AIP The Journal of Chemical Physics

Monte Carlo study of dynamics of the multichain polymer system on the tetrahedral lattice@fa@f)

Andrzej Koliński and Piotr Romiszowski

Citation: J. Chem. Phys. **79**, 1523 (1983); doi: 10.1063/1.445944
View online: http://dx.doi.org/10.1063/1.445944
View Table of Contents: http://jcp.aip.org/resource/1/JCPSA6/v79/i3
Published by the American Institute of Physics.

Monte Carlo study of dynamics of the multichain polymer system on the tetrahedral lattice[a)]

Andrzej Koliński and Piotr Romiszowski

Department of Chemistry, University of Warsaw, 02-093 Warsaw, Poland

(Received 23 November 1981; accepted 16 November 1982)

Diffusion of the chain molecules in the concentrated solutions was studied by means of the computer simulation method. The computations were made for various chain lengths and polymer concentrations. It was observed that the rate of diffusion of the polymer chains strongly depends on the chain length according to the relation $D \propto n^{-b}$. It was found that the value of exponent b increases with the polymer concentration.

INTRODUCTION

The dynamics of the flexible polymer chains in the solution has been intensively studied during the last years, based on the pseudostochastic model proposed by Verdier and Stockmayer.[1] The development of the model was also made by other authors.[2–7] In these works the polymer chains were represented by a string of beads on the regular lattice. The micro-Brownian motions of polymer segments were simulated by means of the pseudorandom process consisting in small succesive modifications of the chain conformation. Such a model enabled the investigation of relaxation of the end-to-end distance of the polymer chain[1–4] and the diffusion processes in the solution.[8] Most of the works published so far related to the case of diluted solutions. Recently, several papers concerning the equilibrium properties of the multichain lattice systems have also been published.[9–11]

The purpose of this paper is to show the application of the *V–S* model to simulation of the classical concentration-gradient experiment in order to determine the diffusion constants.

MONTE CARLO MODEL

The model presented here is based on the tetrahedral (diamond-type) lattice. This lattice seems to be more adequate for models of flexible polyethylene or polyester chains than the cubic lattices. Each of the model chains under consideration consists of N polymer beads placed in the lattice points (Fig. 1). The links connecting polymer beads are the vectors from the following set:

$$\begin{aligned} \alpha_1 &= |1,1,1| \,, & \alpha_1 &= -\beta_1 \,, \\ \alpha_2 &= |-1,-1,1| \,, & \alpha_2 &= -\beta_2 \,, \\ \alpha_3 &= |-1,1,-1| \,, & \alpha_3 &= -\beta_3 \,, \\ \alpha_4 &= |1,-1,-1| \,, & \alpha_4 &= -\beta_4 \,. \end{aligned} \tag{1}$$

For a chain on the diamond lattice successive vectors must be chosen alternately from the two groups α and β. Thus, all valence angles in the model chain are tetrahedral. Rotations around the links are restricted to three discrete values corresponding to *trans* and two *gauche* conformations. The proper volume of the polymer is included in the model by forbidding the double occupancy of the lattice sites. Figure 2 shows the hypothetical Monte Carlo cell. The walls of the cell are perpendicular to the planes of Cartesian coordinate system. The cell is divided into two sections. Cubical section A is formed by 1000 fundamental cells of the diamond lattice. There are 8000 sites accessible for polymer beads. Section B, elongated in positive direction of x-axis, contains 16 000 lattice sites. The periodic boundary conditions[12] were introduced for both Y and Z directions to minimize the cell-size effect.

The initial configuration of several polymer chains is generated in section A as follows:

(1) A lattice site in section A is randomly chosen.

(2) The chosen point is treated as the origin of N-meric chain. The pseudorandom generation of the chains does not exclude the possibility of finding some terminal chain segments in section B, since the wall dividing the Monte Carlo cell into two sections is penetrable, whereas the opposite wall of section A is quite impenetrable.

(3) The double occupancy check is performed, taking into consideration that the periodic boundary conditions[12] exist in the Y and Z directions.

(4) The double occupancy of any lattice site leads to

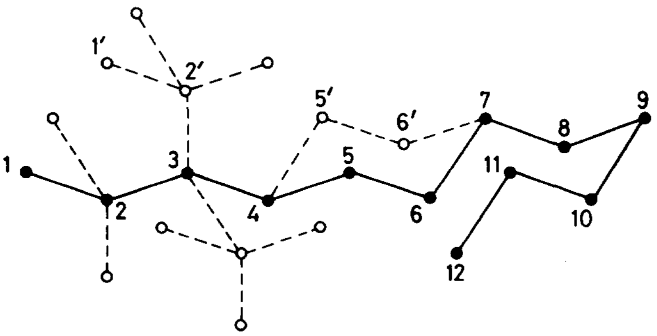

FIG. 1. Conformation of the model chain on the tetrahedral lattice. Some of the allowed modifications are marked with dashed lines. Moves from positions 5 and 6 to 5' and 6' correspond with Eqs. (2) and (2a). The displacements from positions 1 and 2 to 1' and 2' correspond with random modifications of chain ends (see the text).

[a)] This work was supported by The Polish Academy of Sciences (research problem No. 03.10).

0021-9606/83/151523-04$02.10

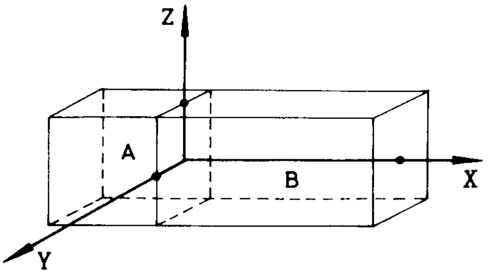

FIG. 2. Illustration of the location of Monte Carlo cell in the coordinates system (see the text).

the removal of the chain from the system and the new trial of generation is made according to steps (1)–(3). The fraction of lattice sites occupied by polymer beads is treated as polymer concentration.

Micro-Brownian motion of the polymer is simulated by randomly choosing a chain and two neighboring i and $i+1$ beads of this chain and then moving only this part of the chain according to fixed rules. Intrachain motion rules maintaining chain connectivity are the following:

$$r'_i = r_{i-1} + r_{i+2} - r_{i+1} , \qquad (2)$$

$$r'_{i+1} = r_{i-1} + r_{i+2} - r_i , \qquad (2a)$$

where r_i and r_i are the vectors from the center of coordinate system to the ith bead of the chain for the old and new positions, respectively. Application of Eqs. (2) and (2a) in the case of planar (*trans*) conformation of the chosen fragment of the chain does not change the positions of the beads.

Chain ends (the case of $i = 1$ or $i + 1 = N$) are treated separately. In this case, the chosen beads are removed and new conformation of the chain end is generated at random. Modification of chain conformation is accepted after the double occupancy check. If the new conformation leads to double occupancy of a lattice site the chain is moved back to its former position. Figure 1 shows some examples of chain movements

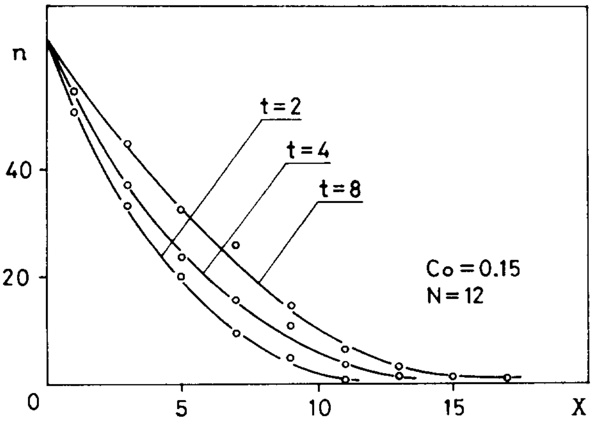

FIG. 3. Plots of polymer beads density distribution in section B for the case of $c_0 = 0.15$ and the chain length $N = 12$. n is the number of polymer beads present in the particular layer of section B at the time moment t indicated near the lines. The thickness of single layer is $\Delta x = 2$.

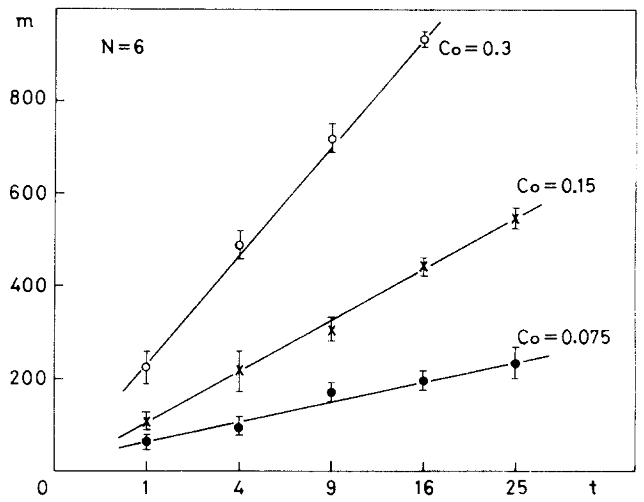

FIG. 4. The total number of polymer beads in section B as a function of time for the case $N = 6$ and various values of c_0 indicated near the lines. The points represent the mean values obtained from three independent simulation runs for each set of initial data. The marked error bars correspond to standard deviation of the mean value.

Micro-Brownian motions of polymer chains result in the diffusion of polymer from section A to section B. During the simulation, the distribution of polymer concentration along the x-axis is computed. Also the total quantity of polymer penetrating into section B is counted.

It is assumed that the number of cycles in which trials of modification of the chain are made is proportional to the time of the modeled process. It is evident that the choice the time unit is made arbitrarily. On the other hand, in the time unit, a constant average number of trials per 1 mer should be done, irrespectively of the chain length. In our computations 1000 trials are made in one time unit for a chain of 24 beads (500 for $N = 12$, and 250 for $N = 6$).

RESULTS AND DISCUSSION

Simulations were carried out separately for the systems containing chains of $N = 6$, 12, and 24 beads of varying initial polymer concentration $c_0 = 0.075$, 0.15, and 0.3. The classical concentration-gradient experiment, which is the subject of simulations, consists in the contact of two solutions of different concentrations.[13] If the solutions are sufficiently extended along the x-axis the starting conditions are as follows:

$$c_{t=0} = \begin{array}{ll} c_0 , & x \leq 0 , \\ 0 , & x > 0 . \end{array} \qquad (3)$$

Under these conditions the following expression describes the concentration gradient-time dependency:

$$\frac{dc}{dx} = -\frac{c_0}{2(\pi D t)^{1/2}} \exp(-x^2/4Dt) . \qquad (4)$$

Figure 3 shows typical distributions of polymer concentrations along the x-axis, obtained during the course of

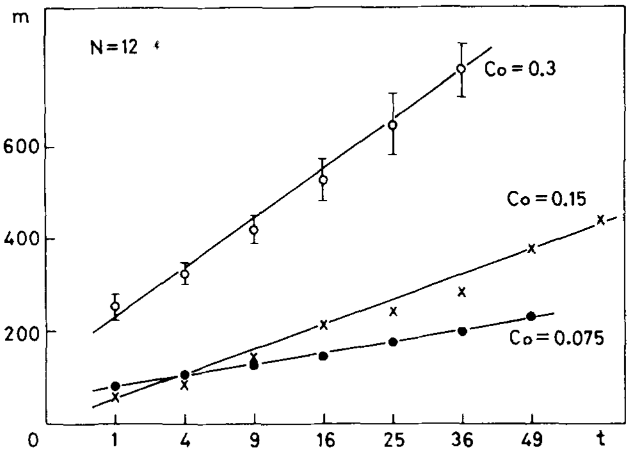

FIG. 5. The total number of polymer beads in section B as a function of time for $N = 12$.

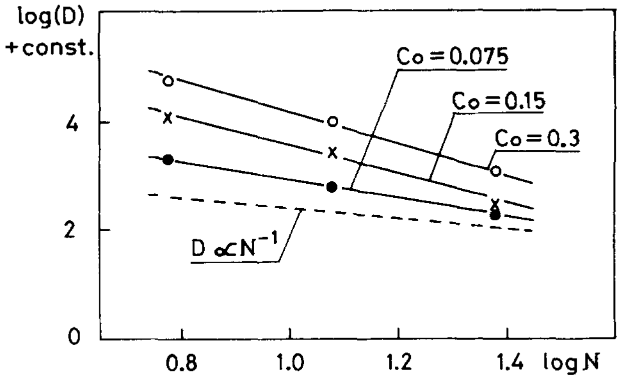

FIG. 7. Comparison of dependencies of the diffusion coefficient on chain length for various values of initial polymer concentrations. Dashed line corresponds to the case of infinitely diluted solution.

simulation. The shapes of these curves are close to the theoretical distribution for the problem defined by Eqs. (3) and (4). However, for the simple determination of the diffusion coefficient D it is sufficient if the solution of the problem is gaussian in the point $x = 0$. Then according to Fick's law

$$\frac{dm}{dt} = -D\frac{dc}{dx}, \tag{5}$$

where dm/dt is the velocity of polymer penetration into section B. The total mass of polymer in section B can be determined as a function of simulation time. The mass is proportional to square root of time

$$m \propto c_0(Dt)^{1/2}. \tag{6}$$

In Figs. 4–6 the mass of polymer present in section B is plotted vs $(t)^{1/2}$. Each of the straight lines in these figures is drawn on the basis of three independent simulation runs. The slopes of the lines K are the simple functions of the diffusion coefficient D, particularly

$$\log(D) + \text{constant} = 2\log(K/c_0). \tag{7}$$

In Fig. 7 the dependencies of D on chain length N are plotted on a log–log scale for different initial polymer concentrations. The theory of the diffusion of flexible polymer chains predicts that $D \propto N^{-b}$ and, for short chains (the case of quite penetrable coil), $b = 1$ (see Ref. 14). This value of exponent b was obtained by Yosukawa and Murakami[8] in MC simulation for infinitely diluted solution. In our computations, concerning concentrated solutions, the dependencies obtained are much stronger (see Fig. 7). For $c_0 = 0.3$ the value of b is slightly greater than 2.5, for $c_0 = 0.075$ it is about 1.5. The value $b = 1$ is expected for considerably smaller concentrations. Our results for higher concentrations are close to scaling prediction of the dependence of translational diffusion coefficient in semidilute solutions on molecular weight. DeGennes[15] obtained $b = 2$ in the case of theta solvent and $b = 9/5$ in a good solvent.

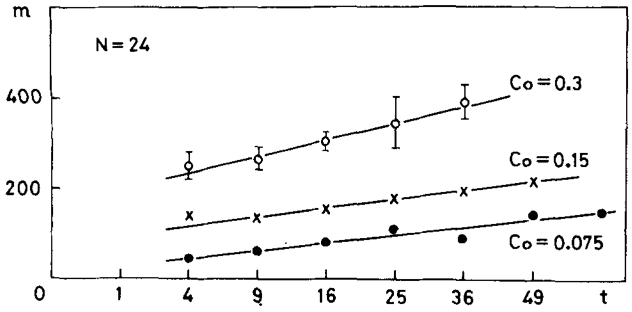

FIG. 6. The total number of polymer beads in section B as a function of time for $N = 24$.

CONCLUSIONS

The results of our computations suggest that the rate of polymer diffusion strongly depends on the chain length according to the relation $D \propto N^{-b}$. The exponent b quickly increases as the polymer concentration increases. This phenomenon can be satisfactorily explained by the entanglement of longer polymer chains in concentrated solutions, when the overlapping of polymer coils is significant. A similar strong dependence of diffusion rate on concentration and polymer length can be the base of the explanation of changes of biradical termination rate with the degree of polymerization and conversion.[16]

[1] P. H. Verdier and W. H. Stockmayer, J. Chem. Phys. 36, 227 (1962).
[2] P. H. Verdier, J. Chem. Phys. 59, 6119 (1973).
[3] H. J. Hilhorst and J. M. Deutch, J. Chem. Phys. 63, 5153 (1975).
[4] D. E. Kranbuehl and P. H. Verdier, J. Chem. Phys. 67, 361 (1977).
[5] M. Lax and C. Brender, J. Chem. Phys. 67, 1785 (1977).
[6] F. Geny and L. Monnerie, J. Polym. Sci. Polym. Phys. Ed. 17, 131 (1979).
[7] F. Geny and L. Monnerie, J. Polym. Sci. Polym. Phys. Ed. 17, 147 (1979).
[8] T. Yosukawa and K. Murakami, Makromol. Chem. 175, 2769

(1976).

[9] A. Baumgärtner and K. Binder, J. Chem. Phys. **75**, 2994 (1981).

[10] H. Okamoto, J. Chem. Phys. **70**, 1690 (1979).

[11] K. E. Evans and S. F. Edwards, J. Chem. Soc. Faraday Trans. 2 **77**, 1891 (1981).

[12] J. G. Curro, J. Chem. Phys. **61**, 1203 (1974).

[13] H. Morawetz, *Macromolecules in Solution* (Wiley, New York, 1965).

[14] H. Yamakawa, *Modern Theory of Polymer Solutions* (Harper and Row, New York, 1971).

[15] P. G. deGennes, *Scaling Concepts in Polymer Physics* (Cornell University, New York, 1979).

[16] K. Ito, J. P lym. Sci. Polym. Chem. Ed. **13**, 1297 (1975).