for uniform chains[3]) should be adequate to observe scattering from internal modes. Since $\langle l^2 \rangle_e^{1/2}$ is proportional to $Z^{1/2}$ for random coils, this means that degree of polymerization Z can be decreased fourfold.

Comparison of Figures 1–3 indicates that the most favorable case is that with the chain labeled at one end. However, the other labeling patterns are also predicted to give rise to significant scattering from internal modes. Since each weights the various normal modes differently, it would be desirable to employ all three labeling patterns to help unravel the many components of the scattering spectrum.

The experimental feasibility of this approach remains to be demonstrated. Hopefully, by using clusters of heavy metal atoms conjugated to organic moieties, as in strongly scattering markers used in electron microscopy, it will be possible to satisfy the dual criteria for the label of high scattering power and small size ($\ll \langle l^2 \rangle_e^{1/2}$). The latter criterion ensures that the hydrodynamic perturbation from the label is negligible. It must also be possible to find a solvent in which the polymer is soluble, which has the same refractive index as the polymer, and in which the label is stable. Work along these lines is in progress in our laboratory.

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A Distribution Function for Polymer Lengths[1]

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ABSTRACT: Taking cognizance of excluded volume effects in the theory of macromolecular configurations, a simple distribution function is proposed for describing end-to-end separations of flexible polymer chains. The function, when projected on one axis, is $C(1 + \beta^2x^2) \exp(-\beta^2x^2)$ where β is a parameter simply related to the mean-square end-to-end separation and C is a normalization constant. This simple modification of the Gaussian distribution provides excellent agreement with exact counts for short chains and moderately good agreement for reduced moments extrapolated to chains of infinitely long contour lengths. The one-component distribution function can easily be converted into a spherically symmetric radial distribution function. The tractability of the proposed formula is such that it should prove useful in describing actual high polymer length distributions.

Flexible polymer chains exhibit a great many distinguishable configurations, so it is quite natural that statistical methods are used for describing them. Mean-square end-to-end separations and average moments of inertia are among the quantities used to characterize flexible polymers, although the distributions of such lengths and moments would be even more useful.[2a] It is the purpose of this paper to present a simple distribution function that can be applied to polymer chain lengths. In establishing this function, we take limited cognizance of the excluded volume effect, a constraint that has generally proved to be frustrating in the theoretical treatment of polymer dimensions.[2b]

The distribution function that we shall describe is a one-parameter function which we believe will be useful for characterizing polymer molecules. The one parameter involved is the mean-square end-to-end distance, a quantity we should like, of course, to be able to predict. If, however, that average distance can be obtained or estimated by other means, then the distribution of lengths can be set forth with reasonable confidence.

In our discussions, we shall initially be concerned with components of lengths and their distribution in one dimension, let us say the x direction of a Cartesian coordinate system. When work on this subject was first initiated by numerous investigators years ago, there was a natural disposition to assume a Gaussian distribution, which would be correct were it not for the effect of excluded volume which precludes double occupancy of any sites in space. A Gaussian distribution is readily derived from the completely random walk model which is often used as a first approximation for describing a polymer chain.[3,4] On the other hand, a better description of a flexible polymer is a non-self-intersecting random walk or string of beads, a model that implies a volume constraint sufficient to render non-Gaussian the distribution of component lengths along some axis.

If $F(x)dx$ is the probability that a polymer chain possesses an x component of end-to-end separation in the range x to $x + dx$, then it can be shown for non-self-intersecting chains that[5,6]

$$(d^2F/dx^2)_{x=0} = 0 \tag{1}$$

To derive eq 1, it is only necessary to assume spherical symmetry for the three dimensional distribution and to stipulate that the end of a polymer chain cannot occupy the same site as its beginning. Spherical symmetry is reasonable to expect for long chains and the noncoincidence of the beginning and end of the chain is inherent in the excluded volume constraint. Since the Gaussian function does not satisfy eq 1, it appears that requiring the second derivative of F to vanish for $x = 0$ may lead to a better description.

To develop a suitable distribution function, we shall modify the Gaussian by multiplying it by a polynomial. The simplest symmetrical, even powered, polynomial that comes to mind consistent with eq 1 is a two-term quadratic consisting of a constant and a second degree term. Hence we shall write

$$F(x) = C(1 + \beta^2x^2) \exp(-\beta x^2) \tag{2}$$

Table I
Projected Distributions on the x Axis of Self-Avoiding Walks of N Steps on a Tetrahedral Lattice

x	$T(x)$	$\mathfrak{N}F(x)$	$\mathfrak{N}E(x)$	$\mathfrak{N}G(x)$
		$N = 5$		
1	74	77	78	85
3	56	60	55	52
5	32	22	21	20
Total	324	318	308	314
		$N = 10$		
0	10,708	10,741	10,889	12,480
2	10,572	10,610	10,420	11,300
4	8,864	9,208	8,487	8,388
6	6,208	6,028	5,481	5,105
8	3,072	2,772	2,661	2,547
10	1,024	880	929	1,042
Total	70,188	69,737	66,845	69,244
		$N = 15$		
1	1,812,890	1,768,423	1,785,738	2,024,365
3	1,719,616	1,729,429	1,679,251	1,792,585
5	1,475,172	1,533,722	1,416,862	1,405,598
7	1,118,592	1,145,858	1,038,319	975,963
9	716,288	693,660	643,974	600,063
11	372,736	335,413	330,446	326,701
13	139,264	129,161	137,510	157,505
15	32,768	39,660	45,564	67,240
Total	14,774,652	14,750,652	14,155,448	14,700,400
		$N = 20$		
0	317,727,164	307,056,718	311,274,488	356,267,666
2	314,980,912	306,307,183	306,507,642	341,775,085
4	294,030,340	296,640,746	285,252,885	300,472,782
6	254,611,216	265,117,520	244,718,193	242,426,283
8	201,340,944	209,610,648	189,964,517	179,499,852
10	142,390,528	143,140,288	131,364,507	121,971,485
12	88,003,584	83,541,149	79,823,513	76,061,056
14	45,776,896	41,527,694	42,097,428	43,528,752
16	19,136,512	17,579,116	19,050,751	22,861,247
18	5,767,168	6,344,141	7,319,881	11,018,778
20	1,048,576	1,954,991	2,364,370	4,873,901
Total	3,041,900,516	3,050,583,672	2,928,201,862	3,045,246,108

It is easily shown that eq 1 holds for $F(x)$. The constant C can be determined by normalization to be

$$C = 2\beta/3(\pi)^{1/2} \tag{3}$$

Finally, if we evaluate $\langle x^2 \rangle$, the mean-square x component of the end-to-end separation, we see that $\langle x^2 \rangle = 5/6\beta^2$; hence

$$F(x) = \left\{\frac{10}{27\pi\langle x^2\rangle}\right\}^{1/2}(1 + 5x^2/6\langle x^2\rangle) \times \exp(-5x^2/6\langle x^2\rangle) \tag{4}$$

Equation 4, which gives the desired result, involves only one parameter, $\langle x^2 \rangle$; yet, as will be shown, it appears to be more effective than other equations that have heretofore been proposed. Equation 4 can readily be converted into a radial distribution function. If $p(r)$ is the radial function so that $4\pi r^2 p(r)dr$ is the probability of finding an end-to-end separation in the range r to $r + dr$, regardless of angular direction, then it can be shown that[5,6]

$$p(r) = -F'(r)/(2\pi r) \tag{5}$$

From this we conclude that

$$p(r) = \left\{\frac{10}{27\pi\langle x^2\rangle}\right\}^{1/2}\left\{\frac{25r^2}{36\pi\langle x^2\rangle^2}\right\} \exp(-5r^2/6\langle x^2\rangle) \tag{6}$$

Since $\langle r^2 \rangle = 3\langle x^2 \rangle$ from symmetry, we can rewrite eq 6 as

$$p(r) = \left\{\frac{10}{\pi\langle r^2\rangle}\right\}^{1/2}\frac{25r^2}{12\pi\langle r^2\rangle^2} \exp(-5r^2/2\langle r^2\rangle) \tag{7}$$

It is easily shown that $p(r)$ is normalized to unity, that the average value of r^2 is indeed $\langle r^2 \rangle$, and that the most probable value of r is $(4\langle r^2\rangle/5)^{1/2}$.

Either the projected distribution, given by eq 4, or the radial distribution, eq 7, can be compared with available data or with other formulas used to describe the distribution of polymer configurations. The best data for such comparisons are obtained by direct count of self-avoiding walks on a lattice; for longer walks it may be necessary to use results obtained by Monte Carlo studies.[7] Since counts on a discrete lattice are most easily expressed in terms of numbers projected onto an axis, eq 4 will be used. The data

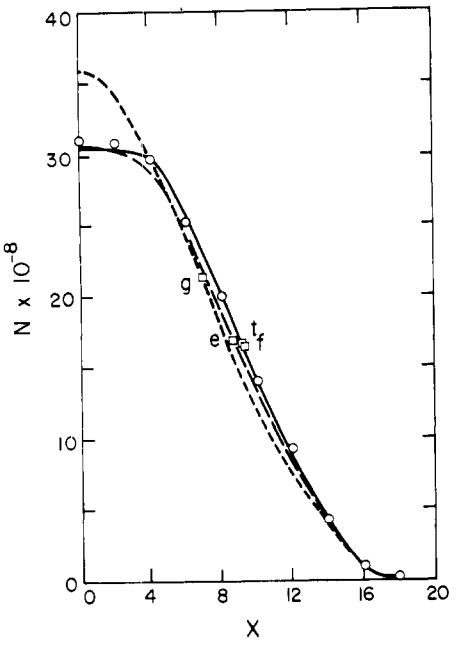

Figure 1. Number distributions projected on x axis for chains of 20 links. Values of $T_{20}(x)$ are indicated by ○, (—) denotes $F(x)$, (— —) denotes $E(x)$, (- - -) denotes $G(x)$. Points of inflection, indicated by □, are further identified by corresponding lower case letters.

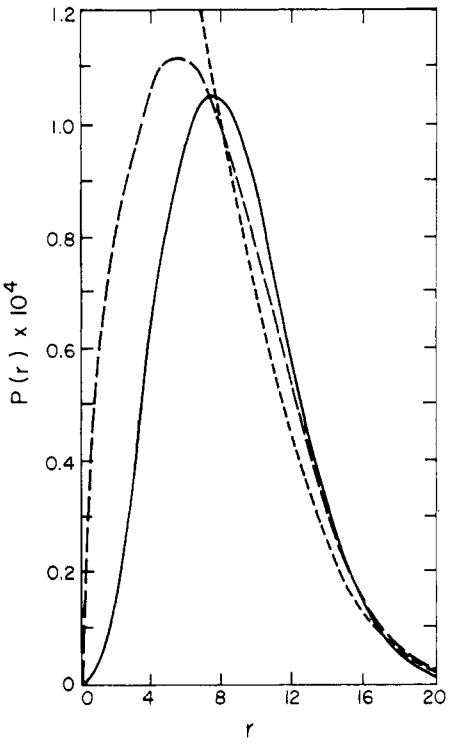

Figure 2. Radial probability distributions for chains of 20 links. $F(r)$ is denoted by (—), $E(r)$ by (— —), and $G(r)$ by (- - -). The functions are normalized to unity when multiplied by $4\pi r^2$ and integrated over the range $0 < r < \infty$.

Table II
Mean-Square Deviations for Self-Avoiding Walks on a Tetrahedral Lattice Using Exact Counts Relative to Calculated Values

N	S_F	S_E	S_G
5	2.381×10^{-3}	2.629×10^{-3}	5.353×10^{-3}
10	1.070×10^{-4}	3.605×10^{-4}	1.550×10^{-3}
15	7.604×10^{-5}	1.776×10^{-4}	8.463×10^{-4}
20	7.727×10^{-5}	1.295×10^{-4}	5.943×10^{-4}

available concerning restricted random walks consist of explicit counts for short walks; these can be extrapolated to learn about trends for infinitely long contours. Although the end-point distributions for short walks depend on the nature of the lattice, it appears that certain extrapolated moments are lattice independent. Since a great deal of numerical information is available for the tetrahedral lattice,[8] we shall use such data as a standard for comparison purposes. We shall denote the discrete tetrahedral distribution by $T_N(x)$ where N is the number of steps and x the component of length in the x direction.

To judge the correctness of our distribution equation, we shall compare it directly against exact numbers for short walks as well as with extrapolated trends for infinitely long walks. For small values of N, it is expedient to treat the problem by fitting curves to a set of points and then determining the closeness of fit. Before comparing two distributions, it is desirable that both be normalized to the same value. For convenience, we have chosen to multiply $F(x)$ by the total number of walks, $\mathfrak{N}$, for which exact counts are available when N is small.

Several other distributions have been used to describe the restricted random walk,[3,4,9-11] but we will here consider only two one-parameter functions for comparison purposes. Historically the Gaussian function was first proposed[3]

$$G(x) = \{2\pi\langle x^2\rangle\}^{-1/2} \exp(-x^2/2\langle x^2\rangle) \qquad (8)$$

Later Domb, Gillis, and Wilmers[5] suggested the function

$$E(x) = \{5/[4\beta\Gamma(2/5)]\} \exp(-|x|/\beta)^{5/2} \qquad (9)$$

provided $\beta = \{\langle x^2\rangle\Gamma(2/5)/\Gamma(6/5)\}^{1/2}$. Theoretical justification for $E(x)$ has been given by Fisher[12] and by Chay[13] using arguments involving the asymptotic behavior of generating functions.

In Table I, $F(x)$, $E(x)$, and $G(x)$ are compared against $T(x)$ for walks of 5, 10, 15, and 20 steps.[8] (The total numbers of walks corresponding to $F(x)$, $E(x)$, and $G(x)$ are not equal to the total for $T(x)$ since it was their integrals that were normalized and not their discrete sums.) Figure 1 shows the projected distributions for walks of 20 steps and Figure 2 shows the equivalent radial distributions. Evidently, $T(x)$ is crudely fitted by all of the three functions but not exactly by any of them.

To determine the closeness of fit, let us define

$$S_f = \sum_x [T(x) - f(x)]^2 / \sum_x T(x)^2 \qquad (10)$$

so that S_f represents the mean-square deviation of points on the analytic curve from the points $T(x)$. From the results shown in Table II, it becomes evident that there is indeed a difference in the fits of the three curves and that $F(x)$ is best, $E(x)$ intermediate, and $G(x)$ least good. Because Table I was constructed by rounding off values to the nearest whole numbers, there is significant round-off error in the lowest values, but the ranking of fit is clear in longer length walks. It is perhaps surprising that a simple modification of a Gaussian to guarantee spherical symmetry in conjunction with nondouble occupancy at the origin should improve the analytic fit by an order of magnitude.

As mentioned earlier, the second derivative of $F(x)$ vanishes at the origin. This is also true for $E(x)$ but not for $G(x)$. Since the second derivative should vanish for $x = 0$, $G(x)$ is definitely deficient on that score. In addition, all

Table III
Points of Inflection of the x Component Distribution of End Points of Self-Avoiding Walks on a Tetrahedral Lattice from Exact Counts and by Analytic Formulas

N	T	F	E	G
5	4	3.8427	3.6291	2.8642
10	6.6122	6.0202	5.6854	4.4871
15	7.8753	7.6949	7.2671	5.7091
20	9.1090	9.1572	8.6480	6.8253

Table IV
Reduced Moments for Self-Avoiding Walks on the Tetrahedral Lattice as Given by Exact Counts and by Analytic Formulas

	T_{20}	T_∞	F	E	G
m_4	2.50	2.65	2.52	2.631	3
m_6	9.08	10.8	9.72	10.66	15
m_8	41.19	58.0	49.90	57.08	105

three functions exhibit points of inflection for one value of $|x|$ different from zero. Fitting values of $T(x)$ in the neighborhood of such an inflection point to a third-order polynomial, namely

$$ax^3 + bx^2 + cx + d = 0$$

we see that the inflection point of interest should occur for $x = -b/3a$. Inflection points determined in this way for $T(x)$ can be compared with those obtained using $F(x)$, $E(x)$, and $G(x)$. The observed and predicted inflection points are compared in Table III. It appears that $F(x)$ gives the closest prediction to the values calculated from exact counts, whereas $E(x)$ and $G(x)$ have inflection points too near to the origin.

Two distributions are identical if all their moments are the same. Accordingly, it is reasonable to compare the lower moments, at least, to test the validity of a formula. The utility of fitting such average properties for a set of points is obvious; for that reason, we chose the second moment as a parameter in writing $F(x)$. To facilitate further comparison, let the reduced moment, $m_{2K}(f)$, associated with a distribution, $f(x)$, be defined by

$$m_{2K}(f) = \int_{-\infty}^{\infty} x^{2K} f(x)\mathrm{d}x \Big/ \left\{ \int_{-\infty}^{\infty} x^2 f(x)\mathrm{d}x \right\}^K \qquad (11)$$

Then for the three functions discussed, we obtain

$$m_{2K}(F) = (3/5)^K(1 + 2K/3)(2K - 1)!! \qquad (12)$$

$$m_{2K}(E) = \frac{\Gamma[(4K + 2)/5]}{\Gamma(2/5)}\left(\frac{\Gamma(2/5)}{\Gamma(6/5)}\right)^K \qquad (13)$$

$$m_{2K}(G) = (2K - 1)!! \qquad (14)$$

where $(2K - 1)!! = (2K - 1)(2K - 3) \cdots (3)(1)$.

Several reduced moments for chains on a tetrahedral lattice are given in Table IV for $N = 20$ and for extrapolated values as $N \to \infty$. In addition, values calculated using eq 12, 13, and 14 are shown for comparison. Evidently, for $N = 20$, the function $F(x)$ gives the best agreement. On the other hand, $E(x)$ is best when compared to values extrapolated to large values of N. The Gaussian distribution is not as good as either of the others for $N = 20$ or for $N \to \infty$. The superiority of $E(x)$ for large N is clear, whereas $F(x)$ is better for small N. It is likely that the two functions are probably equally good for N in the neighborhood of a few hundred.

We might well ask if $F(x)$ could not be improved by adding an x^4 term to the polynomial factor to produce agreement with $m_4(F)$; presumably an x^6 correction could also be added to improve $m_6(F)$ followed by an x^8 term for $m_8(F)$, etc. Such a procedure might be used, although it is aesthetically displeasing because of the need for more parameters. If this is attempted, however, something interesting occurs at the outset. Retaining the requirement that the second derivative vanish at the origin, but changing eq 2 by the addition of $\gamma^4 x^4$ to the polynomial, one obtains

$$F(x) = Ce^{-\beta^2 x^2}(1 + \beta^2 x^2 + \gamma^4 x^4) \qquad (15)$$

A little analysis discloses that, for real values of γ^4, the maximum value of $m_4(F)$ occurs when γ^4 is equal to zero. Since the value previously predicted by $F(x)$ is too low, a fourth-order term by itself cannot improve the reduced fourth moment, so a sixth-order term would be required.

Overall, it is clear that radial symmetry in conjunction with exclusion of double occupancy at the origin leads to a simple modification of the Gaussian function that provides a very good formula for the distribution of polymer lengths. This new function, $F(x)$, is a tractable expression that embodies excluded volume corrections to an extent sufficient to give a satisfactory distribution of lengths of restricted random walks on a tetrahedral lattice.

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