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LETTER TO THE EDITOR

Mean end-to-end distance of branched polymers

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Abstract. We use Monte Carlo methods to calculate the mean end-to-end distance of randomly branched polymer molecules. Molecular realisations are brown on the square and simple cubic lattices, and consist of N bifunctional monomers and N_f polyfunctional branching units of functionality f. We treat three cases in which the monomer branches are either random walks, self-avoiding walks (SAW), or SAW's except that different branches may join at their end points to form closed loops. For the first case, we find that the mean end-to-end distance L varies with N as $L \sim N^{1/4}$ for fixed branching probability p, consistent with previous theoretical predictions. For the latter two cases we find that for fixed p, $L \sim N^{\nu}$, where $\nu = 0{\cdot}57 \pm 0{\cdot}06$ on the square lattice and $0{\cdot}45 \pm 0{\cdot}06$ on the simple cubic lattice. Although the number of closed loops formed per realisation is quite small, it does appear possible that loop formation may play a dominant role in the $N \to \infty$ limit.

An important class of polymer configurations is formed when N bifunctional monomers and N_f polyfunctional branching units of functionality f connect in a *random* way to form a branched structure (see figure 1). The theoretical treatment of such randomly branched polymer configurations was initiated by Zimm and Stockmayer (1949), who calculated the radius of gyration when the number of polyfunctional units is a small fixed number. Subsequently, de Gennes (1968) considered a more general problem in which the number of branching units is variable. Using diagrammatic techniques, de Gennes calculated the probability distribution for the branched structure given the probability distribution function for the linear chain.

These two analyses were restricted only to the case in which the monomer branches formed random walks. (This is often called the 'Gaussian' branched polymer.) This approximation is used to describe the theta temperature, where the Van der Waals attraction of neighbouring molecules is balanced by the excluded volume constraint. Under this restriction, de Gennes showed that the mean end-to-end distance L varies as†

$$L \sim N^{\nu_{sc}} \langle N_f \rangle^{-\mu} \tag{1a}$$

where $\nu_{sc} = \frac{1}{2}$ is the exponent for the single-chain random walk, and $\mu = \frac{1}{4}$ in all dimensions d. Thus for a fixed number of branching units single-chain behaviour occurs. If N_f is not fixed, but is determined by a random probability, then $\langle N_f \rangle \sim N$ and hence equation (1a) can be rewritten as

$$L \sim N^{\nu}. \tag{1b}$$

† This result was derived only for the case of branching units with functionality $f = 3$. It is possible to generalise de Gennes' analysis, and show that the exponents are independent of f.

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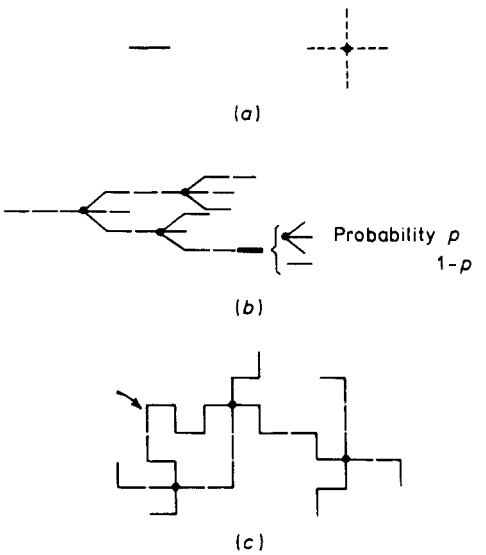

Figure 1. (*a*) The constitutents of the branched polymer are the bifunctional monomers (represented by a bond), which react to form the branches of the polymer, and the *f*-functional branching units (represented by a site). We assume that all the chemical bonds of these units react immediately, so that it may be represented as a site with *f* monomers (shown as broken lines) attached. (*b*) Schematic structure of a typical polymer molecule for a random branching process. The molecule is drawn in a suggestive fashion to illustrate our growing algorithm. One of the branches is chosen at random to be 'current'. At the end point of this branch (shown by the bold line), a branching unit is added with probability *p* or a monomer is added with probability 1-*p*. (*c*) Example of a self-avoiding branched polymer on the square lattice. The arrow indicates where two branches have joined to form a closed loop.

Here $\nu = \nu_{sc} - \mu = \frac{1}{4}$ for all d, in contrast with the single-chain exponent of $\nu_{sc} = \frac{1}{2}$. These exponent predictions have recently been rederived by Lubensky and Issacson (1978), who used field-theoretical methods applied to a generalised spin model (Lubensky *et al* 1978) to treat randomly branched polymers and various related problems.

In this Letter we present preliminary results of a Monte Carlo investigation of the mean end-to-end distance of randomly branched polymers when excluded volume effects are accounted for. We consider a lattice model with bifunctional monomers represented by lattice bonds, and polyfunctional branching units represented by lattice sites (see figure 1(*a*)). The branches of the molecule are formed by monomers joining end-to-end. We assume that all the bonds of the branching unit react immediately, so that no further branches may originate from or terminate at a branching unit at a later stage. We first study the case when the monomer branches are random walks, where our Monte Carlo simulations may be compared with known results. Secondly, we treat the case of branches which are self-avoiding walks (SAW), in order to model the excluded volume constraint. Finally, we consider the case where different branches of the self-avoiding polymer may join at their end points to form closed loops.

The Gaussian branched polymer. We grow molecules on a lattice using an algorithm which may be understood by considering the molecule after it has been partly constructed so that it possesses a tree topology (see figure 1(*b*)). One of the existing

branches is then chosen at random to be 'current', and a branching unit may attach to the monomer at the end point of the current branch with a given probability p. If the branching unit does join, then z additional monomers† immediately attach, which radiate from the branch site, where z is the lattice coordination number. If the branching unit does not attach, then another monomer is added to the current branch. Finally, a new current branch is chosen and the process is repeated.

Once a realisation is generated, the end-to-end distances are computed for each of the $[N_f(f-2)+2][N_f(f-2)+1]/2$ pairs of end points. We then calculate L by treating each pair as statistically independent‡. We have taken data for $10<N<10\,000$ and $0{\cdot}001<p<0{\cdot}2$, and from this information we have studied the dependence of the mean end-to-end distance on: (i) N with N_f fixed; (ii) N with p fixed; and (iii) $\langle N_f\rangle$ with N fixed (see figure 2). For fixed N_f, we find the single-chain behaviour of $L\sim N^{1/2}$. If p is fixed, then we find that $L\sim N^{\nu}$, with $\nu=0{\cdot}26\pm0{\cdot}04$ and $\nu=0{\cdot}29\pm0{\cdot}04$ for the square and cubic lattices respectively, consistent with equation (1a). Thus the effect of branching is

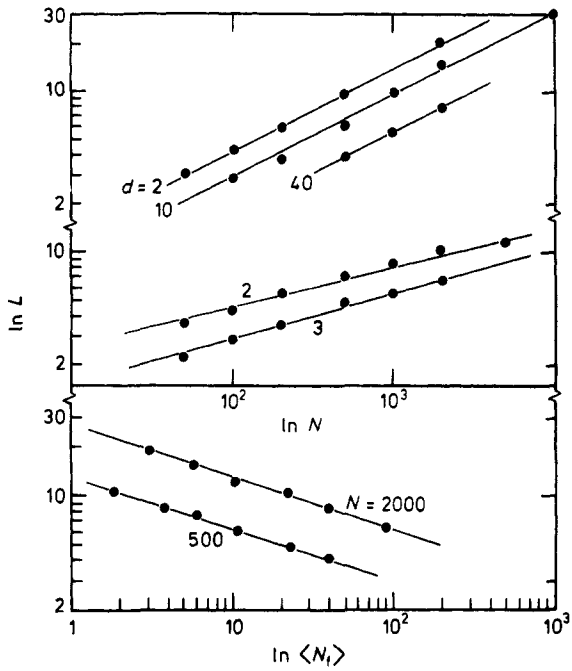

Figure 2. Dependence on $\ln N$ and on $\ln\langle N_f\rangle$ of $\ln L$ for the Gaussian branched polymer. In the upper part of the figure, data from the square lattice are shown with the number of branch points fixed at 2, 10 and 40. A linear least-squares fit yields slopes of 0·512, 0·530 and 0·501 respectively for these data. In the middle of the figure, data are shown when the branching probability is fixed to be 0·01. The data is approximately linear with a slope determined by least-squares fitting to be 0·26 and 0·29 on the square and cubic lattice respectively. In the lower portion, N is fixed at 500 and 2000 to investigate $\langle N_f\rangle$ dependence. Data from the square lattice are fitted by lines of slope −0·31 for both cases.

† Notice that one of the added monomers must retrace along the path of the current branch. This construction is the most natural for the random walk case, and the functionality is thus $z+1$.

‡ This procedure yields results that are virtually identical with the more usual method of weighting each molecular realisation equally. However, at large N, generation of each molecular realisation is relatively time-consuming, and thus to obtain sufficient data we utilise each pair as an independent realisation.

to shrink the molecules substantially. In fact, for $d<4$, the Gaussian approximation predicts that the molecular size should be even more compact than a solid d-dimensional object. This indicates that the Gaussian approximation for the theta temperature will break down for $d<4$. Finally, for fixed N, we find that $L\sim\langle N\rangle^{-\mu}$, with $\mu = 0{\cdot}31\pm0{\cdot}04$ for both lattices. This is slightly larger than predicted by equation (1a) and we are not able to resolve this discrepancy at present.

The self-avoiding branched polymer. In the self-avoiding case, it is most natural to consider now branching units with functionality z. We account for the excluded volume constraint in our growing algorithm by immediately discarding trials if branch intersections occur. Consequently, for large N, very few of the trials initiated become successful realisations. This attrition imposes severe limitations on the maximum molecular size that can be studied, and for this reason, our preliminary data is limited to $N\leqslant 70$†. However, even this data is sufficient to show the quantitatively new effects due to the excluded volume constraint. From studying the dependence of L on N with p fixed, we estimate that $\nu = 0{\cdot}57\pm0{\cdot}06$ on the square lattice, and $\nu = 0{\cdot}45\pm0{\cdot}06$ on the cubic lattice (see figure 3). These numbers are smaller than the best estimates of $\nu_{sc}=0{\cdot}74$–$0{\cdot}75$ and $\nu_{sc}=0{\cdot}59$–$0{\cdot}61$ for the single-chain SAW in two and three dimensions respectively (see e.g. McKenzie 1976, Moore and Bray 1978). Thus the effect of branching is again to shrink molecules, although not to the same degree as in the Gaussian case. Equivalently, we can restate this by saying that the excluded volume constraint is relatively more important for the branched configuration.

We can gain some insight into this interesting result by considering separately the excluded volume constraint within each branch and the repulsion between branches. If

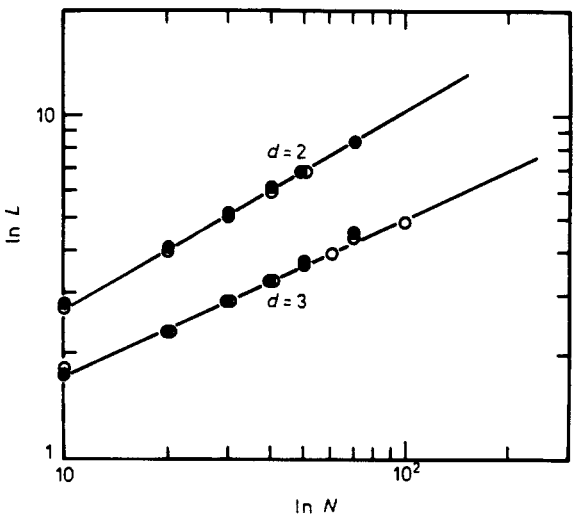

Figure 3. Dependence on ln N of ln L for the self-avoiding branched polymer on the square and cubic lattice with $p=0{\cdot}1$. For the two lattices the data are fitted by lines of slope 0·57 and 0·45 respectively. Data are shown for both the case of loops (○) and the case of no loops (●).

† For the single-chain SAW, the attrition can be partially surmounted by employing sample 'enrichment' or 'dimerisation' methods (Wall *et al* 1963, Alexandrowicz 1969). A similar technique will be required to extend our study to larger N.

we neglect the second effect, then by using the probability distribution for the single-chain SAW (Domb *et al* 1965, Fisher 1966, McKenzie and Moore 1971, des Cloiseaux 1974) we can generalise the diagrammatic treatment of de Gennes (1968) to find the mean distance of a branched polymer with SAW branches, but no repulsion between branches. We find for this structure that $\nu \cong \gamma/4 = \frac{1}{3}$ and $\frac{7}{24}$ for $d = 2$ and 3 respectively, where γ is the exponent that gives the N dependence of the total number of SAWs. Thus the repulsion between chains makes a major contribution in increasing ν from the mean-field value of $\frac{1}{4}$.

We have also looked at the dependence of L on N with N_f fixed, and on $\langle N_f \rangle$ with N fixed. However, in view of the difficulties in obtaining data consistent with equation $(1a)$ for the Gaussian branched polymer, we do not expect good estimates for μ where we are limited to $N \leqslant 70$, and this was found to be the case.

The self-avoiding branched polymer with loops. We have also studied a natural generalisation of the previous model, in which different branch ends may now join to form closed loops†. In this case sample attrition is reduced, and we obtain data for $N \leqslant 100$. We find that estimates for ν are virtually the same as those for the self-avoiding polymer without loops. It appears that the only effect of allowing loops is to reduce the molecular size slightly.

It is most interesting, however, to investigate the dependence of the average number of loops $\langle l \rangle$ on molecular size. While this number is quite small, both the fraction $\langle l \rangle / N$ and the fraction of branches that form closed loops grow with N. Thus it is possible that in the limit of $N \to \infty$ closed loops may be very important (table 1). This feature is quite intriguing in the light of the recent work by Lubensky and Issacson (1979), who argue that the dilute limit of branched polymers with and without loops belong to different universality classes. According to our numbers, this difference is not evident at $N = 100$ and it is likely not to be apparent until N is very large.

We have used Monte Carlo methods to study the mean end-to-end distance of randomly branched polymer molecules. Three types of molecular configurations are considered in which the monomer branches are either random walks, self-avoiding walks, or self-avoiding walks with the possibility that different branches may join at

Table 1. Dependence of the average number of loops in the self-avoiding polymer on the number of monomers, and on the average number of branches. Data is from the cubic lattice, and the branching probability is fixed to be 0·1.

N	No. of loops/monomer	No. of loops/branch
10	0·006	0·018
20	0·018	0·060
30	0·022	0·077
40	0·024	0·087
50	0·024	0·097
70	0·022	0·099
100	0·031	0·133

† In principle, this growing algorithm seems to be capable of generating all clusters that occur in the percolation problem. However, the statistical weights assigned to a given realisation in the two problems are different. Although the exponents quoted here yield a value for the fractal dimensionality for branched polymers that is close to that found for percolation clusters, the relation between these two problems has not yet been clarified (see e.g. Stanley 1977, Harrison *et al* 1978).

their ends to form closed loops. For the first case we confirm approximately that the end-to-end distance varies as $L \sim N^{1/2}\langle N_f\rangle^{-1/4}$ for both the square and the cubic lattice. The latter two cases are used to model excluded volume effects, and we find $L \sim N^{\nu}$, with $\nu = 0{\cdot}57 \pm 0{\cdot}06$ and $\nu = 0{\cdot}45 \pm 0{\cdot}06$ for the square and cubic lattice respectively. When closed loops are allowed, there is no change in our estimates for ν. However, it appears that loops may become very important in the asymptotic $N \to \infty$ limit.

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