Monte Carlo simulation of a confined random-walk chain

Wu Dacheng
Department of Polymer Materials, Chengdu University of Science and Technology, Chengdu, People's Republic of China

and Zhao Delu and Qian Renyuan
Institute of Chemistry, Academia Sinica, Beijing, People's Republic of China
(Received 2 August 1985)

The mean square end-to-end distances $\langle h^2(c)\rangle$ of confined random walks (RW) and confined self-avoiding walks (SAW) have been obtained by means of Monte Carlo simulation on a simple cubic lattice. The geometry of confinement considered includes: a cubic box or a sphere, an infinite tube of square or circular cross-section, and a gap between two parallel infinite plates, corresponding to confinements in three, two and one dimensions respectively. The $\langle h^2(c)\rangle$ value of a confined RW chain decreased monotonically with decreasing confinement size and approached to a value of 0, $\frac{1}{3}$ and $\frac{2}{3}$ of $\langle h^2(0)\rangle$ for three-, two- and one-dimensional confinement respectively, where $\langle h^2(0)\rangle$ is the mean square end-to-end distance of a RW chain without any confinement. A SAW chain confined in a cubic box also showed a continuous decrease of $\langle h^2(c)\rangle$ with decreasing confinement size. However, a SAW chain confined in two and one dimensions showed a minimum value of $\langle h^2(c)\rangle/\langle h^2(0)\rangle$ with decreasing confinement size.

(Keywords: Monte Carlo simulation; mean square end-to-end distance; confined random walk; confined self-avoiding walk)

INTRODUCTION

Random walk has been a classical model for the conformation of a flexible polymer chain in solution and for the theory of rubber elasticity[1,2]. Wiedmann *et al.*[3] were the first to consider the case of confined random walk and attempted an analytical solution for the end-to-end distance by solving the diffusion equation. The problem of confined random walk has been of interest since the development of gel permeation chromatography. Casassa[4] obtained the entropy change of a random-walk chain confined in a sphere, in an infinite tube, and in the gap between two parallel infinite plates. De Gennes[5] has also discussed such problems. Recently one of the present authors has considered the confined random walk in a sphere as a model for the effect of interchain interaction on the coil dimension of polymer molecules in solution and thus to explore the concentration dependence of the coil dimension in semidilute solutions[6]. As Monte Carlo simulation is a convenient means to get the coil dimension of a single chain[7] we shall report here the results of such computation for the cases of a random-walk (RW) chain and a self-avoiding-walk (SAW) chain on a simple cubic lattice confined in a cubic box or a sphere, in an infinite tube, and between two parallel infinite plates of various sizes of confined space.

UNCONFINED RANDOM WALK

A simple cubic lattice with lattice spacing of unit length was used. Following every walk step the following step was assumed to have five possible choices of direction, with the probability of a right-angle turn being w, that of a straight forward step being $1-w$ and that of a backward step being zero. As there are four possible cases of a right-angle turn, each will have a probability $w/4$. A sequence of pseudo-random numbers representing the five possible choices produced by a computer was used to generate the walk. For such a RW it has been shown that the mean square end-to-end distance of N steps is given by[8]:

$$\langle h^2(0)\rangle = N(2/w-1) - 2(1-w)/w^2 \simeq N(2/w-1) \quad (1)$$

Results of Monte Carlo simulation of such a walk of 1000 steps with the value of w taken as 1, $\frac{4}{5}$, $\frac{2}{3}$, $\frac{1}{2}$ and $\frac{1}{4}$ are shown in *Table 1*. The values of $\langle h^2(0)\rangle$ averaged over 100–1000 specimen walks are compared with the value given by equation (1). The agreement is within a few per cent for 1000 specimen walks. The convergence of $\langle h^2(0)\rangle$ of 1000 steps with increasing number of walk specimens is shown

Table 1 The mean square end-to-end distances of 1000 RW steps averaged over n specimen walks obtained by Monte Carlo simulation on a five-choice cubic lattice

n	$w=1$	$\frac{4}{5}$	$\frac{2}{3}$	$\frac{1}{2}$	$\frac{1}{4}$
100	982	1490	1957	2746	5966
200	1001	1424	1989	3140	6727
300	945	1415	2006	3120	6627
400	953	1448	1956	3064	6816
500	954	1479	1903	3064	6763
600	977	1537	1906	3030	6718
700	976	1533	1899	3020	6840
800	991	1528	1863	2981	6738
900	986	1521	1872	2985	6817
1000	973	1521	1875	2984	6814
Eqn. (1)	1000	1500	2000	3000	7000

0032-3861/86/071087-04$03.00

in *Figure 1*. The components of $\langle h^2(0)\rangle$, owing to symmetry, are evidently equal to each other and

$$\langle h_x^2(0)\rangle \simeq \langle h_y^2(0)\rangle \simeq \langle h_z^2(0)\rangle = \langle h^2(0)\rangle/3 \qquad (2)$$

CONFINED RANDOM WALK

For confined random walks, $w=\frac{4}{5}$ was adopted. When a step reached the confinement wall the following step was made to go back to the position of the previous step. The number of steps taken was 500–5000 and the number of specimen walks was 100–1000. For the comparison of $\langle h^2(c)\rangle$ of RW confined in three, two and one dimensions of various sizes, the same sequence of pseudo-random numbers generating the walk was used.

Results of $\langle h^2(c)\rangle$ from Monte Carlo simulation of RW chains confined in three, two and one dimensions with varying size of confinement D_j, $j=3, 2, 1$ respectively, are shown in *Figure 2* normalized to the value $\langle h^2(0)\rangle$ without any confinement. For three-dimensional confinement, D_3 is the side length of a cubic box or the diameter of a sphere. D_2 is the side length of square cross-section or the diameter of circular cross-section of an infinite tube for two-dimensional confinement. D_1 is the gap height between two parallel infinite plates for one-dimensional confinement. In the figure the confinement size D_j has

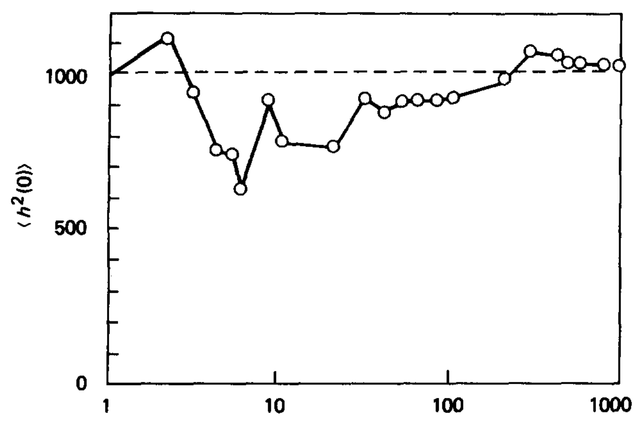

Figure 1 Convergence of the value of $\langle h^2(0)\rangle$ of 1000 RW steps with increasing number of specimen walks

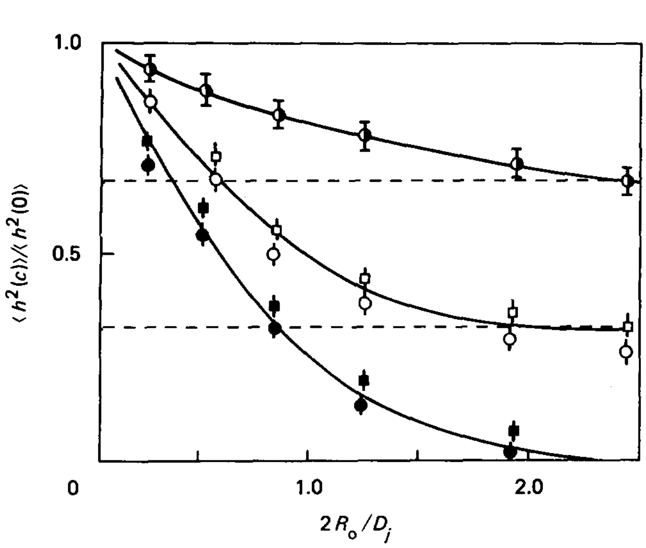

Figure 2 Plots of $\langle h^2(c)\rangle/\langle h^2(0)\rangle$ vs. $2R_0/D_j$ for RWs confined in slits (◑), tubes of square (□) and circular (○) cross-sections and cubic boxes (■) and spheres (●)

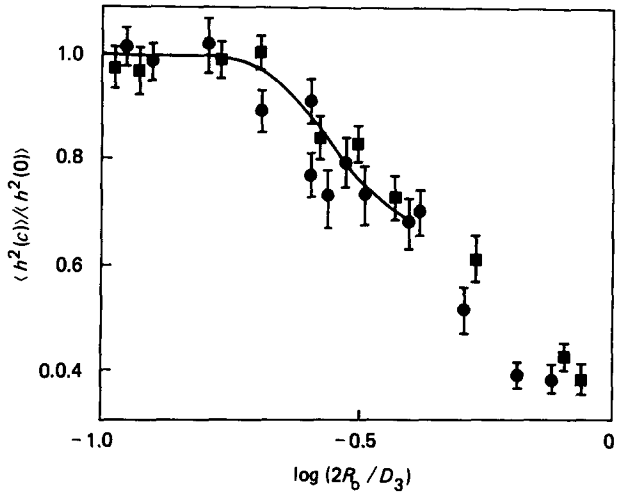

Figure 3 Comparison of $\langle h^2(c)\rangle/\langle h^2(0)\rangle$ as a function of $2R_0/D_3$ for RWs confined in cubic boxes (■) or spheres (●) of sizes D_3 by Monte Carlo simulation to the analytical result of equation (3) (full curve)

been normalized to twice the r.m.s. radius of gyration of the RW chain, i.e. $R_0=[\langle h^2(0)\rangle/6]^{1/2}$. The decrease of $\langle h^2(c)\rangle$ with tighter confinement is clearly shown. At very large values of $(2R_0/D_j)$, i.e. very small values of D_j, $\langle h^2(c)\rangle$ approached a value of 0, $\langle h^2(0)\rangle/3$ and $2\langle h^2(0)\rangle/3$ for three-, two- and one-dimensional confinement respectively.

According to the model of interchain segmental interaction, to be represented by a spherical reflecting wall of diameter D_3, the value of $(2R_0/D_3)^3$ will be proportional to the concentration of polymer chains in the solution if the chains do not interpenetrate each other. From *Figure 2* it is seen that the major portion of the decrease of chain dimension with increasing $2R_0/D_3$ takes place in the range of $0.17<2R_0/D_3<1.3$. A comparison of the result of three-dimensional confinement with the analytical result of Huang and Qian[6] is shown in *Figure 3*. Good agreement is observed in the range of $D_3<2\sqrt{6}R_0$ which supports the correctness of the analytical result:

$$\langle h^2(c)\rangle = \langle h^2(0)\rangle[1-2(3/2\pi)^{1/2}t^3\exp(-3t^2/2)] \qquad (3)$$

$$t=D_3/2\langle h^2(0)\rangle^{1/2}$$

It should be pointed out here that, in the analytical treatment[6], the spherical reflecting wall is centred at each chain segment so that the confinement of the RW chain closely approximates a sphere as in Monte Carlo simulation only when t in equation (3) is much larger than unity. Outside this region the relation $c\propto t^{-3}$ will no longer be valid because of the interpenetration of RW chains. This explains the discrepancy between equation (3) and the Monte Carlo result in the region $D_3>2\sqrt{6}R_0$.

The components $\langle h_x^2(c)\rangle$, $\langle h_y^2(c)\rangle$ and $\langle h_z^2(c)\rangle$ for RW confined in a cubic box of size D_3 all decreased with increasing values of $2R_0/D_3$, and

$$\langle h_x^2(c)\rangle \simeq \langle h_y^2(c)\rangle \simeq \langle h_z^2(c)\rangle \qquad (4)$$

For RW confined in an infinite tube of square cross-section of size D_2 the components in the confined directions $\langle h_j^2(c)\rangle$ decreased with increasing $2R_0/D_2$, while the component in the unconfined direction $\langle h_i^2(c)\rangle \simeq \langle h^2(0)\rangle/3$ was unaffected by the confinement in the other directions. For RW confined in a gap of height D_1 between two parallel infinite plates, only the component $\langle h_j^2(c)\rangle$ in the confined direction decreased with increasing $2R_0/D_1$, while the components $\langle h_i^2(c)\rangle \simeq \langle h^2(0)\rangle/3$ were unaffected by the confinement in the other direction. The change of $\langle h_j^2(c)\rangle/h^2(0)\rangle$ in the confined direction with increasing $2R_0/D_j$ appeared to follow the same curve irrespective of the dimensionality of confinement, as shown in *Figure 4*. It is interesting to mention here the recent experimental finding of Maconnachie, Allen and Richards[9] that, on uniaxially stretching polystyrene of $M_w = 1 \times 10^5$ at 120°C to draw ratios up to 1.9, the radius of gyration of the polymer coil in the direction perpendicular to deformation as determined by SANS is virtually unchanged. For a RW chain confined in an infinite tube the mean square end-to-end distance parallel to the tube axis should, according to our result, approach $\langle h^2(0)\rangle/3$, which is in disagreement with the result of de Gennes from scaling arguments[5].

CONFINED SELF-AVOIDING WALK

The same five-choice succeeding walk step on a cubic lattice was used for SAW with a hard core repulsion of the size of a lattice site. As the definition of a SAW requires that no lattice site is visited more than once, a check must be done before every following step of a SAW to ensure that this requirement is fulfilled. If the neighbouring site has been occupied, the probability of reaching it for the following step will be zero. The other four sites will be chosen with the same probability according to the sequence of pseudo-random numbers. In the case where more than one neighbouring site has been occupied by previous walk steps, the probability of the following step reaching the occupied sites was put equal to zero. In this way the walk must be abandoned if all five neighbouring sites have been occupied.

We calculated first the mean square end-to-end distance of SAW of N steps without any confinement. For a collection of SAW of step number $N = 30$–450 each having 10–1000 specimen walks, the statistical averages of the square end-to-end distance, evaluated according to the method of Rosenbluth and Rosenbluth[10], in which

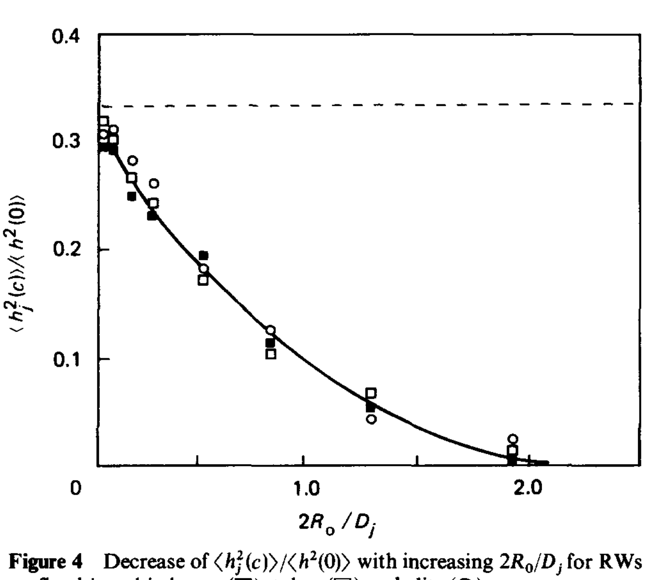

Figure 4 Decrease of $\langle h_j^2(c)\rangle/\langle h^2(0)\rangle$ with increasing $2R_0/D_j$ for RWs confined in cubic boxes (■), tubes (□) and slits (○)

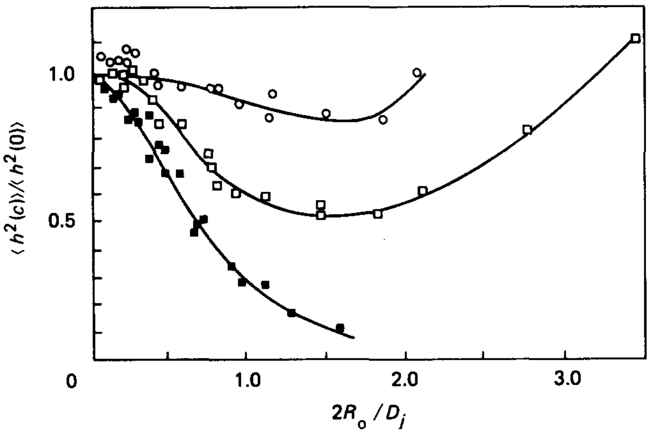

Figure 5 Plots of $\langle h^2(c)\rangle/\langle h^2(0)\rangle$ vs. $2R_0/D_j$ for SAWs confined in cubic boxes (■), tubes (□) and slits (○)

intersegmental interactions could be considered, followed the following relations:

$$\langle h^2(0)\rangle = 1.107N^{1.194} \quad \text{for an athermal state} \quad (5)$$

$$\langle h^2(0)\rangle = 1.732N^{1.001} \quad \text{for a theta state} \quad (6)$$

These results fit nicely with the predictions of other authors[10,11]. At the same time this led to confidence in our computer program for the generation of SAW.

The same geometrical confinements as previously discussed for confined RW were considered for SAW, deleting only the cases of a confining sphere and a tube of circular cross-section for convenience of computation. Analytical solutions for the confined SAW are lacking at present. This makes Monte Carlo simulation even more attractive. When the walk reached a site close to the wall of confinement, the neighbouring lattice site on or beyond the wall was considered as if it were occupied already so as to simulate the confinement by the reflecting wall. The main results of confined SAW calculations are shown in *Figure 5*.

It is apparent from *Figure 5* that the change of square end-to-end distance of a SAW chain confined in a cubic box of decreasing size D_3 is similar to the case of a confined RW chain. The value of $\langle h^2(c)\rangle$ decreased monotonically with increasing $2R_0/D_3$. However for a SAW chain confined in an infinite tube of square cross-section or in a gap between two parallel infinite plates there appeared a minimum in the value of $\langle h^2(c)\rangle/\langle h^2(0)\rangle$ with decreasing D_j. The minimum value of $\langle h^2(c)\rangle/\langle h^2(0)\rangle$ for a SAW chain confined in an infinite square tube was 0.5–0.6 at $2R_0/D_2 \sim 1.6$. Further decrease of D_2 led to an increase of $\langle h^2(c)\rangle/\langle h^2(0)$. This behaviour seems to be reasonable. If we consider the limiting case of D_2 being equal to twice the step length, there will be only one conformation possible for a SAW chain in such a thin confining tube, i.e. a fully extended chain with $h^2(c) = N^2$. For a SAW chain confined in a gap of height D_1 between two parallel infinite plates the minimum of $\langle h^2(c)\rangle/\langle h^2(0)\rangle$ with increasing $2R_0/D_1$ was not pronounced, the minimum value being around 0.9 at $2R_0/D_1$ between 1 to 2. Further increase of $2R_0/D_1$ led to a sharp increase of $\langle h^2(c)\rangle/\langle h^2(0)\rangle$. The increase of coil dimension in the unconfined directions with tighter confinement in the other directions is a manifestation of the intersegmental repulsion as the segment density will

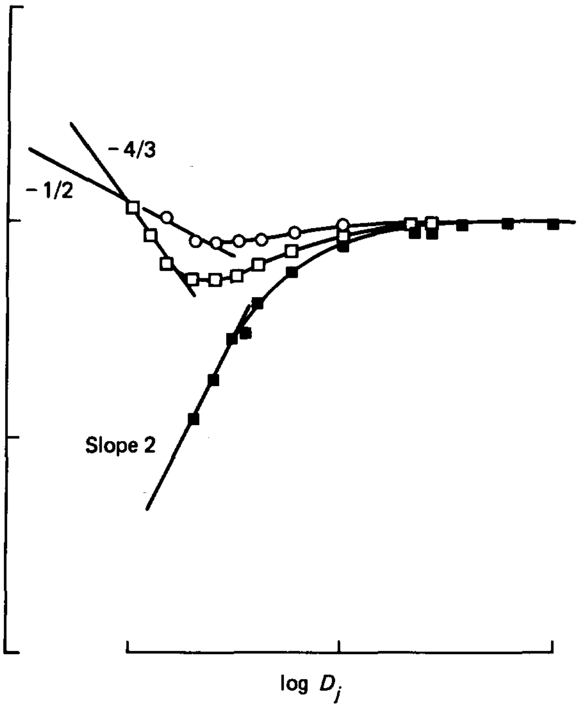

Figure 6 Plots of $\log\langle h^2(c)\rangle$ vs. $\log D_j$ for SAWs confined in cubic boxes (■), tubes (□) and slits (○). 800 walk steps. (Scales represent one decade difference)

certainly increase with tighter confinement in the other directions.

Following the scaling arguments of Wall *et al.*[12] we put

$$\langle h^2(c)\rangle \propto \langle h^2(0)\rangle (R_0/D_j)^m \quad (7)$$

As $\langle h^2(0)\rangle \propto N^{2\nu}$, $\nu=\frac{3}{5}$, we have

$$\langle h^2(c)\rangle \propto N^{\nu(2+m)}D^{-m} \quad (8)$$

For a SAW confined in a sphere of diameter D_3, when $D_3 \to 0$, $\langle h^2(c)\rangle$ will approach zero, being independent of N, so $\nu(2+m)=0$, which gives $m=-2$. That is, the limiting behaviour at small values of D_3 is given by

$$\langle h^2(c)\rangle \propto N^0 D_3^2 \quad (9)$$

For a SAW confined in a tube of diameter D_2, when $D_2 \to 0$, $\langle h^2(c)\rangle \propto N^2$, so $\nu(2+m)=2$, which gives $m=\frac{4}{3}$, and then

$$\langle h^2(c)\rangle \propto N^2 D_2^{-4/3} \quad (10)$$

in agreement with results of Wall *et al.*[12] and Whittington[13]. For a SAW confined in a gap of height D_1, when $D_1 \to 0$, $\langle h^2(c)\rangle \propto N^{3/2}$, so $\nu(2+m)=\frac{3}{2}$, which gives $m=\frac{1}{2}$, and then

$$\langle h^2(c)\rangle \propto N^{3/2} D_1^{-1/2} \quad (11)$$

in agreement with the result of Whittington[13]. These limiting behaviours, (9)–(11), seem to be borne out by the results of Monte Carlo calculations with respect to the D_j dependence, as shown in *Figure 6*.

REFERENCES

1 Kuhn, W. *Koll. Z.* 1934, **68**, 2
2 Guth, E. and Mark, H. *Monatsh.* 1934, **65**, 93
3 Wiedmann, J. J., Kuhn, H. and Kuhn, W. *J. Chim. Phys.* 1953, **50**, 226
4 Casassa, E. F. *Macromolecules* 1975, **9**, 182
5 de Gennes, P. G. 'Scaling Concepts in Polymer Physics', Cornell University Press, Ithaca, 1979, pp. 49, 91
6 Huang, Y. and Qian, R. *Polymer* 1985, **26** (*Commun.*), 242
7 Wall, F. T., Hiller, L. A., Jr and Wheller, D. J. *J. Chem. Phys.* 1954, **50**, 1036
8 Birshtein, T. M., Skvortsov, A. M. and Sariban, A. A. *Macromolecules* 1977, **10**, 202
9 Maconnachie, A., Allen, G. and Richards, R. W. *Polymer* 1981, **22**, 1157
10 Rosenbluth, M. N. and Rosenbluth, A. W. *J. Chem. Phys.* 1955, **23**, 356
11 McCrakin, F. L., Mazur, J. and Guttman, C. M. *Macromolecules* 1973, **6**, 859
12 Wall, F. T., Seitz, W. A., Chin, J. C. and de Gennes, P. G. *Proc. Natl. Acad. Sci.* 1978, **75**, 2069
13 Whittington, S. G. *Adv. Polym. Sci.* 1982, **51**, 35