Subchain Expansion in Generator Matrix and Monte Carlo Treatments of Simple Chains with Excluded Volume

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ABSTRACT: Expansion of subchains in a linear polymethylene chain with excluded volume is evaluated by two methods: (1) Monte Carlo chains in which methylene groups participating in long-range interactions behave as impenetrable spheres with a diameter of 300 pm, and (2) generator matrix calculations in which expansion is produced without any effect on the probability of a trans placement in an infinitely long chain. The Monte Carlo calculation shows that subchain expansion has a larger effect on its end-to-end distance than on its radius of gyration. Location of the subchain within the main chain has an appreciable effect on its expansion, the largest dimensions being obtained for a subchain situated in the middle of the main chain. This behavior arises due to repulsive interaction of the subchain with atoms elsewhere in the main chain. It causes certain subchains to have a larger expansion of their end-to-end distance than does the main chain. Generator matrix calculations reproduce these features if they are parameterized in a manner which assumes the perturbation is felt preferentially in the middle of the chain. Neither Monte Carlo nor generator matrix calculations provide support for assumptions made in simple applications of the blob hypothesis.

Chains with intramolecular excluded volume have larger mean dimensions than do chains unperturbed by long-range interactions. Several configuration-dependent properties of perturbed simple chains can be reproduced by using a model susceptible to rapid, accurate evaluation via generator matrices.[1,2] This model assumes the probability of finding a trans placement in an infinitely long chain is unaltered by the excluded volume effect. The perturbation does, however, modify the distribution of these placements. There is assumed to be a greater tendency for segregation of similar rotational states. These assumptions can be used to construct a model in which $(\alpha_s^5 - \alpha_s^3)/n^{1/2}$ attains a nonzero asymptotic limit at large n, as must be the case for any realistic model.[3] Here α_s^2 is $\langle s^2\rangle/\langle s^2\rangle_0$, where $\langle s^2\rangle$ denotes the mean-square radius of gyration for a perturbed chain of n bonds and $\langle s^2\rangle_0$ is the mean-square radius of gyration when the chain is unperturbed by long-range interactions.

The preceding paper[2] compared the overall expansion of finite polymethylene chains in which the perturbation was introduced via the generator matrix method with the expansion of Monte Carlo chains in which atoms participating in long-range interactions behave as impenetrable spheres. Both approaches yield $\alpha_r^2 > \alpha_s^2$ for chains of moderate size, where α_r^2 is $\langle r^2\rangle/\langle r^2\rangle_0$, the ratio of perturbed and unperturbed mean-square end-to-end distances. Expansion of finite chains is found to be asymmetric in both cases. It enhances the asymmetry of individual chain configurations. Extrapolation of the behavior of finite Monte Carlo chains suggests the asymmetric expansion is retained by chains in which n has become infinite. This result is not obtained by the generator matrix treatment if it is assumed that the perturbation is felt uniformly throughout the chain. However, infinitely long generator matrix chains do experience an asymmetric expansion if the computation is performed in a manner which causes the perturbation to be felt preferentially in the middle of the chain.

Our objective here is to explore the implications of this observation by a detailed examination of the behavior of subchains. Results are found to have bearing on assumptions used in the blob hypothesis.[4]

Calculations

Calculation of the overall chain dimensions is described in the preceding paper.[2] We describe here only those additional relationships required in order to characterize the behavior of subchains.

The mean-square dimensions of a subchain depend on its location within the chain and the number of bonds within the subchain. Let $\langle s_{ij}^2\rangle$ denote the mean-square radius of gyration of a subchain made up of bonds indexed from $j - (i-1)/2$ through $j + (i-1)/2$. Thus i denotes the number of bonds in the subchain and j specifies the location of the middle of the subchain. The radius of gyration of this subchain in the unperturbed state is denoted by $\langle s_{ij}^2\rangle_0$. Define an expansion factor for this subchain as

$$\alpha_{sij}^2 = \langle s_{ij}^2\rangle/\langle s_{ij}^2\rangle_0 \tag{1}$$

The average expansion of all subchains containing i bonds is denoted by α_{si}^2 and defined as

$$\alpha_{si}^2 = (n-i+1)^{-1}\sum_{j=(i+1)/2}^{n-(i-1)/2}\alpha_{sij}^2 \tag{2}$$

Equivalent definitions hold for α_{rij}^2 and α_{ri}^2.

Mean-square unperturbed dimensions for subchains were computed with the rotational isomeric state model developed by Flory and co-workers[5,6] for unperturbed linear polymethylene.

$$\langle r_{ij}^2\rangle_0 = Z^{-1}\mathbf{J}^*\mathbf{U}_2\mathbf{U}_3\ldots\mathbf{U}_{j-(i+1)/2}\mathbf{G}_{j-(i-1)/2}\mathbf{G}_{j-(i-3)/2}\ldots \mathbf{G}_{j+(i-3)/2}\mathbf{G}_{j+(i-1)/2}\mathbf{U}_{j+(i+1)/2}\ldots\mathbf{U}_{n-1}\mathbf{J} \tag{3}$$

$$\langle s_{ij}^2\rangle_0 = Z^{-1}(i+1)^{-2}\mathbf{J}^*\mathbf{U}_2\mathbf{U}_3\ldots\mathbf{U}_{j-(i+1)/2}\mathbf{G}_{j-(i-1)/2}\mathbf{G}_{j-(i-3)/2}\ldots \mathbf{G}_{j+(i-3)/2}\mathbf{G}_{j+(i-1)/2}\mathbf{U}_{j+(i+1)/2}\ldots\mathbf{U}_{n-1}\mathbf{J} \tag{4}$$

Here the appropriate generator matrices,[1,6] formulated from the bond length, bond angle supplement, rotational state dihedral angles, and statistical weight matrix for the unperturbed chain, are denoted by **G** with a subscript indexing the bond for which that matrix is used. All other terms in eq 3 and 4 are defined above or in the preceding paper.[2]

Generator matrix calculations of the mean-square dimensions for *perturbed* subchains differ from those shown above for unperturbed subchains only in the formulation of the statistical weight matrices, as described in the preceding paper.[2]

Monte Carlo methods were used to evaluate $\langle r_{ij}^2\rangle$ and $\langle s_{ij}^2\rangle$ for chains in which atoms participating in long-range

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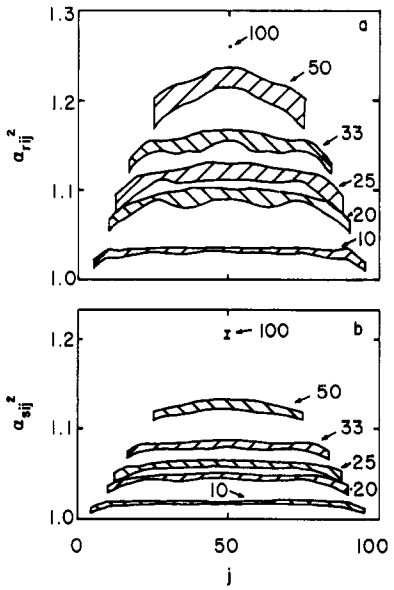

Figure 1. Subchain expansion factors for chains in which atoms participating in long-range interactions behave as impenetrable spheres with a diameter of 300 pm. The number of bonds in the chain is 100 and m is 8. The width of the line is ±1 standard deviation for each α_{rij}^2 (part a) or α_{sij}^2 (part b). The number of bonds in the subchain is noted for each curve.

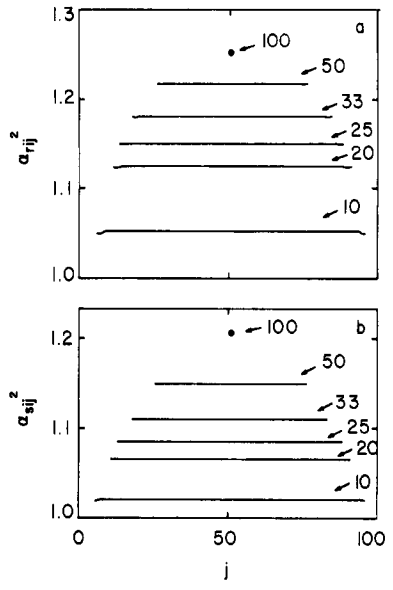

Figure 2. Subchain expansion factors for generator matrix chains with n = 100 and $b = K$ = 0.384. The number of bonds in the subchain is noted for each curve.

interactions behave as impenetrable spheres. The preceding paper[2] describes the procedure for generation of representative samples of such chains.

Position Dependence of Subchain Expansion

Chains Composed of Impenetrable Spherical Atoms. Figure 1 depicts subchain expansion factors calculated for a chain of 100 bonds in which atoms participating in long-range interactions behave as impenetrable spheres with a diameter of 300 pm. The parameter m, defining the shortest interaction considered to be of long range,[2] is assigned a value of 8. Thus the calculations for which results are depicted in Figure 1 were performed in the same manner as the hard-sphere calculations described in Figures 2–6 of the preceding paper.

Expansion factors for the entire chain are about 1.206 for α_s^2 and 1.260 for α_r^2. Long-range interactions produce a larger effect on the end-to-end distance than on the radius of gyration, as expected.[2] Expansion factors for subchains become smaller as the subchain length decreases. In every case for which results are depicted in Figure 1, expansion of the end-to-end distance of a subchain is larger than the expansion of its radius of gyration.

Subchains containing a given number of bonds experience maximal expansion if the subchain is located in the middle of the main chain. Position dependence of subchain expansion is more dramatic with α_{rij}^2 than with α_{sij}^2. The position dependence is barely detectable for very short subchains. For example, subchains with only ten bonds have nearly the same α_{sij}^2 (or α_{rij}^2) for $20 < j < 80$. Expansion factors for this subchain become appreciably position dependent only if the subchain is located near a chain end. In contrast, α_{sij}^2 and α_{rij}^2 are position dependent throughout the entire range if the subchain contains as many as 50 bonds.

Uncertainty in individual α_{rij}^2 and α_{sij}^2 prohibits a precise specification of the shape of their position dependence. For fairly large subchains, such as those containing 50 bonds, a parabolic dependence on position clearly serves as an adequate first approximation. A parabolic dependence might also be a useful approximation for shorter subchains, provided the curvature of the parabola were to approach zero as the number of bonds in the subchain becomes very small.

Generator Matrix Chains with the Perturbation Felt Uniformly throughout the Chain. Figure 2 depicts subchain expansion factors calculated via the generator matrix approach for a chain of 100 bonds. This calculation employs a value of unity for b/K, meaning that the perturbation is felt uniformly throughout the chain (the same statistical weight matrix is used for bonds 3–99).[2] The value of K has been assigned so that α_s^2 for the entire chain is identical with that obtained for the chains considered in Figure 1. No uncertainty need be indicated for the expansion factors depicted in Figure 2 because the generator matrix calculation achieves an exact averaging over all chain configurations.

Comparison of expansion factors depicted in Figures 1 and 2 reveals two features in common. Expansion factors decrease as the number of bonds in the subchain decreases, and a given subchain always has $\alpha_{rij}^2 > \alpha_{sij}^2$. The major difference in subchain expansion factors computed by the two methods lies in their dependence on location within the main chain. Subchain expansion factors depicted in Figure 2 are nearly independent of position. The small position dependence seen is confined to the extreme ends of the chain. It is less noticeable with long subchains (50 bonds) than with short subchains (10 bonds). Can the generator matrix calculation yield a position dependence more closely resembling that seen in Figure 1 if b/K is reassigned so that the perturbation is felt preferentially in the middle of the chain?

Generator Matrix Chains with the Perturbation Felt Preferentially in the Middle of the Chain. Generator matrix calculations cause the perturbation to be felt preferentially in the middle of the chain if b/K is less than unity.[1,2] Figure 3 depicts subchain expansion factors computed using b/K = 0.64, the smallest physically sensible value for this ratio.[1] The value assigned to K has been elevated to 0.41 so that α_s^2 for the entire chain is identical with that depicted in Figures 1 and 2.

Figure 3 has in common with Figures 1 and 2 the feature that $\alpha_{rij}^2 > \alpha_{sij}^2$ for any subchain, and subchain expansion decreases as the number of bonds in the subchain decreases. When attention is focused on the curvature of the

Table I
Comparison of Expansion Factors for Subchains Located in the Middle and at the End of the Main Chain

	$\alpha_{r,i,50}^2 - \alpha_{r,i,(i+1)/2}^2$					$\alpha_{s,i,50}^2 - \alpha_{s,i,(i+1)/2}^2$				
i	MC[a]	0.64[b]	0.82[b]	1.00[b]	1.053[b]	MC[a]	0.64[b]	0.82[b]	1.00[b]	1.053[b]
10	0.02	0.026	0.013	0.003	−0.001	0.010	0.011	0.007	0.002	0.001
20	0.04	0.044	0.022	0.001	−0.005	0.015	0.024	0.012	0.001	−0.002
25	0.04	0.047	0.024	0.001	−0.005	0.015	0.027	0.013	0.000	−0.003
33	0.04	0.046	0.022	0.000	−0.006	0.015	0.027	0.013	0.001	−0.004
50	0.04	0.031	0.015	0.001	−0.004	0.015	0.021	0.010	0.000	−0.003

[a] Approximate value from Figure 1. [b] Generator matrix calculation with indicated value for b/K.

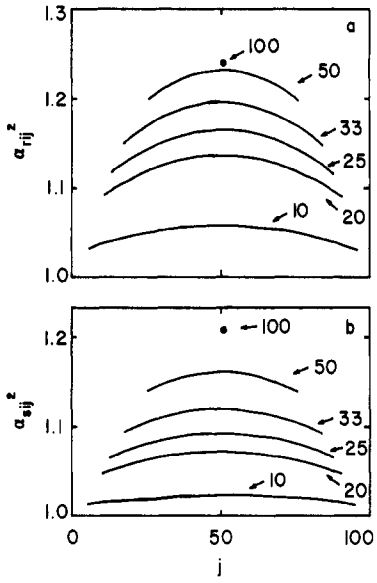

Figure 3. Subchain expansion factors for generator matrix chains with $n = 100$, $K = 0.41$, and $b/K = 0.64$. The number of bonds in the subchain is noted for each curve.

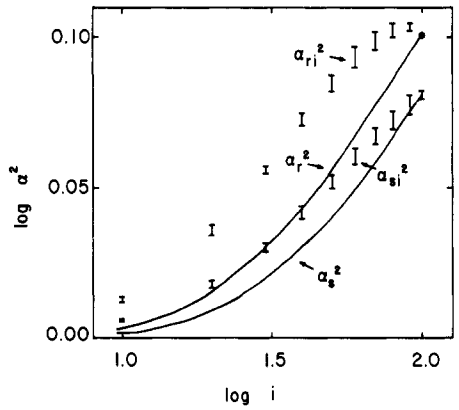

Figure 4. α_{ri}^2 and α_{si}^2 for a polymethylene chain of 100 bonds. Bars denote subchain expansion factors obtained from a Monte Carlo calculation in which atoms participating in long-range interactions behave as impenetrable spheres of 300-pm diameter. Solid lines denote expansion factors (α_r^2 or α_s^2) for *isolated* chains containing i bonds, computed by the same Monte Carlo procedure. These α_r^2 and α_s^2 are from Figure 2 of the preceding paper.[2]

lines, it is clear that Figures 1 and 3 resemble one another, both being different from Figure 2. One means of assessing the curvature is to examine the difference in expansion factors for subchains located in the middle and at the ends of the main chain. Table I reports these differences for the subchains for which results are depicted in Figures 2 and 3 and also for additional generator matrix calculations in which b/K was 0.82 or 1.053. Position within the main chain is seen to be of most importance when the subchain contains about 25–33 bonds. Table I also reports approximate differences in expansion factors for subchains in which atoms participating in long-range interactions behave as impenetrable spheres. The approximate values from the Monte Carlo calculation match up best with generator matrix results obtained when b/K is between 0.64 and 0.82.

Average Subchain Expansion Factors

Chains Composed of Impenetrable Spherical Atoms. Subchain expansion factors, evaluated without regard to position within the main chain, are denoted by α_{si}^2 and α_{ri}^2. Equation 2 gives the relationship between α_{si}^2 and the $n - i + 1$ α_{sij}^2. An analogous expression relates α_{ri}^2 to the α_{rij}^2. Figure 4 depicts α_{ri}^2 and α_{si}^2 for a chain of 100 bonds in which atoms participating in long-range interactions behave as impenetrable spheres of diameter 300 pm. Here m is 8, as was the case in computation of the α_{rij}^2 and α_{sij}^2 depicted in Figure 1.

Figure 4 demonstrates that α_{si}^2 increases continuously as i increases. The bars describe a slightly sigmoid curve, with $d^2(\log \alpha_{si}^2)/d(\log i)^2$ being positive at low i and becoming slightly negative as i approaches n. At any i, α_{ri}^2 is greater than α_{si}^2, as is expected from properties of position-dependent subchain expansion factors considered in Figure 1. An additional important difference in the α_{ri}^2 and α_{si}^2 lies in their behavior as i approaches n. At large i, $d^2(\log \alpha_{ri}^2)/d(\log i)^2$ becomes sufficiently negative so that it causes α_{ri}^2 to pass through a maximum. Subchain expansion factors for the end-to-end distance experience a maximum when i is about 90. Previous Monte Carlo studies of chains on a cubic lattice also found α_{ri}^2 experiences a maximum when i is slightly less than n.[7]

Solid lines in Figure 4 denote expansion factors for *isolated* Monte Carlo chains containing i bonds. These expansion factors are taken from Figure 2 of the preceding paper. Solid lines in Figure 4 must merge with the bars denoting α_{si}^2 and α_{ri}^2 when i becomes 100. If the number of bonds is less than 100, however, the isolated chain experiences a smaller expansion than does a subchain containing the same number of bonds. The extra expansion seen in the subchain must arise from its repulsive interaction with atoms elsewhere in the main chain. This extra expansion is felt both in the end-to-end distance and in the radius of gyration but is of greater consequence in the former case. The sigmoid character of the α_{si}^2 and the maximum experienced by the α_{ri}^2 are both seen to be consequences of the extra expansion, which exerts its largest effect when the subchain is somewhat shorter than the main chain. Curro and Schaefer[7] also attributed their maximum in α_{ri}^2 to the consequence of interaction of the subchain with atoms elsewhere in the main chain.

Generator Matrix Chains with the Perturbation Felt Uniformly throughout the Chain. Figure 5 repeats from Figure 4 bars denoting subchain expansion factors for a polymethylene chain of 100 bonds in which methylene groups participating in long-range interactions behave as impenetrable spheres of diameter 300 pm. Solid lines

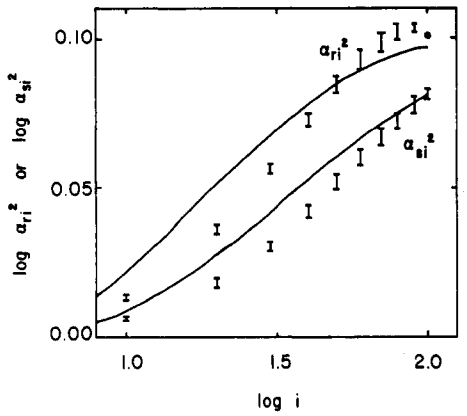

Figure 5. α_{ri}^2 and α_{si}^2 for a polymethylene chain of 100 bonds. Bars denote subchain expansion factors for chains in which methylene groups participating in long-range interactions behave as impenetrable spheres of diameter 300 pm (from Figure 4). Solid lines denote subchain expansion factors computed via generator matrices using $b = K = 0.384$.

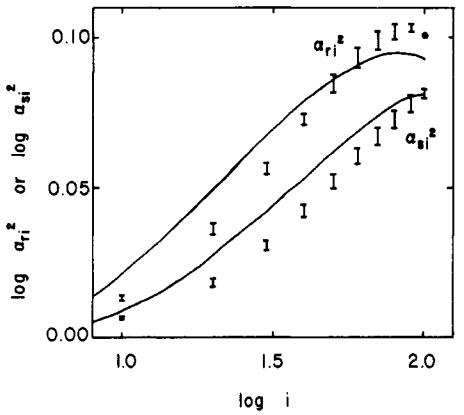

Figure 6. α_{ri}^2 and α_{si}^2 for a polymethylene chain of 100 bonds. Bars denote subchain expansion factors for chains in which methylene groups participating in long-range interactions behave as impenetrable spheres of diameter 300 pm (from Figure 4). Solid lines denote subchain expansion factors computed via generator matrices using $b = K = 0.384$.

denote subchain expansion factors using generator matrices parameterized so that the perturbation is felt uniformly throughout the chain and α_s^2 for the entire chain is the same as that obtained in the Monte Carlo, impenetrable-sphere computation. Both computational procedures find α_{ri}^2 is larger than α_{si}^2. Small subchains are found to experience a larger expansion of the radius of gyration when the computation is carried out using generator matrices. This behavior is hardly surprising because the generator matrix calculation also yields a larger expansion of the radius of gyration for short isolated chains.[2] The major qualitative difference between generator matrix and Monte Carlo results depicted in Figure 5 lies in their shape. While both log α_{ri}^2 and log α_{si}^2 have a sigmoid dependence on log i in the generator matrix calculation, neither experiences a maximum. In contrast, the Monte Carlo calculation produces a definite maximum for α_{ri}^2.

Generator Matrix Chains with the Perturbation Felt Preferentially in the Middle of the Chain. Figure 6 repeats from Figures 4 and 5 bars denoting subchain expansion factors for a polymethylene chain of 100 bonds in which methylene groups participating in long-range interactions behave as impenetrable spheres of diameter 300 pm. Solid lines are now computed via generator matrices using $b/K = 0.64$, with K selected so that α_s^2 for the entire chain is in agreement with that found in the Monte

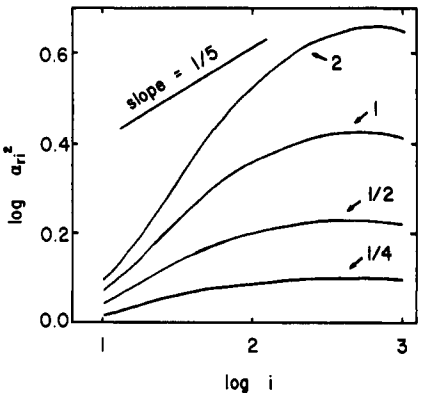

Figure 7. α_{ri}^2 and α_{si}^2 for a polymethylene chain of 100 bonds. Bars denote subchain expansion factors from Figure 4. Solid lines denote subchain expansion factors computed via generator matrices using $K = 0.41$ and $b/K = 0.64$.

Carlo calculation. The major difference in the solid lines depicted in Figures 5 and 6 is in the behavior of α_{ri}^2 as the number of bonds in the subchain approaches the number in the main chain. This subchain expansion factor goes through a maximum only if the generator matrix calculation is carried out in a manner which causes the perturbation to be felt preferenetially in the middle of the chain. Another less apparent difference in Figures 5 and 6 is in the behavior of α_{si}^2. A more sigmoid log α_{si}^2 vs. log i is obtained when the perturbation occurs preferentially in the middle of the chain.

The fact that the intramolecular excluded volume effect produces the largest changes in the middle of the chain is conclusively demonstrated in Figure 1 for chains composed of atoms which act as impenetrable spheres. Generator matrix calculations can reproduce the observed dependence of α_{rij}^2 (or α_{sij}^2) on j if b/K is between 0.64 and 0.82. Generator matrix calculations demonstrate that two consequences of the perturbation being felt preferentially in the middle of the chain are the apprearance of an asymmetric expansion for inifinite as well as finite chains[2] and also appearance of a maximum for α_{ri}^2 when i is somewhat smaller than n.

Behavior of Longer Chains. Concern thus far has been with behavior of subchains in a chain of only 100 bonds. Consideration was restricted to such short chains because the enormous computational resources required for accurate Monte Carlo studies of much longer chains exceed those at our disposal. Generator matrix calculations, in contrast to Monte Carlo calculations, demand relatively little expenditure of computational resources. Consequently generator matrix calculations can be used to estimate subchain expansion in a chain containing an order of magnitude more bonds than the one considered in the Monte Carlo computations described above.

Figures 7 and 8 depict subchain expansion factors computed via generator matrices for a polymethylene chain of 1000 bonds. In each computation the perturbation is felt preferentially in the middle of the chain ($b/K = 0.64$). The value for K ranges from 1/4 to 2. After lengthening of the chain from 100 to 1000 bonds, α_{ri}^2 still goes through a maximum (Figure 7) and log α_{si}^2 still shows a sigmoid dependence on log i (Figure 8). These features are retained over a wide range of K, corresponding to a wide range for the excluded volume parameter z.[1]

It is of interest to compare the subchain behavior depicted in Figures 7 and 8 with predictions obtained with the blob concept.[4] A simple form of this theory asserts subchains behave ideally if they contain fewer than some critical number, n_c, of bonds. The real chain of n bonds

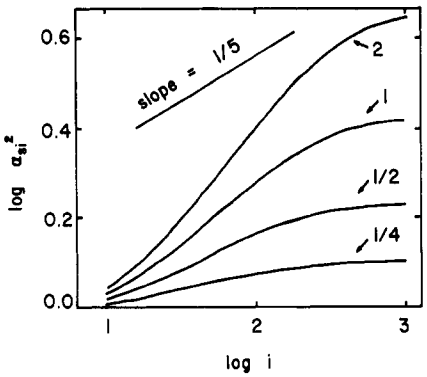

Figure 8. Generator matrix α_{ri}^2 for a polymethylene chain of 1000 bonds. Each computation uses $b/K = 0.64$, and the value for K is shown for each curve. The straight line segment has a slope of 1/5.

is then approximated as a chain of n/n_c blobs. Changes in the environment of the chain are assumed to affect its dimensions through a change in the value for n_c. This theory predicts $\alpha_{si}^2 = \alpha_{ri}^2 = 1$ for $i < n_c$ and that $d(\log \alpha_{si}^2)/d(\log i)$ and $d(\log \alpha_{ri}^2)/d(\log i)$ are 1/5 for $i > n_c$. Modification of the simple blob theory may replace the discontinuous change from ideal to excluded volume statistics by a progressive crossover.[8]

Figures 7 and 8 include a line segment whose slope is 1/5. Lines describing computed behavior of the subchains may have a slope of 1/5 at some value of log i. However, the range of log i over which this slope is observed is not large. Furthermore, there is no indication that the slope tends toward 1/5 as log i becomes large. Indeed, the slope actually becomes negative at large log i in Figure 7. Neither our generator matrix nor Monte Carlo calculations provide support for the blob concept. A major difficulty with simple applications of the blob concept is that they do not properly account for the consequences of the repulsive interaction of the subchain with atoms elsewhere in the main chain. These consequences are a position dependence to the expansion of a subchain (Figures 1 and 3), a maximum for α_{ri}^2 at $i < n$ (Figures 4, 6, and 7), and a pronounced sigmoid character to log α_{si}^2 vs. log i (Figures 4, 6, and 8). A maximum for α_{ri}^2 at $i < n$ has also been seen with chains on a cubic lattice and recognized as being incompatible with simple applications of the blob concept.[7]

Subchain expansion factors could be measured by performing angle-dependent neutron scattering measurements on perturbed polymers in which the isotopic composition of the subchain was different from that of the remainder of the chain. Whether or not these subchains exhibit maximal expansion when they comprise somewhat less than the main chain will depend on the precise manner in which the isotopic labeling is accomplished. If α_{si}^2 is obtained from samples in which the label occurs throughout the subchain, a maximum should not be observed (Figure 8). However, if the isotopic label occurs only at the first and last atoms in the subchain, the measurement will yield α_{ri}^2 and a maximum is predicted (Figure 7).

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A Monte Carlo Study of the Collapse of a Polymer Chain

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ABSTRACT: We study, using Monte Carlo techniques, the equilibrium configurational properties of bead–spring model polymer chains with both repulsive and attractive interactions. By varying the temperature, we represent a polymer chain in solvents with differing degrees of solubility. We find that (a) at high temperatures, corresponding to good solvents, the dependence of the chain dimension R on the number of units N follows the same power law as does a chain with purely repulsive interaction ($R^2 \propto N^{2\nu}$, $\nu \simeq 0.6$), (b) there is a temperature $\tilde{\Theta}$ in the neighborhood of Flory's Θ temperature (at which the second virial coefficient of the interaction vanishes) where there is a linear relation between R^2 and N ($\tilde{\Theta} - \Theta$ depends on the "stiffness" of the chain), and (c) at lower temperatures the chain manifests a collapse which becomes more pronounced with increasing N. There is overall qualitative agreement between our results, experiment, and a generalized form of Flory's theory although the behavior in cases b and c appears to depend on more details of the interaction than are taken into account in the latter.

I. Introduction

The configurations of a polymer chain in a very dilute solution are determined by the interplay between the interactions of chain segments among themselves and with the solvent. In a good solvent excluded volume effects result in a swelling of the chain relative to a random coil. In a poor solvent, on the other hand, the polymer segments prefer self-contacts over contacts with the solvent. It is customary in polymer chain theory to represent these effects by considering an effective interaction potential $u(r)$ between polymer segments which have a short-range repulsive part and a longer range attractive part, e.g., a

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