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Statistics of self-avoiding ring polymers

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Abstract. The iterative convolution (IC) technique previously reported for linear self-avoiding sequences is extended to the description of non-intersecting rings of hard-sphere segments. The principal geometrical features of rings of $N = 20$, 40 and 62 segments are determined, including the intersegmental spatial distribution functions, the mean-square intersegmental separations, the radius of gyration, bond correlation function and segment density distribution function. These quantities are compared with independent Monte Carlo estimates, and the results are found to be generally in good quantitative agreement. A sum rule for the bond correlation function is proposed for rings, whilst the segment density distribution is found to exhibit serrations which are unresolved in the Monte Carlo data scatter. These serrations, moreover, occur at integral multiples of the segment diameter and are attributed to entropic processes associated with ring closure.

1. Introduction

The statistical properties of ring polymers have been investigated using a variety of analytical (Zimm and Stockmayer 1949, Casassa 1965, Burchard and Schmidt 1980), exact lattice enumeration (Wall and Hioe 1970, Rapaport 1975) and Monte Carlo (Bruns and Naghizadeh 1976, Baumgärtner 1982) techniques. The general preoccupation, as in the case of linear polymers, is with their description in terms of limiting exponent relations as the number of segments $N \to \infty$. Here, however, we restrict our discussion to finite-ring systems.

Analytical descriptions have generally neglected excluded-volume effects (Zimm and Stockmayer 1949), and whilst these random-flight models permit closed expressions for the principal statistical parameters of the system such as the mean-square intersegmental separations and the radius of gyration, the results do not bear immediate comparison with either realistic systems or the Monte Carlo and exact enumerations, each of which embody excluded-volume effects to a greater or lesser degree. Indeed, the inter-relation between off-lattice and on-lattice estimates is not at all clear (Bruns and Naghizadeh 1976, Croxton 1983), and accordingly we restrict our comparisons to the off-lattice Monte Carlo calculations of Bruns and Naghizadeh (1976) and, with reservation, the results of Baumgärtner (1982).

The fact that ring polymers may be synthesised by anionic methods and the existence of circular deoxyribonucleic acids provides substantial motivation for the analytical description of finite-ring systems. In this preliminary analysis we extend the previously reported iterative convolution (IC) technique (Croxton 1984a, b) to describe closed, perfectly flexible, self-avoiding, hard-sphere rings. As we point out in that publication, the IC technique yields the closest reported agreement between calculated and MC

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estimates for self-avoiding linear polymers of short to intermediate length ($N \leqslant 20$). Although those calculations were for flexibly connected spherical hard-sphere sequences, the incorporation of stereochemical and more complex central and non-central interactions poses no difficulty. The same observations are appropriate in the present case, although here we again restrict ourselves to the description of a flexibly linked sequence of hard-sphere segments for purposes of simplicity and comparison with extant MC data.

2. Theory

We refer the reader elsewhere (Croxton 1983, 1984a, b) for the detailed description of the IC technique. It is, however, appropriate to give an indication of the approach, and refer the reader to the original publication for details. The geometry of the ring is illustrated in figure 1. We are primarily concerned with the intrachain spatial probability distribution of segments $Z(ij|N)$ within the ring of N segments. We note from the outset that translational invariance within the ring (unlike a linear polymer) means that $Z(ij|N)$ depends only upon the difference $|i-j| = n$ for a ring of N segments

$$Z(ij|N) \equiv Z(n|N). \tag{1}$$

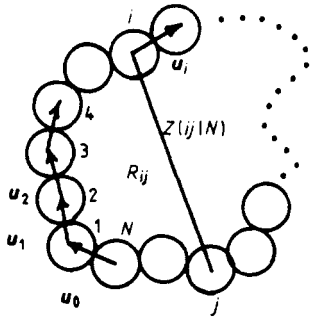

Figure 1. The ring geometry, indicating the principal statistical parameters.

Moreover, these distributions are symmetric

$$Z(n|N) \equiv Z(N-n|N). \tag{2}$$

Correlation between segments (i,j) is established directly through $H(i,j) = \exp(-\Phi(i,j)/kT)$, where $\Phi(i,j)$ is the (i,j) interaction potential, and indirectly through all routes of propagation via other segments in the sequence.

In this paper we take Φ to be the hard-sphere potential with segment diameter $\sigma = 1$.

By virtue of the chain connectivity, these intermediate segments are *physically* (and possibly chemically) distinct, and their contribution to the net correlation of (i,j) requires a mean-field representation of their overall effect. (This is quite different to the correlation of particles (i,j) in a bulk isotropic homogeneous fluid in which any of the neighbouring particles may be taken as representative.) For reasons discussed elsewhere (Croxton 1984a, b) we form the geometric mean of the indirect correlations

and write

$$Z(ij|N) = H(ij) \prod_{k \neq i,j}^{N} \int Z(ik|N) Z(kj|N) \, \mathrm{d}\boldsymbol{k} \tag{3}$$

where Π_k represents the formation of the geometric mean of the convolution integrals through the kth segment, where $1 \leqslant k \leqslant N$, $\neq i, j$. Translational invariance enables us to write

$$Z(n|N) = H(n) \prod_{m} \int Z(m|N) Z(n-m|N) \, \mathrm{d}\boldsymbol{m} \tag{4}$$

where $m = |i-k|$. It is now apparent that equation (4) also satisfies the symmetry condition (2). It is straightforward to cast equation (3) into iterative form (Croxton 1984a, b), whereupon

$$\begin{aligned} Z(ij|N) = \prod_{k}^{N} \int H(ik) \prod_{p \neq i,k}^{N} \int Z(ip|N) Z(pk|N) \, \mathrm{d}\boldsymbol{p} \\ \times H(kj) \prod_{q \neq k,j}^{N} \int Z(kq|N) Z(qj|N) \, \mathrm{d}\boldsymbol{q} \, \mathrm{d}\boldsymbol{k}. \end{aligned} \tag{5}$$

It is a feature of these approximations that excluded-volume effects are progressively neglected with increasing chain length, and the treatment is therefore inappropriate for asymptotically long sequences for which the random walk result would be recovered (Croxton 1984a, b). We therefore restrict our computations and conclusions to finite linear and ring sequences of comparable size to those reported in machine-simulated analyses.

It is appropriate to point out that in the very nature of the approximation made in the IC method, knotted configurations cannot be explicitly excluded, and these will, to a certain but indeterminate extent, contribute to the configurational averages. Equation (5) may be readily evaluated by fast Fourier transform techniques.

With a knowledge of $Z(ij|N)$, the mean-square intrachain distance is readily calculated

$$\langle R_n^2 \rangle_N = 4\pi \int_0^{\infty} Z(n|N) R_n^4 \, \mathrm{d}R_n \tag{6}$$

as is the mean-square radius of gyration

$$\langle S_N^2 \rangle = \frac{1}{N} \sum_{n=1}^{N/2} \langle R_n^2 \rangle - \frac{1}{2N} \langle R_{N/2}^2 \rangle. \tag{7}$$

The vector $\boldsymbol{R}_n$ connecting segments (i, j) may be expressed in terms of the sum of unit bond vectors $\boldsymbol{u}_k$

$$\boldsymbol{R}_n = \sum_{k=i}^{i+n-1} \boldsymbol{u}_k \tag{8}$$

whereupon it follows that

$$2\langle \boldsymbol{u}_0 \boldsymbol{u}_n \rangle = \langle R_{n+1}^2 \rangle - 2\langle R_n^2 \rangle + \langle R_{n-1}^2 \rangle \tag{9}$$

where $\langle \boldsymbol{u}_0 \boldsymbol{u}_n \rangle$ represents the bond correlation function between vectors separated by n segments, where $\boldsymbol{u}_0$ is the bond between segments N and 1 (figure 1).

For non-interacting rings there exists a number of exact results (Zimm and Stockmayer 1949) which provide a useful basis for comparison of the excluded volume results. Designating these quantities by the subscript 0, we have

$$\langle R_n^2\rangle_0 = a^2 n(1-n/N), \qquad \langle S_n^2\rangle_0 = a^2(N/12) \tag{10),(11}$$

where a is the bond length. For an uncorrelated ring of bonds the condition that the sequence returns to the origin is

$$\sum_{i=0}^{n} \boldsymbol{u}_i = -\sum_{i=n+1}^{N} \boldsymbol{u}_i.$$

Forming the scalar product with $\boldsymbol{u}_n$ and averaging yields

$$\langle \boldsymbol{u}_0 \boldsymbol{u}_n\rangle_0 = -1/N \tag{12}$$

that is, the bond correlations are independent of n. This interesting result may perhaps be most readily understood in terms of the equipartitioning of the overall return of the chain to the origin ($\langle\ \rangle = -1$) amongst the N segments of the sequence. This equipartitioning is appropriate only amongst uncorrelated bonds; excluded-volume effects will induce a correlation amongst neighbouring bonds and $\langle \boldsymbol{u}_0 \boldsymbol{u}_n\rangle$ will in general be n-dependent. Nevertheless, the fact that the sequence ultimately returns to the origin implies that in *all* cases we have the sum rule

$$\sum_{n=1}^{N-1} \langle \boldsymbol{u}_0 \boldsymbol{u}_n\rangle = -1 \tag{13a}$$

a result which may be immediately confirmed in the case of rings of uncorrelated bonds (equation (12)). For sequences of identical particles we also have

$$\sum_{n=1}^{N/2} \langle \boldsymbol{u}_0 \boldsymbol{u}_n\rangle = -1/2. \tag{13b}$$

These sum rules provide useful quantitative tests of the adequacy of any theoretical description of ring polymer systems, particularly equation (13a) which applies regardless of chemical sequence or stereochemical structure.

Our fundamental concern in this paper is with the intersegmental distribution function $Z(n|N)$, and it is appropriate to compare this function with its non-interacting, essentially Gaussian (normalised) counterpart

$$Z_0(n|N) = \left(\frac{3N}{2\pi a^2 n(N-n)}\right)^{3/2} \exp\left(\frac{-3NR_n^2}{2a^2 n(N-n)}\right). \tag{14}$$

3. Results

The distribution functions $Z(ij|N)$ and the principal geometric quantities $\langle \boldsymbol{u}_0 \boldsymbol{u}_n\rangle$, $\langle R_n^2\rangle$ and $\langle S_N^2\rangle$ were determined on the basis of the IC approximation for a variety of hard-sphere ring sequences; the results presented here are primarily for rings of $N = 20$, 40 and 62 unit diameter flexibly connected segments. Comparison is made, where possible, with the Monte Carlo data of Bruns and Naghizadeh (1976) and Baumgärtner (1982). Although the latter author criticises the sampling techniques of the former, we do not share his objections which are based on the alleged use of 'dimerisation' techniques, yielding biased ring configurations. In our opinion such techniques are

not used by Bruns and Naghizadeh and their results are not biased in this respect; accordingly we use their data as a primary basis for comparison with our results. Indeed, direct comparison with Baumgärtner's MC data is difficult for two reasons. Firstly, whilst retaining a bond length of unity, he adopts a segment diameter of 0.55. Although we have performed some calculations for such a system, direct comparison with Baumgärtner's MC results is further frustrated by the highly scaled presentation of his data.

3.1. The distributions $Z(n|N)$

The log-log plots of $Z(N/2|N)$ for $N = 20$, 40 (figure 2) and 62 are all characterised by a near-linear rise, peaking just before mid-range, in close qualitative agreement with the results of Baumgärtner. The corresponding non-interacting distributions $Z_0(N/2|N)$ are of similar form, though substantially collapsed into the origin, reflecting the absence of excluded volume effects within the sequence.

Shorter-range distributions ($n < N/2$) show a progressively more pronounced discontinuity or saw-tooth structure towards the end of their range, for given ring size (figure 2), whilst non-interacting sequences remain essentially Gaussian; this we attribute to the strong entropic exclusion operating amongst sequentially close segments.

The mean square separations $\langle R_n^2 \rangle$ within the ring are given by equation (6), which in the case of non-interacting rings reduces to (equation (10))

$$\langle R_n^2 \rangle_0 = n(1 - n/N),$$

which for a bond length of unity within a given ring of non-interacting segments gives

$$\partial \langle R_n^2 \rangle_0 / \partial n = 1 - 2n/N$$

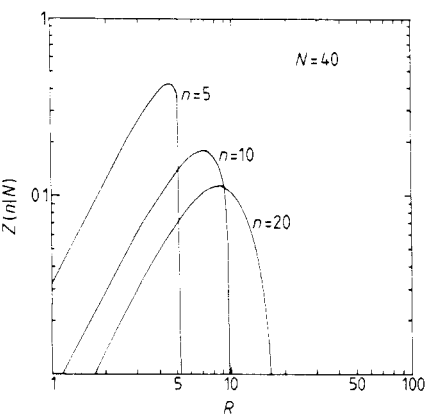

Figure 2. The distributions $Z(n|N)$ ($n = 5$, 10, 20; $N = 40$) for a hard-sphere, self-avoiding ring sequence. The distributions become progressively more discontinuous as n/N decreases.

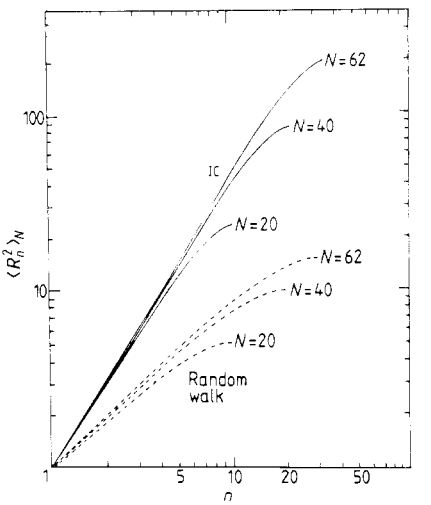

Figure 3. The mean-square separations $\langle R_n^2 \rangle$ within rings of $N = 20$, 40 and 62 self-avoiding hard-sphere segments. The linear region ($0 < n \leq N/4$) has a gradient ~ 2, which decreases substantially over its subsequent range ($N/4 \leq n \leq N/2$). The corresponding curves for self-intersecting rings are also shown for comparison (broken curves).

from which we observe that for small n/N we recover what is essentially linear chain behaviour, whilst as $n \to N/2$ the gradient tends to zero, reflecting the ring closure. These general qualitative features are retained for self-avoiding sequences (figure 3) although excluded-volume effects yield a gradient ~ 2 for $0 < 4 \leqslant N/4$, rapidly decreasing as $n \to N/2$. Even for small n/N, it is evident that the n-dependence differs from that within linear sequences, although precise comparison is difficult since the contribution of end-effects in linear sequences is difficult to eliminate. The conclusion must be that the distinction is attributable to ring closure, and this we discuss further in § 4.

Unfortunately, Bruns and Naghizadeh do not discuss the distributions $Z(n|N)$, but rather consider the segment density distribution

$$\rho(R|N) = \sum_{n=1}^{N-1} Z(n|N) \tag{15}$$

with the corresponding distribution for non-interacting rings

$$\rho_0(R|N) = \frac{3(N-1)}{\pi R(N-2)} \exp\left(\frac{-R^2}{2(N/12)}\right) \operatorname{erf}\left[\left(\frac{3R^2(N-2)^2}{2N(N-1)}\right)^{1/2}\right]. \tag{16}$$

These distributions are compared in figure 4 for a 40 segment ring: the deployment of the chain is seen to be in good agreement with the MC data over the range reported. (Unfortunately in this and subsequent comparisons with the MC data no error bars are quoted by Bruns and Naghizadeh, although they do indicate the scatter of data points; the reader is referred to their original publication for a qualitative estimate of the statistical error involved.)

An immediate consequence of the developing discontinuity in $Z(n|N)$ as $n \to 1$ (figure 2) is the serrated form of the segment density $\rho(R)$ (figure 4). This is not clearly resolved in the MC simulations and may have been lost in the statistical scatter.

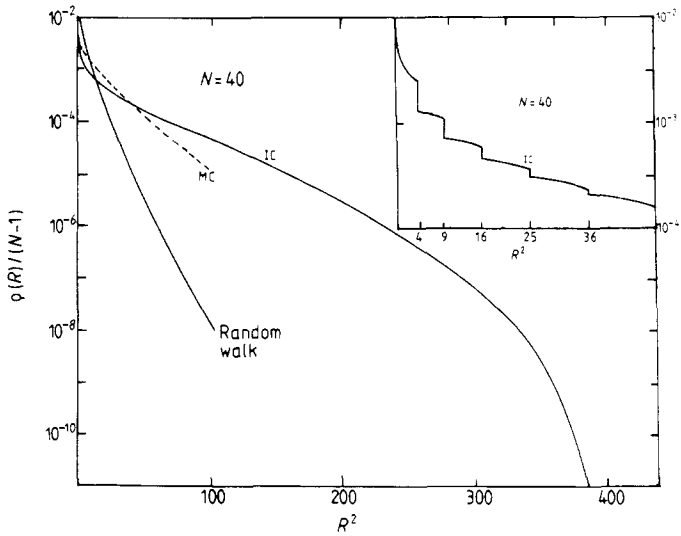

Figure 4. The reduced segment density distribution $\rho(R|N)/(N-1)$ for a self-avoiding ring of $N = 40$ segments. For small intersegmental separations the curve shows a serrated structure (inset), falling to zero at $R = N/2$. The Monte Carlo (broken curve) and random flight distributions are shown for comparison.

However, such a phenomenon has not been observed in our calculations for linear polymers (Croxton 1983, 1984a, b), and we therefore conclude that these serrated segment density distributions are not artefacts of the calculation but are, as we observe elsewhere in this paper, the consequence of the conflicting demands of ring closure and entropic delocalisation of the sequence. We note that these serrations occur at integral multiples of the segment diameter. We directly attribute this short-range structure of the segment density distribution to the small-n components of $\rho(R|N)$ in equation (15). As we observed previously (§ 3.1), the $Z(n|N)$ become progressively more 'saw-toothed' (figure 2) with decreasing n for a ring of given size, the near-discontinuity coinciding with the maximum range of the component distribution. Accordingly the sum (15) will exhibit serrations in the short-range region of the segment density distribution as illustrated in the inset of figure 4.

On the basis of their MC simulations, Bruns and Naghizadeh observe that $\rho(R|N)$ has a functional form similar to the screened-Coulomb potential which arises in the theory of electrolyte solutions. However, statistical scatter fails to resolve any serrated structure in the short-range region of $\rho_{MC}(R|40)$, whilst beyond the range investigated by Bruns and Naghizadeh ($R^2 > 100$), ring connectivity substantially modifies the distribution from screened-Coulomb form ensuring, for example, that $\rho(R_{N/2}|N) \equiv 0$. We shall return to this point later.

The ratio

$$g(R|N) = \rho(R|N)/\rho_0(R|N), \tag{17}$$

designated the radial distribution function by Bruns and Naghizadeh, represents a measure of the deviation from non-interacting behaviour. For a non-interacting ring

$$g_0(R|N) = 1. \tag{18}$$

The agreement with the MC data is seen to be good (figure 5). Clearly the deviation from non-interacting behaviour is pronounced.

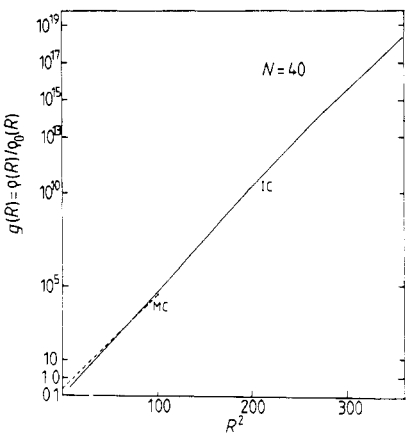

Figure 5. The radial distribution function $g(R|N)$ for $N = 40$. The Monte Carlo result (broken line) is shown for comparison.

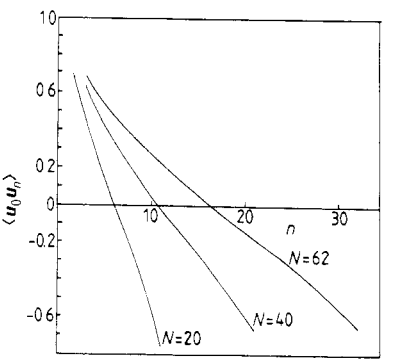

Figure 6. The bond correlation $\langle u_0 u_n \rangle$ for rings of $N = 20$, 40 and 62 hard-sphere segments.

3.2. The bond correlation functions $\langle u_0 u_n \rangle$

The bond correlation functions for rings of $N = 62$, 40, 20 hard-sphere segments are shown in figure 6, and are quite distinct from the non-interacting result $\langle u_0 u_n \rangle = -1/N$ (equation (12)). The bond correlation function is characterised by an initial positive short-range correlation ($n \leqslant N/4$) followed by a negative long-range region ($N/4 \leqslant n < N/2$). In each case the sum rule (equation (13*a*)) is satisfied, and we find

$$\sum_{n=1}^{N-1} \langle u_0 u_n \rangle = \begin{array}{ll} -1.0000 & N = 20 \\ -0.9999 & N = 40 \\ -0.9999 & N = 62. \end{array} \tag{19}$$

Whilst the qualitative form of these bond correlations is similar to those of Baumgärtner, the reduction of excluded volume by a factor of ~ 0.125 probably accounts for his MC bond correlation function crossing the axis at $\sim N/10$. Baumgärtner fits his bond correlation function as follows

$$\langle u_0 u_n \rangle = \frac{1}{N^{2-2\nu}} \left\{ \frac{0.142}{[(n/N)(1-n/N)]^{2-2\nu}} - 5.7 \left[\frac{n}{N} \left(1 - \frac{n}{N} \right) \right]^{2-2\nu} \right\} \tag{20}$$

from which we find, assuming $\nu = 0.59$ (Baumgärtner 1982)

$$\sum_{n=1}^{N-1} \langle u_0 u_n \rangle = \begin{array}{ll} -1.0236 & N = 20 \\ -0.9765 & N = 40 \\ -0.9412 & N = 62 \\ -0.8530 & N = 160 \\ -0.7779 & N = 320. \end{array} \tag{21}$$

The failure of Baumgärtner's sum rule may be attributed to the inadequacy of the scaling function (20), since the sum rule is satisfied regardless of excluded-volume considerations (cf equation (13*a*) *et seq*). In fact, Baumgärtner's scaling function is seriously questioned since the mean-square intrachain distance is given by (Baumgärtner 1982)

$$\langle R_n^2 \rangle = a^2 n + 2 \sum_{j=1}^{n-1} (n-j) \langle u_0 u_j \rangle \tag{22}$$

where a is the bond length. Using equation (20) for $\langle u_0 u_j \rangle$ we should have for $n = N - 1$, $\langle R_n^2 \rangle = 1.00$ ($a = 1$): instead we find

N	20	40	62	160	320
$\langle R_n^2 \rangle$	0.576	1.893	4.526	24.225	71.624

Baumgärtner's results are presented in a highly scaled form and so his estimates of the scaling parameters, in particular his choice of exponents and therefore the fitting of data, may be responsible for the discrepancy. Further resolution of the data is impossible and any attempt to draw more detailed conclusions would be purely speculative and serve no useful purpose here.

3.3. The mean-square radius of gyration $\langle S_N^2 \rangle$

The reduced mean-square radius of gyration $\langle S_N^2 \rangle / N$ determined on the basis of equation (7) is exactly twice that of Bruns and Naghizadeh, who define the radius of gyration in terms of the segment density distribution

$$\frac{\langle S_N^2 \rangle}{N} = \frac{4\pi}{2N^2} \int_0^\infty \rho(R|N) R^4 \, dR. \tag{23}$$

Accordingly, we double their MC estimates for the purposes of comparison with our results (figure 7). The corresponding result for non-interacting rings is $\langle S_N^2 \rangle_0 / N = 0.083$.

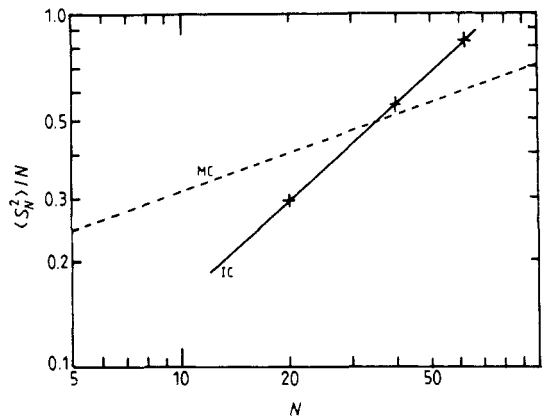

Figure 7. The reduced mean square radius of gyration $\langle S_N^2 \rangle / N$ for self-avoiding hard-sphere rings ($N = 20, 40, 62$) indicated by crosses. The Monte Carlo result is shown for comparison.

The qualitative agreement is good in that both analyses yield a linear relationship for $\ln\langle S_N \rangle / N$ against $\ln N$ for non-intersecting rings. However, the IC estimate is evidently much more strongly N-dependent. The estimate of the mean-square radius of gyration provides a particularly stringent test of the theory, involving as it does the second moment of all internal distributions. The origin of the discrepancy between the MC and IC estimates is not easy to identify since Bruns and Naghizadeh do not explicitly present their distribution functions. However, we observe that the range of $\rho(R|N)$ explored by the machine simulations is substantially less than that required in equation (23) (figure 4); moreover, the fourth moment of the segment density distribution is required, and accordingly we anticipate a substantial underestimate of $\langle S_N^2 \rangle / N$ for large N. We also note that in the case of linear polymers, the IC technique yielded particularly accurate estimates of the radius of gyration (Croxton 1984a, b), and we have no reason to anticipate any poorer performance in the present analysis.

The fact that $\langle S_N^2 \rangle / N$ (MC) is over-estimated for small N, with respect to the IC value, may be attributable to Bruns and Naghizadeh's method of ring generation which certainly tends progressively to overestimate $\langle S_N^2 \rangle$ as the ring size decreases, and $\langle S_N^2 \rangle / N$ even more so. This arises from an ambiguity in their definition of ring closure involving the intersection of two of the N segments to form the closed loop. Whilst relatively unimportant for large rings, this discrepancy becomes progressively more significant with decreasing loop size.

On the basis of a least-squares fit to the data presented in figure 7 we conclude that $\langle S_N^2 \rangle / N$ varies as $N^{0.91}$ whilst Bruns and Naghizadeh report an exponent of 0.24, in close agreement with the result reported for short self-avoiding linear sequences.

4. Discussion

One important conclusion which emerges from this study concerns the ability of the iterative convolution technique to provide a good quantitative description of the principal geometric features of self-interacting polymer sequences on the basis of comparison with their simulated counterparts. The distortion of the spatial ring distributions with respect to both linear polymer (Croxton 1984a, b) and non-interacting systems is striking. In all cases the ring distributions $4\pi R^2 Z(n|N)$ are characterised by a monotonic increase in amplitude, followed by a rapid decrease, tending towards a discontinuity with decreasing n. This we understand in terms of the entropic repulsion which develops amongst closely confined segments (small n) (Croxton 1983). The entropic requirement that the chain be as spatially delocalised as possible conflicts with the condition that the chain ultimately returns to the origin to form a ring, producing the dramatic fall-off in the short-range distributions.

This effect may be most simply demonstrated for the unrestricted random coil. The normalised distribution for the end-to-end distance for such a sequence has already been given (equation (14)). The fraction of configurations permitting the ends of the chain to approach to within a distance b to form a closed loop of size N is

$$\Omega_{\text{ring}}/\Omega = \int_0^b Z_0(R|N)\,\mathrm{d}R.$$

If N is large and b is small, the exponential in (14) can be approximated by unity, whereupon

$$\Omega_{\text{ring}}/\Omega = (3/2\pi N a^2)^{3/2} \int_0^b 4\pi R^2\,\mathrm{d}R = (3/2\pi N a^2)^{3/2} V \qquad (n = N-1)$$

where the approach volume $V = 4\pi b^3/3$. Thus, the entropy change in forming a loop from a linear polymer is

$$\Delta S_{\text{ring}} = -\tfrac{3}{2}kT \ln N + kT \ln[(3/2\pi a^2)^{3/2} V] \qquad \text{(Jacobson–Stockmayer equation)}$$

and the per-segment increase in free energy in closing the linear polymer to form a loop is

$$\Delta G_{\text{ring}} = (1/N)\{\tfrac{3}{2}kT^2 \ln N - kT^2 \ln[(3/2\pi a^2)^{3/2} V]\} \qquad (24)$$

which rises dramatically with decreasing loop length. Whilst such a simplified analysis is not appropriate for the detailed description of self-avoiding systems such as those under consideration here, the model nevertheless provides qualitative support for our discussion of the processes governing short internal ring distributions.

Both on this basis and direct comparison of IC distributions we conclude that the rapid fall-off in the fully extended distribution is *not* an artefact of the technique, but is a real feature of self-avoiding ring distributions. Accordingly, the progressively saw-toothed form of $Z(n|N)$ with decreasing n is attributed directly to ring closure—with the inevitable consequence of a serrated structure in the short-range form of the segment density distribution $\rho(R|N)$. However, these serrations are not resolved in

Bruns and Naghizadeh's MC distributions, although this may be attributable to the breadth of MC data scatter which exceeds the amplitude of the serrations. These authors observe that within the range and statistical scatter of the MC data the distribution appears consistent with a screened-Coulomb function. However, we conclude that neither the short-range nor the long-range form can be described as screened-Coulombic, the departure being specifically attributable to the features of ring connectivity.

We note that the discontinuity in $Z(n|N)$ relaxes uniformly as $n \to N/2$, and accordingly doubt whether the short distributions show a true discontinuity. Indeed, for $n \ll N$ we should expect $Z(n|N)_{\text{ring}} \to Z(n|N)_{\text{linear}}$ where the subset n is far from the ends of the linear sequence. We have no evidence to suggest that ring and internal linear polymer distributions cannot be related by scaling (Baumgärtner 1982).

The estimates of $\langle S_N^2 \rangle$ are in qualitative agreement with the MC data of Bruns and Naghizadeh. However, calculations based on a segment diameter/bond length ratio of 0.55 yield values which substantially exceed Baumgärtner's MC estimates of $\langle R_{N/2}^2 \rangle$ and $\langle S_N \rangle$ for such a system. The reason for the discrepancy is not clear. However, Baumgärtner's scaling of his data is based upon the presumed knowledge of a number of exponents, and an earlier test of his exponent representation of the MC data (§ 3.2) suggests that his choice of exponent may not be entirely correct, and is corroborated in particular by the failure of Baumgärtner's bond correlation function $\langle \boldsymbol{u}_0 \boldsymbol{u}_n \rangle$ to satisfy the sum rule (13*a*).

Acknowledgments

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