Direct Monte Carlo measurement of excluded volume for Pearson walks

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The Pearson walk model of a linear polymer with excluded volume is studied by analogy with a neighbor-avoiding walk on a lattice. The pivot algorithm is used to model the excluded volume directly, with the strength of interaction controlled by bead diameter. The excluded volume per bead is shown to be nonanalytic, with two distinct excluded volume regimes corresponding to geometrically different polymer models.

I. INTRODUCTION

Two-parameter theory of polymers in dilute solution expresses configurational quantities as functions of a single excluded volume variable z; in three dimensions z is proportional to $N^{1/2}\beta$, where N is the chemical length of the chain and β is the binary cluster integral.[1] Relatively little attention has been paid to β, although a good understanding of this quantity is essential to the correct interpretation of polymer models and their relationship to real polymers.

In some special cases, β is known. For a very long linear chain with very small excluded volume, β is effectively that for a dilute gas. For self-avoiding walks (SAWs) on lattices, β is the volume per lattice site. For neighbor-avoiding walks (NAWs) the binary cluster integral is more realistic, in that there is *local sharing* of excluded volume between neighboring monomers along the chain.[2] As with SAWs, the strength of the excluded volume interaction is determined by the lattice geometry. A yet more realistic model is the off-lattice, "stick–bead" chain, or Pearson walk with excluded volume. Like NAWs, Pearson walks exhibit local sharing of excluded volume, but now it is possible to adjust the excluded volume by varying the bead diameter. A final advantage is that the results display no artifacts of lattice structure.

The drunkard's walk proposed by Pearson[3] in 1905 is one of the earliest models of a flexible polymer. It offers a simple and intuitive picture of a random coil, one of considerable utility in the theory of polymer configurations. The model is much less tractable if excluded volume is taken into account, and so has been seldom used as a starting point for excluded volume models. A sequence of $N+1$ hard beads of diameter d is linked linearly by rigid, massless bonds of unit length. Each bead is a perfectly flexible joint between two bonds. The strength of the excluded volume interaction is controlled by the size of the bead diameter, which varies from 0 to 2. Some values of d are interesting for geometrical reasons, the transition from random to SAWs occurs at $d=0$, neighboring beads along the chain share excluded volume at $d=0.5$ and interpenetrate at $d=1$, the transition from SAW to rigid rod occurs at $d=2$.

It is instructive to think of the bond set of the Pearson walk as analogous to a lattice walk. The binary cluster integral represents the effective excluded volume per monomer. For a SAW on a lattice, the binary cluster integral β is by definition the volume per lattice site.[1] For NAWs on a lattice, the effective binary cluster integral is a multiple K of the volume per lattice site.[2] The Pearson walk is viewed as similar to a NAW, $\beta = KV_0$, where V_0 is the volume of a single bead. Then K is analogous to the effective number of lattice sites excluded by each occupied site of the NAW. For a lattice walk, we may identify K with the connective constant[4] μ. (On average, a random walker has μ sites available for the next step. Since immediate reversals are forbidden, the walker is surrounded by $\mu + 1$ effective sites. Excluding these nearest-neighbors and the occupied site but not the two neighbors along the chain gives $K = \mu + 2 - 2 = \mu$.) For a continuum walk K is a well-defined and interesting quantity, although it is not clear what the geometrical interpretation might be.

For NAWs, we define the excluded volume variable (in 3D) by[2]

$$z = \left(\frac{3}{2\pi}\right)^{3/2} N^{1/2} K V_0 .$$

Here the product $K V_0$ is the effective binary cluster integral. The analogous definition for Pearson walks is

$$z = \left(\frac{3}{2\pi}\right)^{3/2} N^{1/2} K \frac{\pi d^3}{6} . \tag{1}$$

It is natural to define the effective excluded volume per monomer as the total volume excluded by the walk, divided by the total number of vertices. For each bead of the chain, we define the *excluding volume* to be the sphere of radius d surrounding the bead. In the limit of small excluded volume, the effective excluded volume per lattice site is simply the excluding volume. For larger values of d the effective excluded volume per site is reduced because of the overlap of excluding volumes (see Fig. 1).

For simulation purposes it is convenient to define the effective binary cluster integral by

$$\beta = \frac{1}{N+1} \sum_{i=0}^{N} \int W_i(\mathbf{r}) d\mathbf{r} . \tag{2}$$

The weight $W_i(\mathbf{r})$ is defined to be 0 if $|\mathbf{r} - \mathbf{r}_i| > d$ and otherwise equal to the reciprocal of the number of monomers within a sphere of radius d centered at $\mathbf{r}$. For example the region of overlap of two excluding volumes must be
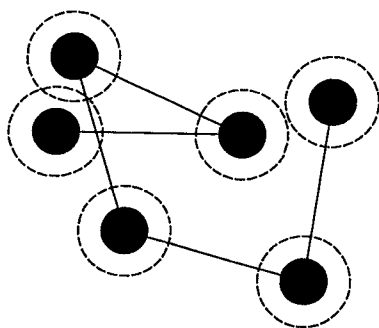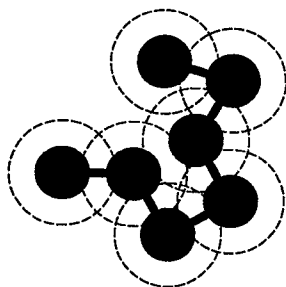
a) d = 0.20

b) d = 0.75

FIG. 1. Binary cluster integral for a freely jointed chain. (a) $d < 0.5$, showing nonlocal sharing of excluding volumes; (b) $d > 0.5$, showing both local and nonlocal sharing.

assigned a weight of $\frac{1}{2}$ to avoid overcounting of the excluded volume (see Fig. 1).

II. MONTE CARLO CALCULATIONS AND RESULTS

The pivot algorithm of Lal,[5] revisited by Madras and Sokal,[6] has proven to be a reliable method for the simulation of chains in the continuum. Modern computers can generate sufficiently large samples using this algorithm that the standard error of the results is well within acceptable limits. Briefly, a bead chosen at random serves as the pivot, and the shorter portion of the chain is rotated through a random angle. If the excluded volume condition is violated, then the original configuration is counted again. If not then the new configuration is counted.

The integral of Eq. (2) is carried out by crude Monte Carlo.[7] It is ideally suited to evaluation by this method, as the domain is complicated, and the integrand highly discontinuous. The integral converges rapidly nonetheless, as seen from the errors quoted in Table I.

TABLE I(a). K and A vs d, 3D Pearson walks.

d	K	A
0.99	5.210 ± 0.005	1.812 ± 0.006
0.75	6.451 ± 0.009	1.764 ± 0.006
0.50	7.702 ± 0.008	1.698 ± 0.006
0.25	7.912 ± 0.002	1.624 ± 0.008
0.10	7.992 ± 0.002	2.631 ± 0.018

TABLE I(b). K and A vs d, 2D Pearson walks.

d	K	A
0.99	2.318 ± 0.006	1.33 ± 0.02
0.75	2.969 ± 0.006	1.34 ± 0.02
0.50	3.820 ± 0.008	1.34 ± 0.03
0.25	3.876 ± 0.009	1.13 ± 0.01
0.10	3.955 ± 0.002	1.16 ± 0.01

For each bead diameter d sampled, 25 samples of 1000 walks each were generated. For each configuration, the integral (2) was estimated using 25 samples of 25 points for each chain vertex. As is the case for NAWs, a fit vs $1/N$ yields accurate estimates of K for infinite chains. The extrapolated results for K appear in Table I and are graphed in Figs. 2 and 3.

Consider Fig. 2. The points represent the measured values of K as a function of d. As d increases from 0 the value of K falls gently until $d = 0.5$, where there is a dramatic and significant decrease that continues until $d = 2$. The dotted curve represents the *local sharing approximation*, the contribution to K from the overlap of the excluding volumes of consecutive beads only. The difference between the two curves represents the contribution of *nonlocal sharing*, that is overlap of excluding volumes of nonconsecutive beads only. As expected, the contribution from nonlocal sharing for $d = 0$ and 2 is nil; it is never very great. The onset of forced local sharing at $d = 0.5$ is by far the most dramatic feature.

It is apparent from Fig. 2 that a fair estimate of K can be obtained from the local sharing approximation. Figure 3 shows a plot of $\beta = KV_0$ vs d (in 3D). The points are the Monte Carlo estimates and the solid curve represents the local sharing approximation. The closeness of the points to the curve emphasizes the value of this approximation. The dashed curve is drawn assuming $\beta = 8V_0$; this cruder approximation holds to about $d = 0.5$.

In the limit of very small bead diameter d, there are no overlaps of excluding volumes, as all beads are well sepa-
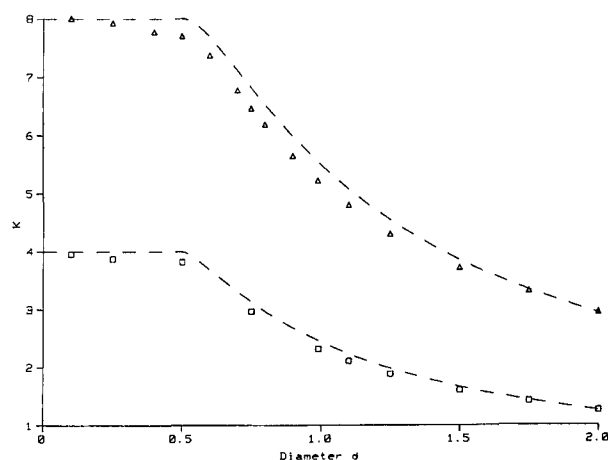
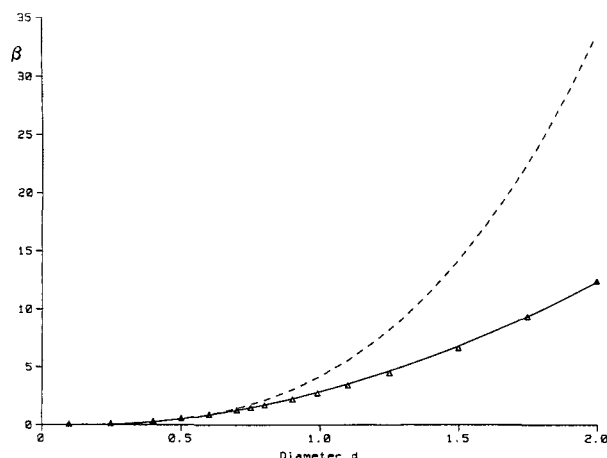FIG. 2. μ vs d. Upper curves, 3D; lower curves, 2D. The dotted curves give the local sharing approximation.

FIG. 3. β vs d. Solid curve, local sharing approximation; dashed curve, $\beta = 8V_0$.

rated. As d is increased to a finite size, there will be occasional overlaps of monomer excluding volumes. If $d < 0.5$, the only such interactions are between monomers at least two units distant along the chain. Interactions between nearest-neighbors along the chain are prevented by the rigid bonds separating them. If $d > 0.5$, the rigid bonds force overlap between these neighboring beads (see Fig. 1).

In the local sharing approximation, a little geometry (see Appendix) suffices to show that for infinite chains in 3D,

$$K = 8 - \begin{cases} 0, & \text{if } d \leqslant 0.5 \\ \dfrac{(2d-1)^2(4d+1)}{2d^3}, & \text{if } d \geqslant 0.5 \end{cases}$$

and in 2D,

$$K = 4 - \begin{cases} 0, & \text{if } d \leqslant 0.5 \\ \dfrac{8}{\pi}\left[\arccos\left(\dfrac{1}{2d} - \dfrac{\sqrt{4d^2-1}}{4d^2}\right)\right], & \text{if } d \geqslant 0.5. \end{cases} \tag{3}$$

It is clear from an examination of these formulas, that $d = 1$ is not a remarkable point, but that there is a discontinuity in the second derivative at $d = 0.5$. In 2D the discontinuity is infinite, in 3D it is finite but large.

We have seen that the contribution to K from local sharing only, ignoring all contributions from overlap of the excluding volumes of nonconsecutive beads, is singular at $d = 0.5$. We are unable to compute the contribution from nonlocal sharing, but excepting the remote possibility that there is an equal, cancelling, singularity in the nonlocal contribution, there is of necessity a singularity in K at $d = 0.5$. The numerical evidence shows that K is dominated by the local sharing contribution, and supports the hypothesis that for $0 < d < 2$, $d = 0.5$ is the only remarkable point.

III. DISCUSSION

The excluded volume of polymers is a complicated quantity, as it involves both geometric and solvent (temperature) effects. The results obtained here demonstrate

clearly that these effects *must* be treated differently; it is not always appropriate to model solvent effects by geometrical features. To emphasize the point, one does not expect a change in solvent condition to induce a singularity in β as can be done by changing d. There are clearly two different kinds of polymer model, those with small geometrical excluded volume and those with significant geometrical excluded volume. Real polymers all belong to the second category; theoretical results obtained for the first category must therefore be applied with caution.

In 3D, the exponent ν in the small excluded volume regime has been calculated by Muthukumar and Nickel,[8] and by DesCloizeaux, Conte, and Jannink[9] to be 0.5886. In the large excluded volume regime it has been computed by LeGuillou and Zinn-Justin[10] to be 0.5880; a very precise numerical estimate is[11] 0.5873, with the other estimates within the error bars. The evidence therefore strongly suggests that the exponent is truly universal; it applies to both categories of excluded volume chain.

In the limit of small excluded volume,[8,9] the amplitude has been computed to be $A = 1.53$. The best numerical evidence,[12] and some RG calculations,[13] suggest a value close to $A = 1.75$ for 3D SAWs. Results for the mean square end-to-end length of Pearson walks have been reported in an earlier publication.[12] The extrapolated amplitudes A have been recomputed using these most recent estimates of K, and are shown in Table I. In 2D, the amplitudes are almost constant, except for apparently anomalous values for $d = 0.10$ and 0.25. In 3D, the amplitudes show a steady decrease with diameter (except for $d = 0.10$). It may be that this decrease is an artifact of the fitting procedure, but it appears not unlikely that A is a function of d.

The Domb–Joyce model[14] provides a helpful framework to discuss the implications of this possibility. Developed for SAWs, Domb–Joyce replaces the definition of z given in Eq. (1) by

$$z_{dj} = \left(\frac{3}{2\pi}\right)^{3/2} N^{1/2}\beta_0 w,$$

where now β_0 represents a purely geometrical excluded volume (the volume per lattice site for SAWs) and w a statistical weight which can be taken as modeling the solvent effect to some extent. The Θ-point is modeled by $w = 0$, and the full effect of geometric excluded volume is represented by $w = 1$. Domb and Joyce claim that the critical point is $w = 0$; for sufficiently long SAWs, evidence shows that,[15] at least to a very good approximation,

$$\alpha^2 \sim A z_{dj}^{4\nu-2} \tag{4}$$

for $0 \leqslant w \leqslant 1$, where the exponent ν and the amplitude A are both universal. In the light of the results presented here, it is possible that universality only exists in the Domb–Joyce sense for Pearson walks. That is

$$\alpha^2 \sim A(d) z_{dj}^{4\nu-2}$$

for all w.

For large N, we expect the power law behavior[8,9]

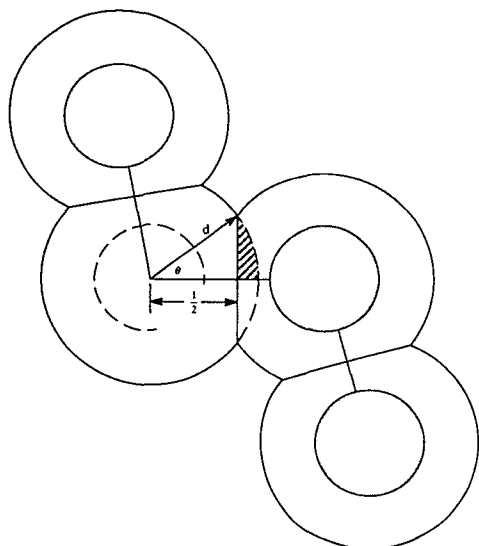$$\alpha^2 = A N^{2\nu-1}(1 + bN^{-\Delta} + \cdots).$$

FIG. 4. Extended two-dimensional chain with unit bond length and $d > 0.5$, showing calculation of the reduced excluded volume.

Recently Nickel[11] has identified two regimes of excluded volume which he calls "two-parameter-like" and "self-avoiding-walk-like," characterized by a change of sign of the amplitude b of the correction-to-scaling term. He reports[16] that this change of sign occurs for a value of d different from the geometrically interesting value $d = 0.5$. The excluded volume, even for this relatively simple model, would appear to be far more complicated than has been previously imagined.

IV. SUMMARY AND CONCLUSIONS

The effective binary cluster integral β of an excluded volume Pearson walk has a singularity for a bead diameter of $\frac{1}{2}$, which results in two distinct excluded volume regimes. The same end-to-end distance exponent applies to both regimes, but the amplitude is a function of diameter; universality for long chains exists only in the Domb–Joyce

sense. The local sharing approximation provides a very good estimate of the geometric excluded volume for an isolated polymer.

ACKNOWLEDGMENTS

APPENDIX

Consider Fig. 4, which represents part of a two-dimensional chain with $d > 0.5$. The overlap of excluding volumes leads to a reduction in K which can be easily calculated. The reduced excluded volume associated with a single monomer is $4V_0$ less 4 times the hatched area, that is

$$4V_0 - 4(\tfrac{1}{2}d^2\theta - \tfrac{1}{2}\cdot\tfrac{1}{2}d \sin \theta) = 4V_0 - 2d^2\theta + d \sin \theta.$$

Equation (3) follows immediately. The 3D result is calculated in a similar fashion.

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