configurations is clearly not the same as the set of self-avoiding random walks on a simple cubic lattice. The agreement previously noted [2] between equilibrium dimensions obtained from self-avoiding random walks [9] and those obtained from our dynamical model therefore suggests that the immobilized configurations do not contribute noticeably to the mean dimensions of the chain.

Computer Realization of the Model

Programming the model we have described on a digital computer is for the most part too straightforward to warrant detailed description. However, it may be relevant to note a few points of technique. For the longest chains studied thus far (64 beads), the longest relaxation times, which are the ones of most interest, require of the order of a quarter of a million individual bead selections and motions. In order to obtain statistically significant samples, we need to run the program for many such relaxation times. There is therefore some justification for writing these sections of the program which actually test and move the chain in such a way as to make them as fast as possible. In this section, we describe some of the methods used for this purpose.

The position of a chain of N beads at any given time is stored in the computer as a set of $3N$ integers between 0 and 63, specifying the x-, y-, and z-coordinates of each bead. If the motion of the chain attempts to cause any bead coordinate to become less than zero or greater than 63, the origin is translated so as to center the chain coordinates in the range (0, 63) before the move is made. The translation applied to the origin is stored for future reference when translational diffusion constants are to be computed. The three coordinates of each bead are packed into one 36-bit computer word, and vector addition and subtraction are carried out directly by performing integer arithmetic upon the complete word. The coordinates are so located in the word that they may be transferred directly to index registers when necessary, without prior unpacking and shifting.

For the models with excluded volume, a second representation of the chain position is maintained. This consists of a "map" of the $64 \times 64 \times 64$ region of the lattice described by the bead position vectors. The map is a large array of core storage in which each bit corresponds to one lattice point. The bit is set to "1" if the lattice point is occupied by a bead, and to "0" otherwise. When a bead is moved, the bit corresponding to its old position is cleared, and the bit corresponding to its new position is set to "1". In order to find out whether a given lattice site is vacant, it is only necessary to locate and examine one bit. The time required for this procedure is essentially independent of the number of beads in the chain.

Similar techniques are described in a recent paper by Mazur and McCrackin [10].

Selection of a bead to be tested and perhaps moved is accomplished by the use of a pseudo-random number generator. In the work to date with the model [2–5], a generator described by Orcutt et al [11] has been used. It is a multiplicative congruential generator with a multiplier of $2^{18} + 3$ and a modulus of 2^{35}. Its statistical properties have been previously investigated and found satisfactory by Hull and Dobell [12]. We use the generator primarily to select "at random" a single bead on a chain of up to 64 beads. We have therefore tested the generator by using it to produce long sequences of integers between 1 and 64, and have tested the properties of the sequences in two ways. In the first test, the autocorrelation [13] in the bead number was obtained for 76 different intervals, consisting of: All intervals from 1 to 64; all powers of 2, 3, 5, and 10 less than 2000; and the interval 2000. The number of samples of the autocorrelation obtained depended upon the interval, but was greater than one million for all intervals less than 100, and greater than half a million for all others except the interval 2000, for which 24576 samples were obtained. For each interval, both the autocorrelation and its sample standard deviation of the mean were obtained. Of the 76 values obtained, 33 were negative and 46 were smaller in magnitude than their own standard deviations of the mean, as compared with expected values of 38 and 52, respectively, for normally distributed random variables. The largest ratio of a magnitude to its standard deviation of the mean, obtained for an interval of 60, was 2.43. These results would be appropriate to a true random number generator.

The bead sequences were further tested by generating about 25 million pairs of bead numbers and obtaining the 1- and 2-dimensional distributions of the values. A chi-squared test was made of the distributions, based on the assumption that all pairs of bead numbers are equally probable. The normalized chi-squared values (defined as the chi-squared found, less the mean and divided by the standard deviation of chi-squared for the assumed distribution) were found to be $+0.81$ and $+1.85$ for the 1- and 2-dimensional distributions, respectively. These values would not be inconsistent with a truly random generator. It can be shown [14] that the distribution of successive triplets for this generator is extremely non-random. However, since triplets have no special significance in the model, one can hope that the seemingly random behavior of pairs of values is sufficient for our purpose. The similarity of the behavior of the computer model without excluded volume to that of a continuous ball-and-spring model, noted elsewhere [4, 5], lends support to this point of view.

When a simulation is begun, the program reads in the initial chain configuration and the initial value of the pseudo-random number, together with parameters specifying the kind and duration of the simulation, the properties to be sampled, etc. The program then selects beads one at a time with the pseudo-random number generator, and tests and moves them in accordance with the foregoing rules.

Periodically the simulation is interrupted and properties of interest (e.g., end-to-end length of the chain) are sampled. Autocorrelation functions are obtained by keeping a table of past values of sampled quantities. Each time a sampled value is obtained, it replaces the oldest value in the table. The products needed for sampling autocorrelation functions are formed periodically from the table entries. When the simulation is completed, means and variances of quantities of interest are printed out and also stored on magnetic tape, to be combined with the results of other such simulations and analyzed. The final chain configuration and pseudo-random number are also punched out on cards, so that they may be used as starting values for the next simulation if desired.

Conclusion

It should be clear that the model described in the preceding sections bears only the most casual resemblance to a real polymer chain. Realism of detail is sacrificed for the sake of speed of computation. Its primary usefulness, therefore, ought to lie in the study of long-range, cooperative motions of chain segments, which should be relatively independent of the precise short-range details of chain structure and motion. The results of studies of chains without excluded volume previously cited, suggest that this is the case. On the other hand, the way in which we introduce and use the excluded volume condition can only be justified by physical intuition at present.

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