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Generator Matrix and Monte Carlo Treatments of Simple Chains with Excluded Volume. Asymmetry and Overall Expansion of Finite Chains

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ABSTRACT: A generator matrix treatment of simple chains with excluded volume was recently described. That treatment properly reproduces the known chain length dependence of the mean-square dimensions in the limit of infinitely long chains. The purpose here is to compare the behavior of finite generator matrix chains with that of Monte Carlo chains in which atoms participating in long-range interactions behave as hard spheres. The model for the unperturbed chain is that developed by Flory and co-workers for polymethylene. Configuration-dependent properties evaluated are expansion of the mean-square end-to-end distance, α_r^2, mean-square radius of gyration, α_s^2, and the expansion along each principal axis of the inertia tensor. Hard-sphere chains examined by Monte Carlo methods contain up to 300 bonds, while generator matrix chains contain up to several thousand bonds. Finite chains have $\alpha_r^2 > \alpha_s^2$ in both treatments. If the generator matrix calculation is parameterized so that the perturbation is felt preferentially in the middle of the chain, the expansion is found to be asymmetric. It serves to enhance the already existing asymmetry of individual configurations. A slightly more asymmetric expansion is experienced by long chains in which atoms involved in long-range interactions behave as hard spheres. The ability of the generator matrix computation to reproduce the chain length dependence of α_s^2 found for short Monte Carlo chains depends on the range of the hard-sphere interaction.

Rotational isomeric state theory has seen considerable success in rationalizing configuration-dependent physical properties of macromolecules unperturbed by long-range interactions.[1] The rotational isomeric state method is particularly attractive when the pertinent physical property can be expressed as a sum of vectors or tensors associated with rigid units in the chain. The statistical mechanical average of the desired property is then extracted from a product of generator matrices.[1] Necessary manipulations are well within the capabilities of most computers. For simple chains the computer time required is trivial.

Evaluation of average configuration-dependent properties is a more difficult task when the chain is significantly perturbed by long-range intramolecular interactions. One fruitful approach dispenses with the actual chain geometry and short-range contributions to rotational potentials and considers instead a smoothed density of chain segments.[2-7] From this approach one concludes $\langle s^2\rangle/\langle s^2\rangle_0$ becomes proportional to $n^{1/5}$ at sufficiently large n.[2] Here n denotes the number of bonds in the chain, while $\langle s^2\rangle$ and $\langle s^2\rangle_0$ denote, respectively, perturbed and unperturbed mean-square radii of gyration.

Chain geometry and short-range interactions can be retained in Monte Carlo studies of macromolecules perturbed by long-range interactions. Long-range interactions are introduced by any of several devices. The simplest approach is rejection of all configurations in which any pair of chain atoms is separated by less than a critical distance. Alternatively, the energy of interaction of each pair of chain atoms can be computed from an expression which includes their distance of separation and terms related to the thermodynamics of polymer–solvent interaction.[8] Each chain is then assigned a weight given by $\exp(-E/kT)$, where E is the total energy for that configuration. Average properties are evaluated from the sample of weighted chains. Unfortunately, a large number of chain configurations must be examined if the computed average is to be in harmony with that which might have been obtained from an infinitely large sample. Consequently a vast amount of computer time is required in Monte Carlo studies. This requirement constitutes a serious obstacle to widespread implementation.

Recently we became interested in modifying generator matrices so that they could be employed in rapid computation of a satisfactory approximation to averaged configuration-dependent properties of simple chains significantly perturbed by long-range interactions. The motivations are easily stated. Generator matrix calculations for a chain of 10^2 bonds require orders of magnitude less computer time than an equivalent calculation in which Monte Carlo methods are employed. The saving in computational effort increases as the chain becomes longer. Chain geometry and short-range interactions pertinent for the unperturbed state are easily retained if the calculation for the perturbed chain can be carried out with generator matrices.

Generator matrices yielding the proper asymptotic behavior for the mean-square *perturbed* dimensions of simple chains with a symmetric threefold rotation potential have recently been described.[9] The modified generator matrices contain an adjustable parameter which can be related to the thermodynamics of polymer–solvent interactions, as expressed either by $\psi_1(1 - \Theta/T)$[10] or by the conventional excluded volume parameter, z.[6] One of the assumptions used in development of these generator matrices is that perturbation of a sufficiently long chain is achieved without alteration in the probability of a trans placement. Validity of this assumption is supported by early Monte Carlo studies of hydrocarbon chains with excluded volume[11] as well as by more recent investigations of linear[12] and branched[13] bolaform electrolytes and of polymethylene chains perturbed through attachment of one end to an impenetrable interface.[14]

A second assumption is that the properties of *perturbed* chains can be reproduced in adequate approximation by appropriately coupled alteration in the probabilities for propagation of the various rotational states.[9] While this assumption cannot be correct in detail, it nevertheless does provide a basis for construction of generator matrices which accurately reproduce the asymptotic behavior of $\langle s^2\rangle/\langle s^2\rangle_0$ for strongly perturbed simple chains. One objective here is to determine whether other properties of perturbed chains are also reproduced by this simple model. We accomplish this end through examination of the asymmetry of the distribution of chain atoms, the overall

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expansion of *finite* chains, and the expansion of subchains.

The model described earlier[9] had several variants. These variants differ with regard to whether the perturbation is felt preferentially near chains ends, perferentially in the middle of the chain, or in like manner throughout the chain. The proper asymptotic behavior of $\langle s^2\rangle/\langle s^2\rangle_0$ could be obtained with any of the variants. A second objective here is to determine whether the details of the manner in which the perturbation exerts its effect on the chain can be more precisely specified when we consider the asymmetry of the distribution of chain atoms, expansion of finite chains, and the behavior of subchains. Finally, we wish to inquire whether the subchains described by the modified generator matrices have properties consistent with those assumed in the blob hypothesis.[15]

This paper focuses on the asymmetry of the distribution of chain atoms and the overall expansion of finite chains. Subchains are described in the accompanying paper.

Calculations

Unperturbed Chain. The unperturbed chain is that described by the rotational isomeric state model developed for linear polymethylene by Flory and co-workers.[1,16] In this model each bond has a length, l, of 153 pm, the bond angle supplement, θ, is 68°, and each internal bond has three rotational states (t, g$^\pm$) with dihedral angles, φ, of 0° and ±120°. Short-range interactions included in this treatment are those between chain atoms i and $i + 3$ and between chain atoms i and $i + 4$. The statistical weight for g$^\pm$ relative to t is denoted by σ, and the weight of g$^\pm$g$^\mp$ relative to tt is $\sigma^2\omega$. At 300 K, $\sigma = 0.432$ and $\omega = 0.034$. These interactions are incorporated in the following statistical weight matrix for bond i:

$$\mathbf{U}_i = \begin{array}{c} \\ \mathrm{t} \\ \mathrm{g}^+ \\ \mathrm{g}^- \end{array} \begin{array}{c} \begin{array}{ccc} \mathrm{t} & \mathrm{g}^+ & \mathrm{g}^- \end{array} \\ \begin{bmatrix} 1 & \sigma & \sigma \\ 1 & \sigma & \sigma\omega \\ 1 & \sigma\omega & \sigma \end{bmatrix} \end{array}, \qquad (1)$$

Columns and rows index the state of bonds i and $i - 1$, respectively. Dimensions of the statistical weight matrix can be reduced to 2×2 due to the symmetric nature of the rotation potential.[1] The configuration partition function, Z, for an unperturbed chain of n bonds is

$$Z = \mathbf{J}^*\mathbf{U}_2\mathbf{U}_3 ... \mathbf{U}_{n-1}\mathbf{J} \qquad (2)$$

where $\mathbf{J}^*$ is either row (1, 0, 0) or row (1, 0), and $\mathbf{J}$ is either col (1, 1, 1) or col (1, 1), depending on whether $\mathbf{U}_i$ is used in the 3×3 or condensed form.

The mean-square unperturbed end-to-end distance, denoted by $\langle r^2\rangle_0$, and mean-square unperturbed radius of gyration for a chain of n bonds are obtained from a serial product of generator matrices in the usual manner.[1]

Asymmetries for unperturbed chains are evaluated from a representative sample of chains generated by Monte Carlo methods. Representative chains are grown using a priori and conditional probabilities deduced from the configuration partition function.[1] The a priori probability that bond i is in state η, denoted $p_{\eta;i}$, is

$$p_{\eta;i} = Z^{-1}\mathbf{J}^*\mathbf{U}_2\mathbf{U}_3 ... \mathbf{U}_{i-1}\mathbf{U}_{\eta;i}'\mathbf{U}_{i+1} ... \mathbf{U}_{n-1}\mathbf{J} \qquad (3)$$

where $\mathbf{U}_{\eta;i}'$ is obtained from the 3×3 representation of $\mathbf{U}_i$ by zeroing all elements except those in the column whose index is η. The a priori probability that bond i is in state η and that bond $i - 1$ is in state ξ, denoted $p_{\xi\eta;i}$, is

$$p_{\xi\eta;i} = Z^{-1}\mathbf{J}^*\mathbf{U}_2\mathbf{U}_3 ... \mathbf{U}_{i-1}\mathbf{U}_{\xi\eta;i}'\mathbf{U}_{i+1} ... \mathbf{U}_{n-1}\mathbf{J} \qquad (4)$$

where $\mathbf{U}_{\xi\eta;i}'$ is obtained from the 3×3 representation of $\mathbf{U}_i$ by nulling all elements except $u_{\xi\eta}$. The conditional probability that bond i is in state η, given that bond $i - 1$ is in state ξ, is

$$q_{\xi\eta;i} = p_{\xi\eta;i}/p_{\xi;i-1} \qquad (5)$$

Representative chains are generated with $p_{\eta;2}$, $q_{\xi\eta;i}$ $(2 < i < n)$, and a random number generator.

The inertia tensor for each configuration, with the nine elements arranged in reading order as a column, is

$$\mathbf{S}_{\mathrm{x}2} = (n + 1)^{-1}\sum_{i=0}^{n}\mathbf{r}_{0i}^{\mathrm{x}2} - (n + 1)^{-2}\Big(\sum_{i=0}^{n}\mathbf{r}_{0i}\Big)^{\mathrm{x}2} \qquad (6)$$

where $\mathbf{r}_{0i}$ denotes the vector from the zeroth to the ith chain atom and x2 as a superscript denotes the self-direct product.[17] Diagonalization of the 3×3 representation of the tensor yields the principal moments, L_i^2, indexed such that $L_1^2 \geq L_2^2 \geq L_3^2$. Averages of corresponding principal moments over all configurations are denoted by $\langle L_i^2\rangle_0$.

Perturbed Chains (Hard Sphere). Monte Carlo methods were used to evaluate average properties for chains in which chain atoms participating in long-range interactions behave as impenetrable spheres of diameter r^*. Representative samples of unperturbed chains were generated by methods described above. Distances between chain atoms i and j, denoted r_{ij}, were examined for all $j - i \geq m$, where m defines the shortest interaction considered to be of long range. A chain was retained only if all such r_{ij} were greater than r^*. Perturbed dimensions and principal moments are denoted by $\langle r^2\rangle$, $\langle s^2\rangle$, and $\langle L_i^2\rangle$, averaging being over surviving chains.

Perturbed Chains (Generator Matrix). The rationale for a generator matrix treatment of chains significantly perturbed by long-range intramolecular interactions is given in ref 9. The statistical weight matrix in eq 1 is written as

$$\mathbf{U}_i = \begin{bmatrix} \tau & \sigma & \sigma \\ 1 & \sigma\psi & \sigma\omega \\ 1 & \sigma\omega & \sigma\psi \end{bmatrix}_i \qquad (7)$$

$$\tau_i = \sigma(\psi_i + \omega) + 2(p_\mathrm{t} - p_{\mathrm{g}\pm})\{2\sigma[1 - (p_\mathrm{t} - p_{\mathrm{g}\pm})^2]\}^{1/2} \qquad (8)$$

Here p_t and $p_{\mathrm{g}\pm}$ are, respectively, the a priori probability that a bond in an infinitely long unperturbed chain is in the trans or either of the gauche states. The correlation between τ_i and ψ_i expressed in eq 8 permits expansion without alteration in the probability of a trans placement in an infinitely long chain.[9] The unperturbed chain is recovered when all $\tau_i = \psi_i = 1$. Proper asymptotic behavior for significantly perturbed chains can be obtained with

$$\tau_i = 1 + [1 - (1 - b/K)(n + 1 - 2i)^2(n - 3)^{-2}]Kn^{1/5} \qquad (9)$$

where K is related to the thermodynamics of polymer–solvent interaction. In good approximation it is[9]

$$K = [10C_M\psi_1(1 - \Theta/T)M_0^{1/2}]^{2/5} \qquad (10)$$

or

$$K = (8.35z/n^{1/2})^{2/5} \qquad (11)$$

The ratio b/K must lie between 0.64 and 1.053.[9] This ratio is unity if the perturbation is felt uniformly throughout the chain (if τ and ψ are independent of i). The perturbation is felt preferentially in the middle of the chain if $b/K < 1$ and preferentially at chain ends if $b/K > 1$.

The previous study,[9] which placed emphasis on asymptotic behavior as n becomes infinite, used eq 9 for all τ_i in the range $1 < i < n$. In the present work τ_2 will always be unity, and eq 9 will be employed only for $2 < i < n$. This change is of no consequence at sufficiently large n.

However, it is necessary if small chains are to have p_t reasonably independent of K and also to have similar end effects at both chain ends.

In order to compute $\langle s^2 \rangle$ and $\langle r^2 \rangle$ via the generator matrix approach, it is only necessary to replace the statistical weight matrices given by eq 1 with those specified by eq 7–11 and a value for b/K. Bond lengths and transformation matrices are the same as those used for computation of $\langle s^2 \rangle_0$ and $\langle r^2 \rangle_0$.

A Monte Carlo calculation is required in order to evaluate $\langle L_i^2 \rangle$ for the perturbed chains specified by eq 7–11. The samples of representative chains were generated from the $p_{\eta;2}$ and $q_{\xi\eta;i}$ ($2 < i < n$) specified through use of the statistical weight matrix from eq 7 in eq 2–5.

Uncertainty in Configuration-Dependent Properties. Generator matrix calculations achieve an exact averaging over all configurations. Consequently there is no uncertainty in the computation of $\langle r^2 \rangle_0$ or $\langle s^2 \rangle_0$. The same statement applies to $\langle r^2 \rangle$ or $\langle s^2 \rangle$ when the perturbed chains are described by the statistical weight matrix in eq 7. Expansion factors defined in eq 12 and 13 therefore have no uncertainty if mean dimensions of the perturbed chains are obtained from generator matrices.

$$\alpha_r^2 = \langle r^2 \rangle / \langle r^2 \rangle_0 \qquad (12)$$

$$\alpha_s^2 = \langle s^2 \rangle / \langle s^2 \rangle_0 \qquad (13)$$

A different situation arises for configuration-dependent properties evaluated from Monte Carlo calculations. The pertinent properties are $\langle L_i^2 \rangle$ for any of the chain models as well as $\langle r^2 \rangle$ and $\langle s^2 \rangle$ for perturbed macromolecules in which chain atoms participating in long-range interactions behave as hard spheres. In each of these cases, three, four, or five independent samples of chains were generated. The desired physical property was averaged over chains in each set. Both the mean and standard deviation were then calculated from these averages. Such data will be presented by one of two methods. If the standard deviation is sufficiently small, a filled circle with radius as large as, or larger than, the standard deviation is plotted. When the standard deviation is larger than the radius of filled circles used in a particular figure, an error bar (of length ±1 standard deviation) is plotted instead.

Overall Chain Expansion

Long-Range Interactions Beginning at Chain Atoms *i* and *i* + 5. Short-range interactions included in treatment of the unperturbed chain are those between chain atoms i and $i + 3$ and between i and $i + 4$. We consider first perturbed chains in which long-range interactions include all interactions other than those operative in the unperturbed chain and atoms participating in long-range interactions behave as impenetrable spheres. Hence surviving chains have all $r_{ij} > r^*$ for $j - i \geq m$, with $m = 5$ and r^* being the diameter of the sphere.

Filled circles and error bars in Figure 1 denote expansion factors computed for such chains when r^* is 300 pm. Computations were not carried out for chains longer than 200 bonds because the computer time required to generate large samples of surviving chains became excessive. At all n examined, different expansions are obtained for the end-to-end distance and radius of gyration, with $\alpha_r^2 > \alpha_s^2$.

Solid lines in Figure 1 denote behavior of expansion factors computed using generator matrices. The parameter K, which can be related to polymer–solvent interaction via expressions such as those in eq 10 and 11, has been assigned so that α_s^2 at $n = 200$ is in agreement with that obtained in the Monte Carlo calculation. Unity was used for b/K. The generator matrix calculation accurately reproduces the chain length dependence for α_s^2 seen in the Monte Carlo calculation in the range $30 < n < 200$. Both calculations yield $\alpha_r^2 > \alpha_s^2$ at $n = 200$, with the difference in these expansion factors being slightly larger in the latter case. The ratio $(\alpha_s/\alpha_r)^3$ is 0.937 from the generator matrix calculation, while Monte Carlo calculations yield a value of about 0.87 ± 0.03. Both of these results are in the range obtained with various lattice chains.[18,19]

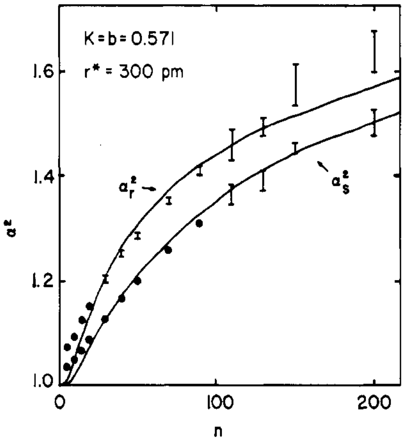

Figure 1. α_r^2 and α_s^2 evaluated using a hard-sphere treatment with $m = 5$ (points and bars) and using generator matrices (solid lines).

Additional generator computations were performed in order to assess the consequences of letting the perturbation exert perferential effects either at chain ends or in the middle of the chain. In these computations b/K was varied over the allowed range (0.64–1.053), K being assigned so that α_s^2 at $n = 200$ was constant. The various generator matrix calculations gave nearly identical chain length dependencies for α_s^2 in the range $30 < n < 200$. There was, however, a small effect on $(\alpha_s/\alpha_r)^3$ at $n = 200$. This ratio varied from as low as 0.935 (when the perturbation was felt preferentially at chain ends) to as high as 0.967 (when the perturbation was felt preferentially in the middle of the chain). The perturbation can alter the mean-square end-to-end distance even if only those bonds near chain ends are affected. In contrast, the mean-square radius of gyration, which depends on the position of all chain atoms, changes but little if the only bonds affected are those near chain ends. Thus $(\alpha_s/\alpha_r)^3$ is smallest when the perturbation is felt perferentially at bonds near the end of a chain.

If n is less than 30, the Monte Carlo calculation yields a larger expansion than does the computation performed with generator matrices. This behavior arises because α_r^2 and α_s^2 from the Monte Carlo calculation remain significantly above unity even for short chains. For example, while atoms separated by five or six bonds only rarely approach within 300 pm of one another in unperturbed chains with $n = 6$, this event nevertheless occurs with sufficient frequency so that deletion of all such configurations from the sample produces significant increases in $\langle r^2 \rangle$ and $\langle s^2 \rangle$ (α_r^2 and α_s^2 are 1.072 and 1.034, respectively). Deletion of these configurations also produces an increase in the probability of a trans placement (p_t rises from 0.621 to 0.666 at $n = 6$).

The increase in p_t at extremely short chains, as well as the occurrence of α_r^2 and α_s^2 greater than unity, suggests the r_{ij} considered to represent long-range interactions should start at $j - i$ somewhat greater than 5. Trial Monte Carlo calculations were performed with various m, where the long-range interactions begin at $j - i \geq m$. If m is raised from 5 to 8, with r^* retained at 300 pm, α_r^2 and α_s^2 become very close to unity at small n, and the perturbation has

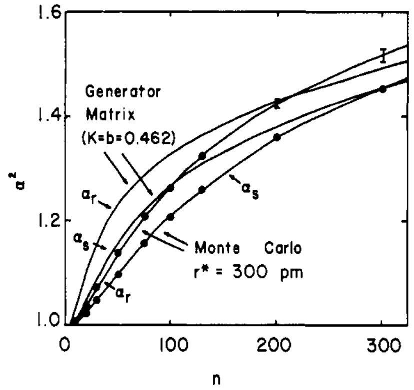

Figure 2. α_r^2 and α_s^2 evaluated using a hard-sphere treatment with $m = 8$ (points and bars) and using generator matrices (lines without points or bars).

little effect on p_t even at large n. Attention is now directed to results of Monte Carlo calculations in which m is 8.

Long-Range Interactions Beginning at Chain Atoms i and $i + 8$. Filled circles and error bars in Figure 2 denote expansion factors computed via Monte Carlo methods with $r^* = 300$ pm and $m = 8$. Chains considered now include those containing as many as 300 bonds. Longer chains could be treated than was the case in Figure 1 because attrition is much less severe when m is raised from 5 to 8. At $n = 200$, for example, 0.3% of the chains survive if m is 5, but the survival rate increases to 16.5% if m is 8. Chain expansion is significantly smaller than that seen in Figure 1. At $n = 200$, α_s^2 falls from about 1.5 in Figure 1 to 1.36 in Figure 2. There is also a decline in the uncertainty in α_s^2 and α_r^2, a direct consequence of larger sample sizes due to less severe attrition.

Winnik et al.[20] recently reported results of rotational isomeric state calculations for hydrocarbon chains in which excluded volume was introduced by various Monte Carlo procedures. One of their procedures uses the same chain geometry and r^* as that employed here. Their E_σ and E_ω (600 and 1900 cal mol^{-1}, respectively) were only slightly different from ours (500 and 2000 cal mol^{-1}, respectively). The longest chain treated in this manner by Winnik et al.[20] had 50 bonds. Their results for this chain were $\alpha_r^2 = 1.07$ and $\alpha_s^2 = 1.05$. Both α_r^2 and α_s^2 were 1.00 for a chain of ten bonds. Monte Carlo results depicted in Figure 2 are $\alpha_r^2 = 1.009 \pm 0.004$ and $\alpha_s^2 = 1.006 \pm 0.001$ at $n = 10$, and $\alpha_r^2 = 1.139 \pm 0.002$ and $\alpha_s^2 = 1.098 \pm 0.001$ at $n = 50$. The smaller expansion seen in the computations reported by Winnik et al.[20] arises in part from their choice of a larger E_σ. Their unperturbed chains contain fewer gauche placements, causing self-intersection to be a less common event in their unperturbed samples. A further contribution to the different chain expansions could be provided by m, which may not have been assigned the same value in the two studies.

Expansion factors were computed with generator matrices in which K and b were both 0.462. The α_s^2 computed at $n = 300$ is then equal to the α_s^2 obtained from the Monte Carlo calculation with $m = 8$. Chain length dependence of the α_s^2 obtained from the generator matrix calculation is depicted in Figure 2. The generator matrix calculation yields a significantly greater expansion for chains having between 10 and 300 bonds than does the Monte Carlo calculation.

Returning to the chain with 300 bonds, results depicted in Figure 2 demonstrate α_r^2 is greater than α_s^2 in both computations, with the difference being somewhat larger in the Monte Carlo calculation. Values for $(\alpha_s/\alpha_r)^3$ are 0.963 and 0.936 ± 0.011 from generator matrix and Monte Carlo calculations, respectively. The two computations yield similar α_r^2 when n is 200, and the generator matrix calculation produces the larger expansion when the chain has between 10 and 200 bonds. As was the case in Figure 1, variation of b/K over the physically sensible range causes only minor changes so long as K is chosen so that α_s^2 at $n = 300$ is constant.

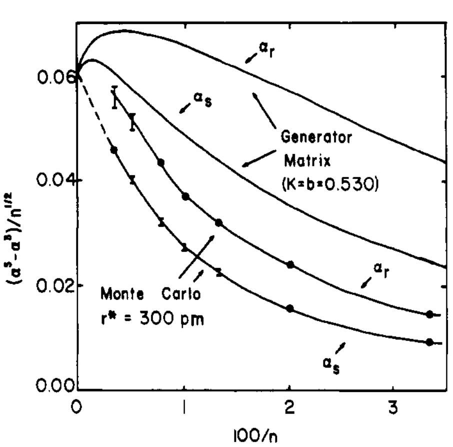

Figure 3. Hard-sphere data from Figure 2 replotted as $(\alpha^5 - \alpha^3)/n^{1/2}$ vs. $1/n$. Generator matrix chains are parameterized to yield 0.06 as the asymptotic limit for $(\alpha_s^5 - \alpha_s^3)/n^{1/2}$.

Results depicted in Figures 1 and 2 can be summarized as follows: Perturbed polymethylene chains containing 30–300 bonds have $\alpha_r^2 > \alpha_s^2 > 1$, $\mathrm{d}\alpha^2/\mathrm{d}n > 0$, and $\mathrm{d}^2\alpha^2/\mathrm{d}n^2 < 0$ according to both generator matrix calculations and Monte Carlo calculations in which interacting chain atoms behave as hard spheres. The second derivative of α^2 with respect to n tends to be more negative in this range of n when dimensions of perturbed chains are evaluated with generator matrices.

Relationship of Finite to Infinite Chains. Attention thus far has been directed toward behavior of chains containing no more than a few hundred bonds because of limitations imposed by the computational resources demanded in Monte Carlo calculations. It is instructive nevertheless to inquire how expansion of finite chains described above is related to expansion of infinitely long chains. Consequently the Monte Carlo results from Figure 2 have been replotted as $(\alpha^5 - \alpha^3)/n^{1/2}$ vs. $1/n$ in Figure 3. A finite intercept on the ordinate is expected because $(\alpha^5 - \alpha^3)/n^{1/2}$ is a constant for sufficiently long perturbed chains.[2]

Monte Carlo data depicted in Figure 3 suggest the asymptotic limit is not reached until n is well above 300. Have the Monte Carlo calculations been carried to large enough n so that extrapolation to $1/n = 0$ can be done with confidence? One might, for example, wish to extrapolate the Monte Carlo data for $(\alpha_s^5 - \alpha_s^3)/n^{1/2}$ to an intercept of about 0.06, as shown by the dashed line in Figure 3. Let us put aside the question of the legitimacy of this extrapolation and inquire instead into the behavior of perturbed chains described by generator matrices and having $[(\alpha_s^5 - \alpha_s^3)/n^{1/2}]_\infty = 0.06$. The speed with which generator matrix calculations are accomplished permits examination of chains long enough so that essentially the entire range of $1/n$ can be explored.

Generator matrix calculations yield $[(\alpha_s^5 - \alpha_s^3)/n^{1/2}]_\infty = 0.06$ if K and b are both 0.530. Chain length dependence of $(\alpha^5 - \alpha^3)/n^{1/2}$ is depicted in Figure 3. Consider first chains whose number of bonds is equal to n in the molecules examined by Monte Carlo methods. In this range for n, both types of calculations yield $\mathrm{d}[(\alpha_s^5 - \alpha_s^3)/n^{1/2}]/\mathrm{d}(1/n) < 0$, and $(\alpha_s^5 - \alpha_s^3)/n^{1/2}$ at a particular n is

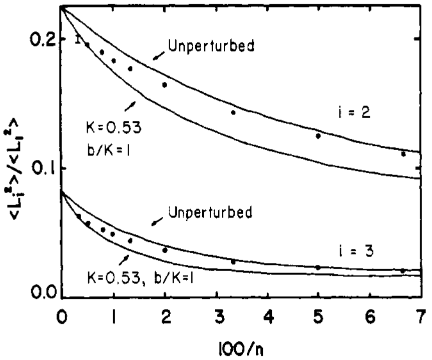

Figure 4. Ratios of averaged principal moments for unperturbed chains and for the perturbed chains considered in Figure 3. Points and the error bar denote perturbed hard-sphere chains.

always larger when the perturbed chain is treated using generator matrices. If attention is confined to chains for which n is between 150 and 300, behavior of $(\alpha_s^5 - \alpha_s^3)/n^{1/2}$ vs. $1/n$ in *both* types of calculations suggests a nearly linear extrapolation to $1/n = 0$ might be appropriate. Computations for perturbed chains having several thousand bonds are readily accomplished using generator matrices, but they are impractical when Monte Carlo methods are employed. Results obtained from the practical generator matrix calculations demonstrate that the proposed extrapolation seriously overestimates the behavior of infinitely long chains. This overestimation arises because $(\alpha_s^5 - \alpha_s^3)/n^{1/2}$ goes through a maximum when n is near 1000.

A search for this maximum in the Monte Carlo calculation would require accurate computations for chains containing well over 1000 bonds. Necessary computational resources far exceed those at our disposal. It may be pertinent, however, to recall that $(\alpha_s^5 - \alpha_s^3)/n^{1/2}$ is known to experience a maximum in certain polymer–solvent systems. For example, polyisobutylene in diisobutylene at 20 °C or in cyclohexane at 30 °C displays a maximum when n is about 3000–7000.[21]

Additional generator matrix calculations were performed for models in which the perturbation was felt differently in the middle of the chain and at chain ends. Chain length dependence of $(\alpha_s^5 - \alpha_s^3)/n^{1/2}$ was similar to that depicted in Figure 3 so long as the asymptotic limit was held constant. The maximum can be removed, however, by increasing the perturbation. Strongly perturbed chains, in which K is much larger than the values used here, have $\mathrm{d}[(\alpha_s^5 - \alpha_s^3)/n^{1/2}]/\mathrm{d}(1/n) < 0$ at all n.[9]

Asymmetry of the Distribution of Chain Atoms

Ratios of Averaged Principal Moments. Averages of corresponding principal moments for individual configurations, denoted by $\langle L_i^2 \rangle$, were computed for unperturbed and perturbed chains. Chain length dependence of ratios of the averaged principal moments is depicted in Figure 4. These ratios have been presented earlier for unperturbed chains at 140°.[12,14,22] Unperturbed chains are characterized by asymptotic limits of $\langle L_2^2 \rangle / \langle L_1^2 \rangle = 0.225$ and $\langle L_3^2 \rangle / \langle L_1^2 \rangle = 0.082$, as must be the case for any flexible unperturbed chain.[17,23-28] Finite unperturbed chains are more asymmetric than infinitely long unperturbed chains, due in part to the bond angle supplement being less than 80°.[28]

Filled circles and error bars in Figure 4 denote $\langle L_i^2 \rangle / \langle L_1^2 \rangle$, $i = 2, 3$, computed for perturbed chains in which chain atoms participating in long-range interactions behave as hard spheres of diameter 300 pm. Here m is 8, as it was in the Monte Carlo computations for which results are depicted in Figures 2 and 3. Perturbed chains containing as many as 300 bonds are found to be more asymmetric than unperturbed chains. Furthermore, perturbation of an infinitely long unperturbed chain would appear to increase its asymmetry if extrapolation of $\langle L_i^2 \rangle / \langle L_1^2 \rangle$ to $1/n = 0$ is approximately linear. Previous studies using a smooth density model,[7] various lattice chains,[25,29] and a perturbation method[30,31] also conclude perturbed chains are more asymmetric than unperturbed chains.

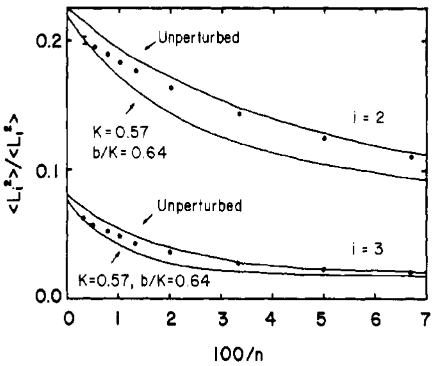

Figure 5. Ratios of averaged principal moments for unperturbed chains and hard-sphere chains from Figure 4. Perturbed generator matrix chains are now parameterized so that the perturbation is felt perferentially in the middle of the chain.

Figure 4 depicts $\langle L_i^2 \rangle / \langle L_1^2 \rangle$ for perturbed chains described by the generator matrices. Parameters used are the same as those employed in computation of expansion factors depicted in Figure 3. Chains containing a finite number of bonds are rendered more asymmetric by the perturbation. Nearly identical asymmetries are obtained in the generator matrix and hard-sphere calculations if chains contain 200–300 bonds. Shorter chains are found to be more asymmetric in the generator matrix treatment. Behavior of the generator matrix treatment as n becomes large shows that the asymmetries of perturbed and unperturbed chains merge as n becomes infinite. This prediction appears to be in conflict with an extrapolation of results depicted for chains in which interacting atoms behave as hard spheres. It also conflicts with conclusions from several previous studies.[7,25,28-31] The conflict can be reduced if the generator matrix calculation is performed in a manner which causes the perturbation to be felt preferentially in the middle of the chain (in Figure 4 it is felt uniformly throughout the chain).

Figure 5 repeats from Figure 4 the $\langle L_i^2 \rangle / \langle L_1^2 \rangle$ for unperturbed chains and for perturbed chains in which interacting atoms behave as hard spheres. The generator matrix treatment of perturbed chains now employs $b/K = 0.64$, instead of $b/K = 1$, as was the case in Figure 4. This assignment causes the perturbation to be felt preferentially in the middle of the chain.[9] The value for K has been adjusted so that the asymptotic limit for $(\alpha_s^5 - \alpha_s^3)/n^{1/2}$ is unchanged. The only significant difference in behavior of $\langle L_i^2 \rangle / \langle L_1^2 \rangle$ from generator matrices in Figures 4 and 5 is that seen at large n. Asymptotic limits for infinite perturbed chains are definitely lower than those for unperturbed chains in Figure 5. Hence one can infer that the perturbation must also be felt preferentially in the middle of the chain when interacting atoms behave as hard spheres. This inference is supported by the behavior of subchains, to be described in the accompanying paper.[32]

Expansion along the Principal Axes. Expansion factors along each of the three principal axes are defined as

$$\alpha_i^2 = \langle L_i^2 \rangle / \langle L_i^2 \rangle_0 \tag{14}$$

The ratio of the expansion along principal axis 2 (or 3) to

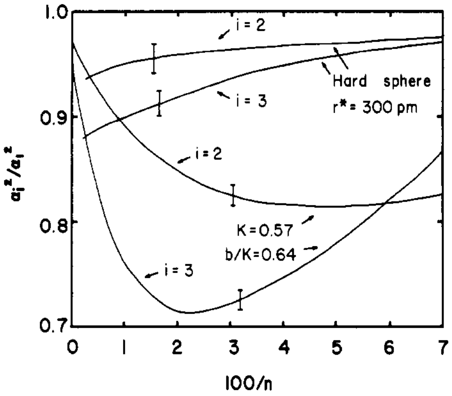

Figure 6. Ratios of expansions along the principal axes for the perturbed chains considered in Figure 5. A representative error bar is shown for each line.

that along the major principal axis can then be assessed from

$$\alpha_i^2/\alpha_1^2 = (\langle L_i^2\rangle/\langle L_1^2\rangle)(\langle L_i^2\rangle_0/\langle L_1^2\rangle_0)^{-1} \qquad (15)$$

Ratios calculated in this manner from the data in Figure 5 are depicted in Figure 6.

All α_i^2/α_1^2 depicted in Figure 6 are less than unity. Expansion of the distribution of chain segments takes place preferentially along the major principal axis. Furthermore, a given type of calculation yields $\alpha_2^2/\alpha_1^2 > \alpha_3^2/\alpha_1^2$ for all but very short chains. Therefore long chains have $\alpha_1^2 > \alpha_2^2 > \alpha_3^2$. This qualitative conclusion is in harmony with results obtained previously using lattice chains,[7,25,29] a smooth density model,[7] and a perturbation method.[30,31] If the generator matrix calculations were carried out in a manner which causes the perturbation to be felt uniformly throughout the chain, infinitely long chains would have $\alpha_1^2 = \alpha_2^2 = \alpha_3^2$ (Figure 4).

The generator matrix treatment and hard-sphere approach yield nearly identical α_i^2/α_1^2 when chains contain about 300 bonds. For smaller chains the generator matrix treatment produces the more asymmetric expansion. If behavior of infinitely long chains in the hard-sphere calculation can be estimated by extrapolation of results depicted in Figure 6, their expansion is more asymmetric than that of infinitely long chains described by the generator matrices.

Generator matrix chains for which data are presented in Figure 6 have asymptotic limits for α_2^2/α_1^2 and α_3^2/α_1^2 of 0.97 and 0.95, respectively. Hard-sphere chains described in this figure also appear to be headed toward limiting values. For α_2^2/α_1^2 the suggested limit is slightly above 0.9, while a limit slightly below 0.9 is expected for α_3^2/α_1^2. These limits are in minor to major disagreement with those suggested by earlier work.

Kranbuehl and Verdier[25] studied chains with up to 62 bonds on a cubic lattice. They found little chain length dependence for α_i^2/α_1^2. Their longest chain had $\alpha_2^2/\alpha_1^2 = 0.88$ and $\alpha_3^2/\alpha_1^2 = 0.80$. Mazur et al.[29] also examined chains on a cubic lattice, the number of bonds now being 50–500. Results for all chains were averaged because there was little dependence on n. In the absence of any attractive interaction (calculation with their Φ set equal to zero), $\alpha_2^2/\alpha_1^2 = 0.90$ and $\alpha_3^2/\alpha_1^2 = 0.79$. These results are in good agreement with those of Kranbuehl and Verdier[25] and slightly lower than the limits obtained in Figure 6. The difference apparently arises because neither perturbed nor unperturbed polymethylene chains conform to a cubic lattice.

The smooth density model employed by Gobush et al.[7] yields limiting values of 0.74 and 0.42 for α_2^2/α_1^2 and α_3^2/α_1^2, respectively, at large z. A less asymmetric expansion was obtained at small z. Their limits are in rather poor agreement with those obtained in Figure 6. Minato and Hatano, using a perturbation method, found α_1^2 increased without limit, but α_2^2 and α_3^2 approached limiting values of 3.39 and 2.12, respectively.[31] Hence their asymptotic limit is zero for both α_2^2/α_1^2 and α_3^2/α_1^2.

Conclusion

Treatment of the intramolecular excluded volume effect via generator matrices permits retention of the bond lengths, bond angles, rotational states, and short-range interactions operative in the unperturbed state. Perturbed polymethylene chains of moderate size are found to have $\alpha_r^2 > \alpha_s^2$, as is to be expected from the behavior of chains in which atoms participating in long-range interactions behave as hard spheres. Details of the behavior of α_r^2 and α_s^2 for chains with up to a few hundred bonds are different in the two treatments. The generator matrix approach for weakly perturbed chains finds $(\alpha_s^5 - \alpha_s^3)/n^{1/2}$ goes through a maximum when n is on the order of 10^3. This maximum is absent in strongly perturbed chains. Infinitely long chains attain a constant value for $(\alpha^5 - \alpha^3)/n^{1/2}$. If the generator matrix treatment is parameterized so that the perturbation is felt perferentially in the middle of the chain, the expansion of both finite and infinite chains is asymmetric. It serves to enhance the existing asymmetry of individual chain configurations. An asymmetric expansion is also seen with chains in which atoms participating in long-range interaction behave as hard spheres.

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