Numerical Study of Self-Avoiding Walks on Lattices and in the Continuum

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ABSTRACT: We propose a consistent description for the mean-square length of self-avoiding walks on lattices and in the continuum, based on careful numerical studies in two and three dimensions. Existing exact enumerations for various lattices are combined with new precise Monte Carlo results and are analyzed according to the best available theoretical models. Small but persistent differences from two-parameter dimensions for walks on different lattices are discussed. The Domb–Barrett equation for the mean-square end-to-end length of a walk is adjusted to reflect the most accurate estimates of the coefficients and exponents, and a similar equation is proposed for two-dimensional walks. Finally, new results for self-avoiding walks in the continuum are interpreted within the framework of the Domb–Joyce model as being consistent with lattice results.

1. Introduction

Polymer scientists have long believed that macroscopic properties of polymers may be described in terms of only a few parameters. That being so, one need only work out the physics for some simple model and then determine the appropriate choice of units for the model to apply to a real polymer. We address here the second part of this program, making use of available physical knowledge. We limit ourselves to the problem of self-avoiding walks on lattices and in the continuum, taking the view that if the suggested program is valid, it should be possible to find a unified, or universal, description of such walks.

There exists a unified description of self-avoiding walks on lattices, proposed some years ago by Domb and Joyce;[1-3] recently Muthukumar and Nickel have offered a similar description of continuum chains.[4] But, to our knowledge, there is no consistent description for all self-avoiding walks, and this is what we will attempt here.

We have two requirements. The first is a set of precise results for self-avoiding walks on lattices and in the continuum. We use available exact enumerations for lattices. In addition, an old Monte Carlo algorithm of Lal,[5] given new respectability by the careful work of Madras and Sokal,[6] provides reliable estimates for self-avoiding chains in the continuum and improved estimates for chains on lattices. The second requirement is a consistent theoretical framework within which the results may be analyzed. We shall use as our theoretical framework the Domb–Joyce model,[1-3] augmented by the recent Borel summation results of Muthukumar and Nickel.[4] The latter provides precise estimates of the asymptotic exponents while the Domb–Joyce model allows for the inclusion of walk geometry in the definition of the excluded-volume variable.

We shall confine ourselves to the mean-square end-to-end vector $\langle R_N^2 \rangle$ for a self-avoiding walk (SAW) of N steps, each step of length a. The most elementary mathematical model of a linear SAW assumes that, in the limit of very long chains, $\langle R_N^2 \rangle$ may be described by a simple power law:

$$\langle R_N^2 \rangle = BN^{2\nu} \tag{1}$$

The exponent ν is believed to be "universal"; that is, the same for all SAWs in a given dimension; the amplitude B is not universal and is dependent on walk geometry. However, if we define the expansion factor as being the ratio of $\langle R_N^2 \rangle$ to the mean-square end-to-end length of random walks

$$\alpha^2 = \frac{\langle R_N^2 \rangle}{Na^2}$$

then there is evidence that α^2 is a universal function, not of N, but of the excluded-volume variable z, which is defined in D dimensions as

$$z = \left(\frac{D}{2\pi}\right)^{D/2} \frac{\beta}{a^D} N^{(4-D)/2}$$

The argument rests, in the first instance, on Flory's 1949 formula[7] for the mean-square end-to-end length of a polymer in dilute solution and on the perturbation series

$$\alpha^2 = 1 + \frac{4}{(4-D)(6-D)} z + \dots \tag{2}$$

derived for long chains with small excluded volume by Teramoto, Fixman, and many subsequent authors.[8] This is called the "two-parameter" theory of polymer excluded volume because α^2 is expressed as a function only of two quantities: the dimensions of ideal chains and the total excluded volume between segments of the chain. Important numerical evidence for this view was provided by Domb[9] when he showed, by analysis of exact enumerations for self-avoiding walks on 3-dimensional lattices, that the expansion factor could be written for long chains as

$$\alpha^2 \sim 1.64 z^{0.4} \tag{3}$$

All details of lattice structure are incorporated into the variable z. Subsequently, Barrett and Domb[2,3] showed that the perturbation series (2) is valid for lattice walks, provided that the definition of z is generalized. Equations 2 and 3 may be combined into a single, simple interpolation formula[2]

$$\alpha^2 = (1 + 6.67z + 12.57z^2)^{0.2} \tag{4}$$

which provides a description of α^2 valid for all long self-avoiding lattice walks. It was supposed that (4) is valid for off-lattice walks as well, but this hypothesis was never fully tested.

A most interesting recent development is the summation of the two-parameter perturbation series (2) by Muthu-

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kumar and Nickel[4] using Borel summation techniques. They find

$$\alpha^2 \sim 1.53z^{0.354}(1 + 0.12z^{-0.95} + ...) \quad (5)$$

DesCloizeaux, Conte, and Jannink[10] have found the same result using a direct renormalization method. These asymptotic results may be combined with the series (2) to produce an equation similar to (4):

$$\alpha^2 = (1 + 7.524z + 11.06z^2)^{0.1772} \quad (6)$$

Since the Muthukumar–Nickel calculation is carried out for the continuum limit of the discrete chain, it appears as if the Domb–Barrett equation (4) cannot be valid for continuum chains. We believe that this interpretation is misleading. First, as discussed elsewhere,[11] the two-parameter behavior of the expansion factor for large excluded volume may not be simply the summation of the series (2). Second, the excluded-volume variable z must be defined carefully if an equation such as (4) or (6) is to have meaning.

We will suggest a revised approximate equation of the form (4), which is suitable for all self-avoiding walks, whether on- or off-lattice. Our program has three steps: (1) to use the most complete exact lattice enumerations available and the most precise simulation data available, in conjunction with the most recent values of the exponents and corrections to scaling to bring equation (4) up-to-date for three-dimensional lattices (It will be seen that, although the result appears quite different, the effect is significant only for large z. A similar formula will be devised for two-dimensional lattices.); (2) to give a definition of the excluded-volume variable z, which is appropriate for any self-avoiding walk, on- or off-lattice (It will be seen that, for any geometry, the excluded volume may be expressed as a multiple K of the volume of a hard sphere situated at each site of the walk. It is possible to compute K exactly for lattices, but only bounds and numerical estimates are as yet available for continuum walks.); (3) to use precise Monte Carlo measurements of continuum walks to estimate the value of the constant K for self-avoiding walks in the continuum.

The result of this program is a master curve on which all lattice and continuum results may be placed. However, there are small but persistent deviations from this master curve for the three cubic lattices. One recalls a fact discussed some years ago by Tanaka,[12] namely, that results for four-choice SAWs on the simple cubic lattice cannot be placed on the master curve unless z is rescaled by an empirical factor. This circumstance is discussed in greater detail below.

2. Pivot Algorithm

The principles of the pivot algorithm are simple. An initial self-avoiding walk of N steps is produced, and from this initial configuration a sample of walks is generated by successively choosing a site of the walk at random and using it as a pivot joint. The shorter portion of the walk is rotated through a random angle, and, if the rotated portion does not intersect the nonrotated portion, the new walk is accepted. Because a SAW is not a very dense object, relatively few attempts are required to produce a new configuration, and indeed a small number of successful moves produces a radically different chain. The pivot algorithm is therefore a particularly efficient method of sampling the configuration space of the chain. Perhaps more important, Madras and Sokal have shown the pivot algorithm to be ergodic; that is, under certain mild conditions on the allowed moves, all possible configurations are sampled by the algorithm. For further details, the interested reader is advised to consult the excellent article of Madras and Sokal.[6]

3. Analysis of Lattice Results

Serious difficulties bedevil any analysis of exact enumeration or simulation data on self-avoiding walks. The reason for this is simple: the behavior of self-avoiding walks is not well understood. It is true that great progress has been made since analysis meant little more than a double-logarithmic fit; the theoretical framework developed over the past several years permits us now to understand (1) as a *critical* equation with ν as a critical exponent. Thus, ν is expected to be *universal* and valid for any self-avoiding walk whatsoever, regardless of its geometry or excluded-volume condition.

The earliest numerical estimates of ν, based on Monte Carlo[13] sampling of lattice walks and subsequently on extrapolations[9] of enumerations of lattice walks, suggested that, for walks in three dimensions, $\nu = {}^6/_5$ and, for walks in two dimensions, $\nu = {}^3/_4$. More recent calculations have refined these estimates. A plausible argument by Nienhuis[14] suggests that ν is indeed ${}^3/_4$ in two dimensions, while for walks in three dimensions LeGuillou and Zinn-Justin[15] have calculated $\nu = 0.588$. The most recent calculation is the Borel summation of Muthukumar and Nickel,[4] which yields $\nu = 0.5886$.

In order to construct a consistent description for self-avoiding walks on lattices, it is essential to estimate the value of the amplitude B of (1). Analytical calculations of B are controversial, and numerical estimates are fraught with great difficulty. The interested reader is advised to read the excellent articles by Guttmann[16] and Rapaport[17] on the estimation of exponents and amplitudes. Numerical estimation of parameters requires a detailed understanding of the functional form being fitted. Since (1) is asymptotic, this means that it is important to know the so-called corrections to scaling.

It is by now known that there must be analytic or Darboux[18] corrections to $\langle R_N^2 \rangle$ (see for example ref 1). That is, there must be corrections of the form $1/N$, $1/N^2$, $1/N^3$, etc. In addition, nonanalytic corrections of the form $1/N^\Delta$ have been found, and each of these in turn spawns a series of analytic corrections $1/N^{1+\Delta}$, etc. Some corrections of this type can be expected to be universal and others to be lattice dependent. For instance, Muthukumar and Nickel[4] find $\Delta = 0.465$ for walks in three dimensions. This correction should be universal. Djordjevic, Majid, Stanley, and dos Santos[19] find for walks on the triangular lattice a numerical estimate of $\Delta = 0.66$. This may represent a universal correction, one valid only for the triangular lattice or some combination of a universal and a lattice-dependent correction. Nienhuis[14] finds a correction exponent of 1.5 for 2-dimensional walks, whereas Rapaport[17] finds no evidence for a nonanalytical correction in either two or three dimensions.

In our ignorance, we have chosen to fit to the general form

$$\frac{\langle R_N^2 \rangle}{N^{2\nu}} = B + \frac{C}{N^\Delta} + \frac{D}{N} + \frac{E}{N^{1+\Delta}} + \frac{F}{N^2} + ... \quad (7)$$

for a number of plausible values of Δ and to record the variability of the leading amplitude B. Fortunately, it has proven to be not too sensitive to the value of Δ.

For 3-dimensional walks, we have fit (7) with $\nu = 0.5886$, using first of all a correction exponent of $\Delta = 0.465$ and then analytic corrections only. We then repeated the process using $\nu = 0.588$ with a correction exponent of 0.47 and then with analytical corrections only. For 2-dimensional walks we have fit using $\nu = 0.75$ and corrections of

$\Delta = 0.66$, $\Delta = 1.5$ and then analytic corrections only. The enumeration data and the Monte Carlo data were fitted separately and then as a single data set. The results in Table II are those obtained from the single data set; the uncertainties given indicate the computed standard error.

Table I displays the enumeration and Monte Carlo data used in this study. The reader interested in seeking sources for the enumerations will find the end of the trail in refs 16 and 17. For each value of N listed, 64 or more samples of 30 000 walks each were generated of lattice walks; 30 or more samples were generated for off-lattice walks. The averages and errors given are for the set of samples. Measurements were taken only for even N for the SC, SQ, and BCC lattices to avoid complications caused by the even–odd alternation of averages for loose-packed lattices. The data for the hexagonal or honeycomb lattice were analyzed in steps of four. The samples were produced using different random number generators and slightly different programs at both our institutions; the results are indistinguishable, which gives us confidence in their precision. We have also included in our analysis the results of Madras and Sokal[6] as well as recent Monte Carlo results with very small errors produced by B. G. Nickel.[20]

The values quoted in Table II have been computed by using the routine SVDFIT, which is based on the singular value decomposition and described in "Numerical Recipes".[21] As a check, other fitting routines were used; all produced the same answers. The χ^2 goodness-of-fit parameter was taken as the sum of squares, each term weighted by the reciprocal variance. This raises the question: what weights should be assigned to the exact enumeration data? We have arbitrarily chosen to apply an *artificial* error of $1/N^2$, since we expect that the asymptotic formula (7) should differ from the exact value by approximately that amount. For instance, although the exact value of α^2 is known to be 1.2 for $N = 2$ step walks on the SC lattice, an asymptotic formula correct to $O(N^{-2})$ can be expected to err by about 0.25. Assigning artificial errors in this way permits the χ^2 goodness-of-fit parameter to be accepted with some confidence.

Table II displays the fitted values of the leading coefficients of (1) and (3). The values of B in Table II are converted into corresponding values of A by exploiting the relationship between N and z. In three dimensions the excluded-volume variable z is

$$z = \left(\frac{3}{2\pi}\right)^{3/2}\frac{N^{1/2}\beta}{a^3}$$

where β/a^3 is the volume per lattice site and has the value 1, $4/3\sqrt{3}$ and $1/\sqrt{2}$ for the SC, BCC, and FCC lattices, respectively. Thus, using the Muthukumar–Nickel values of the exponents, $\nu = 0.5886$ and $\Delta = 0.465$, it follows that

$$A = B\left[\left(\frac{3}{2\pi}\right)^{3/2}\frac{\beta}{a^3}\right]^{-0.3544}$$

If we take as our "two-parameter" amplitude the average of those in Table II, we find

$$\alpha^2 \sim (1.75 \pm 0.03)z^{0.3544} - (0.07 \pm 0.03)z^{-0.5856}$$

The leading amplitude is close to the value of 1.732 obtained by Douglas and Freed[22] but is substantially different from that of (5). Moreover, as noted by Nickel,[20] the sign of the first correction term is opposite to that given in (5).

Equations 4 and 6 are constructed by writing

$$\alpha^2 = (1 + az + bz^2)^c$$

and then choosing a, b, and c so that series expansion is correct to first order, and asymptotic expansion yields the correct amplitude. With the Muthukumar–Nickel values of the exponents, we obtain

$$\alpha^2 = (1 + 7.524z + 23.53z^2)^{0.1772}$$

An equation that is more precise for intermediate values of z is obtained by using the first two terms of the perturbation series and the asymptotic correction:

$$\alpha^2 = (1 + 15.05z + 79.78z^2 - 249.9z^3 + 553.5z^4)^{0.0886} \quad (8)$$

This curve is not recommended for use near $z = 1$ where it has a very slight inflection. It is plotted in Figure 1, together with (4) and (6), on the same axes as the data of Table I. In this plot we have followed Tanaka's advice[12] and replaced the factor $N^{1/2}$ in the definition of z by $N^{1/2}(1 - 1/N)$ to better account for small-chain effects. It is worth noting that the difference between (4) and (8) for larger z is entirely due to the extension of the enumerated series and the availability of precise Monte Carlo results. The former was constructed solely on the basis of the exact enumerations available in 1971.

In two dimensions[8,23]

$$\alpha^2 = 1 + \frac{1}{2}z + \ldots \quad (9)$$

where from (5)

$$z = \frac{1}{\pi}\frac{\beta}{a^2}N$$

For lattices, β/a^2 represents the area per lattice site and has the values 1, $\sqrt{3}/2$, and $3\sqrt{3}/4$ for the square, triangular, and hexagonal lattices, respectively. Values of B and A for 2-dimensional lattices are also quoted in Table II; A is obtained from B in a manner similar to that used for 3-dimensional lattices. Averaging, we find

$$\alpha^2 \sim 1.37 \pm 0.03z^{0.5} \quad (10)$$

We compute the approximate two-parameter formula for two-dimensional walks to be

$$\alpha^2 = (1 + 2z + 3.52z^2)^{0.25} \quad (11)$$

A graph of (11) and the data of Table I are shown in Figure 1. Small-chain effects are partially corrected by replacing the factor of N in z by $N - 1$.

4. Definition of z for Continuum Walks

The variable z, as defined in D dimensions, contains the factor β/a^D, which is taken as the volume per lattice site. For self-avoiding walks in the continuum, this is a more subtle problem.[24] We define a self-avoiding walk in the continuum to be the bond set of a freely jointed chain, which has bonds of constant length a and a hard sphere of diameter d at each vertex. We expect that the characteristics of these walks will depend on the ratio of bead diameter to bond length. If, for any bead diameter, we imagine a *random network*, such that a self-avoiding walk on the network is indistinguishable from a walk in space, then we may equate the excluded volume of the latter with the volume per site of the former. Let us assume that our network has n sites contained in a volume V. We may then define the *site density* of the network as

$$\rho = \lim_{V\to\infty}(n/V) \quad (12)$$

On average, each lattice site requires a volume $1/\rho$, and it is this volume that is excluded when the site is occupied by a bead of the walk.

Table I
Enumeration and Monte Carlo Data for $\langle R^2 \rangle$

3D Lattices: Enumerations

N	SC: $\langle R_N^2 \rangle$	BCC: $\langle R_N^2 \rangle$	FCC: $\langle R_N^2 \rangle$	N	SC: $\langle R_N^2 \rangle$	BCC: $\langle R_N^2 \rangle$	FCC: $\langle R_N^2 \rangle$
1			1.000	9			12.905
2	2.400	2.286	2.182	10	16.817	15.258	14.638
3			3.496	11			16.407
4	5.554	5.124	4.908	12	20.953	18.973	18.207
5			6.397	14	25.228		
6	9.071	8.294	7.950	16	29.627		
7			9.556	18	34.135		
8	12.845	11.689	11.209	20	38.742		

3D Lattices: Monte Carlo

	SC		BCC		FCC	
N	$\langle R_N^2 \rangle$	±	$\langle R_N^2 \rangle$	±	$\langle R_N^2 \rangle$	±
26	53.079[a]	0.0004				
36	78.382[a]	0.0009				
50	116.18	0.13	104.30	0.16	100.25	0.19
52	121.641	0.002				
72	179.330	0.004				
100	265.10	0.48	238.32	0.50	228.82	0.45
104	277.829	0.007				
144	409.024	0.016				
150	429.23	0.64	384.47	0.83	369.46	0.77
200	602.40	1.23	540.75	0.92	521.15	1.30
208	632.800	0.033				
250	788.74	1.16	704.27	1.83	678.32	1.38
288	930.478	0.074				
300	978.00	2.39	876.02	2.22	840.31	1.97
350	1170.99	2.07	1049.08	2.40	1013.73	2.12
400	1365.20	3.02	1232.06	3.04	1186.61	2.91
416	4138.098	0.154				
450	1577.02	2.76	1414.52	3.40	1360.75	2.72
500	1784.00	4.83	1600.59	3.48	1541.05	3.90
576	2113.048	0.356				
600	2217.00	5.32	1987.66	4.53	1910.82	4.01
700	2660.00	6.15	2370.26	5.37	2297.66	5.22
750	2877.69[b]	11.60				
800	3121.60	9.24	2793.67	7.45	2693.10	7.46
832	3261.866	0.756				
900	3571.20	8.42	3199.53	7.95	3084.58	7.58
1000	4050.0	10.7	3627.26	8.38	3501.43	9.12
1152	4789.081	1.794				
1250	5288.41[b]	20.49				
1664	7388.548	3.923				
2000	9197.5	17.7	8237.1	25.0	7901.4	19.5
2304	10846.921	9.542				
3000	14775.8	29.0	13234.5	36.0	12734.1	35.5
3328	16745.239	21.449				

2D Lattices: Enumerations

N	SQ: $\langle R_N^2 \rangle$	Tri: $\langle R_N^2 \rangle$	Hex: $\langle R_N^2 \rangle$	N	SQ: $\langle R_N^2 \rangle$	Tri: $\langle R_N^2 \rangle$	Hex: $\langle R_N^2 \rangle$
1		1.0000		15		43.2197	
2	2.6667	2.4000	3.0000	16	51.9925	47.5189	61.1324
3		4.2174		17		51.9497	
4	7.0400	6.3495	8.2500	18	61.7665	56.5084	72.5270
5		8.7406		19		61.1912	
6	12.5744	11.3631	15.0000	20	72.0765		84.4624
7		14.2039		22	82.8958		97.0096
8	19.0128	17.2422	22.5000	24	94.2010		110.0859
9		20.4665		26	105.9719		123.7028
10	26.2425	23.8664	31.1823	28			137.8200
11		27.4325		30			152.4333
12	34.1871	31.1473	40.3410	32			167.5176
13		35.0339		34			183.0648
14	42.7864	39.0564	50.4855				

2D Lattices: Monte Carlo

	SQ		Tri		Hex	
N	$\langle R_N^2 \rangle$	±	$\langle R_N^2 \rangle$	±	$\langle R_N^2 \rangle$	±
50	278.85	0.63	257.15	0.81	322.39	0.81
100	777.52	2.13	721.14	1.95	902.02	2.12
150	1428.51	3.87	1310.44	4.50	1646.90	5.72
200	2195.2[c]	6.5	2002.46	7.15	2511.31	9.94
250	3066.86	9.13	2816.4	10.9	3517.5	12.3

Table I (Continued)

2D Lattices: Monte Carlo

	SQ		Tri		Hex	
N	$\langle R_N^2 \rangle$	±	$\langle R_N^2 \rangle$	±	$\langle R_N^2 \rangle$	±
300	3998.2	15.0	3721.3	13.9	4624.9	15.3
350	5083.6	16.1	4645.1	17.6	5834.7	23.0
400	6153.9[c]	20.5	5756.0	23.0	7093.8	22.1
450	7404.0	25.0	6805.6	30.3	8476.7	29.4
500	8628.5	33.8	8061.6	34.3	10039.0	41.3
600	11335.5[c]	39.4				

3D Continuum

	$d = 0.1$		$d = 0.25$		$d = 0.50$		$d = 0.75$		$d = 0.99$	
N	$\langle R_N^2 \rangle$	±	$\langle R_N^2 \rangle$	±	$\langle R_N^2 \rangle$	±	$\langle R_N^2 \rangle$	±	$\langle R_N^2 \rangle$	±
50	50.82	0.17	57.22	0.25	88.25	0.26	123.86	0.38	157.36	0.49
100	101.35	0.62	120.65	0.63	200.45	0.64	288.64	0.96	366.47	1.29
150	153.59	0.76	187.51	0.70	322.77	1.23	466.65	1.45	595.84	1.76
200	204.55	1.02	257.24	1.28	457.83	1.91	661.89	3.32	846.18	3.35
250	258.49	1.22	326.92	1.32	591.35	2.16	867.16	3.66	1099.09	4.55
300	307.62	1.58	400.73	1.61	731.95	2.89	1071.01	4.07	1367.32	4.69
350	360.91	1.74	474.48	2.44	875.83	2.97	1291.59	5.57	1636.29	8.59
400	411.79	2.02	550.21	1.97	1023.60	3.78	1511.12	5.93	1924.5	10.3
450	464.12	2.52	626.59	3.16	1173.02	5.15	1742.50	7.66	2216.8	12.3
500	523.62	2.05	713.85	3.14	1336.52	7.47	1973.22	9.73	2524.8	10.9
600	630.80	3.15	864.57	3.74	1672.49	8.17	2460.9	11.1	3148.0	17.0
700	726.24	3.34	1026.62	5.40	1993.50	8.02	2951.1	13.1	3766.6	24.4
800	844.83	4.31	1209.20	5.97	2329.1	10.2	3431.0	16.6	4398.3	24.1
900	951.76	4.23	1370.89	6.34	2667.2	14.7	3936.9	23.5	5039.5	29.4
1000	1053.33	5.00	1527.19	6.64	3060.8	13.2	4458.4	24.7	5712.7	29.9

2D Continuum

	$d = 0.1$		$d = 0.25$		$d = 0.50$		$d = 0.75$		$d = 0.99$	
N	$\langle R_N^2 \rangle$	±	$\langle R_N^2 \rangle$	±	$\langle R_N^2 \rangle$	±	$\langle R_N^2 \rangle$	±	$\langle R_N^2 \rangle$	±
50	63.44	0.24	111.32	0.40	237.67	0.81	308.64	1.01	365.70	0.17
100	147.35	0.48	300.83	1.04	667.03	2.13	863.69	2.50	1022.57	3.72
150	246.68	0.96	542.11	1.68	1229.82	4.51	1582.30	6.32	1873.25	1.12
200	360.13	0.40	831.51	3.04	1891.02	6.66	2428.60	8.83	2851.41	9.85
250	484.96	1.74	1157.61	5.00	2620.0	12.7	3407.5	12.0	4010.34	2.49
300	625.45	2.15	1520.15	5.87	3451.3	16.8	4469.4	14.1	5286.9	23.0
350	777.61	3.21	1918.89	6.13	4355.5	21.0	5615.6	23.7	6630.28	4.48
400	931.35	4.26	2347.4	11.3	5311.7	19.2	6880.3	28.1	8098.5	32.1
450	1106.94	5.01	2772.1	10.4	6311.5	28.2	8189.4	36.6	9659.74	6.71
500	1290.58	6.40	3284.5	14.3	7409.5	37.3	9627.5	40.2	11247.0	52.5
600	1663.71	6.45	4325.0	17.9	9789.6	41.8	12628.1	57.7	14809.4	53.1
700	2106.80	9.04	5347.6	23.3	12268.9	64.0	15939.7	69.7	18681.4	95.6
800	2536.8	11.2	6394.8	28.9	14946.5	80.0	19450.3	98.3	22917.8	99.0
900	3018.4	10.0	7841.8	47.5	17887.4	96.3	23239.5	75.5	27233	124
1000	3544.4	12.1	9211.4	48.9	20931.9	83.2	27272	122	31728	122

[a] Nickel, B. G., private communication. All values with N an even multiple of 26 or 36 were provided by Professor Nickel. [b] Reference 6. All points recorded on p 161 of this reference are included in the fit. [c] These points are obtained from ref 6. All points listed on pp 148 and 149 of this reference are included in the fit.

One convenient way of expressing the factor β for the walk is as

$$\beta = KV_0$$

where V_0 represents the volume of a bead of the chain. For a nearest-neighbor lattice walk, the bead diameter is equal to the lattice spacing. Thus, for a simple cubic lattice, K represents the ratio of the volume of a unit cell to that of a sphere of diameter 1; that is, $K = 6/\pi$. For a continuum walk in D dimensions, $K = 2D/\rho\pi d^3$.

The exact value of K for a given continuum walk is not easily computed; however, it is a simple matter to establish bounds (but the result quoted in ref 11 is incorrect). As an extreme, consider the chain beads to comprise a random, close-packed hard-sphere fluid. The density of this fluid is known[25] to be 0.637, and so $K > 1/0.637 = 1.57$. Note that this limit is independent of bond length. An upper bound may also be computed. A single bead excludes a volume of $8V_0$ to the centers of other beads, but this must be shared with other beads whose own excluded volume intrudes on this space. If the only sharing beads are nearest neighbors along the chain, then the excluded volume is a sphere of radius d that has three subvolumes: two regions where the excluded-volume spheres of neighboring beads overlap, and a region excluded solely by the bead under consideration. We find $K < 5.5$ if $d = a$. If $d < a/2$, then there may be no sharing beads, and so for this case $K < 8$. As $d \to 0$, we anticipate that K should approach 8, the limit for an infinitely dilute hard-sphere gas. We do not know the density of a random, close-packed hard-disk fluid, but crude experiments with pennies suggest that the lower limit of K should be close to 1.15. As $d \to 0$, we expect that K will tend to 4. Values of the bounds on K for the values of d used in this study are listed in Table III.

5. Analysis of Continuum Results

Table I summarises the results for continuum walks, both in two and three dimensions as a function of the diameter d with $a = 1$. Table III shows the values of K obtained by inverting (8) or (11) and fitting this value of z versus $N^{1/2}$ or N. This procedure appears less reliable as d decreases, so for $d < 0.5$ we have roughly interpolated

Table II
Fitted and Extrapolated Coefficients

lattice	B	B'	A	A'
	3D Lattices			
	$\frac{\langle R_N^2\rangle}{N^{1.1772}} = B + \frac{B'}{N^{0.465}} + \ldots \alpha^2 = Az^{0.3544} + A^{-0.5756} + \ldots$			
SC	1.1995 ± 0.0021	−0.196 ± 0.046	1.78 ± 0.01	−0.01 ± 0.03
BCC	1.0727 ± 0.0032	−0.137 ± 0.087	1.74 ± 0.01	−0.06 ± 0.03
FCC	1.0334 ± 0.0034	−0.115 ± 0.100	1.73 ± 0.01	−0.05 ± 0.03
	$\frac{\langle R_N^2\rangle}{N^{1.176}} = B + \frac{B'}{N^{0.47}} + \ldots \alpha^2 = Az^{0.352} + A'z^{-0.588} + \ldots$			
SC	1.2121 ± 0.0021	−0.282 ± 0.048	1.79 ± 0.01	−0.15 ± 0.03
BCC	1.0844 ± 0.0013	−0.276 ± 0.089	1.76 ± 0.01	−0.12 ± 0.03
FCC	1.0449 ± 0.0034	−0.209 ± 0.100	1.74 ± 0.01	−0.09 ± 0.03
	$\frac{\langle R_N^2\rangle}{N^{1.1772}} = B + \frac{B'}{N} + \ldots \alpha^2 = Az^{0.3544} + A'z^{-1.6456} + \ldots$			
SC	1.187 ± 0.001	−1.30 ± 0.02	1.758 ± 0.05	−0.21 ± 0.01
BCC	1.065 ± 0.001	−0.90 ± 0.04	1.73 ± 0.05	−0.09 ± 0.01
FCC	1.026 ± 0.001	−0.93 ± 0.03	1.72 ± 0.05	−0.08 ± 0.01
	2D Lattices			
	$\frac{\langle R_N^2\rangle}{N^{1.5}} = B + \frac{B'}{N^{0.66}} + \ldots \alpha^2 = Az^{0.5} + A'z^{-0.16} + \ldots$			
SQ	0.77 ± 0.01	0.12 ± 0.01	1.37 ± 0.01	0.10 ± 0.03
Tri	0.71 ± 0.01	0.16 ± 0.10	1.35 ± 0.01	0.13 ± 0.08
Hex	0.88 ± 0.01	0.12 ± 0.05	1.37 ± 0.01	0.11 ± 0.01
	$\frac{\langle R_N^2\rangle}{N^{1.5}} = B + \frac{B'}{N} + \frac{B''}{N^{1.5}} + \ldots \alpha^2 = Az^{0.5} + A'z^{-0.5} + A''z^{-1} + \ldots$			
SQ	0.77 ± 0.01	1.06 ± 0.05	1.37 ± 0.01	0.34 ± 0.02
Tri	0.71 ± 0.01	0.94 ± 0.13	1.36 ± 0.01	0.26 ± 0.03
Hex	0.88 ± 0.01	1.77 ± 0.36	1.38 ± 0.01	0.73 ± 0.15
	$\frac{\langle R_N^2\rangle}{N^{1.5}} = B + \frac{B'}{N} + \frac{B''}{N^2} + \ldots \alpha^2 = Az^{0.5} + A'z^{-0.5} + A''z^{-1.5} + \ldots$			
SQ	0.77 ± 0.01	0.75 ± 0.01	1.37 ± 0.01	0.42 ± 0.01
Tri	0.71 ± 0.01	0.55 ± 0.03	1.36 ± 0.01	0.29 ± 0.02
Hex	0.89 ± 0.01	1.33 ● 0.01	1.38 ± 0.01	0.86 ± 0.01

to estimate K. The fitted value for $d = 0.99$ is slightly less than the upper bound, reflecting the low monomer density of an isolated chain. For small values of d, we estimate that K is close to the value for an ideal chain.

The approximate values of K of Table III were used to compute the values of z used in the plot of Figure 2, showing the Monte Carlo values of α^2 as a function of z on the same axes as (8) and (4). It will be seen that there is good correspondence between the points and the curve, except for the smaller values of d.

6. Discussion and Conclusions

Figure 1 shows small but distinct differences between the values obtained for the different lattices. These differences are more evident for the 3D data but are displayed by the 2D data as well if plotted over the same range of z. It is not clear whether these differences are due to inaccuracies in the exponents or corrections to scaling we have used, but the following discussion considers the possibility that they arise from other sources.

The two-parameter hypothesis claims that, for sufficiently long chains, the only relevant physical quantities are the total excluded volume between chain segments

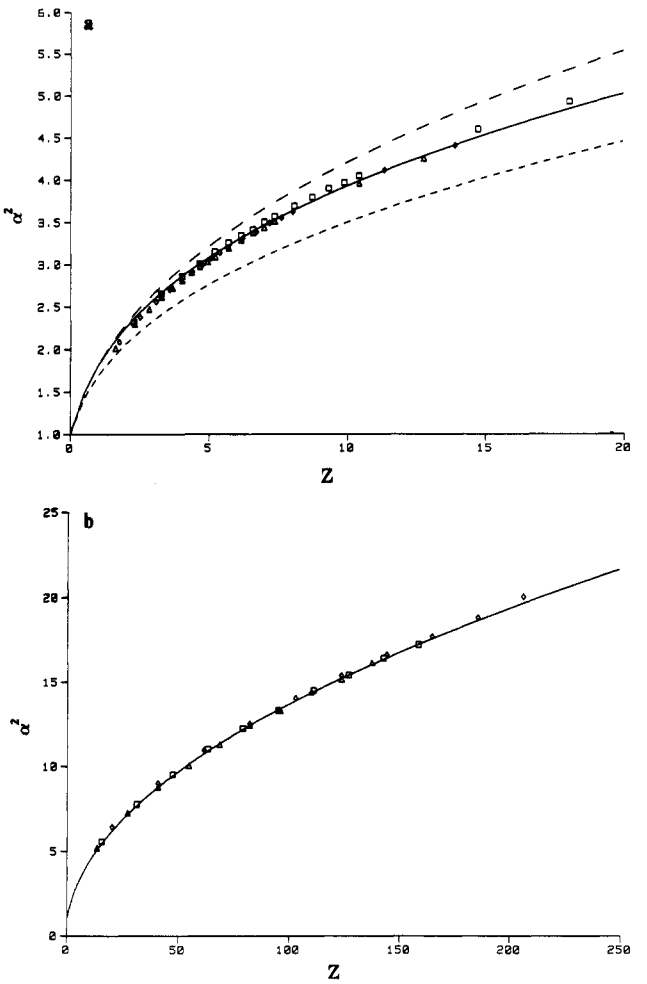

Figure 1. (a) 3-Dimensional lattice data vs z: (□) simple cubic lattice; (◇) body-centered cubic lattice; (△) face-centered cubic lattice. Lower curve, eq 6; middle curve, eq 8; upper curve, eq 4. (b) 2-Dimensional lattice data vs z: (□) square lattice; (◇) hexagonal lattice; (△) triangular lattice. Curve: eq 11.

Table III
Maximum and Fitted/Interpolated Values of K

	3 dimensions		2 dimensions	
diameter	K_{max}	K_{fit}	K_{max}	K_{fit}
1.00	5.5		2.436	
0.99	5.5453	5.5 ± 0.4	2.4582	2.2 ● 0.1
0.75	6.8148	6.5 ± 0.4	3.1236	2.8 ± 0.2
0.50	8	7.4 ± 0.4	4	3.7 ● 0.2
0.25	8	~7.9	4	~3.9
0.10	8	~8	4	~4

and the dimension of ideal chains. If we accept this, then the most likely source of the differences is the definition of the effective excluded volume between monomers, β. The great advantage of a lattice in problems of this type is that all occupiable sites are clearly separated, and there is no overlap of the excluded volume of one monomer with that of another. One is therefore tempted to believe that the excluded volume associated with a monomer is the volume associated with the lattice site. A counterexample was discussed some years ago by Tanaka[12] following a question raised by Yamakawa,[26] namely, that computed values of α^2 vs z for the cubic lattices may be placed on a single composite curve but that values of α^2 for four-choice self-avoiding walks on the simple cubic lattice fall significantly below this composite curve. The short-range geometrical constraint limiting the walker to four choices must somehow be equivalent to modifying the effective excluded volume, which is a long-range effect. Consider a "four-choice random walker" who has arrived at a given

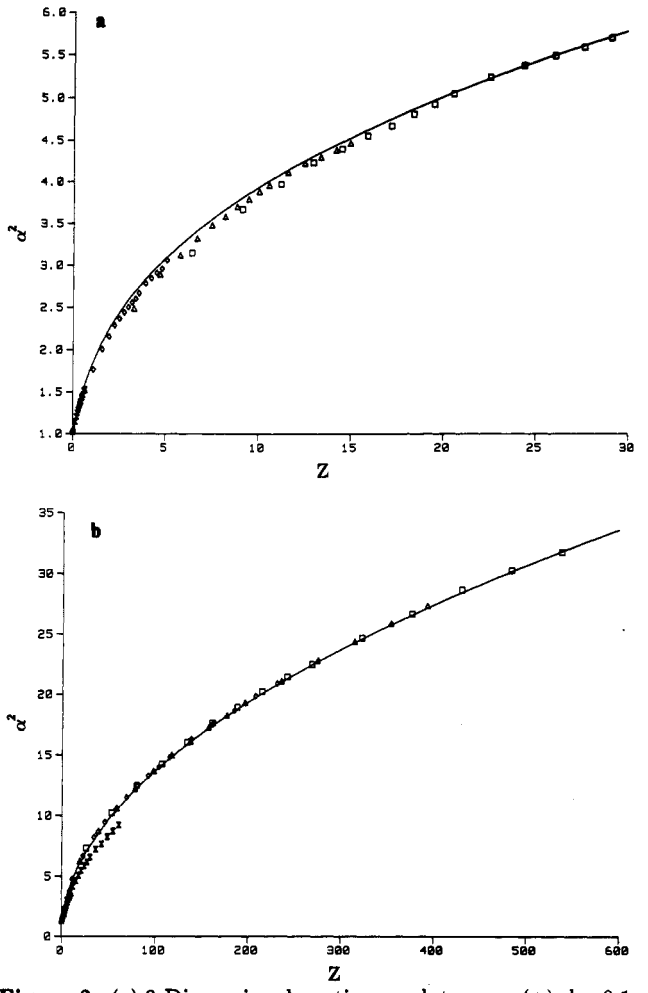

Figure 2. (a) 3-Dimensional continuum data vs z: (▲) $d = 0.1$; (⧖) $d = 0.25$; (◊) $d = 0.50$; (△) $d = 0.75$; (□) $d = 0.99$. Curve: eq 8. (b) 2-Dimensional continuum data vs z. Symbols as in (a). Curve: eq 11.

lattice site. Any of the six surrounding sites are available for the next step, except the site immediately behind, the site immediately ahead, and any of the four remaining sites that happens to be occupied, but, in this respect, the walker is not different from a "five-choice random walker" for whom the site immediately ahead is occupied. It is very difficult to compute the effective excluded volume for such a walk, but if we define *two steps* of the four-choice walk to be a single "Kuhn step", then we consider an $N/2$ step walk for which the short-range geometrical constraint has been reduced (though not eliminated). We thus expect the dimensions of these walks to be intermediate between $N/2$ step walks on the FCC lattice and N step walks on the SC lattice, and this is in fact the case.[27] The clear implication of the above discussion is that β is not always just the volume per lattice site. The question is presently under more detailed study.

Putting aside the question of these small discrepancies, it remains clear that the mean-square end-to-end distance of a self-avoiding walk on a lattice or in the continuum may be well described by an *approximate* two-parameter theory. The calculation of the quantity K is in itself a many-body problem, but we believe the viewpoint proposed here to be useful. The agreement shown in Figure 2 is very satisfying, though not conclusive. It is always possible to choose values for K so that the data will fit many equations very well, although any appropriate choice must be consistent with lattice walk data.

The very fact that the summation of the two-parameter series does not yield the correct asymptotic amplitude for lattice walks demonstrates that the traditional two-parameter theory is not strictly correct. It is probable that the two-parameter series (2) is but a limiting case of the small z expansion of the true, unknown, function. As excluded volume increases, higher order terms, which have hitherto been unimportant, become increasingly significant. There is yet much fascinating work to be done on the two-parameter expansion.

In view of the above comments, (11) and (8) must be seen as a crude cobbling together of two results that have dissimilar theoretical bases. Nonetheless, for practical purposes, these formulas can be expected to provide a reasonably accurate description of the mean-square length of self-avoiding walks, nor is there any real obstacle to the construction of similar two-parameter formulas for other quantities of interest, such as the radius of gyration and second osmotic virial coefficient.

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