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Configurational properties of self-interacting linear polymer chains in a three-dimensional continuum: I. End-to-end probability and molecular span

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Received 16 January 1979

Abstract. A diagrammatic method of comparable status to the exact enumeration machine techniques is developed for the determination of the configurational properties of isolated self-avoiding polymer chains of freely jointed hard sphere segments. A close upper bound on the exponent in $\langle R_{1N}^2 \rangle \sim n^\gamma$ is determined to be $1.26 > \gamma > 1.0$, which is a substantial improvement upon earlier diagrammatic analyses ($\gamma = 2.0$). Moreover, the end-to-end distribution function has a non-zero contact value, indicating the possible development of closed ring configurations—again contrary to earlier diagrammatic analyses.

1. Introduction

Despite general agreement on the properties of self-avoiding walks on regular lattices, it is nevertheless apparent that dimensionality, flexibility and connectivity play an important role. Monte Carlo simulations of such systems, together with exact enumeration techniques, seem to suggest that for long chains of N segments asymptotic behaviour of the mean square end-to-end separation varies as $\langle R_n^2 \rangle = an^\gamma$, where $n = N - 1$ is the number of links, a is a constant dependent only on link length and the nature of the lattice, while γ is a constant exponent dependent only on the dimensionality. The mean square radius of gyration appears to exhibit a similar limiting dependence $\langle S_n^2 \rangle = bn^{\gamma'}$, where b and γ' are again constants depending on the lattice and the dimensionality respectively. Moreover, machine studies strongly suggest that $\gamma = \gamma' \sim 1.2$ for a three-dimensional walk on a regular lattice. Recently, Morita (1976) has analytically investigated the conventional self-avoiding walk for a class of generalised Bethe lattices, obtaining the exact result $\gamma = 2$. Clearly, both the dimensionality and the connectivity of the space essentially modify the asymptotic behaviour—indeed, in the asymptotic limit $N \rightarrow \infty$ the Bethe lattices become effectively of infinite dimension. Nonetheless, the apparent independence of the three-dimensional machine investigations on the nature of the lattice suggests that γ may be a universal constant, and that the conclusions bear extension to three-dimensional continuum systems incorporating excluded volume effects. Indeed, Edwards (1965), working in a mean field approximation which incorporated excluded volume effects, found $\langle R_n^2 \rangle = l^2(v/l^3)^{2/5}n^{6/5}$, where l is the segment length and v the excluded volume per segment. This formula has limiting validity as $n \gg l^6/v^2$, and is seen to be of the form reported on the basis of lattice studies. Reiss (1967), using a somewhat similar approach, found $\gamma = \frac{4}{3}$; however, a refinement due to Yamakawa gave $\gamma = \frac{6}{5}$.

Increased computing capabilities have permitted the Monte Carlo investigation of off-lattice configurations, and initial complacency has given way to some concern that the lattice results do not bear even qualitative extension to continuum polymer systems (Edwards 1970). For example, there is a considerable body of evidence which suggests that the exponent γ is a function of excluded volume. We do have the exact result for zero excluded volume ($\gamma = 1$), and while Edwards' result can, in principle, shed no light on the matter, the question as to how the transition in the exponent between non-zero and zero excluded volume is accomplished is not at all clear. Fleming (1967), for example, finds a steady decrease in γ with excluded volume on the basis of Monte Carlo investigations, smoothly approaching $\gamma = 1$ as the excluded volume tends to zero, and attaining the lattice exponent only beyond some critical value of the excluded volume. Grishman (1973) also reports an off-lattice exponent in close agreement with the lattice results for spherical segments. It is apparent that the dependence or otherwise of the exponent γ upon excluded volume requires further investigation and cannot be imputed from the lattice results. Again, machine evidence seems not inconsistent with the conclusion $\gamma = \gamma'$ for lattices: the same conclusion cannot yet be drawn regarding continuum systems, and certain investigators appear to find $\gamma \neq \gamma'$ for off-lattice self-avoiding walks (Smith and Fleming 1975a, b).

While there appears no chance of an exact analytical solution of the excluded volume problem in polymers, nevertheless there have been a number of theoretical models yielding a variety of quantitative and qualitative results with which the machine studies may be compared. We have already mentioned the results of Edwards and of Reiss (modified by Yamakawa), both of which suggest $\gamma = \frac{6}{5}$, but which appear difficult to reconcile with the substantial body of 'experimental' data, which seems to suggest a different exponent which, moreover, is dependent on excluded volume. It may be, however, that substantially longer Monte Carlo chains would modify this conclusion. A Percus-Yevick (PY) treatment of the excluded volume problem in polymers by Curro *et al* (1969) suggests a strong dependence of the exponent γ on excluded volume, ranging from $\gamma = 2$ for spherical segments to $\gamma = 1$ for zero excluded volume. While $\gamma = 2$ represents a substantial overestimate of the N dependence of the mean square end-to-end separation, it nevertheless provides support for an excluded volume dependent exponent. Unfortunately, this particular development utilising the PY approximation, which has proved so useful in the theory of fluids, yields some qualitatively incorrect results in the case of polymers. For example, the end-to-end contact probability is found to be zero, prohibiting the development of closed rings, which are known to occur. Moreover, the complicated interaction amongst the diagrammatic subsets retained in the graphical expansion of the partition function prohibits even a qualitative assessment of the approximation, and certainly provides no means of systematic refinement.

A further variety of analytical approaches has yielded a corresponding variety of exponents γ (Alexandrowicz 1967a, b, des Cloiseaux 1970, Whittington and Dunfield 1973). In each case both the qualitative and quantitative features are obscured by the approximation, and it proves difficult to assess their effect. Nevertheless, collectively they provide a useful complement to the machine investigations.

Since we are necessarily resigned to approximation, the most we can hope from a theory is one which provides a degree of quantitative (perhaps in the form of lower or upper bounds) and qualitative insight, and whose approximations, moreover, bear assessment and do not consist of virtually inscrutable associations of cancelling errors. In this paper we present what we believe to be a simple theoretical model which satisfies

In this diagrammatic expansion two classes of diagram arise: the nodal N_{1N} and elementary E_{1N} classes. We may therefore write

$$Z_{1N} = N_{1N} + E_{1N}, \tag{7}$$

where the class N_{1N} is characterised by the development of one or more *nodes* or articulation points within the diagram at which a cut would cause the graph to separate into two or more completely disconnected components. The class E_{1N} is simply the non-nodal residue of Z_{1N} . Curro *et al* (1969), working in what is essentially the PY approximation, are able to generate many of the elementary diagrams from the ζ_i diagrams; thus they write for the elementary diagrams of order i

$$\epsilon_i(1N) \sim h_{1N} \zeta_{i-1}(1N) \tag{8}$$

and then

$$E_{1N}^{PY} \sim \sum \binom{N-1}{2} \epsilon_i(1N) (-1)^i. \tag{8a}$$

Clearly, in this approximation only those elementary diagrams having an h_{1N} loop will be generated. Moreover, it is straightforward to show (Curro *et al* 1969) that this subset of diagrams may be written

$$E_{1N}^{PY} \sim \frac{-h_{1N}}{H_{1N}} Z_{1N} \begin{cases} = 0, & r_{1N} \geq 1.0 \\ \neq 0, & r_{1N} < 1.0, \quad N > 3. \end{cases} \tag{9}$$

However, there remain unaccounted for all those elementary diagrams which *do not* have an h_{1N} bond. We may generate these by taking the zero-order ζ diagram $\zeta_0(1N)$ consisting of $N - 1 = n$ unit links which are non-avoiding, and then permuting 1 up to some maximum number, \hat{l} , of h bonds on this $\zeta_0(1N)$ framework, with the restriction that no h_{1N} bond is included.

It may be shown quite easily (Croxton 1974), when due account is taken of the topological degeneracies and the sign of the diagrams, that the derivatives of the ζ_0 diagram self-interfere to yield a fully netted residue where each vertex i is linked to every non-nearest vertex k by a $1 - h_{ik}$ bond. Two separate proofs of this central result are given in appendixes 1 and 2.

These fully netted $\zeta_0(1N)$ diagrams will, however, generate not only the elementary diagrams neglected in the PY approximation, but also the nodal diagrams, which have been already incorporated. So, at order $N = 5$, for example, the neglected elementary residue \hat{E}_{1N} is

$$\hat{E}_{15} = \text{[Diagram: A diamond-shaped graph with 5 vertices and 10 edges, where each vertex is connected to all other vertices except its two immediate neighbors on the boundary]} - N_{15} \tag{10}$$

and the *total* elementary contribution is

$$E_{15} = E_{15}^{PY} + \hat{E}_{15}. \tag{11}$$

Combining equations (7), (9) and (11), we immediately obtain the *exact* result

$$Z_{15} = \text{[Diagram: A diamond-shaped graph with 5 vertices and 10 edges, where each vertex is connected to all other vertices]} \tag{12}$$

which is in retrospect self-evident since (12) expresses the geometrical exclusion

operating amongst the segments constituting the polymer. Clearly, these diagrams are positive and non-zero at $r_{1N} = 1.0$, and tend to zero as r_{1N} tends to its maximum range $(N - 1)\sigma$. Analogous diagrams, i.e. fully netted $\zeta_0(1N)$ exclusion graphs, describe each of the higher-order distributions Z_{1N} . The problem therefore reduces to the evaluation of these exclusion diagrams.

Since PY yields the exact distribution for $N = 3$, the first diagram to be considered arises at $N = 4$, and we have

$$Z_{14} = \text{[Diagram: A square with an 'X' inside, representing an excluded volume diagram for N=4.]}$$

which may be readily evaluated numerically. As we shall see in the next section, on the basis of this diagram we obtain the exact mean square length $\langle R_{14}^2 \rangle = 4.31$ which is to be compared with the result of Curro *et al.*, $\langle R_{14}^2 \rangle_{PY} = 4.50$.

At higher orders, numerical evaluation of the fully excluded diagram becomes prohibitively difficult and computationally impracticable. We have therefore approximated the distributions by two convolution models designated Z_{1N}^I and Z_{1N}^{II} . In each case the normalised distribution Z_{1N} is approximated by a normalised nested convolution: $Z_{1N} \sim (1 - h_{1N}) \int Z_{1,N-1} \delta_{N-1,N} d(N-1)$; in the case of Z_{1N}^{II} the convolution is started from the exact (numerically determined) Z_{14} . In this way the dependence of the lower-order distributions on the omission of exclusion bonds can be assessed. In principle a series of convolutions may be developed in parallel, assuming we have the exact initial distributions Z_{15}, Z_{16}, \dots . In fact, these lower-order distributions are currently being developed numerically using the Ree-Hoover techniques which were so successful in the evaluation of the hard sphere virial coefficients. Padé approximants may also be formed.

We may compare the approximations explicitly for $N = 5$:

$$\text{[Diagram: A cube with one corner cut off, representing Z_{15}^I]} \quad Z_{15}^I = (1 - h_{15}) \int (1 - h_{14}) \int Z_{13} \delta_{34} d3 \delta_{45} d4, \tag{13a}$$

Z_{15} (exact)

$$\text{[Diagram: A cube with one corner cut off, representing Z_{15}^{II}]} \quad Z_{15}^{II} = (1 - h_{15}) \int Z_{14} \delta_{45} d4. \tag{13b}$$

It is straightforward to show that, in such a nested convolution model in which the highest exact distribution is of order r , the fraction of bonds omitted in the distribution Z_{1N} will be $1 - r/(N - 1)$. Thus in Z_{1N}^I the fraction omitted is $1 - 2/(N - 1)$ ($n \geq 2$), while for Z_{1N}^{II} it is $1 - 3/(N - 1)$ ($n \geq 3$). Clearly, both Z_{1N}^I and Z_{1N}^{II} will tend to the zero excluded volume result as $N \rightarrow \infty$, i.e. $\gamma \rightarrow 1$ as $N \rightarrow \infty$. Both these convolution approximations may, of course, be readily evaluated by fast Fourier transform techniques. It is clear that the convolution approximations, in neglecting several of the internal exclusion bonds, will permit unphysical 'over-collapsed' configurations to contribute to the probability distributions and the $\langle R_{1N}^2 \rangle$. However, the convolution approximation is *qualitatively* correct at intermediate N . Moreover, the effect will be cumulative as N increases. Nevertheless, the approximation is not quite as serious as it might at first appear, since we are interested in the higher moments of these distributions, e.g. $\langle R_n^2 \rangle$, and these will be more sensitive to the extended configurations of the exclusion diagram which, fortuitously, predominantly sample those regions of space incidentally satisfying the complete exclusion condition.

The PY approximation may be readily shown consistently to overestimate the molecular span, for equation (7) may be written

$$\begin{aligned} Z_{1N} &= N_{1N} + E_{1N} = N_{1N} - h_{1N}N_{1N} - h_{1N}\mathcal{N}_{1N} + \mathcal{N}_{1N} \\ &= (1 - h_{1N})N_{1N} + (1 - h_{1N})\mathcal{N}_{1N}, \end{aligned} \quad (14)$$

where $h_{1N}N_{1N}$ represents those elementary diagrams formed by applying an h_{1N} bond across a nodal diagram (which reverses its sign), while $h_{1N}\mathcal{N}_{1N}$, \mathcal{N}_{1N} represent those non-nodal diagrams with and without h_{1N} bonds respectively, and these complete the set of elementary graphs.

Now the PY approximation sets $h_{1N}\mathcal{N}_{1N} + \mathcal{N}_{1N} = 0$ —while this is true for $r_{1N} < \sigma$, it is not true for $r_{1N} > \sigma$ and requires $\mathcal{N}_{1N} \equiv 0$. The only condition for this to be the case is in the fully extended configuration, and so the PY approximation incorporates these elementary diagrams insofar as they are fully extended. Consequently, the end-to-end distribution function is radially shifted outwards and is zero in the end-to-end contact configuration. The situation is exacerbated in the determination of the higher moments, e.g. $\langle R_n^2 \rangle$, and may be expected to overestimate substantially the mean square lengths.

3. The end-to-end probability distributions Z_{1N}

The normalised probability distributions $4\pi r_{1N}^2 Z(r_{1N})$ in the various approximations are compared in figure 1 for various N . For $N = 4$ the distribution Z_{14}^{II} is exact. The netted ring convolutions are seen to be qualitatively distinct from the PY distributions of Curro *et al.* The end-to-end contact probabilities $Z_{1N}(\sigma)$ are seen to be non-zero in the former case, while they are zero in the latter, prohibiting the development of closed

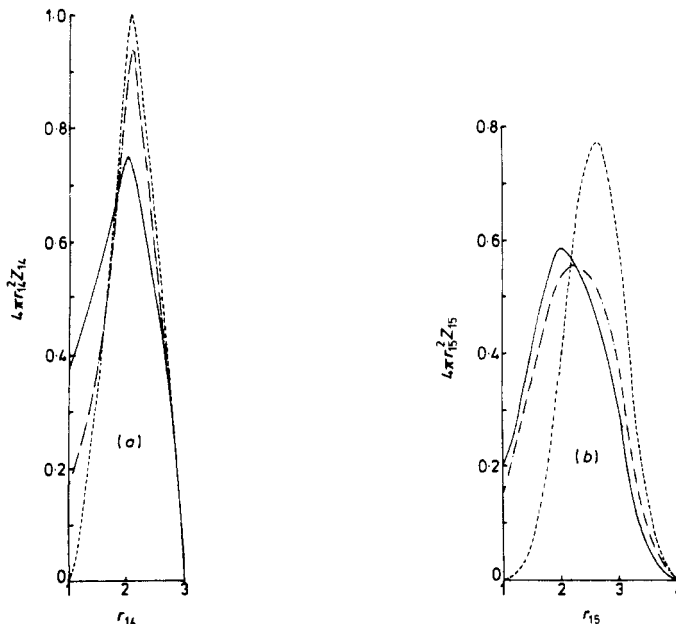


Figure 1. (continued on next page)

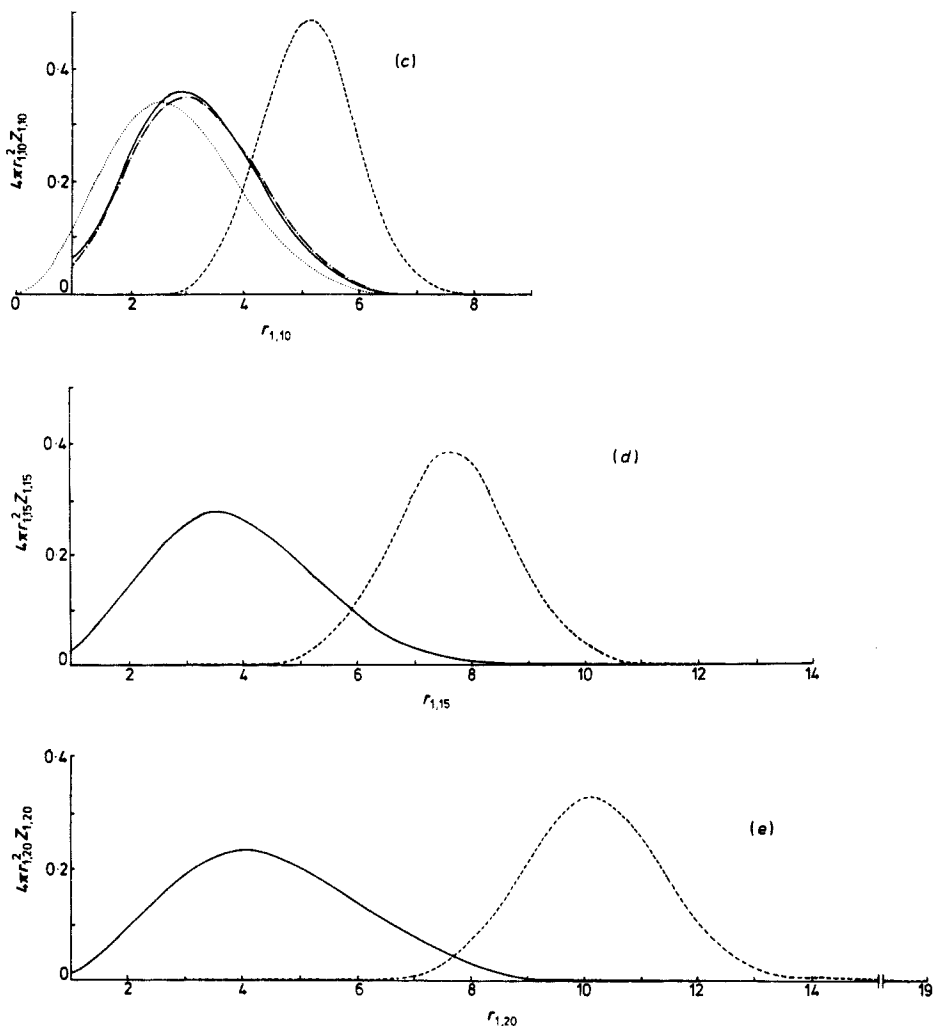


Figure 1. Normalised end-to-end probability distributions: — convolution approximation beginning $N = 4$, etc; - - - convolution approximation beginning $N = 3$, etc; - - - - Curro *et al*'s PY approximation $N = 4$, etc; ···· unrestricted random walk; (a) Z_{14} ; (b) Z_{15} ; (c) $Z_{1,10}$; (d) $Z_{1,15}$; (e) $Z_{1,20}$.

ring configurations. In particular we draw attention to the fact that $Z_{1N}^{\text{II}}(\sigma) > Z_{1N}^{\text{I}}(\sigma) > Z_{1N}^{\text{PY}}(\sigma) = 0$ throughout, although this is most apparent for shorter chain lengths. The peak in the PY distributions is consistently overdeveloped and shifted outwards with respect to the two convolution approximations, both of which become coincident as N increases. In consequence, the PY approximation may be expected to overestimate substantially the mean square end-to-end separation, implying as it does an over-rigidity in the system. The Z_{10} distribution for unit rods ($\epsilon = 0$) is also shown for comparison.

We point out that the higher-order convolution distributions become progressively collapsed with respect to the exact (but unknown) distribution, while the PY distributions become over-extended.

4. The mean square end-to-end distance $\langle R_n^2 \rangle$

As we mentioned in the Introduction, the relevance of Monte Carlo and exact enumeration studies of the self-avoiding walk on regular lattices to the continuum problem is not obvious. Connectivity and dimensionality play an important role; for example, the Ising model exhibits mean field behaviour on tree lattices, but on regular lattices shows interesting non-classical behaviour.

Monte Carlo investigations for a continuum polymer chain have been made by Fleming (1967), who finds that the exponent γ in

$$\langle R_n^2 \rangle = an^\gamma, \quad n = N - 1, \quad (15)$$

appears to increase with the excluded volume ratio ϵ , and suggests that the generally assumed value $\gamma = \frac{6}{5}$ is attained only for $\epsilon \geq 0.5$. This effect may, however, disappear for chains of length impracticable for machine simulation. Certainly the excluded volume ratio ϵ must have an effect on the exponent and is not entirely contained within the constant a as assumed, for example, in Edwards' mean field theory. This is apparent from the result for $\epsilon = 0$ (zero excluded volume—hinged rod polymer) for which both the convolution models and the PY model of Curro *et al* yield the known result $\gamma = 1$ (while that of Edwards does not), and show an increase of γ with ϵ . Fleming finds a relatively weak dependence of γ on ϵ for his Monte Carlo simulations, while Curro *et al* find a much stronger dependence on the excluded volume ratio ($\epsilon = 0, \gamma = 1; \epsilon = 1, \gamma = 2$). Of course, in the present netted ring convolution approximation we would expect the exponent to tend to the zero excluded volume result ($\gamma = 1$), since the fraction of exclusion bonds omitted increases with N , and this we see in figure 2. We have made the usual linearisation of the exponent relation (15),

$$\gamma_n = n(\langle R_{1N}^2 \rangle / \langle R_{1N-1}^2 \rangle - 1), \quad (16)$$

where γ_n is the exponent estimated on the basis of the two consecutive mean square molecular spans $\langle R_{n+1}^2 \rangle$ and $\langle R_n^2 \rangle$. The PY curve is also shown and is seen to exhibit a quite distinct behaviour.

While we cannot make a numerical estimate of the asymptotic value of γ , since the model degenerates to the zero excluded volume system as $n \rightarrow \infty$, the results nevertheless strongly suggest that $1.33 > \gamma > 1.0$ —an unremarkable conclusion, but nonetheless an improvement on the PY result. Confidence in this result is based on figure 2(a), which shows the *exact* curve for $\sigma = 0$, and the $\sigma = 1$ result on the basis of the present convolution approximation. Since we know qualitatively that $\gamma(\sigma = 1) > \gamma(\sigma = 0)$ at all orders, it follows that the only *qualitatively correct* region of the $\sigma = 1$ curve is that which lies above the $\sigma = 0$ curve, the intersection occurring at $\gamma = 1.33$. Of course, this represents an upper limit on the exponent for the self-avoiding system. We may obtain a better estimate by forming an extrapolation as follows. Knowing $\langle R_{1N}^2 \rangle$ on the basis of the approximations Z_{1N}^I, Z_{1N}^{II} and Z_{1N}^0 (zero excluded volume), which represent fractions $1 - 2/(N - 1), 1 - 3/(N - 1)$ and 100% of the bonds missing respectively, we may fit a quadratic curve to yield an estimate of $\langle R_{1N}^2 \rangle$ for 0% bonds omitted. Clearly this is likely to be of any accuracy at all only for small N . However, this is just the region in which we shall form our upper bounds on the estimate of γ . In figure 2(b) we show the $\sigma = 0$ and $\sigma = 1$ (extrapolated) curves, and we see that we are now able to propose $1.26 > \gamma > 1.0$ —a result in closer agreement with other determinations. Incidentally,

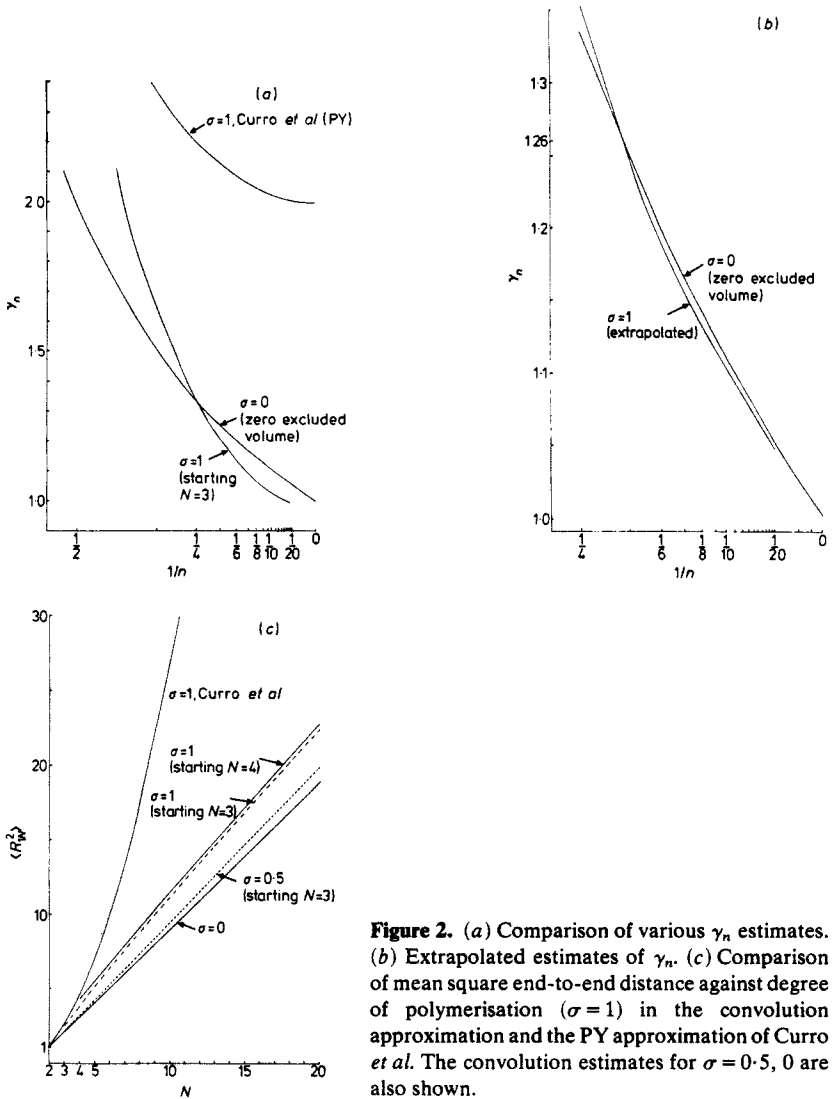


Figure 2. (a) Comparison of various γ_n estimates. (b) Extrapolated estimates of γ_n . (c) Comparison of mean square end-to-end distance against degree of polymerisation ($\sigma=1$) in the convolution approximation and the PY approximation of Curro *et al.* The convolution estimates for $\sigma=0.5, 0$ are also shown.

we should point out that in figures 2(a) and (b) the $\sigma=1$ curve dips below $\gamma=1$ before attaining its asymptotic value of unity, since the $\ln\langle R_{1N}^2 \rangle$ against $\ln n$ curve has an *initial* slope $\gamma > 1$ for small n .

Certainly $\gamma=2$ as predicted by PY is too great. Confidence in these relatively short chains is based upon the agreement found between the exact enumeration and Monte Carlo studies; the suggestion of Flory and Fisk that asymptotic behaviour will not set until $N > 10^6$ has been refuted in a number of studies.

Although there was some evidence of a dependence of γ on ϵ , given the nature of the approximations it was felt that no useful conclusions could be drawn at this stage.

The 'numerical noise' in these investigations is very small; the exact PY exponents for $\epsilon=1.0$ ($\gamma=2$) and $\epsilon=0$ ($\gamma=1$) were reproduced by the same numerical procedures to within ± 0.0001 .

5. Conclusions

On the basis of a diagrammatic approximation, a close upper bound on the exponent γ was determined to be $\gamma \leq 1.26$ for relatively short flexible three-dimensional polymer chains having hard sphere segments of excluded volume ratio $\epsilon = 1$. The dependence of this exponent on ϵ appears much weaker than that predicted by Curro *et al*, on the basis of a PY approximation to the excluded volume problem. The end-to-end probability distributions are qualitatively different to those of the PY analysis, being radially collapsed, of smaller amplitude, and having a non-zero end-to-end contact probability, suggesting the possible development of closed ring configurations. Although the present probability distributions are radially collapsed with respect to the exact (but unknown) functions, they are nevertheless believed to be qualitatively correct, degenerating to the zero excluded volume results as $N \rightarrow \infty$.

Acknowledgments

It is a great pleasure to acknowledge Ruby Turner for her computational assistance and discussions throughout this project, in particular concerning appendix 2. I should also like to thank Tom Osborn for his evaluation of the diagram \boxtimes . I should like to thank the ARGC for financial support.

Appendix 1. Identification of Z_{1N} with the fully netted vertex graph

The elementary graphs neglected in the PY approximation are those non-nodal diagrams with a $1 - h_{1N}$ exclusion bond (see equation (8)). At any given order $N > 3$, these may be generated from a $\zeta_0(1N)$ diagram by permuting 0 up to a maximum number, l , of h bonds between non-adjacent vertices. l will depend on the order N . It is straightforward to show that, since the h bonds are of range σ for hard sphere segments, and are of value 0 or 1, and that the sign of the resulting diagram is $(-1)^l$ if l bonds have been applied to ζ_0 , then the net value of the diagrammatic interference amongst the derivatives is

$$\zeta_0(1N) \left(1 + \sum_{l=1}^{\infty} \frac{(-1)^l l!}{l! (l-1)!} \right). \quad (\text{A1.1})$$

Note that this result holds only if every vertex is within the range σ of every other vertex. If that is the case, then the Σ term may be recognised as the binomial coefficient in the expansion of $(x-1)^{-1}$ with x set to zero. Provided this condition is met, then all the diagrams self-interfere completely and (A1.1) is identically zero. If the range of one or more of the inter-vertex h bonds exceeds σ , then the contribution of the derivatives is zero and (A1.1) reduces to $\zeta_0(1N)$. The derivatives of order N may therefore be expressed as fully netted $\zeta_0(1N)$ graphs with *exclusion* bonds $1 - h$ operating between all non-adjacent vertices. We have, however, inadvertently included the nodal diagrams in the prescription, which we subsequently subtract out; an example at order $N = 5$ is given in equation (10) *et seq.*, resulting in the simple exclusion netted ring representation of Z_{15} in (12).

Appendix 2. An alternative derivation of the result in appendix 1

We first note that for an N -segment polymer chain there are

$$\binom{N}{2} = \frac{N(N-1)}{2}$$

pairs of segments which may interact. Of these, $N-1$ pairs interact through δ bonds, leaving $N(N-1)/2 - (N-1) = (N-1)(N-2)/2$ possible distinct h bonds. For notational convenience we set $M = (N-1)(N-2)/2$.

The set of all diagrams of order N is equivalent to the set of all subsets of the set of possible h bonds, and this set has exactly 2^M elements. In fact, if we first order the set of h bonds, we can then denote each diagram by an M -bit binary number which has the i th bit = {1 if the diagram contains the i th h bond, 0 if it does not}. Note that there are exactly 2^M M -bit binary numbers, so we obtain the 'full set'.

Now sum the diagrams by combining the binary numbers according to the following rules:

- (i) only two numbers at a time are combined, and the two numbers to be combined must differ in exactly one bit, which is 1 in one number and 0 in the other;
- (ii) the 'sum' of the two numbers has an x (for a $1-h$ bond) in the bit where the two summands differ, and is the same as the summands in all other bits;
- (iii) the resulting numbers (containing 0's, 1's and x 's) may be recombined using the same rules.

By induction on the number of bits, any 'full set' of binary numbers (i.e. any set containing all 2^p p -bit binary numbers) summed according to the above rules adds to a single number, every bit of which is an x . Clearly, for $p = 1$, 0 and 1 combine to x . For $p > 1$, first combine pairs which differ only in the p th bit. This leaves 2^{p-1} numbers, each of which has x in the p th bit and a (distinct) $(p-1)$ -bit binary number in the rest. By inductive hypothesis the $(p-1)$ -bit numbers combine to all x 's, and the x in the p th bit is unchanged, giving a p -bit number of all x 's, i.e. exclusion bonds, and the identification with Z_{1N} is again established after the nodal diagrams have been subtracted.

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