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LETTER TO THE EDITOR

Molecular dynamics simulation of polymer chains with excluded volume

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Abstract. Molecular dynamics simulation techniques have been used to study the equilibrium configurational properties of freely moving polymer chains constructed from linked elastic spheres. The mean square end-to-end distance and radius of gyration are found to vary exponentially with chain length, and the results are similar to those obtained in Monte Carlo and self-avoiding walk studies. It is suggested that molecular dynamics is capable of yielding results of the same quality as Monte Carlo, while avoiding the inherent sampling problems.

In this Letter we describe the results of applying molecular dynamics computer simulation techniques to the study of the configurational properties of a polymer chain in dilute solution. Over the past twenty years, molecular dynamics studies of elastic discs and spheres have proved highly successful in exploring phenomena such as the melting transition and the nature of fluid transport at a microscopic level (Alder 1973). However, no application of these methods to a study of the equilibrium properties of long chain polymer molecules appears to exist.

One of the original papers on molecular dynamics (Alder and Wainwright 1959) included a detailed discussion of the principles involved, with emphasis on a system of hard spheres interacting via a square well potential. The essence of the method, which is suitable for systems involving step potentials, is that all the atoms (i.e. spheres or discs) move with constant velocity until any two of them encounter a change in their mutual interaction potential, at which stage an elastic collision occurs. The evolution of the system is thus characterised by a sequence of binary collisions; the two kinds of computation involved in the simulation are the prediction of the next collision, if any, between a pair of atoms, and the determination of the outgoing velocities following a collision.

A model of a freely moving polymer chain which fits into the above scheme, and whose simulation involves computations of the kind just mentioned, is constructed in the following way. The chain is composed of $N + 1$ hard spheres of diameter D attached to each other in 'necklace' fashion by sliding links connecting their centres. The length of each link—the bond length—is free to vary over the range L to $(1 + \delta)L$, with $\delta > 0$. When the link length reaches either of its limits an elastic collision occurs between the two spheres involved, the result of which is a change in their velocity components parallel to the link. No other interaction energy is associated with the link. Pairs of spheres which are not adjacent chain members obey the excluded volume condition in that they collide elastically when their centres approach to a

distance D . By relaxing the constraint of fixed bond length we have converted the complicated equations of motion of a chain of tightly coupled spheres ($\delta = 0$) into a problem of essentially independent colliding spheres ($\delta > 0$) which move with constant velocity between collisions.

In choosing a suitable value for δ there are two conflicting requirements which must be satisfied. The results are later to be compared with those obtained by Monte Carlo analysis, and with numerical results for self-avoiding walks on lattices, both of which correspond to the case $\delta = 0$; consequently δ should be chosen as small as possible. However, the magnitude of δ determines how large a fraction of the collisions in the system involve adjacent chain members. This fraction grows rapidly as δ decreases, and since computation time is proportional to the total number of collisions which occur, the simulation will be unable to adequately sample configuration space if the fraction is too large. A compromise value of $\delta = 0.1$ was adopted, and appears to fulfil both requirements.

It should be pointed out that in this simplest of models the spheres are freely linked and that there is no attempt to restrict the angles between consecutive bonds, nor are there any intra-chain interactions present apart from the excluded volume. Such improvements to the model are readily incorporated and are currently being studied. Furthermore, the model neglects modifications to the motion due to the presence of other chains or the solvent, though the simulation can be extended to include these effects as well.

Chains of various lengths ranging from $N + 1 = 10$ to 50, with $L = D = 1$, were simulated, and several chains of each length were studied. The initial state (whose influence faded rapidly) was taken to be a regular helix, but the initial velocities were assigned random values. A chain was first allowed to evolve for a period of time to eliminate the effects of the initial state, and then the configurational properties—mean bond length, end-to-end distance, and radius of gyration (i.e. the root mean square distance of the spheres from their centre of mass)—were measured at regular time intervals. These intervals were sufficiently long for there to be little correlation between consecutive measurements. The overall average estimates of the mean square end-to-end distance $\langle R^2 \rangle$ and radius of gyration $\langle S^2 \rangle$, based on 1000–2000 measurements for each N , are summarised in table 1, and plotted against N on a log-log scale in figure 1.

Table 1. Results for chains with $D = 1$, $L = 1$. n_s is the number of measurements made, and the error estimates are the standard deviations obtained by dividing the data into eight groups.

$N + 1$	n_s	$\langle R^2 \rangle$	$\langle S^2 \rangle$
10	1420	17.26 ± 1.18	2.83 ± 0.11
12	1112	22.40 ± 0.70	3.58 ± 0.07
16	1112	32.34 ± 1.63	5.24 ± 0.16
20	1112	42.88 ± 1.24	6.86 ± 0.14
24	1428	54.41 ± 2.95	8.73 ± 0.29
28	1904	66.04 ± 1.44	10.53 ± 0.09
32	1775	79.14 ± 1.60	12.70 ± 0.18
40	1675	97.94 ± 2.37	16.33 ± 0.16
50	2080	142.85 ± 1.91	22.36 ± 0.42

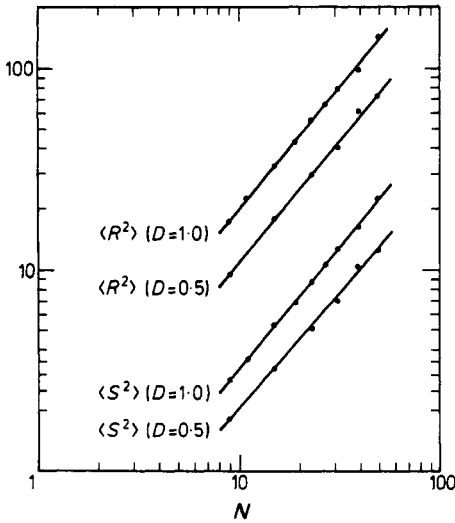


Figure 1. Log-log plots of $\langle R^2 \rangle$ and $\langle S^2 \rangle$ against N . The straight lines indicate the results of least square fits to the data.

Studies of the self-avoiding walk model of a polymer chain on three-dimensional lattices, using exact enumeration and Monte Carlo methods, have established that asymptotically $\langle R^2 \rangle \sim a_R N^{2\nu_R}$ and $\langle S^2 \rangle \sim a_S N^{2\nu_S}$ (where N is the number of steps), with $2\nu_R = 2\nu_S = 1.20$ (e.g. Domb 1969, Rapaport 1975). The apparent lattice independence of the exponents ν_R and ν_S (universality) suggests that the same asymptotic forms might also apply to free chains not confined to a lattice. In order to test this idea we have performed least square fits of $\ln\langle R^2 \rangle$ and $\ln\langle S^2 \rangle$ to $\ln N$ and the results obtained are $2\nu_R = 1.220 \pm 0.016$, $2\nu_S = 1.213 \pm 0.016$, with $a_R = 1.12 \pm 0.07$, $a_S = 0.184 \pm 0.010$. The straight lines corresponding to these values are included in figure 1. The variable bond length could only be incorporated into the analysis in an approximate manner by multiplying N by the average bond length (equal to 1.052 for each N studied), but the exponent values themselves are not affected by this correction. The error estimates given are the standard deviations obtained by dividing the raw data into eight groups and fitting each group separately; they are not given in order to establish firm bounds on the results, but merely to provide some idea of the dispersion involved. The values of $2\nu_R$ and $2\nu_S$ exceed the accepted lattice estimates by 1–2%, but in view of the errors we feel that the possibility of 1.20 being the correct result is not excluded.

One question which can be legitimately raised is whether asymptotic behaviour can be expected from chains of lengths in the range 10 to 50. The fact that the data points in figure 1 lie close to the straight line is evidence that this may indeed be the case. Further support for asymptotic behaviour at these values of N , at least for $\langle R^2 \rangle$, is obtained from a self-consistent field analysis of the excluded volume problem (Edwards 1965) which predicts $\langle R^2 \rangle \sim a_R N^{1.20}$ for $N \gg L(L/D)^6$, and since $L = D = 1$ in the simulation, even the shortest chains satisfy this criterion. Finally, lattice based self-avoiding walk studies using exact enumeration techniques are limited to small N (in the range 10–20, depending on the lattice), and here too asymptotic behaviour is generally observed.

The freely linked hard sphere chain had previously been studied using Monte Carlo methods, and for the case $L = D$ the exponent estimates obtained are as follows. Grishman (1973) obtained $2\nu_R = 1.20-1.22$ using chains with $N \leq 500$, and in a similar study with $N \leq 1024$ Bruns (1977) found that $2\nu_R \approx 2\nu_S = 1.19-1.20$. Smith and Fleming (1975) used a different sampling scheme involving inexact configuration weights, and obtained $2\nu_R = 1.21$, $2\nu_S = 1.16$ for $N \leq 100$; however in view of the other estimates (both molecular dynamics and Monte Carlo) it appears that this low ν_S value is incorrect, possibly due to the weighting scheme whose influence on the results cannot be predicted. Overall it seems reasonable to conclude that both $2\nu_R$ and $2\nu_S$ lie in the range 1.19-1.22. It will be noticed that Bruns' estimates of $\langle R^2 \rangle$ and $\langle S^2 \rangle$, and consequently a_R and a_S , are significantly larger than those obtained here; we are unable to offer an explanation for this at present.

We have also applied the molecular dynamics technique to chains with $D = 0.5$, $L = 1$, and the results are shown in table 2 and figure 1. The least square fits to the data yield $2\nu_R = 1.216 \pm 0.054$, $2\nu_S = 1.150 \pm 0.027$ and $a_R = 0.62 \pm 0.12$, $a_S = 0.135 \pm 0.013$; the larger errors than for $D = 1$ are a consequence of fewer simulation runs. ν_R seems to be unchanged from $D = 1$, but ν_S has decreased considerably.

The Monte Carlo exponent estimates for this case are as follows: Grishman (1973) $2\nu_R = 1.20-1.23$; Bruns (1977) $2\nu_R = 1.174$, $2\nu_S = 1.169$; Smith and Fleming (1975) $2\nu_R = 1.165$, $2\nu_S = 1.07$ (this value is obtained by interpolation). Thus while there appears to be general agreement that $2\nu_S$ is definitely below 1.20, the ν_R values obtained by molecular dynamics and Monte Carlo fall into two distinct groups. In view of the fact that much longer chains may be required to obtain full asymptotic behaviour for $D < 1$, further analysis of the various sets of data taking this into account may help resolve this issue.

In conclusion, it has been demonstrated that molecular dynamics simulation is a successful technique for studying the *static* configurational properties of polymer models. Simulation represents a true numerical experiment whose advantages over the Monte Carlo method are that it does not require a source of random numbers (with whatever subtle errors the possible irregularities in the random number generator may introduce into the results), nor does it require decisions regarding the relative weights of the sampled configurations. Furthermore, it is capable of reproducing dynamic behaviour, and a study of this topic, together with a more extensive analysis of the static properties will be presented in subsequent articles.

Table 2. Results for chains with $D = 0.5$, $L = 1$.

$N+1$	n_s	$\langle R^2 \rangle$	$\langle S^2 \rangle$
10	808	9.51 ± 0.53	1.81 ± 0.06
16	965	17.85 ± 1.01	3.21 ± 0.15
24	965	29.12 ± 2.28	5.11 ± 0.18
32	1010	40.20 ± 1.13	6.99 ± 0.10
40	1100	61.51 ± 5.04	10.31 ± 0.40
50	802	72.45 ± 5.36	12.42 ± 0.48

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