

# Monte Carlo studies on the freely jointed polymer chain with excluded volume interaction

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We have carried out computer simulations of the freely jointed polymer chain with an excluded volume interaction using a dynamic Monte Carlo method for chain lengths  $N$  between  $N = 8$  and  $N = 100$ . The equilibrium values of end-to-end distances and radius of gyration approach the asymptotic form  $\sim N^\nu$  for  $N \gtrsim 70$  (scaling limit) and excluded volume parameter  $d/l = 1.0$ . The scaling limit decreases to lower  $N$  for lower  $d/l$ . Here  $l$  is the length of a chain unit and  $d$  is the excluded volume distance. The exponent is  $\nu \approx 0.6$  for  $d/l \neq 0$  and  $\nu = 0.5$  for  $d/l = 0$ . The structure function varies as  $S(k) \sim q^{-1/\nu}$  ( $q = kN^\nu$ ) over a wide range of  $q$ . This asymptotic behavior for large  $N$  is found for  $N \gtrsim 16$  and  $d/l \neq 0$ . Our results are carefully compared to previous studies on the same model where other types of Monte Carlo methods are used.

## I. INTRODUCTION

The effect of intramolecular forces on the mean size of chain molecules in dilute solution has attracted considerable attention in the past.<sup>1-10</sup> In particular, computer simulations have been used<sup>3,11-17</sup> to generate on-lattice<sup>11,12,16</sup> or off-lattice<sup>13-15</sup> random walks simulating polymer configurations. In the case of random walks on lattices the interatomic forces between chain atoms are simulated by the condition that the walk does not intersect itself. So far, three methods of polymer simulation have been developed: molecular dynamics,<sup>17</sup> static Monte Carlo,<sup>11-15</sup> and dynamic Monte Carlo methods.<sup>18</sup>

In the present work we have used a dynamic Monte Carlo method to investigate an off-lattice polymer: the freely jointed chain with an excluded volume potential, i. e., a chain of hard spheres, "pearl-necklace" model. This model has been studied previously by static Monte Carlo methods.<sup>13-15</sup> However, there are distinct numerical discrepancies between some of the numerical results of the various groups.<sup>13-15</sup> The main aspect of our paper is to test the application of our dynamic method to the freely jointed polymer chain and to re-examine equilibrium data obtained by static Monte Carlo methods, and critically compare the accuracy of the various methods. Our studies should also be considered as a first step to the investigation of a more realistic model, the freely jointed chain of molecules interacting via a Lennard-Jones potential, which yields the thermodynamics of a polymer in solution. This will be published elsewhere.<sup>18</sup>

In Sec. II we describe our Monte Carlo technique and outline the means by which the quantities of interest may be estimated. The reliability of these estimates is then discussed. In Sec. III the Monte Carlo results are presented and are compared to previous results.<sup>13-15</sup>

## II. THE POLYMER MODEL AND MONTE CARLO TECHNIQUE

The freely jointed polymer chain with excluded volume interaction consists of  $N + 1$  hard spheres of diameter  $d$  indexed from 1 to  $N + 1$ , which are connected by  $N$  bonds of length  $l = 1$  (Fig. 1). The angles between neigh-

boring bonds are not restricted. The quantities we are interested here are the mean square end-to-end distance

$$\langle R_N^2 \rangle = \langle (\mathbf{r}_1 - \mathbf{r}_{N+1})^2 \rangle \quad (1)$$

and the mean square radius of gyration

$$\langle S_N^2 \rangle = \left\langle \sum_{i=1}^N \sum_{j=i+1}^{N+1} (\mathbf{r}_i - \mathbf{r}_j)^2 \right\rangle / (N+1)^2, \quad (2)$$

where  $\mathbf{r}_i$  are the coordinates of the  $i$ th sphere and the brackets  $\langle \dots \rangle$  denote the average over all possible configurations  $\{\mathbf{r}_1, \dots, \mathbf{r}_{N+1}\}$ . Often one is interested in the structure function<sup>10</sup> defined as

$$S(k) = \left\langle \left| \frac{1}{N+1} \sum_{i=1}^{N+1} \exp(i\mathbf{k} \cdot \mathbf{r}_i) \right|^2 \right\rangle, \quad (3)$$

where  $\mathbf{k}$  is the wave vector. For small  $k$ , one gets the Debye moment expansion<sup>19</sup>

$$S(k) = 1 - \langle S_N^2 \rangle k^2 / 3 + O(k^4); \quad k \ll \langle S_N^2 \rangle^{-1/2}. \quad (3a)$$

For  $k \gg \langle S_N^2 \rangle^{-1/2}$  the spheres are uncorrelated and  $S(k) \sim 1/N$ . In the case of vanishing excluded volume parameter  $d/l = 0$  it is well known that<sup>1</sup>

$$\langle R_N^2 \rangle = l^2 N, \quad (4a)$$

$$\langle S_N^2 \rangle = l^2 \frac{N(N+2)}{6(N+1)}, \quad (4b)$$

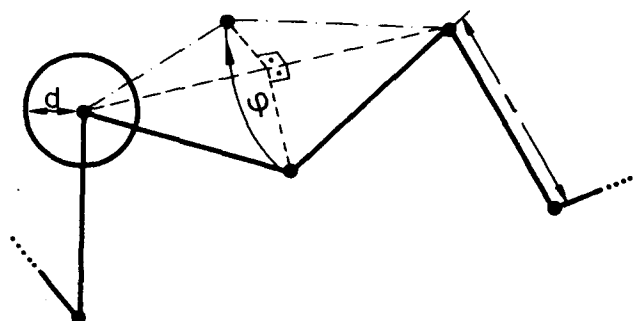


FIG. 1. Local motion of the freely jointed chain. A connection point of two segments is moving collisionlessly on a circle from its old place to a new one located an angle  $\phi$  away, keeping the neighboring segment-segment connection points in space fixed.

$$S(k) \propto k^{-2} \quad (\text{for } \langle S_N^2 \rangle^{-1/2} < k < l^{-1}) . \quad (4c)$$

For  $d/l \neq 0$  no exact relation is known. There exist several analytical approaches<sup>1-10</sup> which support a power law in the limit  $N \rightarrow \infty$

$$\langle R_N^2 \rangle \propto N^{2\nu} \quad (5a)$$

$$\langle S_N^2 \rangle \propto N^{2\nu} \quad (5b)$$

$$S(k) \propto k^{-1/\nu} \quad (\text{for } \langle S_N^2 \rangle^{-1/2} < k < l^{-1}) \quad (5c)$$

where  $0.6 \lesssim \nu \lesssim 0.588$ . This exponent  $\nu$  should be universal; i. e., the same for all  $d/l \neq 0$  and independent of the polymer model.<sup>5</sup> Throughout the paper we have adopted if necessary for our analysis of the data the values  $\nu = 0.588 \pm 0.001$  which has been obtained by field-theoretical renormalization group calculations.<sup>9</sup>

Estimates for the quantity defined in Eqs. (1)–(3) at  $d/l \neq 0$  may be obtained by means of the Monte Carlo technique, which was first introduced by Metropolis *et al.*<sup>20</sup> in the computations of the equation of state of a hard-sphere gas. In addition, this scheme allows one to deal directly with the system at the microscopic level, and it is therefore possible to get an insight into the detailed behavior of the system. For a detailed discussion of this scheme we refer to Refs. 20 and 21.

In our Monte Carlo method one starts with an arbitrary initial configuration  $\{\mathbf{r}_1, \dots, \mathbf{r}_i, \dots, \mathbf{r}_{N+1}\}$ . After the  $i$ th sphere has been chosen by a random-number generator the sphere is moving collisionless on a circle from its old place  $\mathbf{r}_i$  to a new one  $\mathbf{r}'_i$  located a randomly chosen angle  $\varphi$  away, keeping the neighboring spheres  $\mathbf{r}_{i-1}$  and  $\mathbf{r}_{i+1}$  fixed (see Fig. 1). If the  $i$ th sphere at  $\mathbf{r}'_i$  is penetrating another sphere of the chain this attempt is rejected and the  $i$ th sphere remains at  $\mathbf{r}_i$ , otherwise the configuration has changed to  $\{\mathbf{r}_1, \dots, \mathbf{r}'_i, \dots, \mathbf{r}_{N+1}\}$ . In this manner a sequence of new configurations is generated. Since the system tends to equilibrium by construction, there is a correspondence between the time lapse and the number of configurations. So that the time unit does not depend on the chain length  $N$ , this unit is defined as a sequence in which, on the average, any sphere has the possibility to move once. This is the so-called Monte Carlo step per particle, containing a sequence of  $N$  chain configurations. Thus, for describing the evolution of the system we may use a parameter  $t$ , called the time, which takes on the sequential values  $t_k = k/N$ ,  $k = 1, 2, \dots$ . Of course, there is only a superficial analogy to the time evolution of an actual chain in solution, evolving according to Hamiltonian equations of motion, while in our case the "time" evolution is described by a Markovian master equation.<sup>21</sup> One may now define time-dependent quantities. For example, the time-dependent end-to-end distance at time  $t$  is defined as

$$R(t) = |\mathbf{r}_1(t) - \mathbf{r}_{N+1}(t)| . \quad (6)$$

In Fig. 2 a characteristic behavior of the time-dependent average square end-to-end distance

$$\langle R^2(t) \rangle = \frac{1}{t} \int_0^t dt' R^2(t') \quad (7)$$

is shown. For time  $t$  large enough good estimates of

the equilibrium values (4a) or (5a) may be obtained. We estimate that the time needed to reach equilibrium increases with chain length  $N$  as  $N^2$ ,<sup>18</sup> while corresponding dynamic Monte Carlo studies on lattices<sup>16</sup> involve an increase of relaxation time  $\propto N^3$ .<sup>22</sup> Types of the data shown in Fig. 2 have been collected throughout the simulations, to check that equilibrium was actually obtained. Since the *same* slowing down occurs for chains without excluded volume interaction as well, it is an important accuracy check that we easily reproduced the exact results for the case  $d/l = 0$ . Of course, with  $d/l \neq 0$  it may happen that the system is nonergodic, since the phase space could split into several "pockets" mutually inaccessible from each other. Then every dynamic simulation which investigates one pocket only could involve a systematic error. To cope with this difficulty we made runs with several different starting configurations of the chain (particularly for  $d/l = 1$ ). We always observed the averages to settle down to the same limiting values, irrespective of the starting configurations. Therefore we think that nonergodicity in practice is not a serious problem in our case.

### III. RESULTS

Our results for various chain lengths  $N$  and excluded volume parameters  $d/l$  are summarized in Table I and Figs. 3 and 4. The data for  $d/l = 0$  are given by Eqs. (4a, b) which have been reproduced by simulation within an error of about 1% (compare also Figs. 2 and 4). For chain lengths much larger than 100 our program would need a computer time (IBM 370/168) which seems to us to be unreasonably high. However, from Fig. 3 one deduces that at  $N \approx 100$  the "asymptotic limit  $N \rightarrow \infty$ " is reached within the numerical error, so that for calculating  $\langle R^2 \rangle$  and  $\langle S^2 \rangle$  it seems to be unnecessary to go far beyond  $N \approx 100$  in our case of the freely jointed chain

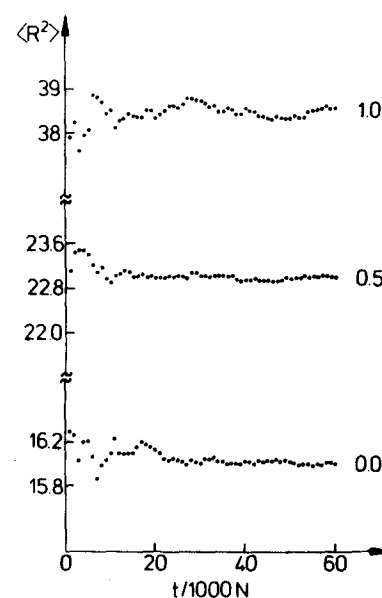


FIG. 2. Time evolution of the mean square end-to-end distance  $\langle R^2 \rangle$  as defined by Eq. (7) demonstrated for chain length  $N = 16$  and three excluded-volume parameters  $d/l = 1, 0.05$ , and  $0.0$ .

TABLE I. Mean square end-to-end distances,  $\langle R^2 \rangle$ , and mean square radius of gyration,  $\langle S^2 \rangle$ , for chains of  $N$  steps and excluded volume ratio  $d/l = 1.0$ .

| $N$ | $\langle R^2 \rangle$ | $\langle S^2 \rangle$ | $\langle R^2 \rangle / \langle S^2 \rangle$ |
|-----|-----------------------|-----------------------|---|
| 8   | $15.90 \pm 0.08$      | $2.48 \pm 0.01$       | $6.41 \pm 0.03$                             |
| 16  | $38.55 \pm 0.15$      | $5.86 \pm 0.02$       | $6.58 \pm 0.03$                             |
| 32  | $94.30 \pm 0.6$       | $14.2 \pm 0.1$        | $6.64 \pm 0.04$                             |
| 50  | $165.0 \pm 3.0$       | $25.3 \pm 0.3$        | $6.52 \pm 0.1$                              |
| 100 | $380.0 \pm 6.0$       | $59.0 \pm 0.5$        | $6.44 \pm 0.1$                              |

model. This point of view is also supported by the structure function  $S(k)$  in Fig. 4. The remarkable insensitivity to the number of beads indicates that even a chain length of 16 is near the asymptotic limiting behavior already as long as distances larger than  $l$  are probed.

In contrast to previous static Monte Carlo calculations<sup>14,15</sup> we find no contradiction to universality. For  $d/l = 0.5$  and  $d/l = 1.0$  the same exponent  $\nu$  is found (Figs. 3 and 4), so that it supports the idea<sup>5</sup> that the exponent  $\nu$  drops discontinuously from  $\nu \approx 0.6$  for  $d/l \neq 0$  to  $\nu = 0.5$  for  $d/l = 0$ . In Fig. 5 the deviations between our work and previous results<sup>13-15</sup> are shortly summarized.

The discrepancies with the results of Refs. 13 and 15 may be explained as follows. Using the "dimerization" method of Alexandrowicz<sup>9</sup> a number of  $L$  short chains of length  $n$  are successively randomly connected taking into account the excluded volume restriction. So one generates a polymer chain of length  $N = Ln$ . But in doing so one has added short polymer chains with an end-to-end distribution function of the scaling form<sup>8</sup>

$$P_n(r) = \frac{1}{l^3 n^{3\nu}} f\left(\frac{r}{ln^\nu}\right) \quad (8)$$

which obviously yields not the distribution function of the final chain

$$P_N(r) = \frac{1}{l^3 n^{3\nu} L^{3\nu}} f\left(\frac{r}{ln^\nu L^\nu}\right) \quad (9)$$

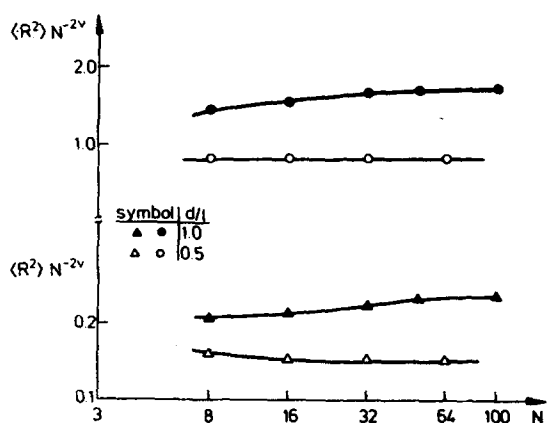


FIG. 3. The asymptotic behavior of the scaled mean square end-to-end distance  $\langle R^2 \rangle N^{-2\nu}$  and the scaled mean square radius of gyration  $\langle S^2 \rangle N^{-2\nu}$ , where  $\nu = 0.588$ .

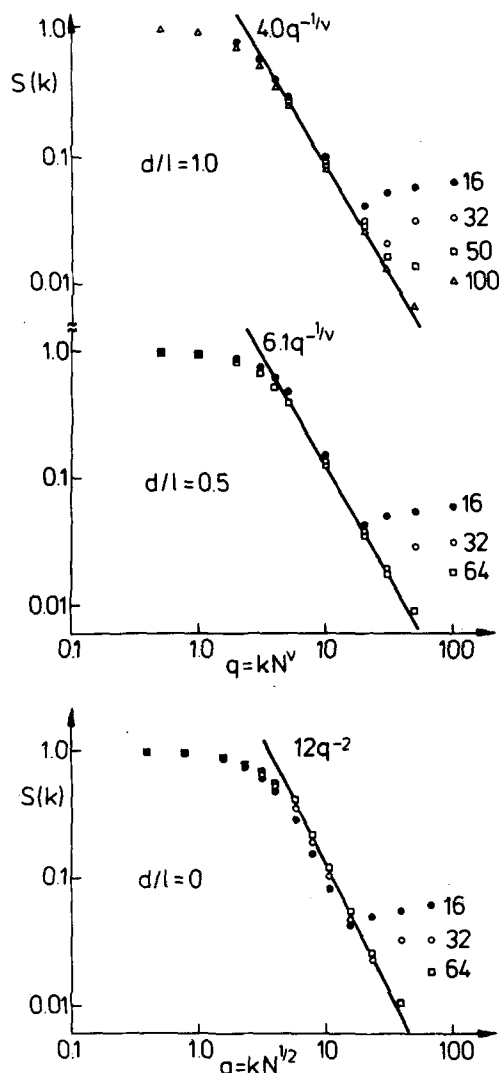


FIG. 4. The structure function  $S_N(k)$  vs  $q$ , where  $q = kN^\nu$  and  $\nu = 0.59$  for  $d/l = 1.0, 0.5$  and  $\nu = 0.5$  for  $d/l = 0$ . The symbols represent the results of different values of  $N$  (see right-hand notations). The structure function in the intermediate  $q$  range is indicated by the line  $S_N(k) = \text{const.} \times q^{-1/\nu}$ .

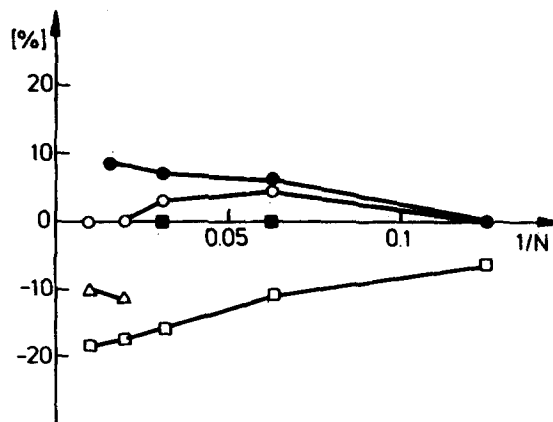


FIG. 5. Deviations per cent between our results and Ref. [15] (circles), Ref. [14] (squares), Ref. [13] (triangles) as a function of chain length  $N$ . The full symbols correspond to  $d/l = 1.0$ , the open symbols to  $d/l = 0.5$ .

TABLE II. Mean square end-to-end distances,  $\langle R^2 \rangle$ , and mean radius of gyration,  $\langle S^2 \rangle$ , for chains of  $N$  steps and excluded volume ratio  $d/l = 0.5$ .

| $N$ | $\langle R^2 \rangle$ | $\langle S^2 \rangle$ | $\langle R^2 \rangle / \langle S^2 \rangle$ |
|-----|-----------------------|-----------------------|---|
| 8   | $10.20 \pm 0.02$      | $1.78 \pm 0.002$      | $5.73 \pm 0.01$                             |
| 16  | $23.0 \pm 0.2$        | $3.80 \pm 0.03$       | $6.05 \pm 0.05$                             |
| 32  | $52.3 \pm 0.5$        | $8.46 \pm 0.06$       | $6.18 \pm 0.06$                             |
| 64  | $117.5 \pm 1.0$       | $18.95 \pm 0.15$      | $6.20 \pm 0.05$                             |

This general statement is supported by the following phenomenological arguments. It is well known<sup>1,10</sup> that the excluded volume interaction swells the coil and scaling laws hold only if (Ginzburg criterion)

$$(d/l)^3 \gg N^{-1/2} \quad (10)$$

which leads for large  $N$  to a characteristic internal chain length<sup>10,5</sup>

$$n_c \approx (l/d)^6 \quad (11)$$

such that all distances  $\langle r_n^2 \rangle$  ( $n \geq n_c$ ) are swollen and all distances  $\langle r_n^2 \rangle$  ( $n < n_c$ ) are unperturbed. The total mean end-to-end distance is then given by

$$\langle R_N^2 \rangle = \left( \frac{N}{n_c} \right)^{2\nu} n_c l^2 \quad (12)$$

Consequently the "dimerization" method approximately works only if

$$(d/l)^3 \gg n^{-1/2} \quad (13)$$

Thus if one chooses as subchain length  $n = 8$  (as done in Ref. 15) the "dimerization" method is expected to yield fairly accurate results for  $d/l = 1.0$  but rather inaccurate results for  $d/l = 0.5$ . This expectation is fully borne out by Fig. 5. The fact that for large  $L$  and  $d/l = 1.0$  the results approach the correct ones seems to be fortuitous in this method, because the fusion of a large number of dense subchains leads (by taking into account the excluded volume restriction) to a swollen total chain, but with a detailed structure which is very different from the correct one. This interpretation should be proven by calculating the structure function of "dimerized" polymer chains. These arguments are supported by the fact that for  $d/l = 1.0$  and  $L = 2, 3$  ( $N = 16, 32$ ) the fusion of dense subchains leads to higher average values.

Using subchains of  $n = 50$  for  $d/l = 1$ <sup>13</sup> the "dimerization" method should yield reasonable results for  $\langle R_N^2 \rangle$ . But we guess that using "biased" subchains as done in Ref. 13, which have too low values of  $\langle R_n^2 \rangle$  the total chain size must be underestimated, consistent with that we find in Fig. 5. Possibly for large  $L$  the correct value of  $\langle R_N^2 \rangle$  is approached. But whether the final distribution [Eq. (9)] is correctly realized is an open question.

However, in spite of these objections most of the results obtained with the "dimerization" method seem not to be as far off as the results obtained with the technique of "inversely restricted sampling"<sup>14</sup> for  $d/l = 1$ . But for  $d/l = 0.5$  this method yields results which agree with ours. It is not clear what the reason of this behavior is; perhaps the statistics obtained by that method be-

comes the worse the higher the excluded-volume parameter  $d/l$ .

In most cases our estimates lie in between the estimate of Refs. 13, 15, and 14. Since the discrepancies between these results was of the order 10% typically, it is clear the exponent estimates which can be obtained from that type of data can not yet be very accurate either.

#### IV. CONCLUSION

It is clear that the freely jointed chain with an hard-core potential should not be regarded as a model which faithfully describes phenomena occurring in certain real systems. Also the dynamics introduced to calculate equilibrium quantities does not simulate the time-dependent behavior of real polymers. But nevertheless, if one is mainly interested in the general properties of a polymer chain in solution and believes in the "universality principle" invoked in second order phase transitions (to which the asymptotic behavior of polymer chains is related),<sup>5</sup> then the freely jointed chain should be a good starting point. One serious defect of the present model is that the hard-core interaction yields no realistic thermodynamics. So investigations on the collapse phase transition ( $d/l \rightarrow 0$  continuously) and related phenomena cannot be carried out within the frame work of this model. Therefore we have restricted our attention only to three excluded volume parameters  $d/l$ .

Detailed studies on the collapse phase transition of the freely jointed chain with a more realistic interaction (Lennard-Jones potential) will be published elsewhere.<sup>18</sup> There also the dynamics of the polymer chain will be discussed. Although the kind of dynamics produced by our Monte Carlo method is somewhat unrealistic<sup>22,23</sup> (no hydrodynamics, etc.), it gives a valuable insight into the behavior of the system at the collapse transition.<sup>18</sup> In conclusion, we think we have demonstrated that our dynamic version of Monte Carlo simulation for off-lattice polymer chains yields results of reliable accuracy, comparable or even better than previous static methods. But the advantage of our scheme is that it is not restricted to excluded volume interaction, but is readily generalized to arbitrary pair-potentials between the molecules forming the polymer chain.

*Note added in proof:* A recent reanalysis of the data of Ref. 15 revealed a bias in the original data evaluation (W. Bruns, private communication). The corrected data are in very good agreement with our present results in Table I and II, confirming the accuracy of our method.

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