# Conformation of Linear Polymers in Three Dimensions

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By significantly extending the existing exact enumeration results, and by combining several independent analysis methods, the authors obtain accurate estimates of the leading "scaling" exponent and the amplitudes for the $d=3$ linear-polymer radius-of-gyration problem. Specifically, they find that the mean square end-to-end distance of an $N$-step self-avoiding walk on an fcc lattice is given by the expression $\rho_N \sim AN^{2\nu}[1+B/N^{\Delta}+C/N]$ with $\nu \cong 0.5875$, $\Delta \cong 0.470$, $A \cong 1.05$, $B \cong -0.3/A$, and $C \cong 0.25$.

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What is the shape of a long polymer molecule? This question has intrigued the best minds for many decades, and stimulated a variety of disciplines ranging from mathematics and physics to chemistry and biology. It soon became clear that the simplest model for the structure, assuming the position of each successive link in the polymer to be a random variable, was unrealistically simple. The chain must be enlarged simply because of the fact that two links of the chain cannot be in the same position of space. This "excluded-volume effect" is incorporated by describing the chain not as a random walk but as a self-avoiding walk, and an elegant formula was advanced by Flory to describe the dependence of the rms radius of gyration $R_g$ on the polymerization index $N$: $R_g \sim N^{\nu}$, with $\nu = 3/(d+2)$.[1]

The modern era of polymer statistics has been characterized by a long-standing ambivalence[1] concerning the domain of validity of the Flory formula; it works perfectly for $d=1$ and for $d \geq 4$, and recently an argument has been advanced to support the Flory prediction $\nu = \frac{3}{4}$ for $d=2$.[2] Thus it is tempting to expect that it works for $d=3$ also. Indeed experimental data are frequently analyzed by assuming $\nu = \frac{3}{5}$, and this value is consistent with most Monte Carlo calculations.[3] With the advent of the renormalization group (RG), there arose the possibility that $\nu < \frac{3}{5}$, and the most accurate calculations[4,5] now suggest $\nu = 0.5880 \pm 0.0015$. A subsequent analysis of some *experimental* data suggested that possibly $\nu = 0.5860 \pm 0.0040$.[6] Nonetheless, what has traditionally been the *most* accurate[7] method of scaling exponent calculation—extrapolation from exact enumeration—gives the Flory value.[8]

Our purpose here is to demonstrate clearly that $\nu$ is significantly *less* than the Flory value for $d=3$. To this end, we have accomplished the following two nontrivial tasks: (a) We have extended existing enumeration data significantly by calculating two *new* terms for $\rho_N$ for the fcc lattice, representing roughly 100 times as much computer time as previously expended on this problem, and (b) we have combined a number of independent extrapolation procedures, all of which incorporate "corrections to scaling," in an effort to isolate the correct value of the leading scaling exponent $\nu$. Here $\rho_N$ is the mean square end-to-end distance of a self-avoiding walk (SAW)—a random walk with only the steric excluded-volume constraint that two monomers cannot be in the same place. Asymptotically, $\rho_N$ scales in the same fashion as $R_g^2$, with the general form

$$\rho_N = AN^{2\nu}[1+B/N^{\Delta}+C/N+\ldots]. \quad (1)$$

Previous series work has neglected the presence of the leading nonanalytic and analytic correction-to-scaling terms $B/N^{\Delta}$ and $C/N$. Our main result is that with careful incorporation of the correction terms, we can obtain an estimate of the leading exponent that is of the same accuracy as that obtained from RG calculations:

$$\nu = 0.5875 \pm 0.0015. \quad (2)$$

As a by-product, we also obtain the first series estimate of the amplitudes $A$, $B$, $C$.

*Exact enumerations for the fcc lattice.*—We focus attention on the close-packed fcc lattice, since oscillations due to the two-sublattice structure are not present. However, the large coordination number ($z=12$) means that at each successive order there are about 10 times as many walks as at the previous order. Roughly 85 h of central-processing-unit time on an IBM 3081 computer were required to enumerate exactly the $c_{11} = 176\,064\,704\,412$ and $c_{12} = 1\,791\,455\,071\,068$ walks of 11 and 12 steps, respectively. We find the results $\rho_{11}c_{11} = 1\,144\,305\,206\,478$ and $\rho_{12}c_{12} = 16\,308\,699\,430\,896$. (Since almost 1000 h of computer time would be required to enumerate the roughly $18\times10^{12}$ walks with 13 steps, this calcu-

lation was not attempted. Several checks were carried out, based on recent exact results concerning the end-point probability distribution.)

*Analysis of extended series: the correlation length exponent* $\nu$.—The key problem is to estimate the "true" value of $\nu$ from the knowledge of the first twelve values of $\rho_N$. We found that standard methods like Padé approximants and their variations[9] do not work well because of the significant influence of the correction-to-scaling terms in (1). Fortunately, however, we shall see that a delicate combination of different methods does produce consistent exponent estimates. The main lesson that is illustrated by our analysis is that reliance on only one or two methods can produce results that are internally consistent yet nonetheless are wrong. For example, we show in Fig. 1(a) the predictions of three methods, I, II, and III; other methods were used, but these three gave the most reliable and consistent results for all lattices and all cases studied. Plotted as the top and bottom curves are the functions

$$\nu_{\mathrm{eff}}{}^{\mathrm{I}}(N) = \tfrac{1}{2}N\left(\frac{\rho_{N+1}}{\rho_N}-1\right) = \nu - \frac{B}{2N^{\Delta}} - \frac{C}{2N} + \frac{\nu(2\nu-1)}{2N} + \cdots, \tag{3a}$$

$$\nu_{\mathrm{eff}}{}^{\mathrm{II}}(N) = \tfrac{1}{2}\frac{\ln(\rho_N/\rho_{N-1})}{\ln[N/(N-1)]} = \nu - \frac{B}{2N^{\Delta}} - \frac{C}{2N} + \cdots, \tag{3b}$$

where the second equalities of (3a) and (3b) follow from substitution in (1). An eyeball fit to the exact points suggests that possibly $\nu = \frac{3}{5}$ (see arrow). However, we see from the form of (3a) and (3b) that if the correction-to-scaling exponent $\Delta$ satisfies $\Delta < 1$, then the limiting slope is $+\infty$ providing that the amplitude factor $B$ is negative. Thus the data for $\nu_{\mathrm{eff}}{}^{\mathrm{II}}(N)$ must have a *maximum*. We note in passing that this situation parallels that of the $d=2$ triangular lattice,[10] for which $B$ is positive so that both curves approach $\nu$ with slope $-\infty$ and hence $\nu_{\mathrm{eff}}{}^{\mathrm{I}}(N)$ has a *minimum*.

The third set of data shown are for method III, which eliminates the $1/N$ analytic correction that is present in both (3a) and (3b):

$$\nu_{\mathrm{eff}}{}^{\mathrm{III}}(N) = \frac{(\rho_{N+1}-\rho_N)(\rho_N-\rho_{N-1})}{\rho_N{}^2 - \rho_{N+1}\rho_{N-1}} = \nu + O(N^{-\Delta}). \tag{3c}$$

To some extent, this method corresponds to taking successive intercepts of estimates of the sort

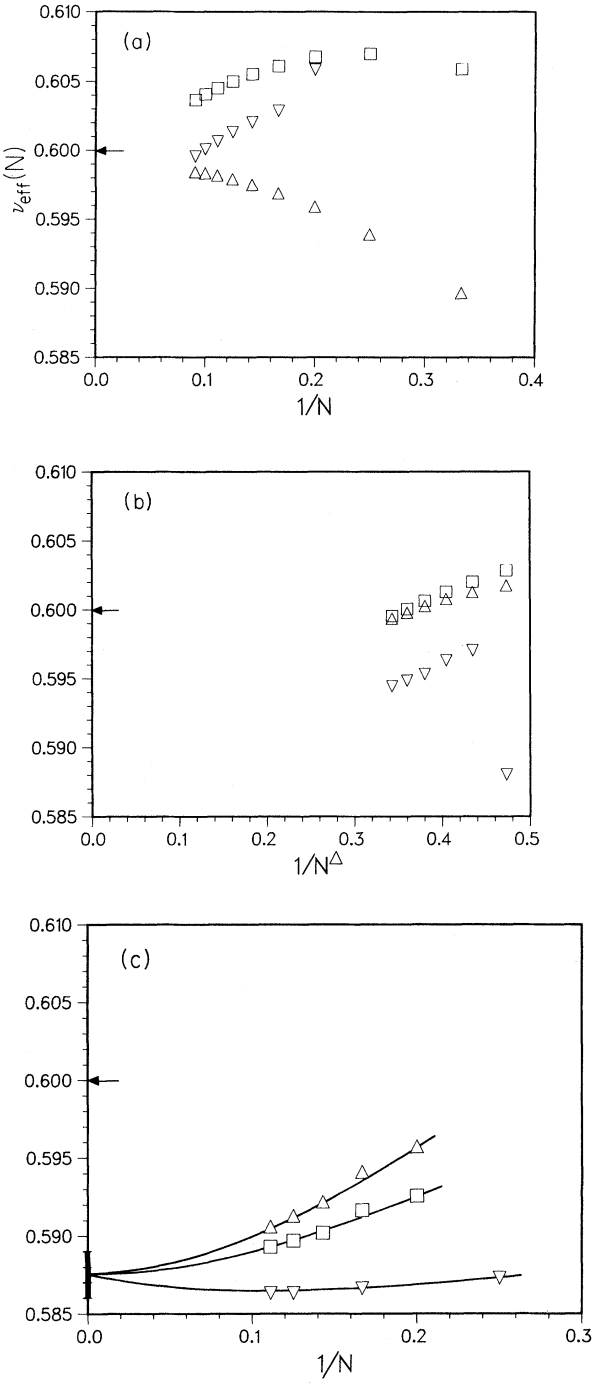


FIG. 1. (a) The dependence on $1/N$ of the three sequences of successive approximations $\nu_{\mathrm{eff}}(N)$ to the correlation length exponent $\nu$ for the fcc lattice SAW problem. Squares, Eq. (3a); triangles, Eq. (3b); and inverse triangles, Eq. (3c). (b) The sequence of "first intercepts," obtained by placing a straight-line segment through successive pairs of points in (a). (c) The "second intercepts." The arrow denotes the Flory value $\nu = \frac{3}{5}$.

formed in methods I and II; therefore it is not surprising that this method serves to extrapolate the very small degree of curvature present in curves I and II and therefore suggests that $\nu < \frac{3}{5}$. Note that Ref. 8 calculates (3c) through order $N = 10$ but does not extrapolate the trend indicated in Fig. 1(a), and hence concludes that $\nu = \frac{3}{5}$.

We now address the rather subtle question of how to extrapolate the trends present in methods I, II, and III. The essential point is that one must choose the appropriate variable $x$ to use as the abscissa in order that the slight curvature is minimized and reliable extrapolation can be made.

All our definitions of $\nu_{\rm eff}(N)$ [e.g., Eqs. (3a)–(3c)] are of the form

$$\nu_{\rm eff}(N) = \nu_{\rm true} + 1/N^{\Delta} + 1/N . \quad (4a)$$

Our estimates of $\nu_{\rm true}$ are based on forming a sequence of intercepts of successive pairs of points (called "first intercepts") and then plotting these first intercepts against a suitable abscissa. We then repeat the procedure and form an improved sequence of estimates of $\nu_{\rm true}$ (called "second intercepts"). This procedure can be continued until the points cease to be smoothly behaved.

One must be prudent in choosing the abscissa, since this choice will determine the curvature of the resulting plot. For certain choices of the abscissa, data obeying (4a) asymptotically should become roughly linear, thereby enabling reliable estimates to be made for $\nu_{\rm true}$. To see this, let $u = 1/N^{\theta}$, where $\theta$ is a free parameter. Substituting in (4a), we find $\nu_{\rm eff}(u) = \nu_{\rm true} + u^{\Delta/\theta} + u^{1/\theta}$. The first intercepts are then of the form

$$I(u) = \nu_{\rm true} + (1 - \Delta/\theta)u^{\Delta/\theta} + (1 - 1/\theta)u^{1/\theta} . \quad (4b)$$

Two very useful choices are as follows: (i) $\theta = 1$ [here (4b) predicts that the last term is zero, and hence there is no maximum and the behavior is monotonic; thus we plot the sequence $I(u)$ against $u^{\Delta/\theta} = N^{-\Delta}$], and (ii) $\theta = \Delta$ [here the second term in (4b) is zero, so that we plot $I(u)$ against $u^{1/\theta} = 1/N$]. Both methods give comparable final estimates for $\nu_{\rm true}$.

As an example of the sort of plots that result, we set $\theta = 1$ and show in Fig. 1(a) the functions plotted against $1/N$. In Fig. 1(b) the successive intercepts are seen to be nonhorizontal, indicating that the original data have considerable curvature. The intercepts extrapolate toward a value of $\nu$ considerably *lower* than $\frac{3}{5}$, and on this basis

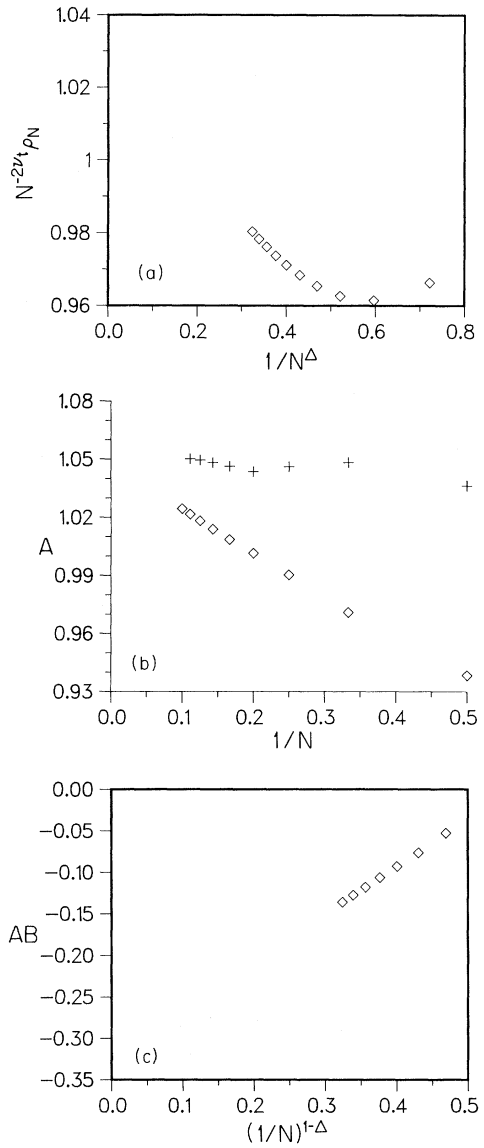


FIG. 2. Sequences of estimates used to obtain the amplitudes $A$ and $B$. (a) The dependence on $(1/N)^{\Delta_t}$ of the function $N^{-2\nu_t}\rho_N$. The limiting intercept of this graph should be $A$, while the limiting slope should be $BA$. Accordingly, in (b) we show the first intercepts (diamonds) and also the second intercepts (crosses), while in (c) we show the slopes of line segments joining successive pairs of points of (a). All graphs assume the trial values $\nu_t = 0.5875$ and $\Delta_t = 0.470$; the reason for the relatively large error bars quoted in the text is that both $A$ and $B$ depend rather sensitively on both $\nu_t$ and $\Delta_t$.

we feel that we can exclude with some degree of confidence the possibility that the Flory formula is correct for $d = 3$. To obtain the most precise estimate of $\nu$, we show in Fig. 1(c) the second intercepts. Again, considerable regularity is

displayed. Successive estimates must approach $\nu_{\text{true}}$ with *zero* slope if plotted against $1/N$.

The amplitudes $A$, $B$, and $C$ in Eq. (1) were obtained *seriatum*. Firstly, we multiply both sides of (1) by $N^{-2\nu_t}$, where $\nu_t$ is a trial value of $\nu$. The left-hand side is then plotted against $1/N^{\Delta t}$, where $\Delta_t$ is a trial value of $\Delta$. A plot using the choice $\nu_t$ of (2) and $\Delta_t = 0.470^4$ is shown in Fig. 2(a). The amplitudes $A$ and $B$ are then obtained from the intercept and slope, respectively. By studying the dependence on $N$ of the sequence of intercepts obtained by successive pairs of points [Fig. 2(b)], we find $A \cong 1.05 \pm 0.03$. The estimate $B \cong -0.30/A$ is similarly obtained by studying the sequence of successive slopes [Fig. 2(c)]. *Unbiased* estimates of $B$ may be obtained by calculating the limiting slopes of Fig. 1(b). Comparable final estimates are obtained. $C$ can be similarly obtained by changing the $x$ axis of Fig. 1(a) to $1/N^{\Delta}$, and Fig. 1(b) to $1/N$. We find $C \cong 0.25$ from the limiting slopes.

In summary, then, the situation for the $d=3$ SAW problem (the $n=0$ limit of the $n$-vector model) is somewhat parallel to that for the $n=1$ problem a few years ago, when series analysis predicted $\gamma = \frac{5}{4}$ yet RG predicted a value roughly 1% lower. Largely through the careful and clever efforts of Nickel and others,[7] this discrepancy was resolved: Analysis of extended series incorporating correction-to-scaling factors indicated that the RG results are indeed correct. We claim in this work to have successfully carried out the analogous efforts for the $n=0$ problem, and again it appears that the RG results are correct. Thus the Flory formula, while correct for the integer values $d=1$, 2, and 4, *fails for the most physically interesting case* $d=3$.

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