

Excluded-volume expansion of polymer chains: A Monte Carlo study of the scaling properties

I. Webman and Joel L. Lebowitz

Departments of Mathematics and Physics, Rutgers University, New Brunswick, New Jersey 08903

M. H. Kalos

Courant Institute of Mathematical Sciences, New York University, New York, New York 10012

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Results are presented of Monte Carlo simulations of continuum-model polymer chains which results confirm the idea that for long chains the degree of expansion due to excluded volume depends on the interaction range σ , on N , the number of links, and on the link size a through a single variable $z \propto (\sigma/a)^3 \sqrt{N}$. The expansion factor $\psi(z)$ is very close in form to that found by Lax, Barrett, and Domb for lattice models of a polymer. For $z \geq 2$, $\psi(z)$ follows a power law predicted by Flory. For finite chains there are corrections to $\psi(z)$ which depend on N and on the form of the interaction.

I. INTRODUCTION

In this note we describe Monte Carlo studies of the swelling of a polymer chain in a good solvent resulting from excluded volume interactions. The pioneering work of Flory,¹ as well as more recent studies,²⁻⁵ agree that for a chain of N units of length a , with a repulsive interaction $U(r)$ between any two units,

$$R^2/Na^2 = \alpha^2(z, N) - \psi(z) \quad \text{as } N \rightarrow \infty. \quad (1)$$

Here R^2 is the squared end-to-end distance of the chain which can depend generally on N and the form of the potential $U(r)$:

$$z = (3/2\pi)^{3/2} B \sqrt{N} / a^3, \quad B = \int (1 - e^{-\beta U(r)}) d\vec{r}. \quad (2)$$

In our model system $U(r)$ is strongly repulsive for small values of r and vanishes for larger r . For a real polymer in a solvent, $U(r)$ will be some effective interaction between parts of the chain which depends both on the polymer and on the solvent.

The physical idea behind this simple universal dependence of α^2 on N and U is that as $N \rightarrow \infty$, the density of the monomers, $\rho \propto N/R^3$, goes to zero, so that the dominant term in the free energy comes from binary interactions in which the dependence on $U(r)$ enters only through B . Indeed, one can obtain a formal power series in z whose coefficients approach a well-defined limit when $N \rightarrow \infty$.^{2,3} This series, however, is not expected to be convergent (it may be asymptotic),⁶ and is thus not useful for finding α^2 for a given U and N . It is therefore in practice supplemented by a power law which was first derived by Flory from the formula

$$\alpha^5 - \alpha^3 = \frac{3}{2} \sqrt{3} z, \quad (3)$$

which for $z \gg 1$ gives

$$\alpha^2 \sim z^{2(2\nu-1)}, \quad \nu = \frac{3}{5}. \quad (4)$$

More recent renormalization-group computations of the critical exponent ν give $\nu \approx 0.588$,⁷ very close indeed to Flory's value. While the asymptotic N dependence of R^2 implied by Eq. (3), $R^2 \sim N^{1.2}$, has been verified (within a few percent) both experimentally² and by computer simulations,⁸ the general validity of Eq. (1) has been checked directly only for lattice systems.

Lax, Barret, and Domb (LBD)⁹ found evidence for the dependence of α^2 solely on z as $N \rightarrow \infty$ and $B \rightarrow 0$. Furthermore, a single function $\psi(z)$ could be fitted to the results on various lattices.

The question then naturally arises of whether Eq. (1) is also valid for more realistic continuum models of polymers. Also of interest are the finite N corrections to α^2 . We describe here Monte Carlo computations which were designed to investigate some of these questions.

II. MODEL AND RESULTS

We studied a continuum chain of beads connected by rigid links. Models of this character are much used in polymer theory for the study of excluded-volume effects. The units in this model represent statistical segments of the polymer molecule rather than single monomers, since the angular correlations between neighbors which characterize real polymer chains are not represented in the model. Any pair of beads along the model chain interacts via the repulsive potential

$$U(r) = \begin{cases} 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 + \frac{1}{4} \right], & r \leq 2^{1/6} \sigma \\ 0, & r > 2^{1/6} \sigma \end{cases} \quad (5)$$

with $\beta\epsilon = 0.1$.

The parameter z in Eq. (2) can be rewritten as

$$z = (3/2\pi)^{3/2} A (\beta\epsilon) \sigma^3 \sqrt{N} / a^3. \quad (6)$$

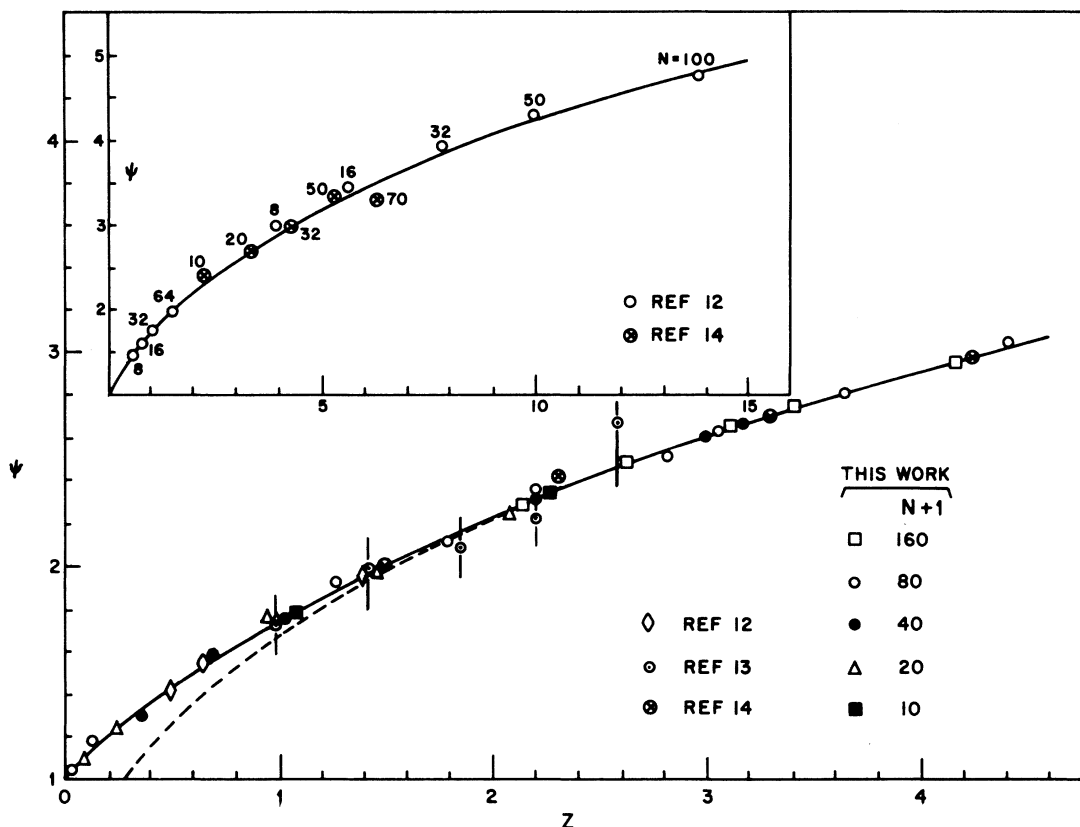


FIG. 1. The data points represent the extrapolated values $\alpha^2(z, N) + Cz/\sqrt{N}$: $C=0.8$ for our results, $C=0.7$ for the results of Ref. 12, $C=1.0$ for the results of Refs. 13 and 14. Solid curves: Eq. (8). Dashed curve: Eq. (9). The error bars of our results are 2–3%. (Numbers in the inset denote values of N .)

[For hard-sphere potentials $A=4\pi/3$, while $A(0.1)=3.22$.]

Equilibrium configurations of chains with N links, $N=4$ –159 and values of σ/a between 0.16 and 0.8, were generated by reptation Monte Carlo dynamics.¹⁰ The results for $\alpha^2(z, N)$ at fixed z increase with N and appear to converge to a limit as $N \rightarrow \infty$. Their behavior is consistent with the relationship

$$\alpha^2(z, N) = \psi(z) - Cz^\mu N^{-\sigma}, \quad (7)$$

with $\sigma=0.5$, $\mu=1.0 \pm 0.1$, and $C \approx 0.8$. The accuracy of Eq. (7) may be judged from Fig. 1 where we plot $(R^2/Na^2 + 0.8z/N^{0.5})$ vs z using all our data. The solid curve is given by the following formula:

$$\psi^{15} = 1 + 20z + 156z^2 + 592z^3 + 2500z^6 \left(1 + \frac{486}{2500} z^{-2}\right). \quad (8)$$

Equation (8) has the same form as Eq. (42) of LBD constructed to fit their lattice results—the only difference is the coefficient of z^6 which was adjusted to fit our results for large z ,

$$\psi(z) \approx (1.68 \pm 0.03)z^{0.4}. \quad (9)$$

When one averages the coefficients of the corresponding equation given by LBD over the lattices they treated, one gets the value 1.663. The values of the first three coefficients in Eq. (8) were obtained by Barrett¹¹ from the series expansion of $\psi(z)$ in powers of z for lattice models. The lattice values of these coefficients agree with those obtained for a continuum model by cluster-expansion calculations.² Thus, while the form of Eq. (8) is *ad hoc*, the coefficients contain only two adjustable parameters which have similar values for lattice and continuum systems.

Baumgärtner and Binder¹² have studied continuum chains of hard-sphere beads connected by rigid links. Their results, extrapolated using the correction term of Eq. (7) with $C \approx 0.7$, are included in the inset of Fig. 1. Although their potential is harder than that of Eq. (5), the corrected results fit the curve given by Eq. (8). Also represented in Fig. 1 are the results for the bead-spring model chains of Ceperley, Kalos, and Lebowitz,¹³ and the results of Bishop, Ceperley, Frisch, and Ka-

los.¹⁴ In these models, the distance between beads is not fixed and a^2 is the average squared distance between adjacent beads. The interactions between beads in these studies is of the same form as Eq. (5) in this work; the values of $\beta\epsilon$ are 0.1 in Ref. 13 and 1.0 in Ref. 14. The results were extrapolated using the correction term in Eq. (7) with $C \approx 1.0$. Our curve lies within the error range of the adjusted results. Thus it seems that the correction to the asymptotic $\psi(z)$ is not universal but depends on the type of potential and on the nature of the distribution function of bond lengths.

We have also evaluated the values of the squared radius of gyration, S^2 . We find that for $z \geq 2$, $R^2/S^2 \approx 6.34$ with no significant z dependence. This ratio approaches 6.0 as $z \rightarrow 0$. In Fig. 2 we compare $\psi_s(z) \equiv S^2(z)/S^2(0)$ with the experimental data on swelling of polystyrene chains in various solvents compiled and analyzed by Ackasu and Han.¹⁵ The values of z for the data were determined from the relation $z = A\tau\sqrt{M}$ where M is the molecular weight, $\tau = (T - \theta)/\theta$, and A is a constant which we adjusted to obtain a fit of the data to our curve in the high- z regime: $A = 9.6 \times 10^{-3}$. Also represented in Fig. 2 are $\psi_F(z)$, the solution of Flory's formula Eq. (3), and $\bar{\psi}_F(z)$, the solution of a modified version of Eq. (3), $\alpha^3 - \alpha^3 = Qz$ where Q was adjusted so that $\bar{\psi}_F(z) \approx \psi_s(z)$ for large values of z . It is apparent that $\psi_F(z)$ approaches the asymptotic power-law behavior more gradually than either $\psi_s(z)$ or the experimental data.

We note that Eq. (7) may be written in the form

$$\alpha^2(z, N) = \psi(z)[1 - K(\sigma/a)^3/\psi(z)], \quad (10)$$

where $K = 0.85$ for our data. For fixed σ/a and N sufficiently large so that $z \approx 2$, $R^2(N)$ will be given by

$$R^2 \propto a^2 N^{2\nu} [1 - K_1(\sigma/a)^{1.8} N^{-0.2}], \quad (11)$$

where $K_1 = K/1.72$. The very slow decay of the correction term in Eq. (11) will result in a modified effective exponent

$$2\nu(\sigma, N) \cong 2\nu + 0.2K_1(\sigma/a)^{1.8} N^{-0.2}, \quad (12)$$

which is slowly varying function of N and σ . The corrections to $\psi(z)$ will therefore be manifested as a correction to the exponent obtained from a power-law fit to the data for finite chains. Indeed, the fact that some of the continuum results for bead chains give exponent values $2\nu = 1.21-1.23$ (Refs. 12 and 14) which are higher than $2\nu \approx 1.2$ obtained for lattice walks indicates a slower approach to the purely z dependent region in continuum chains.

III. DISCUSSION

The data presented here support the hypothesis that for excluded-volume interactions, as represented by short-range repulsive potentials, the expansion factor α^2 is a function of a single parameter z for long chains. For $z \geq 2$, $\psi(z)$ follows a power law $\psi \propto z^{0.4}$ consistent with an excluded-volume exponent $\nu \sim 0.6$. The values of $\psi(z)$ agree with the results for lattice walks with pseudopotential interactions. We also find good agreement with experimental data in both the asymptotic and crossover regimes.

For finite chains we find that α^2 depends on N as well as z , and can depend on the details of the potential. For fixed potential range σ , the approach to the asymptotic limit $N \rightarrow \infty$ is rather slow. Accordingly, the deviation from a power law of the N dependence of R^2 for short chains is not pronounced, and is manifested in somewhat increased values of effective exponents.

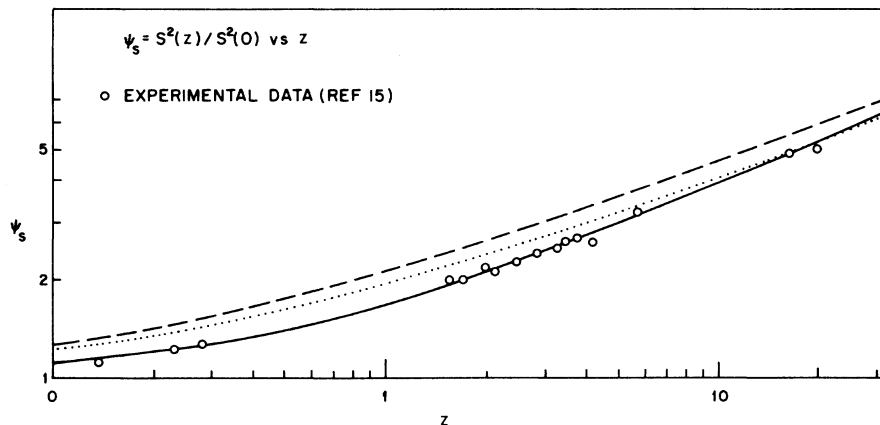


FIG. 2. Experimental data for $\psi_s = S^2(z)/S^2(0)$ for polystyrene in various solvents vs z (Ref. 15). Solid curve: Eq. (8). Dashed curve: Flory's formula Eq. (3). Dotted curve: modified Flory formula (see text).

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