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Monte Carlo studies of the excluded volume problem for polymer chains in the continuum
I. Use of inversely restricted sampling techniques

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Abstract. Recent publications on the configurational properties of polymer chains subject to excluded volume restraints, as deduced from studies of off-lattice model chains, are briefly reviewed. It is shown that the data for such models cast doubt on the validity of the frequently quoted equations $\langle R_N^2\rangle = aN^{6/5}$ and $\langle S_N^2\rangle = a'N^{6/5}$ where $\langle R_N^2\rangle$ and $\langle S_N^2\rangle$ are respectively the mean square end-to-end length and mean square radius of gyration of N-link chains, and a and a' are constants. The use of the technique of inversely restricted sampling to generate off-lattice model chains, with either freely varying or fixed bond angles, and free rotation about bonds, is described. An analysis of the configurational properties of such chains is presented in the following paper.

1. Introduction

In recent years the theoretical study of the configurational properties of real polymer chains has attracted considerable interest. Approximate analytical solutions of the excluded volume problem, ie the determination of the chain expansion due to the fact that no two monomers can occupy the same volume, as distinct from a completely free random walk model, have been presented by several authors, eg Flory (1949), Edwards (1965), Flory and Fisk (1966), Reiss (1967), Alexandrowicz (1967a, b), Naghizadeh (1968), Yamakawa (1968, 1971), Freed (1971), and de Gennes (1972). Two other numerical approaches have also been employed, namely direct enumeration of short chain configurations (Domb 1960) and Monte Carlo techniques (Wall *et al* 1954). A comprehensive bibliography has been published by Domb (1969).

It has been suggested in many of these analytical and numerical papers that the mean square end-to-end length $\langle R_N^2\rangle$ of a three-dimensional polymer chain of N links, subject to excluded volume restraints, is given at large N by

$$\langle R_N^2\rangle = aN^{\gamma} \tag{1}$$

where $\gamma = \frac{6}{5}$ and a is a constant determined by link length, and, in the case of chains confined to a lattice framework, the type of lattice. The Monte Carlo and direct enumeration results also suggest that the mean square radius of gyration $\langle S_N^2\rangle$ has the same functional dependence on N, and that

$$\langle S_N^2\rangle/\langle R_N^2\rangle = 0{\cdot}157 \pm 0{\cdot}002. \tag{2}$$

A large majority of the direct enumeration and Monte Carlo results have been compiled from analyses of chains constructed on various lattice frameworks, eg simple cubic, body-centred cubic, tetrahedral. The main advantages of on-lattice construction,

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as distinct from a régime in which varying bond angles and free rotation about bonds are permitted, are the relative simplicity of checking for violation of the excluded volume conditions, and the reduced incidence of such violation. Furthermore, since values very close to $\frac{6}{5}$ for the exponent γ of equation (1) have been obtained on a variety of lattices, together with $\langle S_N^2\rangle/\langle R_N^2\rangle$ ratios in good agreement with the figure 0·157 of equation (2), it has been conjectured (Domb 1963) that the dimensionality of the lattice, rather than its stuctural detail, determines in large measure the configurational properties of the chains. The corresponding equations in two dimensions, as determined from direct enumeration and Monte Carlo studies, are

$$\langle R_N^2\rangle = bN^{3/2}$$

$$\langle S_N^2\rangle/\langle R_N^2\rangle = 0{\cdot}140 \pm 0{\cdot}002.$$

Despite the agreement between several independent workers on the properties of on-lattice chains, it is not yet certain that a lattice model is appropriate to real polymers (Edwards 1970), and hence the dependence of $\langle R_N^2\rangle$ and $\langle S_N^2\rangle$ on N quoted above may not be correct for such systems. This would imply important consequences for many areas of polymer physics research, eg light scattering, diffusion viscosity, sedimentation and osmotic pressure, in which specific configurational models are usually assumed in order to interpret experimental data.

We consider now the evidence against $\gamma = \frac{6}{5}$. The analytical treatment of Alexandrowicz (1967a, b), in which excluded volume interactions are treated in terms of Gaussian probabilities for intersegmental contacts, predicts $\langle R_N^2\rangle$ asymptotically proportional to $N^{1{\cdot}236}$. Reiss (1967) used a variation principle to develop a single-segment self-consistent field treatment, somewhat similar to the method introduced by Edwards (1965), and found $\langle R_N^2\rangle$ proportional to $N^{4/3}$; however a refinement due to Yamakawa (1968) gave $\gamma = \frac{6}{5}$. Des Cloizeaux (1970) treated the case of repulsive interactions between all points of the chain, using a minimal Gaussian approximation, and also obtained $\gamma = \frac{4}{3}$. The Lagrangian theory of de Gennes (1972) yields $\gamma \sim 1{\cdot}195$. Whittington and Dunfield (1973), using an approach analogous to the Born–Green–Yvon analysis of liquids, estimated $\gamma = 1{\cdot}569$ and $1{\cdot}574$ for square and triangular two-dimensional lattices respectively, and $\gamma = 1{\cdot}258$ and $1{\cdot}246$ for simple cubic and face-centred cubic three-dimensional lattices respectively. Although the differences between lattice types of the same dimensionality are small, their departure from the widely accepted $\frac{3}{2}$ (two-dimensional) and $\frac{6}{5}$ (three-dimensional) ratios is significant. Authors using Monte Carlo techniques have avoided the limitations of on-lattice chain construction to varying extents. Unfortunately the much increased computing time requirement has usually restricted the calculations to chains not exceeding approximately 300 links (compare 1700-link chains generated on a lattice by Wall and Erpenbeck 1959). We now list this work in chronological order.

(i) Windwer (1965) generated 100-link chains with alternate tetrahedral and cubic lattice bonds, the bond length remaining constant at $3^{1/2}$, and found, from log–log plots,

$$\langle R_N^2\rangle = 2{\cdot}77N^{1{\cdot}29}$$

$$\langle S_N^2\rangle = 0{\cdot}39N^{1{\cdot}32}$$

$$\langle S_N^2\rangle/\langle R_N^2\rangle = 0{\cdot}158 \text{ (on average).}$$

The small non-systematic variation in the tabulated values of $\langle S_N^2\rangle/\langle R_N^2\rangle$ for various N is surprising, in view of the difference between the two exponents.

(ii) Rice and Windwer (1965) attempted to simulate the effects of varying excluded volume by working on a tetrahedral lattice and discarding varying fractions of the chains which self-intersected. Writing

$$\begin{aligned} \langle R_N^2 \rangle &= aN^{\gamma} \\ \langle S_N^2 \rangle &= a'N^{\gamma'} \end{aligned} \tag{3}$$

they found minimum values of 1·172 and 1·176 for γ and γ' respectively, and a steady increase in both as the excluded volume restrictions were made more stringent. This behaviour contrasts with the analytical predictions of a discontinuity in the value of γ between zero for a completely free random walk and $\frac{6}{5}$ (in three dimensions) for any finite excluded volume.

(iii) Gallacher and Windwer (1966) generated branched chains on a tetrahedral lattice, the branches being of varying lengths but short in comparison with the main chain length of 200 links. The spacing of the branches along the backbone was also varied. Once again values of γ and γ' (equations (1) and (3)) differing significantly from the lattice value of $\frac{6}{5}$ were observed, both indices tending to increase with increasing branch length and decreasing branch spacing. However, the $\langle S_N^2 \rangle / \langle R_N^2 \rangle$ ratio was found to settle down to values close to 0·157 for all branch length/branch spacing choices, in agreement with the results for linear chains constructed on a lattice.

(iv) Fleming (1967, 1968) investigated 100-link chains in the continuum, allowing freely varying bond angles and completely free rotation about bonds. He also varied the size of the excluded volume by varying the diameters of the hard spheres representing the monomer units of the chain with respect to a constant bond length. Defining an excluded volume ratio v by

$$v = \frac{\text{diameter of hard spheres}}{\text{bond length}} \tag{4}$$

he found $\gamma = 1{\cdot}05$, 1·06 and 1·18 for $v = 0{\cdot}1$, 0·2 and 0·5 respectively.

(v) Mark and Windwer (1967) generated self-avoiding walks up to 200 steps on a tetrahedral lattice, and extended the excluded volume condition to incorporate first non-bonded nearest neighbours. They obtained $\gamma = 1{\cdot}255$, in good agreement with some direct enumeration studies of Mazur and Joseph (1963), and interpreted their result as showing the dependence of γ on the excluded-volume parameters, ie γ is not determined uniquely by the dimensionality of the lattice.

(vi) Loftus and Gans (1968) considered chains with a fixed bond length and bond angle of 109·5° (the tetrahedral angle), the monomers being represented by hard spheres with diameters equal to the bond lengths. Allowed rotation about the bonds was varied from three discrete positions (one trans and two gauche) to complete freedom, and chain lengths from 20 to 100 links were investigated. Values of γ and γ' considerably larger than $\frac{6}{5}$ were found, even for rotations as small as $\pm 1°$ about the three discrete lattice positions. The $\langle S_N^2 \rangle / \langle R_N^2 \rangle$ ratio also nearly always fell below the lattice range $0{\cdot}157 \pm 0{\cdot}002$.

(vii) Alexandrowicz and Accad (1971), using a 'dimerization' process introduced by Alexandrowicz (1969) to overcome excluded volume sample attrition, built 8192-link chains on a four-choice cubic lattice and found that $\langle R_N^2 \rangle$, although proportional to $N^{6/5}$ up to about 1500 links, increased more slowly towards the end-points of the chains.

(viii) Lal and Spencer (1971) used an improved model of *n*-alkane molecules which incorporated the known rotational preferences around the C–C bonds in such molecules, different C–C and C–H bond lengths, and representation of long-range intersegmental interactions by Lennard-Jones potentials. Consequently the chains were not constrained to a tetrahedral lattice. They found γ and γ' lying in the ranges 0·79 to 1·25 and 1·07 to 1·35 respectively, although their calculations were restricted to 50-link chains.

(ix) Warvari *et al* (1972) investigated randomly coiling polysarcosine and poly-N-methyl-L-alanine using hard sphere models with relative radii (H, C, N, O, CH_3, NH_3) appropriate to these compounds. Assuming that the peptide bonds were fixed in the planar trans configuration, they limited rotation about the backbone N–C^{α} and C^{α}–C′ single bonds to certain discrete values. From an analysis of chains of around 300 links in length they concluded that there is a continuum of possible γ and γ' values stretching from unity at zero excluded volume to above $\frac{6}{5}$, and that $\langle S_N^2 \rangle / \langle R_N^2 \rangle$ is less than $\frac{1}{6}$.

(x) Lemaire *et al* (1974) restricted their calculations to polyethylene chains on a tetrahedral lattice, and investigated two distinct models, namely one in which it was assumed that the positions corresponding to the three internal rotation angles of 0°, +120° and −120° were equally probable, and a second more realistic model in which the potential energy for rotation about a given bond depended only on the rotational states of the nearest-neighbour bonds. Performing calculations for 2000-link chains, they obtained $\gamma = 1{\cdot}188$ for the first model, a result which they regarded as supporting the $\gamma = \frac{6}{5}$ school, but for the second model they estimated $\gamma = 1{\cdot}09 \pm 0{\cdot}01$.

After consideration of the above data, two questions spring immediately to mind. Firstly, if there exists a unique asymptotic value of γ for three-dimensional lattice-constrained chains, is it $\frac{6}{5}$, and secondly, what is the corresponding value for off-lattice chains? We are concerned here only with the second of these questions. An unambiguous answer has not yet been given, because of the relatively short chains to which calculations have been restricted by computing time requirements. We have therefore investigated longer (up to 504 links) chains over the range of excluded volume ratio (see equation (4)) v = zero to unity, for both freely varying and fixed bond angles, and with free rotation about the bonds in both cases.

In this paper we describe the method of chain generation, in particular the modifications required in order to use the technique of inversely restricted sampling to generate off-lattice chains; in the following paper we present our results and conclusions.

2. Off-lattice chain construction

Following Fleming (1967), the monomer units of the chains are represented as hard spheres, the bond length is set at unity, and the choice of sphere diameter then determines the excluded volume ratio v. The centre of the first sphere of each chain is taken as the origin of coordinates, and two calls to the pseudo-random number generator (Control Data Corporation FORTRAN RANF) then give the values of $\cos\theta$ and $\phi(0-2\pi)$ required to determine the direction of the first link, in the case of freely varying bond angles. Random generation of $\cos\theta$ and ϕ, rather than θ and ϕ, ensures that the probability distribution of the link direction is constant over the surface of a sphere. In the case of fixed bond angles, equated to the tetrahedral angle 109·5°, the value of ϕ only is required. One or two further calls to RANF then give a proposed position for the third sphere, which is accepted or rejected after inspection for intersection with the first sphere. If intersection occurs, another choice of $\cos\theta$ and ϕ (or ϕ only) gives an alternative position

for the third sphere, and the process is continued, if necessary, until an acceptable site is found. In this way, chains of the required number of links can be constructed, the major limitation being computing time.

Neglecting considerations of sample size, unbiased statistics on the configurational properties of the chain would be obtained if the construction of a given chain were discontinued immediately two spheres intersected, ie immediately the excluded volume condition was violated. Since construction was continued, in our calculations, simply by choosing an alternative site, the resulting statistics must be biased. More specifically, we would expect to obtain a smaller value of γ (Fleming 1967). This bias may be removed using a modification of the method of inversely restricted sampling.

3. Inversely restricted sampling

Inversely restricted sampling is one of two techniques commonly used to reduce sample attrition due to violation of excluded volume conditions, the other being the sample enrichment technique of Wall and Erpenbeck (1959). Both were used in this study, mainly the former. The use of the latter in an off-lattice context is straightforward, and will not be discussed further. Hammersley and Morton (1954) have described the method of inversely restricted sampling in detail; Rosenbluth and Rosenbluth (1955) and Mazur and McCrackin (1968) have used it successfully in studies of on-lattice chains. We now briefly describe its use in constructing chains in the continuum.

3.1. Chains with freely varying bond angles

Figure 1 shows a number of shaded spheres of diameter v representing the initial monomers of a chain, the distance between centres of consecutive spheres being unity. Thus the locus of the centre of sphere $N+1$ is a spherical surface with radius unity and centre coincident with the centre of sphere N. If $N \geqslant 2$, a given choice of $\cos\theta$ and ϕ may define a proposed position of sphere $N+1$ such that it would intersect one or more previously added spheres, thereby contravening the excluded volume conditions. More specifically, since the distance of closest approach of the centres of any two spheres is equal to their

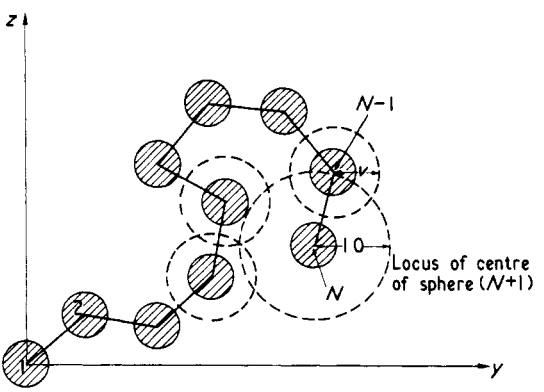

Figure 1. Model polymer chain with freely varying bond angles subject to excluded volume conditions. Each monomer unit is represented by a sphere of diameter v. The distance between centres of consecutively added spheres is unity.

diameter v, an exclusion is indicated when a circle of radius v centred on a previously added sphere intersects the spherical surface which is the locus of the centre of sphere $N+1$. Three such exclusions are shown in figure 1, that due to sphere $N-1$ always being present. Since centre $N+1$ must be positioned elsewhere on the locus, we may define the multiplicity p_N of the Nth link (joining spheres N and $N+1$) by

$$p_N = \frac{\text{total area of locus of centre } N+1}{\text{area of locus not excluded by previously added spheres}}.$$

The size of the excluded area, ie the size of the cap of the larger sphere in figure 2, is

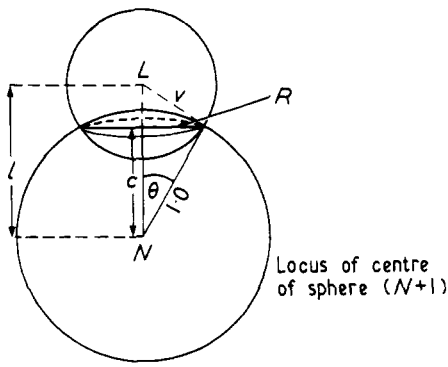

Figure 2. Exclusion of part of the locus of centre $N+1$ by previously added sphere L (freely varying bond angles).

readily calculated. Denoting the L–N inter-centre distance by l, and the height of the cut-off plane above centre N by c,

$$\text{Excluded area on locus} = \int_0^{\cos^{-1}c} 2\pi \sin\theta \, d\theta = 2\pi(1-c)$$

where $c = (1-v^2+l^2)/2l$. The same result is obtained if the centre of the interfering sphere L is located inside the locus of centre $N+1$. The total excluded area E_T is then obtained, in the simplest case, by summing over all interfering spheres i, giving

$$E_T = 2\pi \sum_i (1-c_i)$$

and a multiplicity

$$p_N = \frac{4\pi}{4\pi - 2\pi \Sigma_i (1-c_i)} = \frac{1}{1-[0{\cdot}5 \Sigma_i (1-c_i)]}.$$

Complexities arise when two or more previously added spheres exclude the same part of the locus. A simple summation such as that quoted immediately above would then overestimate the excluded area of the locus. In practice it was found that overlap on the locus involving three or more spheres was a very rare occurrence, less than 1 % of all multiple exclusions, and hence we consider double overlap only, eg that shown in figure 3 for two spheres centred on L_1 and L_2. Overlap occurs when the distance between the centres of the two cut-off planes is less than the sum of their radii, ie when

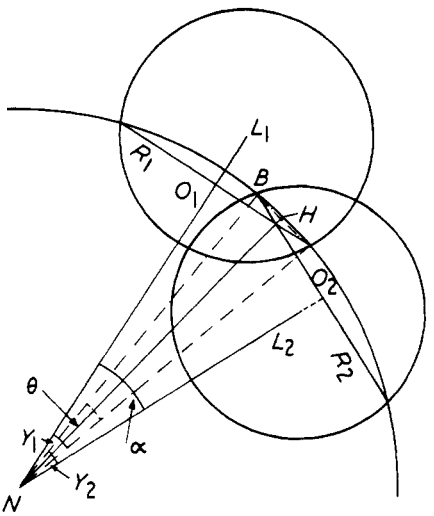

Figure 3. Exclusion of the same part of the locus of centre $N+1$ by previously added spheres L_1 and L_2 (freely varying bond angles).

$O_1O_2 < R_1+R_2$. If the angle subtended at the centre of sphere N by L_1L_2 is α, then, denoting the overlap angle by θ,

$$\theta = \gamma_1+\gamma_2-\alpha$$
$$= \cos^{-1}c_1+\cos^{-1}c_2-\cos^{-1}\left(\frac{l_1^2+l_2^2-(L_1L_2)^2}{2l_1l_2}\right)$$

where l and c are as defined earlier. Although the shape of the overlap surface is generally asymmetric, it may be approximated by a circular cap of radius BH at a height NH above N where

$$BH = \sin(\theta/2) \qquad \text{and} \qquad NH = \cos(\theta/2).$$

Hence the excluded area common to both spheres is $2\pi(1-\cos\frac{1}{2}\theta)$ where

$$\cos\theta = (\cos\alpha)(c_1c_2-R_1R_2)+(\sin\alpha)(R_1c_2+c_1R_2).$$

The correct total excluded area E_T is then

$$E_T = 2\pi\left\{\sum_i(1-c_i)-\sum_{j>i}\left[1-\left(\frac{1+\cos\theta_{ij}}{2}\right)^{1/2}\right]\right\}$$

summing over overlapping pairs i,j. Since the total area of the spherical surface is 4π, the multiplicity p_N of the Nth link is given by

$$(p_N)^{-1} = 1-0{\cdot}5\left\{\sum_i(1-c_i)-\sum_{j>i}\left[1-\left(\frac{1+\cos\theta_{ij}}{2}\right)^{1/2}\right]\right\}.$$

The statistical weight W_N of any N-link chain is then

$$W_N = \prod_{k=1}^{N} p_k^{-1}.$$

3.2. Chains with fixed bond angles

In this slightly more realistic model of a polymer chain the bond angle is fixed at the tetrahedral angle 109·5°, and hence the locus of the centre of sphere $N+1$ is the rim of a cone with sloping side of length unity, making an angle of 70·5° with the direction of the $(N-1)$th link (see figure 4). The calculation of multiplicities for this model is a more complex exercise in geometry, but since it is an obvious extension of the approach just described, further details will not be given.

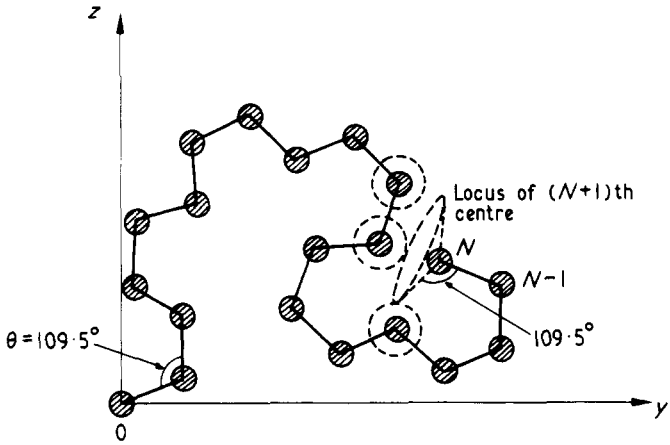

Figure 4. Model polymer chain with fixed bond angles (the tetrahedral angle 109·5°), subject to excluded volume conditions.

4. Computation and timings

Separate programs embodying the freely varying and fixed bond angle models were written in FORTRAN and run on the Monash University Control Data Corporation 3200 computer. The method used to store the coordinates of the individual monomer units in the computer memory, and to check for violation of the excluded volume conditions, was very similar to that described by Fleming (1967). The time taken to generate each link in the chain was approximately constant from the 20th link onwards, and increased only slightly with increasing v. Samples of 1000 100-link freely varying and fixed bond angle chains were constructed in thirty and forty minutes respectively, more time being required in the latter case because of the many coordinate transformations which were necessary. A given chain was abandoned before it reached the required length only in the very rare event that the locus of the centre of the next sphere to be added was totally excluded, ie the end-point was completely surrounded by other spheres.

Values of R_N^2 and S_N^2 and the associated multiplicities p_N for a given chain under construction were held in the computer memory until the chain contained the required number of links. Multiplicity-weighted R_N^2 and S_N^2 were then added to a cumulative total, representing typically 1000 chains, from which the dependence of $\langle R_N^2 \rangle$ and $\langle S_N^2 \rangle$ on N, and any other required information, was deduced. Re-start options were included in the programs so that chain generation, say for a given excluded volume ratio, could be continued through a series of computer bookings.

Exhaustive tests made on the pseudo-random number generator subroutine RANF (CDC3200) showed it to be suitable for this application, eg there was no significant correlation between successive members of the test sequence generated, over the range zero to unity, the numbers also being evenly distributed about 0·5.

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