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Mean Square Dipole Moment of Excluded Volume Polymers

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ABSTRACT: A first-order excluded volume perturbation expansion that includes finite-chain effects is derived for the mean square dipole moment of a polymer chain. In the long-chain limit the Nagai–Ishikawa–Doi expression $(\alpha_\mu^2 - 1)/(\alpha_r^2 - 1) = \langle \mu \cdot \mathbf{r} \rangle_0^2 / \langle \mu^2 \rangle_0 \langle r^2 \rangle_0$ is obtained. A finite-chain correction term proportional to $N^{-1/2}$ is also present. The discrepancy between Monte Carlo calculations and the Nagai–Ishikawa–Doi formula is attributed to this correction term. We also conclude that when $\langle \mu \cdot \mathbf{r} \rangle_0 = 0$, $\langle \mu^2 \rangle$ exhibits a weak excluded volume effect, with α_μ tending to a constant not equal to 1.

Introduction

The mean square dipole moment of a polymer molecule in dilute solution is useful in polymer characterization, and so naturally its excluded volume behavior is of interest. For some time it has been accepted that the mean square dipole moment of any polymer for which $\langle \mathbf{r} \cdot \mu \rangle_0$ is zero, e.g., a polymer whose individual dipole moments lie perpendicular to the chain contour in the unperturbed state, would not exhibit excluded volume effects.[1-3] In 1971 Nagai and Ishikawa[4] derived the following equation:

$$\alpha_\mu^2 - 1 = [\langle \mathbf{r} \cdot \mu \rangle_0^2 / \langle r^2 \rangle_0 \langle \mu^2 \rangle_0](\alpha_r^2 - 1) \tag{1}$$

Here $\mathbf{r}$ and μ represent the end-to-end vector and molecular dipole moment vector, respectively, $\langle\ \rangle$ and $\langle\ \rangle_0$ represent averages over perturbed and unperturbed chain ensembles, respectively, and $\alpha_\mu^2 = \langle \mu^2 \rangle / \langle \mu^2 \rangle_0$ and $\alpha_r^2 = \langle r^2 \rangle / \langle r^2 \rangle_0$ are the dipole moment and end-to-end vector expansion factors, respectively. Nagai and Ishikawa argued that the above equation holds at least through third order in the excluded volume perturbation expansion, and subsequently, Doi[5] argued that it holds to all orders. However, Mattice and Carpenter[6] reported Monte Carlo calculations of model polymers that violate eq 1. Mattice and coworkers[7] later argued that this discrepancy is due to a flaw in the Nagai–Ishikawa and Doi arguments, namely that the unperturbed bivariate distribution function $P(\mathbf{r},\mu)$ is non-Gaussian. In this paper we make a different assertion, namely that $P(\mathbf{r},\mu)$ is Gaussian, that eq 1 is correct in the long-chain limit, and that the discrepancy between the Monte Carlo results[6,7] and eq 1 is the result of finite-chain corrections to eq 1.

Since eq 1 holds in the long-chain limit, we conclude that $\langle r^2 \rangle$ and $\langle \mu^2 \rangle$ exhibit the same scaling behavior for large N whenever $\langle \mathbf{r} \cdot \mu \rangle \neq 0$. However, when $\langle \mathbf{r} \cdot \mu \rangle_0 = 0$, eq 1 does not require $\alpha_\mu = 1$ at large N since α_r diverges. The first-order perturbation expansion developed here indicates that $\alpha_\mu \neq 1$ even though $\langle \mathbf{r} \cdot \mu \rangle_0 = 0$, implying a weak excluded volume effect even when $\langle \mathbf{r} \cdot \mu \rangle_0 = 0$.

Mean Value Theorem

The mean value theorem assures that the end-to-end vector of a flexible polymer chain obeys Gaussian statistics. This theorem follows from the convolution integral

$$P(\mathbf{r},N) = \int d\mathbf{r}'\ P(\mathbf{r}',j) P(\mathbf{r}-\mathbf{r}',N-j) \tag{2}$$

where $P(\mathbf{r},N)$ represents the distribution function of the end-to-end vector, $\mathbf{r}$, of an unperturbed chain of length N.[8] Equation 2 is a result of chain flexibility, expressing the fact that the chain is equivalent to two shorter chains joined through a flexible link. However, an analogous convolution integral can be written for the bivariate distribution function of $\mathbf{r}$ and μ, and it must follow that $P(\mathbf{r},\mu)$ is Gaussian in the long-chain limit. The most general form of $P(\mathbf{r},\mu)$ is[4]

$$P(\mathbf{r},\mu) = (3/2\pi)^3 D^{-3/2} \exp(-3Q/2D) \tag{3a}$$

where

$$Q = \langle r^2 \rangle_0 \mu^2 - 2\langle \mathbf{r} \cdot \mu \rangle_0 \mathbf{r} \cdot \mu + \langle \mu^2 \rangle_0 r^2 \tag{3b}$$

and

$$D = \langle r^2 \rangle_0 \langle \mu^2 \rangle_0 - \langle \mathbf{r} \cdot \mu \rangle_0^2 \tag{3c}$$

It follows from eq 3 that the distribution function of μ for an unperturbed ring polymer (obtained by setting $\mathbf{r} = 0$ in eq 3 and renormalizing) is also Gaussian with characteristic ratio, $C_\mu^{(\mathrm{ring})} = \langle \mu^2 \rangle_0^{(\mathrm{ring})}/N$, given by

$$C_\mu^{(\mathrm{ring})} = C_\mu^{(\mathrm{linear})} - \langle \mathbf{r} \cdot \mu \rangle_0^2 / N \langle r^2 \rangle_0 \tag{4}$$

where $C_\mu^{(\mathrm{linear})}$ is the characteristic ratio of the linear chain, N is the number of bonds in either the ring or linear chain, and the averages shown in the right-most term are taken over a linear chain of length N. All the quantities appearing on the right side of eq 4 can be easily calculated by the usual matrix techniques for unperturbed model polymers,[9,10] so that $C_\mu^{(\mathrm{ring})}$ is calculable. This result will be used below.

Non-Gaussian Contributions to $\langle r^2 \rangle_0$ and $\langle \mu^2 \rangle_0$

For all but the shortest linear chains,[11] the following equations hold:

$$\langle r^2 \rangle_0 = NC_r + D_r \tag{5a}$$

$$\langle \mu^2 \rangle_0 = NC_\mu^{(\mathrm{linear})} + D_\mu^{(\mathrm{linear})} \tag{5b}$$

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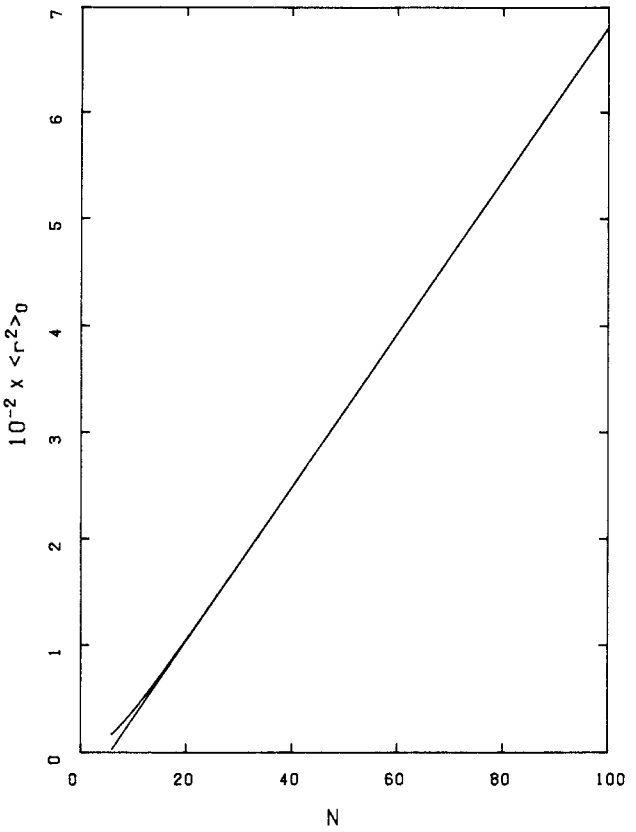

Figure 1. Mean square end-to-end distance of linear model chains A, B, and C as a function of N, the number of bonds. Both the exact expressions and the N^{-1} expansion (eq 5) have been plotted. For these model chains eq 5 is valid for N greater than about 15.

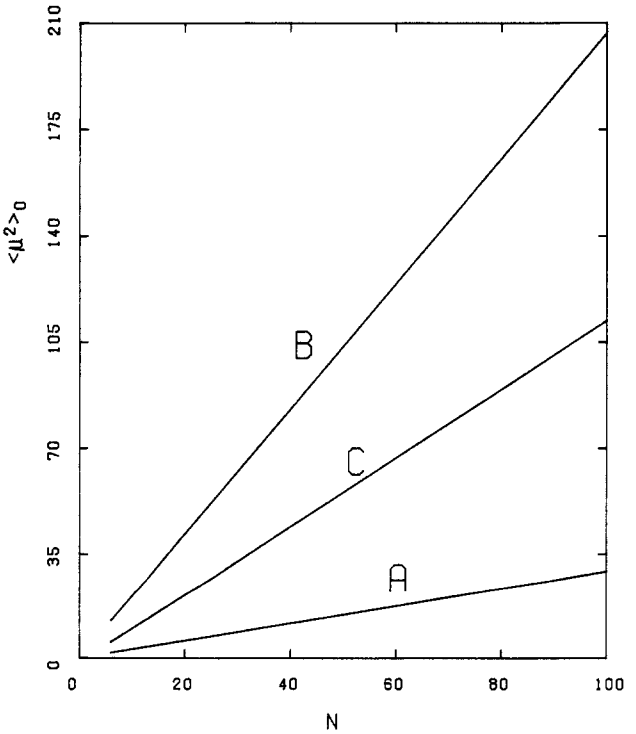

Figure 2. Mean square dipole moments as a function of N, the number of bonds, for linear model chains A, B, and C. Both the exact expressions and the N^{-1} expansions (eq 5) have been plotted for all three cases. The agreement is so good that separate curves are unresolvable, at least for $N > 6$.

These equations are expansions in powers of N^{-1}.[9] Figures 1 and 2 provide some idea of the range of N values over which linearity can be expected, at least for the model

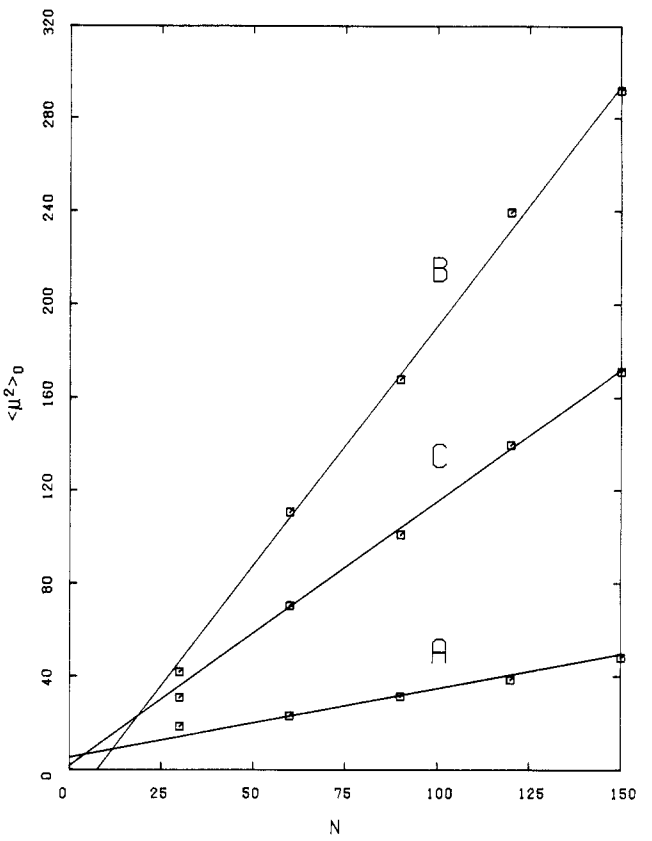

Figure 3. Monte Carlo results for the mean square dipole moments of ring model chains A, B, and C. The solid lines represent linear least-squares fits for which the intercept ($D_\mu^{(ring)}$ was permitted to adjust but for which the slope ($C_\mu^{(ring)}$ was constrained at the value given by eq 4.

chains considered below. (See below for a description of chain models A, B, and C.) As a result of Monte Carlo calculations reported below, it also appears that the mean square dipole moments of ring chains follow a similar form down to rather small N. (See Figure 3)

$$\langle \mu^2 \rangle_0^{(ring)} = NC_\mu^{(ring)} + D_\mu^{(ring)} \tag{5c}$$

We shall employ these results in constructing a first-order perturbation expansion that includes finite-chain effects.

First-Order Perturbation Expansions for $\langle r^2 \rangle$ and $\langle \mu^2 \rangle$

The first-order perturbation expansions for linear chains are[12]

$$\langle \mu^2 \rangle = \langle \mu^2 \rangle_0 + \beta \sum_{j<k} [\langle \mu^2 \rangle_0 \langle \delta(\mathbf{r}_{jk}) \rangle_0 - \langle \mu^2 \delta(\mathbf{r}_{jk}) \rangle_0] \tag{6a}$$

$$\langle r^2 \rangle = \langle r^2 \rangle_0 + \beta \sum_{j<k} [\langle r^2 \rangle_0 \langle \delta(\mathbf{r}_{jk}) \rangle_0 - \langle r^2 \delta(\mathbf{r}_{jk}) \rangle_0] \tag{6b}$$

for β the binary cluster integral. Note that $\langle \mu^2 \delta(\mathbf{r}_{jk}) \rangle_0 / \langle \delta(\mathbf{r}_{jk}) \rangle_0$ is the mean square dipole moment of an ideal linear chain with segments j and k cross-linked, but since the cross-link is flexible, this is just the mean square dipole moment of a ring of length $k - j$ plus the mean square dipole moment of a linear chain of length $N - k + j$.

$$\langle \mu^2 \delta(\mathbf{r}_{jk}) \rangle_0 = [(N - k + j) C_\mu^{(linear)} + (k - j) C_\mu^{(ring)} + D_\mu] \langle \delta(\mathbf{r}_{jk}) \rangle_0 \tag{7a}$$

Likewise

$$\langle r^2 \delta(\mathbf{r}_{jk}) \rangle_0 = [(N - k + j) C_r + D_r] \langle \delta(\mathbf{r}_{jk}) \rangle_0 \tag{7b}$$

In the above

$$D_\mu = D_\mu^{(\text{ring})} + D_\mu^{(\text{linear})} \tag{8}$$

Combining all the above yields

$$\alpha_\mu^2 - 1 = \beta(NC_\mu^{(\text{linear})} + D_\mu^{(\text{linear})})^{-1}\sum_{j<k}[\Delta C_\mu(k-j) - D_\mu^{(\text{ring})}]\langle\delta(\mathbf{r}_{jk})\rangle_0 \tag{9a}$$

and

$$\alpha_r^2 - 1 = \beta C_r(NC_r + D_r)^{-1}\sum_{j<k}(k-j)\langle(\mathbf{r}_{jk})\rangle_0 \tag{9b}$$

where

$$\Delta C_\mu = C_\mu^{(\text{linear})} - C_\mu^{(\text{ring})} = \langle\mathbf{r}\cdot\boldsymbol{\mu}\rangle_0^2/N\langle r^2\rangle_0 \tag{10}$$

To proceed, we must evaluate the sums

$$S_1 = \sum_{j<k}\langle\delta(\mathbf{r}_{jk})\rangle_0 \tag{11}$$

and

$$S_2 = \sum_{j<k}(k-j)\langle\delta(\mathbf{r}_{jk})\rangle_0 \tag{12}$$

For large enough $k-j$, $\langle\delta(\mathbf{r}_{jk})\rangle_0 = (3/2\pi C_r)^{3/2}(k-j)^{-3/2}$. Equation 12 is summed in the usual fashion,[12] by converting the sums to integrals, which yields

$$S_2 = (4/3)(3N/2\pi C_r)^{3/2} + \mathcal{O}(N)^{1/2} \tag{13}$$

where the $\mathcal{O}(N)^{1/2}$ terms are the result of this approximation. Attempting the same approximation with eq 11 would yield an "ultraviolet" divergence, which indicates that the sum is dominated by short-range terms and must be summed explicitly. For all but the smallest values of k, the sum over j quickly converges to some value independent of k that we shall call K. Then it follows that

$$S_1 = KN + \mathcal{O}(N)^0 \tag{14}$$

where the $\mathcal{O}(N)^0$ terms result from small values of k, and where K is given by

$$K = \sum_{j=1}^{\infty}\langle\delta(\mathbf{r}_{0j})\rangle_0 \tag{15}$$

which we recognize as a sum of ring-closure probabilities over chains of all lengths. Since eq 15 is dominated by short-range ring closures, the exact value of K should be model-dependent and difficult to ascertain.

By combining all of the above, we obtain the following expression, valid to first order in the perturbation expansion:

$$(\alpha_\mu^2 - 1)/(\alpha_r^2 - 1) = \langle\mathbf{r}\cdot\boldsymbol{\mu}\rangle_0^2/\langle r^2\rangle_0\langle\mu^2\rangle_0 - W(D_\mu^{(\text{ring})}/C_\mu^{(\text{linear})})N^{-1/2} + \mathcal{O}(N^{-1}) \tag{16}$$

where

$$W = (3K/4)(2\pi C_r/3)^{3/2} \tag{17}$$

At large N, we recover eq 1, although the correction term decays slowly, as $N^{-1/2}$. We show in the next section that this term can have a noticeable effect, especially in shorter polymers, and that in all likelihood it accounts for the departures from eq 1 observed by Mattice and co-workers.[6,7]

Since eq 1 has been shown to be valid to all orders in the limit of large N,[5] it implies that $\langle r^2\rangle$ and $\langle\mu^2\rangle$ scale the same with N when $\langle\mathbf{r}\cdot\boldsymbol{\mu}\rangle_0 \neq 0$. However, when $\langle\mathbf{r}\cdot\boldsymbol{\mu}\rangle_0 = 0$, eq 1 does not imply that $\alpha_\mu = 1$, since α_r diverges. Setting $\langle\mathbf{r}\cdot\boldsymbol{\mu}\rangle_0 = 0$ in eq 9 yields

$$\alpha_\mu^2 = 1 - \beta K D_\mu^{(\text{ring})}/C_\mu^{(\text{linear})} + \mathcal{O}(N^{-1}) \tag{18}$$

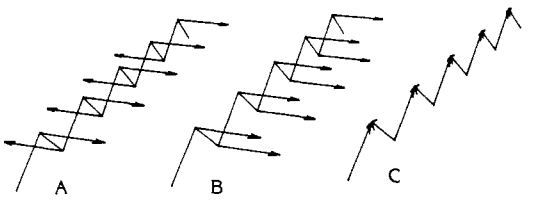

Figure 4. Diagram of the dipole moment arrangements for the three model chains.

Table I
Parameters Determining Unperturbed Mean Square End-to-End Distance and Unperturbed Mean Square Dipole Moment of Chain Models A, B, and C

	A	B	C
C_r	7.210	7.210	7.210
D_r	−40.48	−40.48	−40.48
$C_\mu^{(\text{linear})}$	0.2943	2.064	1.135
$D_\mu^{(\text{linear})}$	−0.0020	0.331	−1.371
$C_\mu^{(\text{ring})}$	0.2943	2.064	1.135
$D_\mu^{(\text{ring})}$	5	−16	2

On the basis of eq 18, combined with the realization that $\langle\mu^2\rangle$ is sensitive only to short-range interactions, we conclude that α_μ tends to a constant different from 1 as N increases whenever $\langle\mathbf{r}\cdot\boldsymbol{\mu}\rangle_0 = 0$. Equation 18 provides an estimate of α_μ valid near the Θ-point. In other words, when $\langle\mathbf{r}\cdot\boldsymbol{\mu}\rangle_0 = 0$, we can expect $\langle\mu^2\rangle$ to exhibit a weak excluded volume interaction, sufficiently strong to affect only the preexponential term of the dipole moment power law.

Comparison with Monte Carlo Calculations

Mattice and Carpenter[6] reported Monte Carlo calculations on a number of model chains. We have selected the three models that yield the largest deviations from eq 1 for comparison with the equations derived above. All three chains have the same polyethylene-like statistical weights[6] and differ only in the arrangement of individual dipoles along the backbone of the chain. These are summarized in Figure 4. Chains A and B are both defined to have individual dipoles normal to the bond vector planes, with either an isotactic or syndiotactic arrangement, as shown in Figure 4. In chain C, individual dipole moments are parallel to the bond vectors but with a head-to-tail arrangement. Chains A, B, and C are identical with models examined by Mattice and Carpenter except for a difference in bond angles. We employed tetrahedral bonds to simplify the ring-chain calculations (see below) while the bond angles of the models in ref 6 are slightly different.

Table I lists the parameters appearing in eq 5 for each of the chain models. The quantities C_r, D_r, $C_\mu^{(\text{linear})}$, $D_\mu^{(\text{linear})}$, and $C_\mu^{(\text{ring})}$ were calculated by the usual matrix methods.[9,10] Figures 1 and 2 display $\langle r^2\rangle_0$ and $\langle\mu^2\rangle_0$ as functions of N as calculated for each of these models. For all three models $\langle\mathbf{r}\cdot\boldsymbol{\mu}\rangle_0 = 0$, so that $C_\mu^{(\text{ring})} = C_\mu^{(\text{linear})}$ and the leading term in eq 16 is zero. We estimated $D_\mu^{(\text{ring})}$ by standard Metropolis Monte Carlo sampling techniques. The initial state of the chain in the Monte Carlo calculation was a ring laid out on the tetrahedral lattice by walking around a cyclohexane chair for the required number, N, of bonds. N was always a multiple of 6 so that the resulting chain was indeed a ring. Individual Monte Carlo steps were performed by selecting at random a sequence of six contiguous bonds within the ring and replacing these bonds by another set of six having the same vector sum. The new set of six bonds was selected randomly from a table of all six bond walks with the given vector sum. These tables had been generated previously and were stored in core memory during program execution. The initial state of the system was randomized by performing $N \times 10^4$ Monte

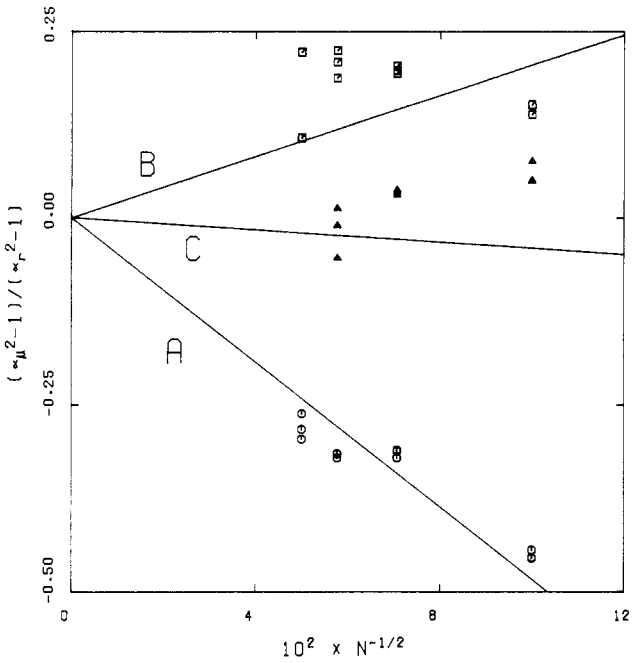

Figure 5. Plot of $(\alpha_\mu^2 - 1)/(\alpha_r^2 - 1)$ vs. $N^{-1/2}$ for the three model chains from the Monte Carlo data of Mattice and Carpenter.[6] The solid curves are from eq 16 with $W = 0.27$.

Carlo steps. Then the square dipole moment of the ring was sampled $N \times 10^3$ times, at intervals of 100 Monte Carlo steps. Approximate values of $D_\mu^{(\text{ring})}$ were taken as the intercept of the best fit least-squares line having the predetermined slope $C_\mu^{(\text{ring})}$, as in Figure 3.

Figure 5 plots values of $(\alpha_\mu^2 - 1)/(\alpha_r^2 - 1)$ as calculated by Mattice and Carpenter and compares these with the prediction of eq 16. The fit in Figure 5 was obtained by using the value $W = 0.270$. It is important to remember that eq 16 is only an approximation, since it neglects higher order terms in both the perturbation expansion and in the $N^{-1/2}$ expansion. Unfortunately, the sampling error appears too large in the Mattice–Carpenter Monte Carlo data to determine unequivocally if higher order terms are important. Nevertheless, Figure 5 indicates that eq 16 predicts both the sign and the relative magnitude of the departures from eq 1 that were observed by Mattice and Carpenter.

The value $W = 0.270$ corresponds to a value $K = 6.13 \times 10^{-3}$. We might ask if that value seems reasonable for the present models. Computing K is undoubtedly possible, since techniques[13] for computing ring-closure probabilities are available. However, these appear too tedious for a study of this scope. It is possible to sum eq 15 for a simpler model, namely a six-choice walk on the simple cubic lattice. Simple combinatorial arguments yield the following equation in that case:

$$K = \sum_{j,k,l} 6^{-(j+k+l)}(j + k + l)![(j/2)!(k/2)!(l/2)!]^{-2} \qquad (19)$$

where the sums range over all nonnegative even-integral values of j, k, and l, except for j, k, and l all simultaneously zero. The above sum yields a value of $K = 0.519$. The K value for the models studied here, which exclude the immediate back-step and include a strong pentane interference, is expected to be much smaller. Therefore, although we have no precise calculation of K, it is not at all reasonable to argue that the actual value of K would be too small to produce the fit shown in Figure 5.

Mattice and co-workers have argued that the change in α_μ, as shown in Figure 5, can be expected on physical grounds.[6,7] For example, one expects a decrease in α_μ with increasing α_r for chain model A, since the more extended conformations yield greater dipole moment cancellation. By the same argument, one expects α_μ to increase for model B. This is indeed correct, with the change in α_μ controlled by the value of $D_\mu^{(\text{ring})}$, as in eq 18.

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