Communications to the Editor

Dimensions of Model Polymer Chains with Variable Excluded Volume

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The effects of excluded-volume interactions upon the mean dimensions of random-coil polymer chains have been the subject of many investigations over the years.[1] These effects are often summarized by the exponent $2\nu = d[\ln\langle l^2\rangle]/d[\ln(N-1)]$ for the power-law dependence of mean-square end-to-end length $\langle l^2\rangle$ (or other mean-square chain dimensions) upon the number $N-1$ of steps in the chain. It seems to be generally agreed that computer simulations of random walks with excluded volume *on lattices* give values of 2ν close to the value $^6/_5$ predicted long ago by Flory self-consistent field theory.[1-3] However, while some analytical models and computer simulations on lattices yield this result, more recent theoretical treatments[4] and lattice-model studies[5] have led to lower values, while *off-lattice* simulations, where the chain conformations are not restricted by a lattice structure,[6-9] have often yielded apparent values of 2ν as high as 1.3.

As part of a computer simulation study of excluded-volume effects upon chain dynamics in the absence of lattice constraints,[10] we have obtained values of $\langle l^2\rangle$ for bead–stick chains with ratios d of bead diameter to step length (stick length) set anywhere between zero (no excluded volume) and unity (bead diameter equal to step length). The ratio d is of course a measure of the magnitude of the excluded-volume effect. It is related to the familiar excluded-volume variable z of two-parameter theory:[1] $z \propto (N-1)^{1/2}d^3$. In this paper, we report preliminary values of 2ν, obtained by least-squares fits of $\ln\langle l^2\rangle$ to linear functions of $\ln(N-1)$ for chains of from 9 to 99 beads, for eight values of d. The results show that the apparent exponent 2ν increases smoothly with bead diameter as d increases from 0 to 1.

A random-coil polymer chain $N-1$ units long is modeled by a string of N beads. The vectors (sticks, steps) connecting the beads along the chain are all the same length. Unlike the lattice models employed in most earlier work, the angle between successive connection vectors is not restricted. The ratio d of bead diameter to connection vector length (step length) may be fixed at any value between 0 and 1. The chain undergoes sequences of random moves, the details of which are reported elsewhere,[10] which prohibit bead overlap. As the chain moves, its configuration is repeatedly sampled, and the sampled values are used to generate values of $\langle l^2\rangle$ and other equilibrium dimensions of interest.

A sequence of random moves was carried out for each chain length and value of d employed. Each sequence of moves was divided into a number of subintervals of equal length, chosen to be much larger than that required for a chain to move from one configuration to a new one independent of the first. The data from each subinterval were averaged, and the means from different subintervals were treated as independent estimates from which overall means and sample standard deviations of the mean were obtained in the usual way.

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 $d = 0.79$. For $d = 0$, $\langle l^2\rangle$ is of course equal to $N-1$ times the step length, and simulation values are obtained and reported only as a check on the precision and accuracy of the simulations. log–log plots of $\langle l^2\rangle$ vs $N-1$ appeared linear for all values of d. The values of $\langle l^2\rangle$ at each value of d were therefore fitted by unweighted linear least squares to the form $\ln\langle l^2\rangle = a + 2\nu\ln(N-1)$. The values of 2ν obtained in this way, fitting data at all chain lengths, were compared with values obtained by omitting first the values of $\langle l^2\rangle$ for $N = 9$ and then the values for both $N = 9$ and $N = 15$. Omitting the data for the shorter chains had no discernable effect on the behavior of 2ν vs d, except for some increase in scatter when the data for both $N = 9$ and $N = 15$ were omitted. We have therefore chosen to report in Table I the values of 2ν obtained by including data at all chain lengths, together with the value for $d = 1$ taken from earlier work.[9]

Table I
Exponents 2ν Obtained by Fitting Mean-Square End-to-End Length $\langle l^2\rangle$ of Off-Lattice Chains of $N-1$ Steps to the Form $\ln\langle l^2\rangle = a + 2\nu\ln(N-1)$ by Unweighted Least Squares, for Chains with Ratios d of Bead Diameter to Step Length between 0 and 1[a]

d	2ν	(sdm)	d	2ν	(sdm)
0.0	0.9948	(0.0052)	0.71	1.2216	(0.0042)
0.30	1.0950	(0.0096)	0.79	1.2403	(0.0079)
0.45	1.1424	(0.0081)	0.87	1.230	(0.012)
0.55	1.185	(0.013)	0.93	1.2410	(0.0036)
0.63	1.2005	(0.0013)	1.0	1.258	(0.003)

[a] Numbers in parentheses (sdm) are standard deviations of the mean in 2ν. Values for $d = 1$ are taken from ref 9.

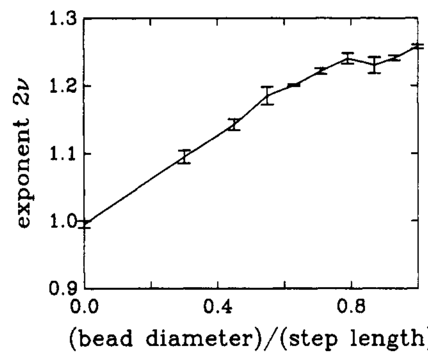

Figure 1. Expansion exponents $2\nu = \partial(\ln\langle l^2\rangle)/\partial[\ln(N-1)]$ for the mean-square end-to-end lengths $\langle l^2\rangle$ of chains of $N-1$ steps, with excluded volume, vs ratios of bead diameter to step length. The vertical lines extend upward and downward one sample standard deviation of the mean from the mean values.

Figure 1 is a plot of the chain expansion exponents 2ν listed in Table I vs the relative bead diameter d. As expected, 2ν is essentially unity when the bead diameter is zero. When the bead diameter is equal to the connection vector length ($d = 1$), 2ν is about 1.26 as reported previously.[9]

Figure 1 shows that the chain-length dependence of the expansion exponent $2\nu = \partial(\ln \langle l^2 \rangle)/\partial[\ln (N-1)]$ is a smooth function of the bead diameter. Further, Figure 1 shows that 2ν is equal to $^6/_5$ only when the ratio d of bead diameter to step length is in the vicinity of 0.6. This result is very different from functional forms previously proposed,[11,12] which imply that 2ν has a constant value of $^6/_5$, independent of d.

Summary. The preliminary results reported here show that, at least for the range of chain lengths employed in this study, the apparent power-law dependence of mean-square end-to-end length upon chain length for off-lattice chains of variable bead size is *not* in general equal to $^6/_5$. Rather, it seems to be a simple, smooth function of the ratio of bead diameter to step length. The value $^6/_5$ is observed only when that ratio is about 0.6. Of course, finite-chain results such as those reported here cannot yield predictions of how 2ν varies with d for infinite chains. However, these apparent exponents *are* relevent to real polymer chains, which are also of finite length.

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References and Notes

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