# Effects of Variable Excluded Volume on the Dimensions of Off-Lattice Polymer Chains

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ABSTRACT: The expansion of bead–stick models of polymer chains by excluded volume has been obtained by Monte Carlo methods for chains with ratios $d$ of hard-sphere bead diameter to stick length between zero (no excluded volume) and unity (connected beads touching) for chains of from 9 to 99 beads. We report values of mean-sauare end-to-end length $\langle l^2 \rangle$ and apparent power-law exponents $2\nu = \partial \ln\langle l^2 \rangle / \partial \ln(N\text{-}1)$ for chains of $N$ beads, for eight values of $d$ from 0.30 to 0.93. For the range of chain lengths reported here, the apparent power-law exponent $2\nu$ is not independent of $d$ but rather shows a smooth, gradual transition from the well-known result for $d = 0$ to the previously-reported value for $d = 1$. The variation of $2\nu$ with bead size is remarkably similar to its variation with short-range attractive energy in other models. The results reported here are compared with those obtained by other workers on and off lattices, for hard-sphere and Lennard-Jones potentials, and with predictions of two-parameter and scaling theories.

Although the effect of excluded volume on the size and shape of polymer chains has been much studied over the years, it remains a subject with many unanswered questions. Of particular interest is understanding the dependence of equilibrium chain dimensions upon chain contour length in the presence of excluded-volume interactions. This dependence is often summarized by the logarithmic derivative $2\nu = \partial \ln\langle l^2 \rangle / \partial \ln(N\text{-}1)$ of the mean-square end-to-end length $\langle l^2 \rangle$ with respect to the number $N$-1 of steps in the chain and by its apparent limiting long-chain values. For sufficiently long random-coil chains without excluded-volume interactions (Θ conditions), $2\nu$ is unity. For sufficiently long chains with excluded volume, the venerable mean-field value $2\nu = {}^6/_5$ was long believed and is still often accepted.[1-4] But while some analytical models and computer simulations on lattices yield this result, more recent treatments have led to lower values,[5-8] often in the vicinity of 1.18, while off-lattice simulations[9-17] have given values of $2\nu$ as large as 1.3. These apparent discrepancies suggest a need to understand the physical consequences which arise from the introduction into a polymer model of an impenetrable volume associated with each unit. A number of questions arise as a consequence of recent analytical and numerical calculations[7,8,18] in this area: How large must $N$ be for $2\nu$ to approach its long-chain limiting behavior? What is the relation of model results to the behavior of real chains, of finite length, and to their properties in regimes between good solvent and Θ-solvent conditions? In particular, what is the nature of the transition between excluded-volume and no excluded-volume conditions, both for finite-length chains and in the long-chain limit?

In the course of computer simulation studies of excluded-volume effects upon chain dynamics in the absence of lattice constraints,[16,19] we have obtained mean-square end-to-end lengths $\langle l^2 \rangle$ for bead–stick chains with varying excluded volume. Here we report the equilibrium dimensions obtained in this study, in which the excluded volume is allowed to assume 10 values ranging from no excluded volume, where the ratio $d$ of bead diameter to step length is zero, to the usual self-avoiding walk, where $d$ is unity.[20] Values of $2\nu$ are obtained by fitting $\langle l^2 \rangle$ to linear functions of $\ln(N\text{-}1)$. Results are obtained for off-lattice chains of from 9 to 99 beads. The results are analyzed in terms of the usual excluded-volume parameter of two-parameter theory and are compared with previous lattice simulation results as well as with those from other analytical and numerical studies.

## Model

In the random-coil off-lattice model of a polymer chain used here, a chain $N$-1 units long is modeled by a string of $N$ impenetrable beads. The vectors ("sticks") connecting bead centers along the chain are each one unit in length. Each bead–stick pair is taken to represent one "statistical segment" in a real polymer chain. In contrast to most earlier work, the ratio $d$ of bead diameter to connecting vector length is allowed to vary from the no excluded-volume limit of a stick chain (freely jointed chain), with $d = 0$, to a "pearl necklace" chain of touching spheres, with $d = 1$. The beads are not constrained to lie on a lattice, and no restriction is placed on the angle between successive connection vectors along the chain. Equilibrium ensemble averages of chain dimensions are obtained by subjecting the chain to sequences of elementary moves, each of which consists of selecting a single bead in the chain at random and attempting a local move of just that bead and its adjacent connecting vectors. For a non-end bead, the attempted move consists of a rotation of the selected bead about an axis passing through the centers of its immediate neighbors along the chain, through an angle chosen at random in the range $(-\pi, \pi)$. For an end bead, with only one neighbor, the rule is modified by first generating the center coordinates of a "phantom" bead at unit distance and a randomly-chosen direction from the selected end bead. The non-end bead move is then carried out on the selected end bead, using the phantom bead as its missing neighbor. (This end-bead move is chosen because, in the absence of excluded-volume effects, it avoids end effects in center-of-mass diffusion constants.) Excluded-volume constraints are introduced by disallowing a move which would place the selected bead less than one bead diameter from another bead. For the chain

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dynamics simulations reported here, an entanglement constraint is also employed which consists of disallowing any move which would cause one connection vector to pass through another as the move takes place. This extra constraint should have no effect upon the values of equilibrium chain dimensions but should merely slow down the process by which they are generated.[21,22]

For each value of $N$ and $d$, equilibrium dimensions are obtained by a two-stage process. In the first stage (initialization), the chain is moved in the manner just described, starting from an arbitrarily chosen chain configuration which does not violate the excluded-volume constraints (usually either a highly extended configuration or an equilibrium configuration from a chain with a larger bead diameter). Simulated motion is continued for a time which is typically at least 10 times the expected longest internal relaxation time $\tau_1$ of the chain (based on previous experience with similar systems), to produce a chain configuration which may be taken as one randomly-selected sample from the equilibrium ensemble for the system. No sampling is done during this first stage, except to check system operation. After the initialization stage has been completed, resulting in a randomly-chosen starting configuration, the second, data-gathering stage of simulation is started. In this stage, simulation continues and mean-square dimensions and other quantities of interest are sampled at various times for the estimation of mean values. This stage of the simulation is continued for a time typically from 300 to 600 times $\tau_1$. Sampled values of the end-to-end vector $\mathbf{l}(t)$ at time $t$ are also stored to form products of the form $\mathbf{l}(t_0)\cdot\mathbf{l}(t_0+t)$, which are used to form estimates of the time-correlation function $\rho(t) = \langle\mathbf{l}(t_0)\cdot\mathbf{l}(t_0+t)\rangle/\langle l^2\rangle$. The long internal relaxation time $\tau_1$ is estimated from $\rho(t)$ by standard methods.[13,14] The values of $\tau_1$ so obtained are then compared with the estimates previously used to set the lengths of the initialization and data-gathering stages, and additional simulations are carried out if necessary. In order to estimate uncertainties in the final average dimensions, we divide the total length of the data-gathering stage of each simulation into a number of subintervals (from 4 to 48 in the work reported here) of equal length. The length of each subinterval is from 29 to 227 times $\tau_1$. Chain dimensions are first averaged over each subinterval. Since the length of each subinterval is much larger than the longest internal relaxation times, the subinterval averages may be taken as *independent* estimates of chain dimensions. These subinterval averages are then combined to form the grand average and its standard deviation, and the sample standard deviation of the mean is obtained in the usual way.

## Results

Values of $\langle l^2\rangle$ were obtained for nine values of $d$ between zero and 0.93, for chains of 9, 15, 33, 63, and 99 beads, except that values were not obtained for 99-bead chains for $d = 0.79$. Values of $\langle l^2\rangle$ and their associated standard deviations of the mean were obtained from subinterval averages as described in the preceding section. The results obtained are shown in Table I, together with the numbers $n_s$ of subintervals employed in each case. Values for $d = 1.0$, also shown in Table I, are taken from an earlier paper.[14]

For $d = 0$, $\langle l^2\rangle$ is of course just equal to $N$-1 times the step length. Simulation values obtained for $d = 0$ are therefore reported only as a check on the precision and accuracy of the simulations. Log–log plots of $\langle l^2\rangle$ vs $N$–1 are shown in Figure 1. They appear to be roughly linear at all values of $d$. The standard deviations in $\langle l^2\rangle$ shown in Table I, which depend upon the lengths of the simulations, are seen to increase with increasing $\langle l^2\rangle$ and are very roughly proportional to $\langle l^2\rangle$ at each value of $d$. The values of ln $\langle l^2\rangle$ at each bead diameter were therefore fitted by unweighted linear least squares to the form ln $\langle l^2\rangle = c + 2\nu \ln(N\text{-}1)$. The values of $2\nu$ and $c$ so obtained[23] are given in Table II together with the values for $d = 1$ taken from ref 14. As a check on whether these values of $2\nu$ have begun to approach long-chain limiting values, the fits were repeated, first omitting the data for $N = 9$ and then omitting data for both $N = 9$ and $N = 15$. The values of $2\nu$ so obtained are also reported in Table II. Plots of $2\nu$ from all three fits vs $d$ are shown in Figure 2. It initially appears from Figure 2 that omitting data for the shorter chains has no significant effect upon the results, apart from increasing the scatter. (We address this observation

**Table I. Values of Mean-Square End-to-End Length $\langle l^2\rangle$ and Their Standard Deviations (SD) for Chains of $N$ Beads and $N$-1 Steps, with Unit Step Length and Bead Diameter $d$[a]**

| $d$ | $N$ | $\langle l^2\rangle$ (SD) | $n_s$ |
|---|---|---|---|
| 0.00 | 9 | 8.05 (0.12) | 12 |
| 0.00 | 15 | 14.34 (0.33) | 12 |
| 0.00 | 33 | 32.43 (0.96) | 12 |
| 0.00 | 63 | 61.7 (1.9) | 12 |
| 0.00 | 99 | 98.5 (2.5) | 12 |
| 0.30 | 9 | 8.50 (0.21) | 12 |
| 0.30 | 15 | 15.28 (0.15) | 48 |
| 0.30 | 33 | 38.41 (0.87) | 12 |
| 0.30 | 63 | 77.3 (1.8) | 12 |
| 0.30 | 99 | 132.9 (2.5) | 12 |
| 0.45 | 9 | 9.70 (0.19) | 12 |
| 0.45 | 15 | 18.40 (0.22) | 48 |
| 0.45 | 33 | 46.46 (0.63) | 12 |
| 0.45 | 63 | 101.3 (3.1) | 12 |
| 0.45 | 99 | 169.0 (7.3) | 4 |
| 0.55 | 9 | 10.74 (0.18) | 12 |
| 0.55 | 15 | 21.25 (0.48) | 12 |
| 0.55 | 33 | 57.30 (0.83) | 12 |
| 0.55 | 63 | 121.1 (3.0) | 12 |
| 0.55 | 99 | 225.3 (7.9) | 5 |
| 0.63 | 9 | 12.08 (0.24) | 12 |
| 0.63 | 15 | 23.70 (0.44) | 12 |
| 0.63 | 33 | 64.0 (1.2) | 12 |
| 0.63 | 63 | 141.1 (3.5) | 12 |
| 0.63 | 99 | 258.3 (9.2) | 4 |
| 0.71 | 9 | 12.622 (0.083) | 48 |
| 0.71 | 15 | 25.30 (0.28) | 12 |
| 0.71 | 33 | 68.7 (1.4) | 12 |
| 0.71 | 63 | 154.7 (3.2) | 12 |
| 0.71 | 99 | 276.7 (6.3) | 4 |
| 0.79 | 9 | 13.19 (0.14) | 12 |
| 0.79 | 15 | 26.99 (0.20) | 12 |
| 0.79 | 33 | 74.73 (0.74) | 12 |
| 0.79 | 63 | 167.8 (3.7) | 12 |
| 0.87 | 9 | 14.65 (0.16) | 12 |
| 0.87 | 15 | 28.97 (0.41) | 12 |
| 0.87 | 33 | 84.1 (1.3) | 12 |
| 0.87 | 63 | 183.5 (1.6) | 12 |
| 0.87 | 99 | 315.2 (5.9) | 12 |
| 0.93 | 9 | 14.95 (0.19) | 12 |
| 0.93 | 15 | 30.47 (0.42) | 12 |
| 0.93 | 33 | 84.1 (1.6) | 12 |
| 0.93 | 63 | 190.8 (3.0) | 12 |
| 0.93 | 99 | 337.3 (7.1) | 12 |
| 1.00 | 9 | 15.96 (0.30) | 7 |
| 1.00 | 15 | 32.13 (0.42) | 7 |
| 1.00 | 33 | 92.40 (0.41) | 7 |
| 1.00 | 45 | 135.9 (2.8) | 7 |
| 1.00 | 63 | 209.5 (4.3) | 7 |
| 1.00 | 99 | 373.1 (9.5) | 7 |

[a] Also shown is the number $n_s$ of equal subintervals, each much longer than the longest internal relaxation time $\tau_1$, into which each simulation has been divided for averaging (see text); the number of degrees of freedom associated with each standard deviation is $n_s$-1.

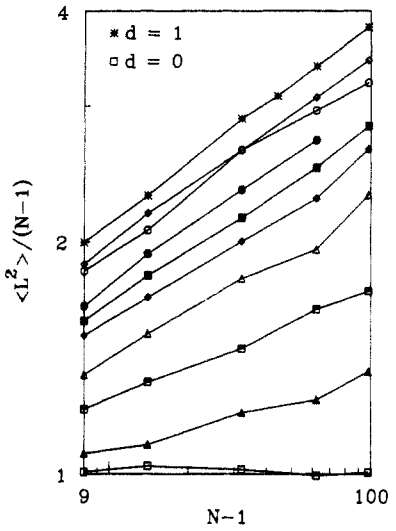


**Figure 1.** Expansion factors $\alpha^2 = \langle l^2 \rangle/(N\text{-}1)$ for the mean-square end-to-end length of off-lattice chains of $N$-1 steps between hard-sphere beads at 10 vaues of ratio $d$ of bead diameter to step length between 0 and 1, given in Table I.

**Table II. Exponents $2\nu$ and Prefactors $c$ Obtained by Fitting Mean-Square End-to-End Length $\langle l^2 \rangle$ of Off-Lattice Chains of $N$-1 Steps to the Form $\ln \langle l^2 \rangle = c + 2\nu \ln(N\text{-}1)$ by Unweighted Least Squares, for Chains with Ratios $d$ of Bead Diameter to Step Length[a]**

| $d$ | $c$ (SD) | $2\nu$ (SD) | $2\nu'$ | $2\nu''$ |
|---|---|---|---|---|
| 0.00 | 0.026 (0.018) | 0.9948 (0.0052) | 0.9877 | 0.9912 |
| 0.30 | −0.150 (0.034) | 1.0950 (0.0096) | 1.1048 | 1.1054 |
| 0.45 | −0.106 (0.026) | 1.1424 (0.0081) | 1.1433 | 1.1555 |
| 0.55 | −0.078 (0.041) | 1.1850 (0.0130) | 1.2017 | 1.2168 |
| 0.63 | −0.0035 (0.0041) | 1.2005 (0.0013) | 1.2215 | 1.2430 |
| 0.71 | 0.000 (0.013) | 1.2216 (0.0042) | 1.2276 | 1.2435 |
| 0.79 | 0.011 (0.025) | 1.2403 (0.0079) | 1.2281 | 1.2238 |
| 0.87 | 0.133 (0.012) | 1.2300 (0.0120) | 1.2250 | 1.1804 |
| 0.93 | 0.132 (0.013) | 1.2410 (0.0036) | 1.2354 | 1.2408 |
| 1.00 | 0.153 (0.011) | 1.2580 (0.0030) | 1.2583 | 1.2492 |

[a] Values of $2\nu$ were previously reported in ref 17. Numbers in parentheses (SD) after values of $c$ and $2\nu$ are standard deviations inferred from the least-squares fits. Also shown are values $2\nu'$ obtained by omitting data for $N = 9$ from the fits and values $2\nu''$ obtained by omitting data for both $N = 9$ and $N = 15$ from the fits.

in greater detail and in the context of other work farther on.) As expected, $2\nu$ is essentially unity when the bead diameter is zero. When the bead diameter is equal to the connection vector length ($d = 1$), the apparent value of $2\nu$ is about 1.26 as reported previously.[13,14] Between these limits the apparent exponent varies *smoothly* with $d$.

Instead of plotting $2\nu$ vs $d$, we may plot $2\nu$ vs $d^3$, which is proportional to the bead volume $v_b = \pi d^3/6$. This plot, in Figure 3, shows a smooth, rapid rise in $2\nu$ as $d^3$ increases from zero to about 0.2, followed by a much more gradual rise as $d^3$ increases to unity. In contrast to the behavior shown in Figure 2, the plot in Figure 3 might seem to suggest a distinct transition between two regions of qualitatively different behavior. However, it is clear from Figure 2 that this "transition" is only an illusion resulting from the choice of abscissa.

Guttman[24,25] has reported $2\nu$ as a function of intramolecular energy for self-avoiding walks on several lattices. Guttman's models differ from ours in several respects. Nevertheless, it is instructive to compare the results obtained for the two kinds of models. In Guttman's models, multiple occupancy of lattice sites is forbidden and there is an attractive energy $\epsilon$ for each pair of beads separated by one lattice distance. Guttman reports values of $2\nu$ as a function of $\sigma\phi$, whre $\sigma + 1$ is the coordination

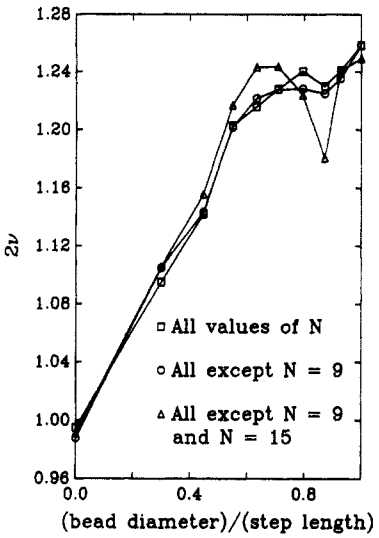


**Figure 2.** Apparent exponents $2\nu$ obtained by fitting mean-square end-to-end length $\langle l^2 \rangle$ for chains of $N$-1 steps and ratios $d$ of bead diameter to step length to the form $\ln \langle l^2 \rangle = c + 2\nu \ln(N\text{-}1)$ as described in the text.

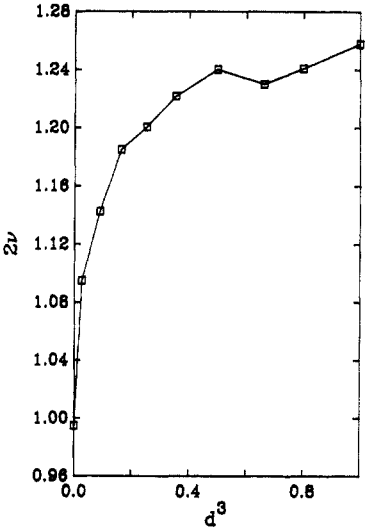


**Figure 3.** "All values of $N$" data of Figure 2, plotted vs $d^3$ instead of $d$.

number of the lattice, $\phi = -\epsilon/kT$, $k$ is Boltzmann's constant, and $T$ is absolute temperature. A plausible off-lattice analogue is a model consisting of touching, impenetrable beads of diameter $a$, with an attractive potential which is $\epsilon$ when the distance between bead centers is between $a$ and $2a$, and zero otherwise. For $\epsilon = 0$, this becomes our model with $d = 1$. Increasing $\epsilon$ from zero decreases the chain dimensions in Guttman's model, as does decreasing the ratio $d$ of bead diameter to stick length in ours. In other words, the size of the bead in our model plays a role analogous to that of the depth of the attractive energy well in Guttman's lattice model. The two approaches can be connected by means of the binary cluster integral $B = \int\{1 - \exp[-V(\mathbf{r})/kT]\}\,d\mathbf{r}$, where $V(\mathbf{r})$ is the interaction energy. For the model with attractive energy, $V(\mathbf{r}) = \infty$ for $0 < r < a$, $V(\mathbf{r}) = -\epsilon$ for $a < r < 2a$, and $V(\mathbf{r}) = 0$ for $r > 2a$. Then we have $B = 4\pi\int_0^\infty\{1 - \exp[-V(r)/kT]\}r^2\,dr = 8v_0(8 - 7e^\phi)$, where $v_0 = \pi a^3/6$ is the volume of a bead whose diameter is equal to the stick length. For our variable bead-size model, $B = 4\pi\int_0^d r^2\,dr = 8v_b = 8v_0 d^3$. Equating the two, we obtain $\phi = \ln[1 + (1 - d^3)/7]$. Figure 4 shows $2\nu$ plotted against $\phi$ as defined above, compared with Guttman's plots of $2\nu$ vs $\sigma\phi$ (Figure 2 of ref 24). The two models differ in the good-solvent regime $\phi = 0$, where

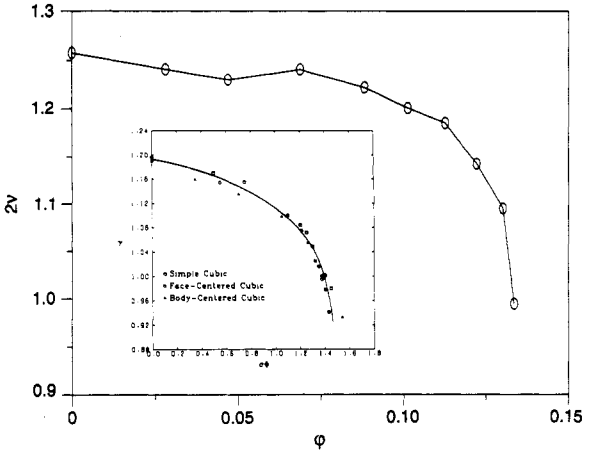


**Figure 4.** Apparent exponents $2\nu$ vs effective attractive energy $\phi = \ln[1 + (1 - d^3)/7]$, obtained as described in the text, for chains with ratios $d$ of bead diameter to step length. The inset shows corresponding results from Figure 2 of ref 24, reproduced with the permission of the publisher.

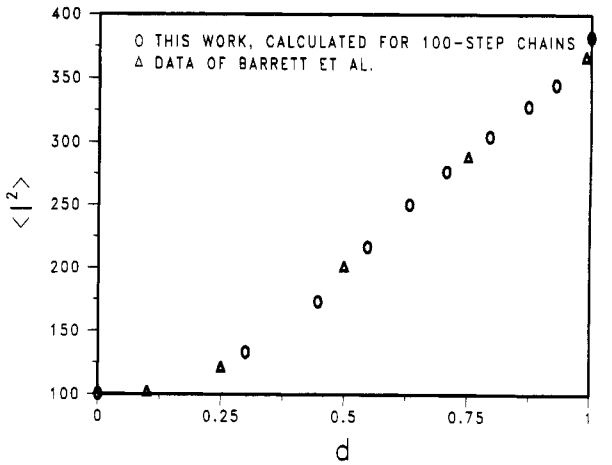


**Figure 5.** Mean-square end-to-end lengths $\langle l^2 \rangle$ for off-lattice chains of 100 steps and ratios $d$ of bead diameter to step length, calculated as described in the text and compared with data of Barrett et al.[8]

Guttman's lattice models give apparent values of $2\nu$ slightly less than 1.20, compared with the off-lattice result of 1.26. However, the overall similarity in their behavior is readily apparent, especiallly in the very rapid variation of $2\nu$ with $\phi$ in the vicinity of the $\Theta$ point ($2\nu = 1$).

Recently Barrett, Mansfield, and Benesch (hereafter BMB)[8] have examined the expansion of $\langle l^2 \rangle$ by beads of varying sizes. They plot the expansion coefficient $\alpha^2 = \langle l^2 \rangle/[(N\text{-}1)a^2]$ versus the familiar excluded-volume variable $z = [3/(2\pi a^2)]^{3/2}(N\text{-}1)^{1/2}\beta$, where $\beta$ is an effective excluded volume related to the bead volume $v_b$, and $a$ is the step length. According to the usual "two-parameter" theory of excluded volume,[4] $\alpha^2$ is a function of $z$ alone in the long-chain limit. The questions of the functional dependence of $\alpha^2$ on $z$, including its asymptotic long-chain limit and the magnitude of $N$ required to approach this limit, and of the relationship between $\beta$ and bead volume are all subjects of current analysis and debate.[7,8,18,26]

First, we compare our values of $\alpha^2$ with those reported by BMB. We note that BMB's results are given in terms of the number of *steps*; our $N$ is the number of *beads*. To demonstrate the consistency of both sets of results, which employ different values of both $N$ and $d$, we have extrapolated our data slightly to predict values of $\langle l^2 \rangle$ at $N\text{-}1 = 100$. For each value of $d$, we have used the fitted values of $c$ and $2\nu$ given in Table II to calculate $\langle l^2 \rangle$ from the relation $\ln \langle l^2(N\text{-}1{=}100) \rangle = c + 2\nu \ln(100)$. The results, plotted in Figure 5, show that our data are indeed consistent with those of BMB.

Next we examine the question of whether BMB's results and ours have reached asymptotic limits. Our results, in the range $8 \le N\text{-}1 \le 98$, and those of BMB, in the range $50 \le N\text{-}1 \le 1000$, both "look" as if they should yield limiting long-chain values of $2\nu$. To see whether they do, we first calculated $2\nu$ by unweighted least squares as previously described for our own data, using all the BMB data. We then recalculated $2\nu$ using only the BMB data in the range $50 \le N\text{-}1 \le 250$, which overlaps the range of our results. Finally, we recalculated $2\nu$ from the BMB data in the range $250 \le N\text{-}1 \le 1000$. The results are shown in Table III. Although the BMB data and ours cover quite different ranges of $N$ and employ different values of $d$, taken together similarities in behavior between the results in Table III and our results in Table II are evident. In both cases, at small values of $d$ the apparent values of $2\nu$ increase as the range of chain lengths over which they are estimated increases, while the opposite is true at large values of $d$.

**Table III. Exponents $2\nu$ Determined from the "3D Continuum" Data of Table I in Reference 8, for Off-Lattice Chains of $N$-1 Steps with Ratios $d$ of Bead Diameter to Step Length, for Ranges of $N$-1 Shown**

| $d$ | $50 \le N\text{-}1 \le 250$ | $250 \le N\text{-}1 \le 1000$ | $50 \le N\text{-}1 \le 1000$ |
|---|---|---|---|
| 0.1 | 0.9943 | 1.0203 | 1.0145 |
| 0.25 | 1.084 | 1.1142 | 1.1012 |
| 0.50 | 1.1856 | 1.1803 | 1.1807 |
| 0.75 | 1.2077 | 1.1856 | 1.1950 |
| 0.99 | 1.2126 | 1.1903 | 1.1977 |

The change in behavior appears to occur between $d = 0.25$ and $d = 0.5$ in the BMB results and between $d = 0.71$ and $d = 0.79$ in ours, but this is scarcely surprising given the different ranges in $N$ involved. *The important point is that there is no evidence to suggest that asymptotic values of $2\nu$ have been reached for any nonzero values of $d$ in the range $8 \le N\text{-}1 \le 1000$.*

We now consider the question of the extent to which $\alpha^2$ can be represented as a function of $z$ alone. In order to investigate this hypothesis, BMB first express $\beta$ as a multiple of bead volume: $\beta = (\pi d^3/6)K$, where $K$ depends only upon $d$ and is presumed to approach the monatomic hard-sphere gas value of 8 as $d$ approaches zero. They then use various theoretically obtained approximate relations between $\alpha^2$ and $z$ to infer values of $K$ from their values of $\alpha^2$ and the relation $z = [3/(32\pi)]^{1/2}(N\text{-}1)^{1/2}d^3K$. Here we choose a more simple-minded approach: If $K$ is indeed independent of $N$, then plots of $\alpha^2$ vs $\ln[(N\text{-}1)^{1/2}d^3]$ for different values of $d$ can be made coincident simply by horizontal translations. Figure 6 shows a plot of the data in Table I plotted in this way. It will be seen that the ranges in $N$ and $d$ are such that the curves for each adjacent pair of $d$-values cover overlapping ranges of $\alpha^2$. Although the scatter in our results is evident, it is clear that these curves can *not* be made to coincide by horizontal translations. In each region where values of $\alpha^2$ overlap, the curve for the higher value of $d$ has the larger slope. The same conclusion may be reached by making similar plots of the "3D continuum" data in Table I of BMB. Their data for smaller values of d (0.1 and 0.25) are not well suited to this purpose, since the range of $N$ they employ does not result in overlapping values of $\alpha^2$. However, their data for $d = 0.50$, 0.75, and 0.99 are shown in Figure 7 and lead to the same conclusion as do our data in Figure 6. Although the differences in slope of adjacent curves are slight, they are significant, given the high precision of the BMB data. In both cases simple translations alone will not make the curves coincide. The greater the value of $d$,

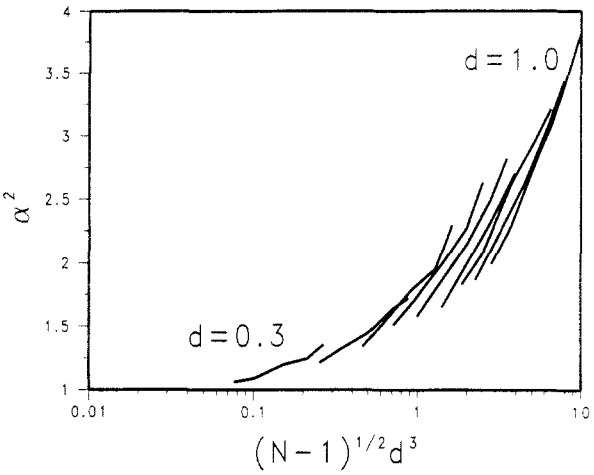


**Figure 6.** Expansion factors $\alpha^2 = \langle l^2 \rangle/(N\text{-}1)$ for chains of $N$ beads with ratios $d$ of bead diameter to step length vs $(N\text{-}1)^{1/2}d^3$, for the values of $d$ given in Table I. Each curve represents a different value of $d$.

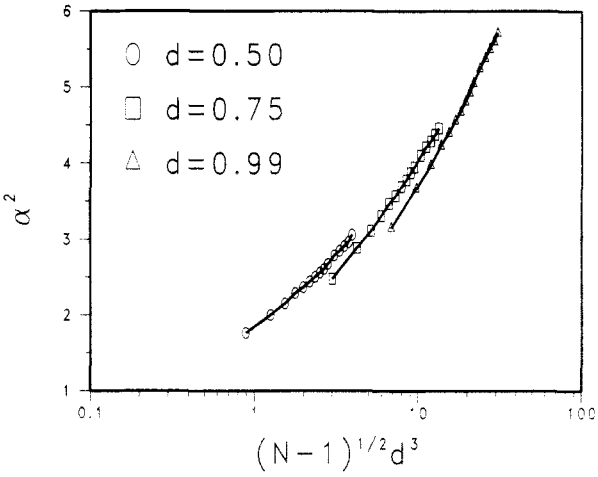


**Figure 7.** Expansion factors $\alpha^2$ obtained from the data of Barrett et al.[8] vs $(N\text{-}1)^{1/2}d^3$, for $d$ = 0.50, 0.75, and 0.99.

the larger the slope at a given value of $\alpha^2$. We conclude that, at least for chains of up to 1000 steps, $\alpha^2$ is *not* simply a function of $(N\text{-}1)^{1/2}$ times a function of $d$ alone.

This analysis does not of course invalidate the two-parameter theory or the possibility of other simplifying approximations at extremely large values of $N$. Rather, it suggests that the binary cluster integral has a coupled functional dependence upon bead size and chain length at the *finite* chain lengths corresponding to real polymers.

Finally, we have compared our data with the scaling proposal put forth by Kremer, Baumgärtner, and Binder[27] (hereafter KBB). KBB suggest that in three dimensions $\alpha^2$ should be proportional to $x^{1/5}$, where $x = (N\text{-}1)d^6$, in the limit as $N$ becomes large but $x$ remains finite. Bishop and Michels[28] have compared several workers' data, including their own, with this prediction. Their models employ a Lennard-Jones potential instead of a hard-sphere potential; they equate the hard-sphere diameter $d$ to an "effective" bead diameter, chosen at the point where the Lennard-Jones potential changes sign. They compare log–log plots of $\alpha^2$ vs $x$ with a straight line of slope $^1/_5$ and conclude that the KBB scaling prediction is obeyed when $x$ is greater than 5.

We can compare our hard-sphere results for 64-bead chains with the results for Lennard-Jones beads by using the values of $c$ and $2\nu$ in Table II to calculate values of $\langle l^2 \rangle$ from the relation $\ln \langle l^2(N\text{-}1\text{=}63) \rangle = c + 2\nu \ln(63)$. The results are shown in Figure 8, together with values for $N$ = 64 taken from Table I of ref 28. It will be seen that the two sets of results are in reasonable agreement. The differences between them are well within the uncertainties given in ref 28. Thus the BMB results in ref 8, the results for Lennard-Jones models shown in ref 28, and our results reported in this paper are all mutually consistent.

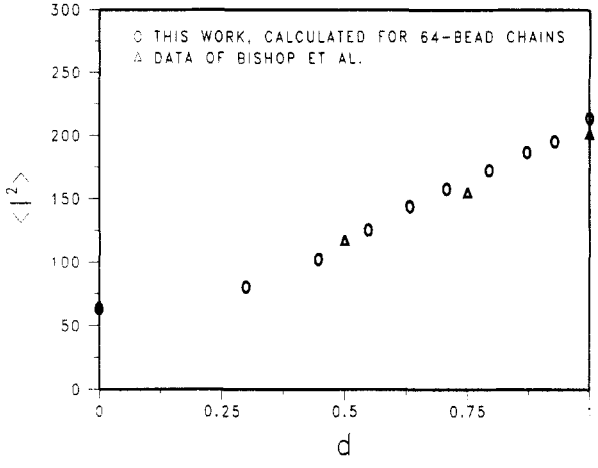


**Figure 8.** Mean-square end-to-end lengths $\langle l^2 \rangle$ for off-lattice chains of 64 beads and ratios $d$ of bead diameter to step length, calculated as described in the text and compared with data of Bishop et al.[28]

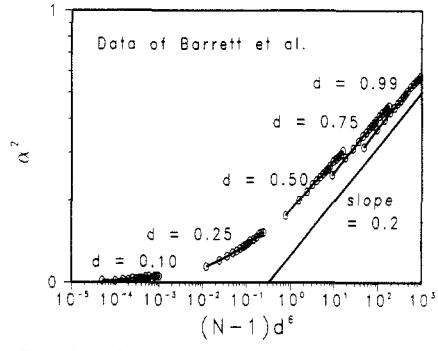


**Figure 9.** Log–log plots of expansion factors $\alpha^2 = \langle l^2 \rangle/(N\text{-}1)$ for chains of $N$ beads with ratios $d$ of bead diameter to step legnth vs $(N\text{-}1)d^6$, data of Barrett et al.[8]

Next, we test the scaling prediction of KBB. As noted in our previous discussion and exhibited both in Figure 6 (our data) and Figure 7 (BMB data), $\alpha^2$ is not simply a function of $x$ but depends upon both $N$ and $d$. Further, Figure 9 shows the BMB results as a log–log plot of $\alpha^2$ vs $x$, the kind of plot employed in Figure 1 of ref 28 and taken there as evidence favoring the KBB scaling prediction. A straight line of slope $^1/_5$ has been added for comparison. The first thing we notice in Figure 9 is that the data for different values of $d$ definitely do *not* lie on a common curve, at least for $x$ greater than 5. Second, the slopes of $\alpha^2$ vs $x$ at constant $d$ for the larger values of $d$ certainly *look* consistent with a limiting value of $^1/_5$, but it is clear from the detailed analyses of both the BMB data and our own that the data do not support this limiting value. We conclude that *plots of this sort are not reliable tests of scaling predictions*. Furthermore, the KBB prediction that $\alpha^2$ is a function of $x$ alone does not appear to hold for chains of up to 1000 beads.

## Conclusions

The results reported here show that, at least for the ranges of chain lengths employed in this work and the work of BMB, the apparent power-law exponent of mean-square end-to-end length for off-lattice chains of variable bead size is *not* constant but seems to be a simple smooth

function of the ratio of bead diameter to step length. In addition, there seems to be no reason to suppose that even 1000-bead chains have reached the region of limiting long-chain behavior.

The variation of $2\nu$ from the excluded-volume to the $\Theta$ or no excluded-volume condition with varying bead volume is remarkably like its variation with nearest-neighbor attractive energy. In both cases $2\nu$ is extremely sensitive to slight changes in excluded volume or attractive energy near the $\Theta$ condition. As bead volume is increased or attractive energy is decreased from the $\Theta$ condition, the apparent value of $2\nu$ increases relatively rapidly until it reaches roughly $^6/_5$; further increases are relatively slow. These observations could be taken to support the notion of a "crossover" between two regimes of qualitatively different behavior. But this is merely a continuous transition, in the region $0.5 < d < 0.7$,from a region near $\Theta$ conditions, where $2\nu$ is strongly dependent on attractive and repulsive interactions, to a region where $2\nu$ varies only slightly with changes in the intramolecular forces.

Real polymer chains are of course of finite length. The question of the correspondence between the number of segments in the models and the chain contour length in real polymers, and in particular the question of the molecular-weight range to which long-chain limiting predictions apply, remains open to conjecture and further study. The results discussed here show that, for off-lattice model chains of up to 1000 steps, the *apparent* exponent $2\nu = \partial \ln \langle l^2 \rangle / \partial \ln(N\text{-}1)$ does not necessarily reach infinite-chain limiting values and increases smoothly with increasing excluded volume.

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(20) Some of these results have previously been reported in preliminary form in ref 17.
(21) There are of course much more efficient (i.e., faster) methods for generating ensembles of equilibrium chain configurations than the one described here, when time-dependent behavior is not being studied and only equilibrium dimensions are wanted. The equilibrium results reported in this paper are byproducts of work[19] aimed primarily at studying the effects of variable excluded volume upon chain dynamics.
(22) A model similar to the one employed here except for the entanglement constraint was used earlier by A. Baumgärtner and K. Binder (*J. Chem. Phys.* **1979**, *71*, 2541) to study the equilibrium properties of chains with $d = 0.5$ and 1.
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