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The shape of polymer chains and rings

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Abstract. Exact enumeration methods are used to study the distribution of units in self-avoiding polymer chains and rings on the FCC lattice. Estimates of the exponents characterizing the size dependence of the moments are derived and compared with those of the chain end-to-end distance distribution. Ratios of the different moment types are also studied and compared with the predictions of cluster theory.

1. Introduction

The self-avoiding chain, or walk, on a lattice has been the subject of numerous studies, both because of its application as a model of a polymer chain in dilute solution and for the possible connection to other problems of statistical mechanics (Domb 1969). The self-avoiding condition represents an attempt to simulate the excluded volume portion of the intrachain interaction. Polymer models which omit this or any other kind of interaction between non-neighbouring chain units are Markovian and, consequently, are amenable to study by straightforward transfer matrix methods (Flory 1969); the incorporation of a long-range type of interaction such as the excluded volume renders these methods inapplicable.

There have been two main approaches to the self-avoiding chain problem—exact enumeration (eg Domb 1969) and Monte Carlo (eg McCrackin *et al* 1973). In the exact enumeration studies the configurational properties of short chains (generally of length 10–20 links, depending on the lattice) are determined by exhaustive generation and, where the results are sufficiently smooth, they are extrapolated to provide the limiting long-chain behaviour. The Monte Carlo investigations are based on suitably generated samples of considerably longer (100–1000 links) chains, here the need to resort to extrapolation is diminished because the chains are usually of sufficient length to display the limiting behaviour. The predictions of the two different approaches tend to agree remarkably well, lending support to the claim that it is possible to deduce many of the limiting properties by extrapolating the short-chain data.

Less extensively studied by either exact or Monte Carlo methods are the properties of the self-avoiding ring polymer on a lattice. Rings are more difficult to study by Monte Carlo methods than chains because the attrition inherent in the process makes generation of adequate samples of the larger rings very difficult (Kumbar and Windwer 1968). The important configurational property of the rings is the mean distribution of the individual units about their centre of mass—essentially the 'shape' of the ring. For chains it is again the shape which is of importance and, in addition, the mean distribution

of the distance between the end-points of the chain. In the exact enumeration studies techniques have been developed for simplifying the end-point calculations, and these have consequently progressed a good deal further than the shape calculations for which no comparable short-cut exists. A further consequence of this lack of a short-cut is that the study of the ring shape has been almost totally avoided.

In this paper we report on exact enumeration studies of the shapes of self-avoiding chains and rings on the face-centred cubic (FCC) lattice. On account of the high co-ordination number ($q = 12$) one expects that the limiting behaviour should become apparent much sooner than for other, less closely packed lattices. Available work supports this contention; for example, the degree of convergence of the results from chains of up to fourteen links on the tetrahedral ($q = 4$) lattice (Kumbar and Windwer 1969) is similar to that from chains of up to about six links on the FCC. In our study the rings have been generated to twelve links, the chains to nine.

2. Generation method

We consider a chain of n links connecting $n+1$ units of equal mass. The units are located at the sites of a regular lattice and the link length is the distance between nearest-neighbour sites. c_n is defined to be the number of self-avoiding (no two units occupying any one lattice site) n-link chains which start out from any given site. Similarly, u_n is the number of n-link (n-unit) self-avoiding rings (first and last sites coincide) which pass through a particular site. On the FCC lattice the c_n have been tabulated as far as $n = 12$ (Martin *et al* 1967) and the u_n to $n = 14$ (Sykes *et al* 1972*b*). Further terms are known for other lattices, although the numerical values of the highest-order terms obtained tend to be smaller than their FCC counterparts. The large numbers involved are quite obviously impossible to compute directly but, through use of a counting theorem (Sykes 1961) and lattice symmetry, computational effort can be reduced substantially.

The counting theorem for self-avoiding chains is based on the observation that, for a given chain, the addition of a further link is more likely to yield a new self-avoiding chain than a chain which visits one of its sites twice. It is therefore preferable to count the possible failures at each stage, and this in turn leads to a recurrence relation for the c_n in terms of graphs which are more readily counted than the chains. A similar simplification is also possible for the self-avoiding rings (Sykes *et al* 1972b).

The configurational properties of the chains are determined by the set $\{c_n(s)|$ all possible $s\}$, where $c_n(s)$ denotes the number of n-link chains with an average distance between the units and the centre of mass equal to s, and by $\{c_n(r)|$ all possible $r\}$, with $c_n(r)$ the number of chains with end-point separation r. For rings the quantity required is $u_n(s)$, the analogue of $c_n(s)$. The moments of the distributions of s and r for the chains are

$$R^p_{n,\mathrm{ch}} = \sum_r r^p c_n(r)/c_n \qquad S^p_{n,\mathrm{ch}} = \sum_s s^p c_n(s)/c_n$$

and for the ring s distribution

$$S^p_{n,\mathrm{ri}} = \sum_s s^p u_n(s)/u_n.$$

For $p = 2$, S^2_n is commonly called the mean square radius of gyration and R^2_n represents the mean square 'length' of the chain.

A recurrence relation method similar to that used for c_n has also been developed to aid in computing the $c_n(r)$ (Martin and Watts 1971), and the calculations for the FCC lattice have been carried out to $n = 10$ (McKenzie 1973). No equivalent development has occurred for $c_n(s)$ or $u_n(s)$. By direct methods the moment $S^2_{n,\mathrm{ch}}$ has been computed to $n = 7$ on the FCC (Domb and Hioe 1969) and somewhat further on other lattices. The only exact enumeration ring study is for the tetrahedral lattice, where $S^2_{n,\mathrm{ri}}$ has been evaluated to $n = 14$ (Kumbar and Windwer 1969).

The results described here form part of a more general study in which the self-avoiding chains and rings contain additional attractive or repulsive interactions between non-adjacent units that approach to nearest-neighbour distance. These interactions further complicate the enumeration problem; for this reason no attempt has been made to look for recurrence relations which would be of help only in the non-interacting limit, and the enumerations were tackled by the direct approach. However, as will be outlined below, some degree of effort was invested into optimizing the computational algorithm, and the lattice symmetry was used to achieve a substantial reduction in the numbers of configurations which had to be generated.

The symmetry reduction arises as follows. The first link of the chain or ring is fixed on any one of the (equivalent) lattice bonds. This produces an immediate twelve-fold reduction in counting effort for the FCC lattice. The second link can now be laid down in four non-equivalent ways out of the possible eleven. Finally, taking into account equivalent three-link configurations produces a further 25% reduction for chains and 50% for rings. This procedure could be carried through to higher order but the additional savings no longer warrant the effort involved. Chains and rings were therefore generated using each of the non-equivalent three-link configurations as a starting point, and the final counts multiplied by the numbers of equivalent configurations of each type.

The computer program used to generate chain and ring configurations is of course coded in assembler language. This ensures a much more effective utilization of the high-speed registers of the processing unit, and thus a reduction in the number of accesses to the comparatively slower main storage than would be achieved by a compiled program written in a higher-level language such as FORTRAN.

A further marked improvement in computing speed derives from not constructing the configurations a single link at a time, but by using a prepared list of short self-avoiding chains (in this case, of up to four links) to enable the addition of several links simultaneously. Since some 30% of four-link random chains on the FCC lattice fail to be self-avoiding, the use of lists means that many of the unsuccessful attempts at generating valid configurations will be avoided. The actual method of list construction, which involves pointers from outside the list and internal linkage between the list elements to permit rapid access to specific groups of stored chains, contributes very significantly to the program efficiency. The net result is a rate of generating self-avoiding configurations of approximately 8×10^6 counts/min on the IBM 370/165 computer. This is double the rate reported for a program used in other work of a similar nature (Martin and Watts 1971—the rate obtained was 10^6 counts/min on a machine operating at roughly a quarter of the speed).

The chains and rings generated are grouped according to their s-values (and, for later use, also according to the numbers of nearest-neighbour pairs). The resulting $c_n(s)$ and $u_n(s)$ are used in the S-moment calculations. The $c_n(r)$ and the R moments of the chains were similarly determined. The moment values are listed in the appendix. Wherever possible the results were checked against previous work and complete agreement was found.

3. Analysis of results

Extrapolation of the exact short chain and ring moments against n to obtain the limiting behaviour is made on the basis of the assumed form

$$M_n^p \sim A_p n^{\gamma_p}\left(1+\frac{a_{1p}}{n}+\frac{a_{2p}}{n^2}+\ldots\right),$$

with M denoting the moments R or S. The procedure is linearized by considering ratios of successive M_n^p:

$$\theta_n^p = n\left(\frac{M_{n+1}^p}{M_n^p}-1\right) \simeq \gamma_p+\frac{b_{1p}}{n}+\frac{b_{2p}}{n^2}+\ldots. \tag{1}$$

The exponents γ_p are the primary targets of the analysis; estimates are found by fitting the known θ_n^p to kth-degree polynomials in $1/n$, for $k = 1, 2, \ldots$. Use of larger values of k in principle allows for more accurate extrapolation, but since each estimate of γ_p requires a set of $k+1$ successive θ_n^p, the expected improvement in accuracy is countered by the increased dependence on smaller values of n. We have tacitly assumed that the finite-n corrections can be expressed in polynomial form; corrections involving non-integral powers or logarithmic terms could well be present, but because the analysis is not particularly sensitive to the details such terms are only included if required by independent arguments (eg Sykes *et al* 1972a). For this reason, too, the values of b_{kp} are not recorded here.

Tables 1 and 2 contain the exponent estimates from the ring and chain S moments for $p = 2$ and 4, together with those from the chain R moments. The $p = 2$ results also appear in figure 1. The entries in table 1 indicate that $\gamma_2 = 1{\cdot}20$ for each of the three kinds of moments; in the ring case the estimate appears more like 1·21–1·22, but reference to the $k = 3$ column suggests that the ring results are not as well converged as those of the chain, and the value 1·20 is still possible.

Table 1. Extrapolated exponent estimates for the $p = 2$ moments obtained by fitting kth-degree polynomials in $1/n$ to the values of θ_n^2, as in equation (1) (cf figure 1). (The actual θ_n^2 values appear in the $k = 0$ column.)

n \ k	0	1	2	3
$\gamma_{2,\mathrm{ri}}(S)$				
9	1·1612	1·2111	1·2948	0·9060
10	1·1663	1·2126	1·2184	1·0402
11	1·1707	1·2143	1·2219	1·2313
$\gamma_{2,\mathrm{ch}}(S)$				
6	1·0901	1·1916	1·2103	1·2087
7	1·1056	1·1985	1·2156	1·2226
8	1·1177	1·2026	1·2148	1·2136
$\gamma_{2,\mathrm{ch}}(R)$				
6	1·2122	1·2057	1·1937	1·1891
7	1·2110	1·2040	1·1998	1·2080
8	1·2100	1·2026	1·1983	1·1957

Table 2. Exponent estimates for the $p = 4$ moments.

n \ k	0	1	2	3
$\gamma_{4,ri}(S)$				
9	2·5002	2·4491	2·5527	1·7601
10	2·4952	2·4505	2·4563	2·2314
11	2·4912	2·4511	2·4536	2·4462
$\gamma_{4,ch}(S)$				
6	2·4169	2·4486	2·4610	2·4476
7	2·4219	2·4517	2·4594	2·4573
8	2·4256	2·4515	2·4509	2·4368
$\gamma_{4,ch}(R)$				
6	2·7461	2·4168	2·4140	2·4004
7	2·6990	2·4166	2·4163	2·4193
8	2·6635	2·4153	2·4112	2·4028

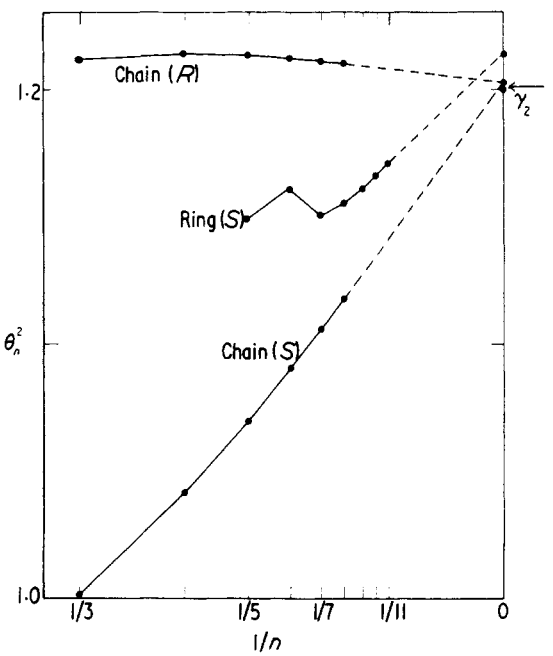

Figure 1. The quantities $\theta_n^2 = n[(M_{n+1}^2/M_n^2) - 1]$ plotted against $1/n$ for the three moment types. The linear extrapolations are based on the last two points only (cf table 1).

In the case of $\gamma_{2,ch}(R)$ the result 1·20 is well established for various three-dimensional lattices (most recently McKenzie 1973, Watts 1974). Monte Carlo analysis supports the claim $\gamma_{2,ch}(R) = \gamma_{2,ch}(S) = 1{\cdot}20$ (McCrackin *et al* 1973). The only existing result for rings is a Monte Carlo estimate of $\gamma_{2,ri}(S) = 1{\cdot}18$ (Kumbar and Windwer 1968), but sampling problems were encountered with the larger rings and, indeed, the generating method is biased in that it is not rings that are constructed, but 'tadpoles'—rings with a

tail. The effect of the tail is to alter the mean s-distribution of the attached rings, although it is not evident whether the results are significantly modified.

The results of table 2 suggest that $\gamma_4 = 2\gamma_2$, and higher-moment results (not shown) that $\gamma_{2p} = p\gamma_2$, although the degree of overestimation of γ_p tends to increase with p. A possible reason for this is that the higher-p moments depend increasingly strongly on the more extended configurations. The geometric constraints make it difficult to form highly compact configurations for small n, particularly in the case of the rings. The mean distribution of mass is consequently less compact, and the moment estimates increased. Larger-n results on the FCC or similar studies on other lattices ought to provide a more definite answer to the question of the relations between exponents.

If it is true that $\gamma_{p,\mathrm{ch}}(R) = \gamma_{p,\mathrm{ch}}(S) = \gamma_{p,\mathrm{ri}}(S)$, it becomes meaningful to examine the limits of the moment ratios

$$\psi_n^p = R_{n,\mathrm{ch}}^p / S_{n,\mathrm{ch}}^p \qquad \phi_n^p = S_{n,\mathrm{ch}}^p / S_{n,\mathrm{ri}}^p.$$

These ratios are evaluated and fitted to polynomials in $1/n$ as before. In the case of ϕ_n^p we are unable to use the ring data for $n > 9$ because the corresponding chain results are unavailable. The results of the analyses appear in tables 3 and 4. There is a strong indication that the ratios approach finite limits (and by a circular argument this provides further evidence for the equality of the exponents).

The limiting value of ψ_n^2 is seen to be 6·41 (table 3). A value of 6·46 was deduced from only seven terms (Domb and Hioe 1969) and the Monte Carlo estimate is 6·26 (McCrackin *et al* 1973). The values reported for other three-dimensional lattices are of similar magnitude. For ϕ_n^2 we see that the limit is close to 1·9 (table 4). Work on the tetrahedral lattice yields a similar value. The fact that similar results for ψ_n^2 and ϕ_n^2 are obtained from different lattices suggests that, at least to a first-order approximation, the ratios depend only on dimensionality. If this is the case, the results should apply also to systems not constrained to a lattice (see Grishman 1973, Stellman and Gans 1972 for opposing views on whether this is the case for exponents). With regard to the moment ratios for higher p, there are no results available for comparison.

Table 3. Extrapolated estimates of the ratios $\psi_n^p = R_{n,\mathrm{ch}}^p / S_{n,\mathrm{ch}}^p$. (The actual ψ_n^p values appear in the $k = 0$ column.)

n \ k	0	1	2	3
$p = 2$				
7	5·7951	6·3838	6·4537	6·4375
8	5·8705	6·3983	6·4417	6·4218
9	5·9299	6·4052	6·4296	6·4052
$p = 4$				
7	41·597	50·989	52·676	52·681
8	42·820	51·384	52·568	52·389
9	43·798	51·615	52·426	52·142
$p = 6$				
7	332·03	450·30	478·48	481·40
8	347·69	457·30	478·30	477·99
9	360·36	461·71	477·17	474·90

Table 4. Extrapolated estimates of the ratios $\phi_n^p = S_{n,\mathrm{ch}}^p / S_{n,\mathrm{ri}}^p$

n \ k	0	1	2
$p = 2$			
7	1·9465	1·8297	1·8107
8	1·9358	1·8610	1·9546
9	1·9280	1·8649	1·8787
$p = 4$			
7	4·1306	3·6946	3·7994
8	4·0885	3·7935	4·0903
9	4·0570	3·8049	3·8449
$p = 6$			
7	9·5124	8·1953	9·1056
8	9·3740	8·4049	9·0337
9	9·2705	8·4430	8·5765

For simple random chains and rings without excluded volume the limiting ratios for $p = 2$ are known exactly—$\phi^2 = 2$ and $\psi^2 = 6$ (Zimm and Stockmayer 1949). Cluster expansion methods have been used to study the way in which the configurational properties of random chains and rings are affected by the introduction of excluded volume. Use of these methods leads to the perturbation expansions (Fixman 1955, Casassa 1965)

$$R_{\mathrm{ch}}^2 = na^2(1 + \tfrac{4}{3}z + \ldots)$$

$$S_{\mathrm{ch}}^2 = \tfrac{1}{6}na^2(1 + \tfrac{134}{105}z + \ldots)$$

$$S_{\mathrm{ri}}^2 = \tfrac{1}{12}na^2(1 + \tfrac{1}{2}\pi z + \ldots)$$

where the expansion parameter $z = (3/2\pi a^2)^{3/2}\beta n^{1/2}$, $\beta(>0)$ is the binary cluster integral which embodies the effect of the excluded volume, and a is the mean link length. From these expressions we obtain the moment ratio expansions

$$\psi^2 = 6(1 + 0{\cdot}057z \ldots)$$

$$\phi^2 = 2(1 - 0{\cdot}295z \ldots).$$

The changes in the ratios predicted by the cluster series, namely that ψ^2 is increased and ϕ^2 reduced when excluded volume is taken into account to first order, agree with the exact enumeration results. The cluster method does not appear to have been applied to compute higher moments. Unfortunately the present nature of the z expansion makes quantitative comparison with the exact enumeration results impossible, although it seems likely that the detailed study of the structure of the cluster series coefficients (Domb and Joyce 1972) will permit such comparison in due course.

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Appendix. Moment values

n \ p	2	4	6
$R^p_{n,\mathrm{ch}}$			
3	3·495727	15·80342	83·90598
4	4·907755	32·00980	250·3935
5	6·397215	55·29974	580·5393
6	7·949826	86·39937	1150·030
7	9·555960	125·9423	2045·532
8	11·20919	174·5019	3363·989
9	12·90455	232·6008	5211·923
$S^p_{n,\mathrm{ch}}$			
3	0·683761	0·505743	0·402135
4	0·912000	0·909746	0·987284
5	1·149501	1·456199	2·022973
6	1·395446	2·158265	3·682270
7	1·648974	3·027667	6·160730
8	1·909412	4·075201	9·675354
9	2·176180	5·310805	14·46326
$S^p_{n,\mathrm{ri}}$			
5	0·577143	0·337600	0·200055
6	0·709794	0·513474	0·378369
7	0·847137	0·732986	0·647651
8	0·986353	0·996757	1·032150
9	1·128753	1·309062	1·560130
10	1·274387	1·672716	2·261765
11	1·423023	2·090093	3·169191
12	1·574471	2·563442	4·316691

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