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Matrix Treatment of Configuration-Dependent Physical Properties for Simple Chains Perturbed by Long-Range Interactions

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ABSTRACT: Matrix methods, widely used to relate configuration-dependent physical properties of unperturbed polymers to chain geometry and short-range contributions to potentials affecting rotation about bonds, have been adapted so that they reproduce several properties of certain chains perturbed by long-range interactions. This objective is achieved through a modification in the significance of certain elements in the statistical weight matrix. Matrices used can be of the same dimensions as those used to successfully treat the unperturbed chain. Illustrative calculations are performed for polymethylene chains containing various numbers of bonds, n, and with different extent of perturbation by long-range interactions. The model yields perturbed chains with the following characteristics: (1) Bond lengths and bond angles are the same as those for the unperturbed chain. (2) $(\alpha_s^5 - \alpha_s^3)/n^{1/2}$ reaches a nonzero asymptotic limit at large n ($\alpha_s^2 = \langle s^2\rangle/\langle s^2\rangle_0$, where $\langle s^2\rangle$ and $\langle s^2\rangle_0$ are the mean-square radius of gyration for perturbed and unperturbed chains, respectively). (3) Large expansions are achieved without alteration in the a priori probability for a trans placement in a long chain. (4) The effect of the perturbation on the ith bond increases as n increases. (5) Long-range interactions exert perturbations preferentially in the middle of the chain. (6) Perturbations are independent of the direction selected for indexing bonds in the chain. The magnitude of the perturbation for a polymer of specified n in a particular polymer–solvent system depends on an adjustable parameter denoted by K. In good approximation, K for polymethylene at 25 °C is found to be $[10C_M\psi_1(1 - \Theta/T)M_0^{1/2}]^{2/5}$. Therefore the model incorporates the thermodynamic character of polymer–solvent interaction as expressed by $\psi_1(1 - \Theta/T)$.

Complete understanding of the behavior of a macromolecule must include the ability to successfully relate configuration-dependent physical properties of the chain to its covalent structure. An impressive variety of configuration-dependent properties exhibited by long chain molecules unperturbed by long-range inateractions has been quantitatively related to the local covalent structure of the polymer through application of matrix methods.[1,2] This approach takes account of the actual structural geometry (bond lengths and bond angles) as well as short-range contributions to potentials affecting rotation about bonds in the chain. Accessible physical properties include size and shape of the unperturbed chain, as reflected by moments of the chain vector and radius of gyration and also by related tensors.[1-6] Several optical properties become accessible when contributions to the dipole moment and anisotropic part of the molecular polarizability tensor are assigned to each rigid group in the macromolecule.[1,2,7-13] Applicability of these matrix methods has been extended to encompass treatment of branched macromolecules unperturbed by long-range interactions.[14-17]

Much effort has been directed toward investigation of the manner in which perturbations produced by long-range interactions alter configuration-dependent properties. A common objective is evaluation of modifications in extension of the chain, as reflected by its mean-square end-to-end distance, $\langle r^2\rangle$, or mean-square radius of gyration, $\langle s^2\rangle$. Much less attention has been given to the actual chain geometry and rotational potentials than is possible in matrix treatments of configuration-dependent properties of unperturbed chains. Indeed, important consequences of perturbations produced by long-range interactions have been obtained from treatments which ignore connectivity of chain atoms and use instead a smoothed density of segments.[18-21] Chain atom connectivity may be recognized by using a pearl necklace model.[22,23] Perturbation of macromolecular dimensions is found to increase without limit as the number, n, of bonds in the chain increases. At sufficiently large n, $\langle s^2\rangle/\langle s^2\rangle_0$ becomes proportional to $n^{1/5}$.[18] Here $\langle s^2\rangle_0$ denotes the mean-square radius of gyration for a chain unperturbed by long-range interactions. Another approach to characterization of configuration-dependent properties of perturbed chain molecules is study of self-avoiding random walks on various types of lattices. Several such studies find representative samples of perturbed chains for which $\langle r^2\rangle/\langle r^2\rangle_0$ becomes proportional to $n^{1/5}$ at sufficiently large n.[24-26]

The power and broad applicability of matrix methods used to treat configuration-dependent properties of unperturbed chains makes it highly desirable to extend their

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range so that they might be used for chains perturbed by long-range interactions. Structural geometry and short-range contributions to potentials affecting rotation about bonds could then be included in a treatment of the perturbed chain. All of the configuration-independent properties susceptible to evaluation by matrix models would become accessible. Such computations require assembly of a statistical weight matrix for each bond about which rotation occurs. Pertinent statistical weight matrices for unperturbed chains are frequently of dimensions $\nu \times \nu$, where ν denotes the number of states assigned for rotation about a bond. A statistical weight matrix with these dimensions may be used if rotation about bond i is dependent upon rotation about bond $i - 1$ but independent of rotation about bond $i - 2$. Reduction in matrix size is possible if the rotational potential is symmetric.[2] Interactions of longer range can be treated by using a larger statistical weight matrix. A statisical weight matrix of dimensions $\nu^j \times \nu^j$ would permit treatment of a chain in which rotation about bond i was dependent on rotation about bonds $i - 1, i - 2, ..., i - j$. In principle, therefore, the contribution of all possible intramolecular interactions in a linear chain of n bonds could be evaluated if one were able to work with, and assign the elements in, a statistical weight matrix of dimensions $\nu^{n-3} \times \nu^{n-3}$. This approach to a matrix treatment of large chain molecules perturbed by long-range interactions is decidedly unattractive. The statistical weight matrices required are simply too large.

Escape from this disappointing state of affairs becomes possible if a slight modification is made in the meaning assigned to elements in a statistical weight matrix. These elements are often formulated as $\exp[-(E_i - E_0)/RT]$, where E_0 is the energy of a short polymer fragment in some reference conformation and E_i is the energy when that fragment has the conformation whose statistical weight is under discussion. Frequently an element may be formulated as a sum of such exponentials, the summation being carried out at appropriately specified intervals over some region of conformational space for the polymer fragment. In any event, the objective is to be able to satisfactorily approximate the entire configurational integral by a sum over discrete states.[1,2] States used for this purpose need not correspond to minima in the conformational energy surface for the polymer fragment.[27]

Statistical weights adopted for the unperturbed state specify a priori probabilities, p_η, $p_{\xi\eta}$, etc., for observation of specified local conformations.[1,2] Here p_η is the a priori probability that a bond will be in state η, $p_{\xi\eta}$ is the a priori probability that a bond is in state η and its predecessor is in state ξ, etc. These a priori probabilities are characterized as first-order, second-order, etc., according to the number of bonds whose state is defined. Thus the a priori probability for finding a chain of n bonds in a specified configuration is an $(n - 2)$-order probability. Perturbations produced by long-range interactions extensively modify the $(n - 2)$-order probabilities. Chain configurations with long-range repulsive interactions experience a reduction in their $(n - 2)$-order probability, and there will consequently be an increase in $(n - 2)$-order probability for chain configurations devoid of such interactions. These perturbations will modify other high-order probabilities as well. The influence of long-range interactions should diminish as one considers probabilities of successively lower order and become negligible for probabilities of first order.

The foregoing discussion provides the rationale for modifying a matrix treatment of an unperturbed chain so that it can be used to evaluate configuration-dependent properties of chains perturbed by long-range interactions. Attribute fundamental significance to the $(n - 2)$-order probabilities because it is these probabilities which dictate the chain configurations to be used in the approximation to the configurational integral. Achieve the perturbation by simply altering the statistical weight matrix in a manner which leaves the p_η unchanged but changes higher order a priori probabilities in a manner which will favor those chain configurations with fewer long-range repulsive interactions. Clearly the necessary alteration in elements of the statisical weight matrix is not to be attributed to a specific interaction energy. It should instead be looked upon as a device which permits a satisfactory approximation to the consequences of a host of long-range interactions.

The objective here is to describe implementation of this rationale for simple symmetric chains with three rotational states (t, g$^\pm$) for each internal bond. Restraints imposed on elements of the statistical weight matrix are characterized and illustrative calculations are performed for polymethylene chains. Cases are considered where consequences of long-range interactions are felt perferentially in the middle of the chain or at chain ends. The proposed treatment can easily be made to yield $\langle s^2\rangle/\langle s^2\rangle_0$ proportional to $n^{1/5}$ at large n.

The Unperturbed Chain

Flory and co-workers[1,2,28] have developed a rotational isomeric state treatment for a simple unperturbed chain with a symmetric rotational potential and three rotational states per bond. Their treatment, which includes statistical weights arising from first- and second-order interactions, will be used for the unperturbed chains considered here. This section reviews the features of their work which are essential to the present matrix treatment of perturbed chains.

The statistical weight matrix for bond i, $\mathbf{U}_i$, can be written as

$$\mathbf{U}_i = \begin{array}{c|ccc} & \mathrm{t} & \mathrm{g}^+ & \mathrm{g}^- \\ \hline \mathrm{t} & \tau & \sigma & \sigma \\ \mathrm{g}^+ & 1 & \sigma\psi & \sigma\omega \\ \mathrm{g}^- & 1 & \sigma\omega & \sigma\psi \end{array}_{\,i} \qquad (1)$$

Columns and rows index the state of bond i and $i - 1$, respectively, and the order of indexing is t, g$^+$, g$^-$. First-order interactions weight gauche states by a factor of σ relative to trans states. Second-order interactions give rise to weighting factors denoted by τ, ψ, and ω. The tt, g$^\pm$g$^\pm$, and g$^\pm$g$^\mp$ states are weighted by factors of τ, ψ, and ω, repectively, relative to tg$^\pm$ and g$^\pm$t states.

The statistical weight matrix in eq 1 can be condensed,[2] without loss of content, to

$$\mathbf{U}_i = \begin{array}{c|cc} & \mathrm{t} & \mathrm{g}^\pm \\ \hline \mathrm{t} & \tau & 2\sigma \\ \mathrm{g}^\pm & 1 & \sigma(\psi + \omega) \end{array}_{\,i} \qquad (2)$$

The configuration partition function, Z, for a chain of n bonds is obtained from this statistical weight matrix as

$$Z = \mathrm{row}\,(1, 0)\,\mathbf{U}_2\mathbf{U}_3 \ldots \mathbf{U}_{n-1}\,\mathrm{col}\,(1, 1) \qquad (3)$$

If statistical weight matrices are identical for all i, the configuration partition function can be expressed in terms of eigenvalues of $\mathbf{U}$.

$$\mathrm{U} = \mathrm{C}\begin{bmatrix} \lambda_1 & 0 \\ 0 & \lambda_2 \end{bmatrix}\mathrm{D} \qquad (4)$$

$$\lambda_{1,2} = \tfrac{1}{2}[\tau + \sigma(\psi + \omega) \pm \{[\tau - \sigma(\psi + \omega)]^2 + 8\sigma\}^{1/2}] \qquad (5)$$

$$\mathbf{C} = \begin{bmatrix} 1 & 1 \\ (\tau - \lambda_2)^{-1} & (\tau - \lambda_1)^{-1} \end{bmatrix} \tag{6}$$

$$\mathbf{D} = (\lambda_1 - \lambda_2)^{-1} \begin{bmatrix} \tau - \lambda_2 & -(\tau - \lambda_1)(\tau - \lambda_2) \\ -(\tau - \lambda_1) & (\tau - \lambda_1)(\tau - \lambda_2) \end{bmatrix} \tag{7}$$

$$Z = [(1 - \tau + \lambda_1)(\tau - \lambda_2)\lambda_1^{n-2} - (1 - \tau + \lambda_2)(\tau - \lambda_1)\lambda_2^{n-2}](\lambda_1 - \lambda_2)^{-1} \tag{8}$$

As n goes to infinity, the configuration partition function becomes proportional to λ_1^n. The second-order a priori probabilities are then obtained as

$$p_{\xi\eta} = u_{\xi\eta}\mathbf{C}_{\eta 1}\mathbf{D}_{1\xi}/\lambda_1 \tag{9}$$

When presented in matrix form, these $p_{\xi\eta}$ are

$$\begin{array}{cc} & \begin{array}{cc} \mathrm{t} & \mathrm{g}^{\pm} \end{array} \\ \begin{array}{c} \mathrm{t} \\ \mathrm{g}^{\pm} \end{array} & \begin{bmatrix} \tau(\tau - \lambda_2) & 2\sigma \\ 2\sigma & -\sigma(\psi + \omega)(\tau - \lambda_1) \end{bmatrix} \end{array} [\lambda_1(\lambda_1 - \lambda_2)]^{-1} \tag{10}$$

from which the first-order a priori probabilities are obtained as

$$p_{\mathrm{t}} = 1 - p_{\mathrm{g}\pm} = [\tau(\tau - \lambda_2) + 2\sigma][\lambda_1(\lambda_1 - \lambda_2)]^{-1} \tag{11}$$

The average number of bonds in a sequence of trans placements is

$$\langle n_{\mathrm{t}} \rangle = (p_{\mathrm{tt}} + p_{\mathrm{g}\pm\mathrm{t}})p_{\mathrm{g}\pm\mathrm{t}}^{-1} = \lambda_1(\lambda_1 - \tau)^{-1} \tag{12}$$

The mean-square unperturbed end-to-end distance is obtained as

$$\langle r^2 \rangle_0 = Z^{-1}\mathbf{F}_1\mathbf{F}_2 \ldots \mathbf{F}_{n-1}\mathbf{F}_n \tag{13}$$

If $\mathbf{U}_i$ and Z are given by eq 2 and 3, respectively, for a chain containing n bonds of length l, with bond angle supplement θ and dihedral angles for the t, g$^+$, and g$^-$ states of 0°, φ, and $-\varphi$, respectively, then[2]

$$\mathbf{F}_1 = \text{row } (1, 2l\cos\theta, 2l\sin\theta, 0, l^2, 1, 2l\cos\theta, 2l\sin\theta, 0, l^2) \tag{14}$$

$$\mathbf{F}_n = \text{col } (l^2, l, 0, 0, 1, l^2, l, 0, 0, 1) \tag{15}$$

$$\mathbf{F}_i = \begin{bmatrix} \tau\mathbf{E}_0\mathbf{F}_0 & 2\sigma\mathbf{E}_0\mathbf{F}_+ \\ \mathbf{E}_0\mathbf{F}_0 & \sigma(\psi\mathbf{E}_+ + \omega\mathbf{E}_-)\mathbf{F}_+ \end{bmatrix}_i \tag{16}$$

$$2 \leqslant i \leqslant n - 1$$

$$\mathbf{E}_0\mathbf{F}_0 = \begin{bmatrix} 1 & 2l\cos\theta & 2l\sin\theta & 0 & l^2 \\ 0 & \cos\theta & \sin\theta & 0 & l \\ 0 & \sin\theta & -\cos\theta & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{bmatrix} \tag{17}$$

$$\mathbf{E}_0\mathbf{F}_+ = \begin{bmatrix} 1 & 2l\cos\theta & 2l\sin\theta & 0 & l^2 \\ 0 & \cos\theta & \sin\theta & 0 & l \\ 0 & \sin\theta\cos\varphi & -\cos\theta\cos\varphi & \sin\varphi & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{bmatrix} \tag{18}$$

The mean-square unperturbed radius of gyration is obtained from eq 20. Generator matrices in eq 20 have

$$\langle s^2 \rangle_0 = (n + 1)^{-2}Z^{-1}\mathbf{F}_1\mathbf{F}_2 \ldots \mathbf{F}_{n-1}\mathbf{F}_n \tag{20}$$

dimensions 1 × 14, 14 × 14, and 14 × 1. They are obtained in the usual manner[2] from generator matrices used to compute $\langle r^2 \rangle_0$.

Experimentally measured unperturbed dimensions,[29] and their temperature coefficient,[30,31] for linear polymethylene, as well as the optical anisotropy exhibited by linear alkanes,[32] have been reproduced by using the preceding rotational isomeric state treatment with l = 1.53 Å, θ = 68°, φ = 120°, E_σ = 500 cal mol^{-1}, E_ω = 2000 cal mol^{-1}, and $E_\tau = E_\psi = 0$.[28,32] At 300 K these energies yield σ = 0.432, ω = 0.034, and $\tau = \psi = 1$. Second-order a priori probabilities obtained from eq 10 are

$$\begin{array}{cc} & \begin{array}{cc} \mathrm{t} & \mathrm{g}^{\pm} \end{array} \\ \begin{array}{c} \mathrm{t} \\ \mathrm{g}^{\pm} \end{array} & \begin{bmatrix} 0.379 & 0.263 \\ 0.263 & 0.094 \end{bmatrix} \end{array} \tag{21}$$

and first-order a priori probabilities are $p_{\mathrm{t}} = 1 - p_{\mathrm{g}\pm}$ = 0.642. There are an average of 2.4 bonds in a sequence of trans placements.

Perturbed Chains with the Same First-Order a Priori Probabilities as Unperturbed Chains

A substantial alteration in mean-square dimensions for a polymer chain would occur if there were an overwhelming drive to propagate placements of the same kind. Each chain would form a rod in the event that the tendency for propagation of placements of the same kind were absolute. Rods containing only trans placements would be expected to have a larger end-to-end distance than rods containing only g$^+$ or g$^-$ placements. Both types of rods would be expected to have r^2 much greater than $\langle r^2 \rangle_0$ for a flexible chain with large n.

The rods would usually be devoid of repulsive long-range interactions, although such need not necessarily be the case. For example, a value of φ near 180° might cause the g$^+$ and g$^-$ helices to be of such low pitch that repulsion would occur between successive turns of the helix. For many polymers of interest, however, the chain geometry and rotational states are such that these conflicts will not occur. Our concern here is with polymers in which repulsive interactions are absent in g$^+$ and g$^-$ helices and in the chain configuration consisting entirely of trans placements.

The foregoing envisions existence of a class of chain molecules for which repulsive long-range interactions are eliminated, and the mean-square end-to-end distance increased, by causing each chain to rigorously propagate a certain rotational state. Of course, it is unlikely that a particular rotational state would be rigorously propagated throughout the chain for most perturbed molecules of interest. Consider instead chains in which the tendency to propagate a particular conformation is not absolute but only somewhat larger than that found in the unperturbed molecule. This situation might well serve to increase the mean dimensions of the chain and to also reduce the number of long-range repulsive interactions. The chain would then have two of the characteristics associated with a polymer in a good solvent: larger dimensions and fewer

$$(\psi\mathbf{E}_+ + \omega\mathbf{E}_-)\mathbf{F}_+ = \begin{bmatrix} \psi + \omega & 2l(\psi + \omega)\cos\theta & 2l(\psi + \omega)\sin\theta & 0 & l^2(\psi + \omega) \\ 0 & (\psi + \omega)\cos\theta & (\psi + \omega)\sin\theta & 0 & l(\psi + \omega) \\ 0 & (\psi + \omega)\sin\theta\cos\varphi & -(\psi + \omega)\cos\theta\cos\varphi & (\psi + \omega)\sin\varphi & 0 \\ 0 & (\psi - \omega)\sin\theta\sin\varphi & -(\psi - \omega)\cos\theta\sin\varphi & -(\psi - \omega)\cos\varphi & 0 \\ 0 & 0 & 0 & 0 & \psi + \omega \end{bmatrix} \tag{19}$$

repulsive long-range interactions than the molecule in its unperturbed state.

The probability for propagation of a sequence of trans placements can be enhanced if the value assigned to τ is increased. If no other change is made in the statistical weights, there would also be an increase in p_t. Similarly, the probability for propagation of a sequence of gauche placements of the same sign is increased if a larger value is assigned to ψ. In the absence of any other change in statistical weights, an increase in ψ will produce an increase in $p_{g\pm}$ and a decrease in p_t. Clearly it should be possible to increase the probability for propagation of a particular type of placement, without altering p_t or $p_{g\pm}$, if increases in τ and ψ are correlated in an appropriate manner. Such chains would be expected to exhibit a larger mean-square end-to-end distance and fewer repulsive long-range interactions than chains with unmodified τ and ψ. This alteration in conformational properties would have been achieved without any change in $p_t = 1 - p_{g\pm}$ or in statistical weights arising from first-order interactions.

Perturbation of the chain through correlated changes in τ and ψ will not, of course, account for all chain configurations whose $(n-2)$-order a priori probability is increased by long-range interactions. However, the objective here is not an exact solution to the configurational integral. Instead we will be content to evaluate configuration-dependent properties for a large number (3^{n-2} in the present case) of suitably weighted chains if numerical answers so obtained represent a sufficiently accurate approximation to those which might have been received from an exact solution to the configurational integral. This objective is attainable because, as will be shown below, it is easy to reproduce $\langle s^2\rangle/\langle s^2\rangle_0$ proportional to $n^{1/5}$ at large n.

The desired connection between τ and ψ can be found by demanding that $p_t - p_{g\pm}$ be constant. From eq 5 and 11, this term is found to be

$$p_t - p_{g\pm} = [\tau - \sigma(\psi + \omega)]\{[\tau - \sigma(\psi + \omega)]^2 + 8\sigma\}^{-1/2} \quad (22)$$

This equation can be recast as a quadratic in τ. Solutions obtained from the quadratic formula are

$$\tau = \sigma(\psi + \omega) \pm 2(p_t - p_{g\pm})\{2\sigma[1 - (p_t - p_{g\pm})^2]^{-1}\}^{1/2} \quad (23)$$

The desired solution is obtained with the "+" sign if $p_t > p_{g\pm}$ and with the "−" sign if $p_t < p_{g\pm}$. Therefore

$$\tau = \sigma(\psi + \omega) + 2(p_t - p_{g\pm})\{2\sigma[1 - (p_t - p_{g\pm})^2]^{-1}\}^{1/2} \quad (24)$$

In the next section we explore the sensitivity of $\langle r^2\rangle$ and $\langle s^2\rangle$ to changes in τ and ψ when the relationship between these statistical weights is that given by eq 24. Expansion factors will be defined as

$$\alpha_r^2 = \langle r^2\rangle/\langle r^2\rangle_0 \quad (25)$$

$$\alpha_s^2 = \langle s^2\rangle/\langle s^2\rangle_0 \quad (26)$$

Here $\langle r^2\rangle_0$ and $\langle s_2\rangle_0$ denote mean-square dimensions obtained from eq 13 and 20, using the τ and ψ appropriate for the unperturbed state. If different τ and ψ are used, the mean-square dimensions are denoted by $\langle r^2\rangle$ and $\langle s^2\rangle$. These computations simply entail treating the chain with a modified statistical weight matrix, the same matrix being used for each internal bond. It is immediately apparent that $\langle r^2\rangle/nl^2$ and $\langle s^2\rangle/nl^2$ must approach asymptotic limits as n goes to infinity. Consequently α_r and α_s, obtained from eq 25 and 26, must also approach an asymptotic limit, α_∞, as n goes to infinity. This behavior is in conflict with the expectation that α_r and α_s should become proportional to $n^{1/10}$ at sufficiently large n.[18] Procedures which yield the proper chain-length dependence for α_r and α_s will be described in a later section.

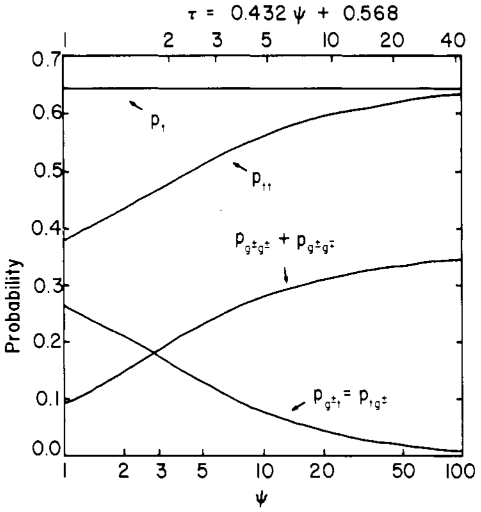

Figure 1. First- and second-order a priori probabilities as n goes to infinity for chains with $\sigma = 0.432$, $\omega = 0.034$, and the indicated τ and ψ. Probabilities are depicted as a function of ln ψ.

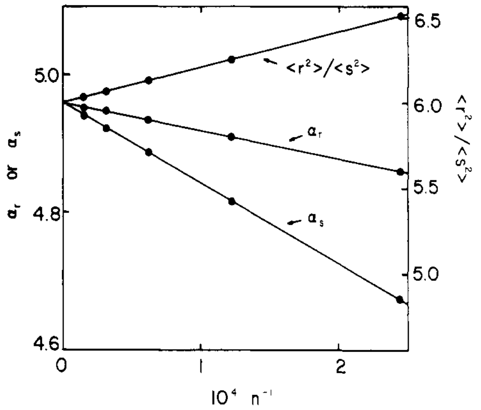

Figure 2. Chain-length dependence for α_r, α_s, and $\langle r^2\rangle/\langle s^2\rangle$ when $\sigma = 0.432$, $\omega = 0.034$, $\psi = 100$, $\tau = 43.8$, $\theta = 68°$, and gauche placements are located at ±120°.

Illustrative Calculations for Polymethylene Chains Using the Same τ for All Internal Bonds

Configuration-dependent physical properties of unperturbed linear polymethylene chains have been successfully treated by using $l = 1.53$ Å, $\theta = 68°$, $\varphi = 120°$, $E_\sigma = 500$ cal mol^{-1}, $E_\omega = 200$ cal mol^{-1}, and $E_\tau = E_\psi = 0$.[28,32] At 300 K these energies yield $\sigma = 0.432$, $\omega = 0.034$, $\tau = \psi = 1$, and $p_t = 1 - p_{g\pm} = 0.642$. For this specific case, eq 24 becomes

$$\tau = 0.432\psi + 0.568 \quad (27)$$

and the average number of bonds in a sequence of trans placements, from eq 12, is

$$\langle n_t\rangle = 1.00 + 1.44\tau = 1.82 + 0.62\psi \quad (28)$$

Computations of $\langle r^2\rangle$, $\langle s^2\rangle$, p_η, and $p_{\xi\eta}$ were carried out for the above l, θ, φ, and statistical weights. Values for ψ ranged up to 100, and the corresponding τ were computed from eq 27. Each computation was carried out for several n ranging from 4 to 65 538. At small n, p_t for chains with $\tau \neq 1$ was frequently quite different from the result obtained at the same n when τ was unity. However, as n increased, p_t approached 0.642 for all values of τ. The variation in p_t at small n is not surprising because eq 9 becomes valid only in the asymptotic limit as n increases. An n of 514 was sufficient to bring p_t to within 1% of the asymptotic value when $\psi \leq 50$. At $\psi = 100$, an n of 1026 was required to approach to within 1% of the limiting value for p_t.

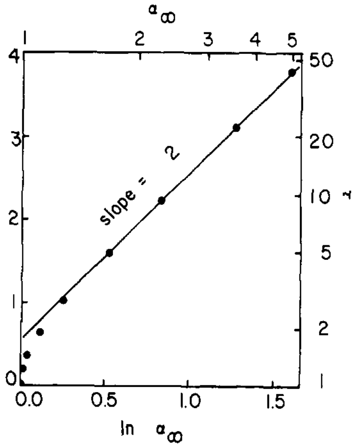

Figure 3. Relationship between ln τ and ln α_∞ when $\sigma = 0.432$, $\omega = 0.034$, $\tau = 0.432\psi + 0.568$, $\theta = 68°$, and gauche placements are located at ±120°.

Figure 1 depicts the dependence of limiting p_t, p_{tt}, $p_{tg\pm} = p_{g\pm t}$, and $p_{g\pm g\pm} + p_{g\pm g\mp}$ on τ and ψ. As expected, p_t at the asymptotic limit is independent of τ. The p_t value defines an upper limit for p_{tt}. Figure 1 demonstrates that p_{tt} approaches this upper limit with an increase in the value assigned to τ. When τ is 40, p_{tt} is smaller than p_t by only 0.01. The increase in ψ provides a greater weight for a pair of bonds having gauche placements of the same sign. Consequently $p_{g\pm g\pm}$ increases as ψ increases. There is a decline in the a priori probability for a pair of bonds in $g^\pm t$ or $tg^\pm$ placements when τ and ψ increase. When ψ is 100, $p_{tg\pm} = p_{g\pm t}$ is only 0.010.

Figure 2 depicts the approach to the asymptotic limit for several properties when ψ is 100, the largest value used. At finite n, α_s lags behind α_r. However, these two expansion factors approach the same value, 4.96, as n goes to infinity. The ratio of the mean-square end-to-end distance to the mean-square radius of gyration exceeds 6 at finite n, but becomes equal to 6 as n goes to infinity. A more rapid convergence of α_r, α_s, and $\langle r^2\rangle/\langle s^2\rangle$ to their asymptotic limits was obtained in cases where ψ was less than 100. In all cases studied the asymptotic limit for $\langle r^2\rangle/\langle s^2\rangle$ was 6, and α_s approached α_r as n went to infinity.

Asymptotic expansion factors rise as τ and ψ increase from unity. Behavior of the limiting expansion factors is depicted in Figure 3. Dependence of ln τ upon ln α_∞ is not linear when τ is only slightly above unity. As τ increases, however, ln τ becomes proportional to ln α_∞. If α_∞ is greater than about 1.4

$$\mathrm{d}\ln\tau/\mathrm{d}\ln\alpha_\infty = 2 \tag{29}$$

The relationship between τ and ψ, eq 27, demands than d ln ψ/d ln α_∞ must also become equal to 2 as α_∞ increases. Comparison of Figure 3 and a plot of ln ψ vs. ln α_∞ (not shown) reveals that ln τ becomes a linear function of ln α_∞ at somewhat smaller α_∞ than does ln ψ.

One of the major failures of the model whose behavior is depicted in Figures 1–3 is that α becomes independent of n at large n, rather than becoming proportional to $n^{1/10}$.[18] The behavior depicted in Figure 3 reveals a simple means by which the proper dependence of α upon n could be obtained. In view of eq 29, the model would necessarily yield

$$(\mathrm{d}\ln\alpha/\mathrm{d}\ln n)_{n\to\infty} = 1/10 \tag{30}$$

if the value assigned to τ were made a function of n according to

$$(\mathrm{d}\ln\tau/\mathrm{d}\ln n)_{n\to\infty} = 1/5 \tag{31}$$

The model would still be deficient in that it implies effects of long-range interactions are felt in like manner in the middle of the chain and near chain ends; i.e., the same τ is used for all internal bonds in a chain of specified n. This problem will be addressed, and rectified, in the next section. Effective use will be made of one feature, specifically eq 31, of the simpler model, where the same τ is used for all internal bonds.

Chains in Which Long-Range Interactions Produce Different Effects in the middle of the Chain and near Chain Ends

In order to modify the model so that long-range effects can manifest themselves differently in the middle of the chain and near chain ends, τ and ψ must be made functions of i. Let the relationship expressed in eq 24, which was originally designed to relate τ and ψ, now relate τ_i and ψ_i instead

$$\tau_i = \sigma(\psi_i + \omega) + 2(p_t - p_{g\pm})\{2\sigma[1 - (p_t - p_{g\pm})^2]^{-1}\}^{1/2} \tag{32}$$

Here σ, ω, p_t, and $p_{g\pm}$ still have the values characteristic of the unperturbed chain. Will use of eq 32 for all i in the range $2 \le i \le n - 1$ continue to yield a constant $p_t = 1 - p_{g\pm}$ for the perturbed chain if τ and ψ become functions of i? At first glance it would appear this feature must be sacrificed if τ and ψ are not constant over the entire chain. The relationship between τ and ψ in eq 24 was obtained by using eq 9. What significance is to be attributed to $u_{\xi\eta}$, $\mathbf{C}_{\eta 1}$, $\mathbf{D}_{1\xi}$, and λ_1 if τ and ψ are functions of i? Indeed the pertinence of the entire diagonalization scheme, presented in eq 4–7, would appear to be called into question if τ and ψ are not constant. Specifically, it must be true that

$$\mathbf{C}_{i-1}\begin{bmatrix}\lambda_1 & 0\\ 0 & \lambda_2\end{bmatrix}_{i-1}\mathbf{D}_{i-1}\mathbf{C}_i\begin{bmatrix}\lambda_1 & 0\\ 0 & \lambda_2\end{bmatrix}_i\mathbf{D}_i = \mathbf{C}_{i-1}\begin{bmatrix}\lambda_1 & 0\\ 0 & \lambda_2\end{bmatrix}_{i-1}\begin{bmatrix}\lambda_1 & 0\\ 0 & \lambda_2\end{bmatrix}_i\mathbf{D}_i \tag{33}$$

if $\mathbf{U}_{i-1} = \mathbf{U}_i$, but eq 33 may be error if $\mathbf{U}_{i-1} \neq \mathbf{U}_i$.

Closer inspection reveals the problem might not be as severe as suggested by a first glance. Initially assign τ and ψ for all bonds in a long chain the values appropriate for the unperturbed state. For a polymethylene chain, this assignment is $\tau = \psi = 1$. The mean-square dimensions are then $\langle r^2\rangle_0$ and $\langle s^2\rangle_0$, and the a priori probability for a trans placement in a long chain is p_t. Now produce a small increase in the τ_i. Let the increase be weakly dependent on i but require $\tau_i = \tau_{n-i+1}$ (properties of the chain should not depend on the direction in which indexing occurs) and relate τ_i to ψ_i by eq 32. On the basis of the behavior of the polymethylene chain described in the previous section, mean dimensions are now expected to be larger than $\langle r^2\rangle_0$ and $\langle s^2\rangle_0$. Since τ_i is now a function of i, there may also have been a change in the a priori probability for a trans placement in the chain. It is not immediately obvious, however, whether p_t should increase or decrease. Indeed, it might be possible that $\langle r^2\rangle$ and $\langle s^2\rangle$ would be much more sensitive than p_t to the changes produced in τ_i and ψ_i. If that is so (and calculations presented below confirm it to be true for polymethylene chains), one could produce significant expansion of the chain, while doing nothing of consequence to p_t, using a scheme in which τ_i and ψ_i were functions of i. We can now explore the manner in which configuration-dependent physical properties of perturbed chains depend on the connection between local consequences of the perturbation and the distance of a bond from a chain end. Information available from this approach will become apparent from a consideration of several examples.

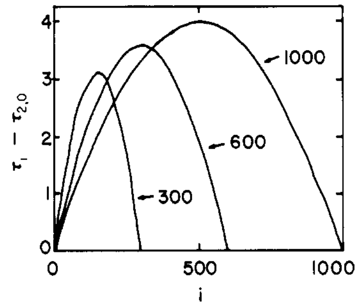

Figure 4. Chains with parabolic τ_i calculated from eq 34 and 36 with $a = {}^1/_5$, $K = 1$, and constant τ_2. The n are noted for each curve.

Perturbations produced by long-range interactions are felt preferentially in the center of the chain if τ_i is parabolic, centered at $i = {}^1/_2(n + 1)$, and $\tau_{(n+1)/2} > \tau_2$

$$\tau_i = \tau_{(n+1)/2} - (n + 1 - 2i)^2(n - 3)^{-2}(\tau_{(n+1)/2} - \tau_2) \qquad (34)$$

If long-range interactions produce no significant effect at chain ends, τ_2 would be assigned the value $\tau_{2,0}$ used for the unperturbed chain. For such chains the relationship between α and n will be dictated by the relationship between $\tau_{(n+1)/2}$ and n. If perturbed chains are to obey eq 30, $\tau_{(n+1)/2}$ is expected to behave in a manner given by the following simple modification of eq 31:

$$(\mathrm{d}\ln \tau_{(n+1)/2}/\mathrm{d}\ln n)_{n\to\infty} = a \qquad (35)$$

where a is an appropriate constant. The desired limiting behavior is obtained with

$$\tau_{(n+1)/2} = Kn^a + \tau_{2,0} \qquad (36)$$

where K is a constant which dictates the size of α_r and α_s at a particular n and a. This constant would be zero if the chain were unperturbed.

Chains with τ_i given by eq 34 and 36 have an undesirable feature which becomes apparent from inspection of Figure 4. Here τ_i is shown as a function of i for various n, K and a being assigned values of unity and ${}^1/_5$, respectively, and τ_2 being held constant. The value specified for many τ_i (e.g., τ_{150}) is seen to decrease when the chain is lengthened from 300 to 1000 bonds. This behavior would suggest the effect of long-range interactions on a subchain might become less severe as the chain is lengthened. Our expectation is that such is not the case in a real chain. We assume the perturbation felt at bond i cannot decrease when the chain is lengthened. Thus a restraint on the recipe used to relate $\tau_{(n+1)/2}$ to n is that $\mathrm{d}\tau_i/\mathrm{d}n$, $1 < i < n$, cannot be negative. At constant τ_2 the indicated derivative is

$$\mathrm{d}\tau_i/\mathrm{d}n = 4Kn^a(i - 2)[a(n - i - 1)n^{-1} - (n + 1 - 2i) \times (n - 3)^{-1}](n - 3)^{-2} \qquad (37)$$

which is nonnegative for $2 < i < n - 1$ if $a > n(n - 5)/(n - 3)(n - 4)$. Thus a must be unity or larger for long chains if τ_2 is to be constant and $\mathrm{d}\tau_i/\mathrm{d}n$ is to be nonnegative. Calculations of $\langle r^2\rangle$ and $\langle s^2\rangle$ were performed as a function of n with $a = \tau_2 = 1$ and various K greater than zero. In all cases the expansion factors at large n increase more rapidly than $n^{1/10}$. Therefore parabolic dependence of τ_i, with τ_2 simultaneously being constant, is not acceptable.

A satisfactory set of parabolas is obtained by using eq 36 in conjunction with eq 38

$$\tau_2 = bn^a + \tau_{2,0} \qquad (38)$$

The ratio b/K governs whether the perturbation is felt preferentially in the middle of the chain or at the ends.

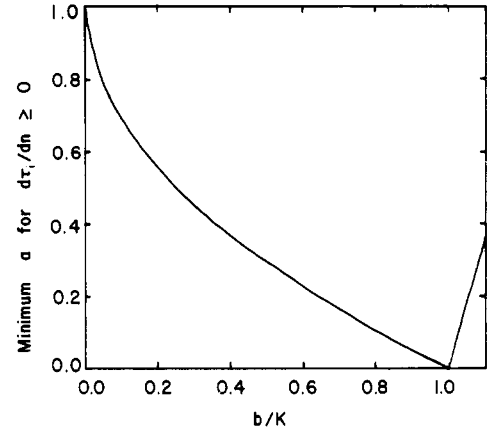

Figure 5. Limiting behavior at large n for a specified by eq 39.

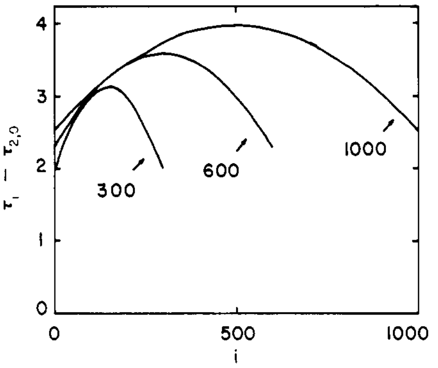

Figure 6. Chains with parabolic τ_i calculated from eq 40 with $K = 1$. The n are noted for each curve.

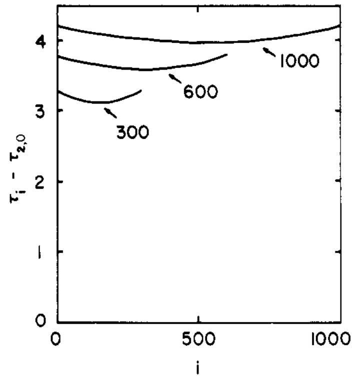

Figure 7. Chains with parabolic τ_i calculated using $b/K = 1.053$, $a = {}^1/_5$, $K = 1$, and the indicated n.

All i in the range $2 \leq i \leq n - 1$ will have $\mathrm{d}\tau_i/\mathrm{d}n \geq 0$ if

$$a \geq 4(i - 2)(1 - b/K)n(n + 1 - 2i)\{(n - 3)[4(i - 2) \times (n - i - 1) + (n + 1 - 2i)^2 b/K]\}^{-1} \qquad (39)$$

Limits imposed by eq 39 on a become independent of n as n increases. The limiting behavior is depicted in Figure 5 as a function of b/K. If a is to be ${}^1/_5$, as suggested by Figure 3 and eq 31, b/K must lie between 0.64 and 1.053. Behavior of parabolas generated with $a = {}^1/_5$ and $b/K = 0.64$

$$\tau_i = \tau_{2,0} + [1 - 0.36(n + 1 - 2i)^2(n - 3)^{-2}]Kn^{1/5} \qquad (40)$$

is depicted in Figure 6 for $K = 1$ and various n. Negative $\mathrm{d}\tau_i/\mathrm{d}n$ are no longer obtained.

The largest τ_i occur at the ends of the chain when b/K exceeds unity. The term b/K can be no larger than 1.053 if a is to be ${}^1/_5$. Parabolas obtained with $b/K = 1.053$, $a = {}^1/_5$, and $K = 1$ are depicted in Figure 7.

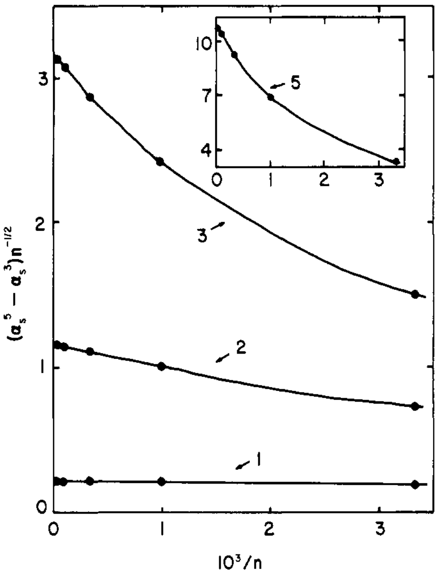

Figure 8. Chain-length dependence of computed $(\alpha_s^5 - \alpha_s^3)/n^{1/2}$ when τ_i is given by eq 40, ψ_i is related to τ_i by eq 32, $\sigma = 0.432$, $\omega = 0.034$, $\theta = 68°$, and gauche placements are located at ±120°. Values used for K are indicated for each curve.

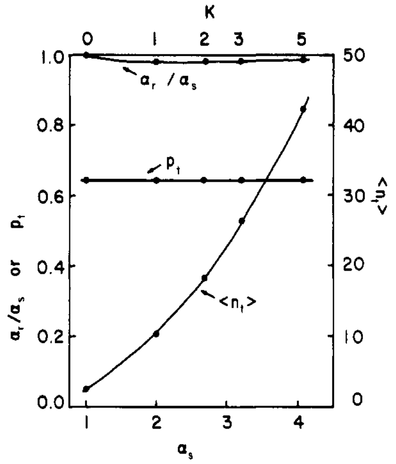

Figure 9. Values of p_t, α_r/α_s, and $\langle n_t \rangle$ for chains of 10^4 bonds. Statistical weights and geometric parameters are the same as those used in Figure 8.

Configuration-dependent physical properties were computed for perturbed polymethylene chains, using eq 40 with K = 1, 2, 3, and 5. Figure 8 depicts chain-length dependence of $(\alpha_s^5 - \alpha_s^3)/n^{1/2}$. At each K for which results are depicted in Figure 8, $(\alpha_s^5 - \alpha_s^3)/n^{1/2}$ reaches an asymptotic limit at large n. Therefore eq 40 yields α_s which become proportional to $n^{1/10}$ at sufficiently large n. As K increases, larger n are required to bring $(\alpha_s^5 - \alpha_s^3)/n^{1/2}$ close to its limiting value.

Certain properties for chains with $n = 10^4$ are depicted in Figure 9. The a priori probability for a trans placement is unaffected by the perturbation. Thus eq 32 successfully relates τ_i and ψ_i even though the $\mathbf{U}_i$ are not identical. This constancy of p_t is obtained even for chains where the expansion is quite large, i.e., α_s as large as 4 at $n = 10^4$. The model can therefore produce perturbed chains which have the following features:

(1) Bond lengths and bond angles are the same for perturbed and unperturbed chains.

(2) The term $(\alpha_s^5 - \alpha_s^3)/n^{1/2}$ attains a nonzero asymptotic limit at large n.

(3) Large expansions are achieved without alteration of the a priori probability for observation of a trans placement in a long chain.

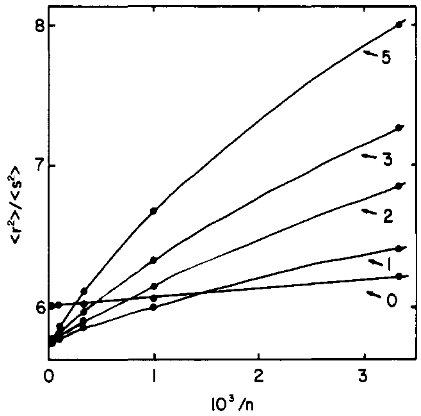

Figure 10. Chain-length dependence of $\langle r^2 \rangle / \langle s^2 \rangle$ for the chains described in Figure 8.

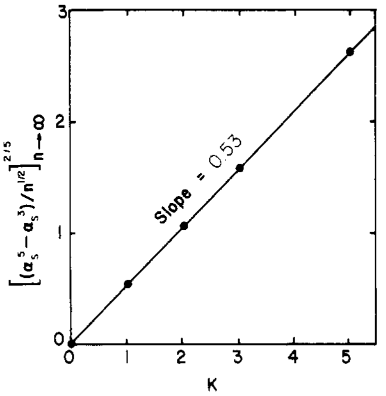

Figure 11. Relationship between the asymptotic limit for $[(\alpha_s^5 - \alpha_s^3)/n^{1/2}]^{2/5}$ and K for the chains described in Figure 8.

(4) The effect of the perturbation on the ith bond increases an n increases.

(5) The effect of the perturbation produced by long-range interactions is felt preferentially in the center of the chain.

(6) Perturbations are introduced in a manner which is independent of the direction selected for indexing bonds in the chain.

The perturbation affects $\langle s^2 \rangle$ and $\langle r^2 \rangle$ differently. Thus α_r/α_s is less than unity for perturbed chains containing 10^4 bonds (Figure 9). Chain-length dependence of $\langle r^2 \rangle / \langle s^2 \rangle$ is depicted in Figure 10. At small n, perturbed chains have larger $\langle r^2 \rangle / \langle s^2 \rangle$ then the unperturbed chain. As n increases, a point is reached at which $\langle r^2 \rangle / \langle s^2 \rangle$ falls below $\langle r^2 \rangle_0 / \langle s^2 \rangle_0$. The n required for this crossover becomes larger with larger K. While $\langle r^2 \rangle_0 / \langle s^2 \rangle_0$ becomes equal to 6 as n goes to infinity, $\langle r^2 \rangle / \langle s^2 \rangle$ for the perturbed chain approaches a value near 5.75.

According to Flory's treatment of perturbed chains, $(\alpha_s^5 - \alpha_s^3)/n^{1/2}$ is equal to $2C_M\psi_1(1 - \Theta/T)M_0^{1/2}$.[33] Here Θ is the theta temperature, ψ_1 is Flory's entropy parameter, M_0 is the mass per chain bond, and C_M is $(3^3/2^{5/2}\pi^{3/2})(\bar{v}^2/v_1 N)(M/\langle r^2 \rangle_0)^{3/2}$. A relationship between K of the present model and the thermodynamics of polymer–solvent interactions, as expressed by $\psi_1(1 - \Theta/T)$, is accessible if $2C_M\psi_1(1 - \Theta/T)M_0^{1/2}$ is identified with the asymptotic limit for $(\alpha_s^5 - \alpha_s^3)/n^{1/2}$ in Figure 8. Figure 11 demonstrates that a straight line is obtained if the $^2/_5$ power of the limiting $(\alpha_s^5 - \alpha_s^3)/n^{1/2}$ in Figure 8 are plotted as a function of K. Therefore a good approximation for polymethylene chains is

$$K = [10C_M\psi_1(1 - \Theta/T)M_0^{1/2}]^{2/5} \qquad (41)$$

Preliminary calculations executed by using other values

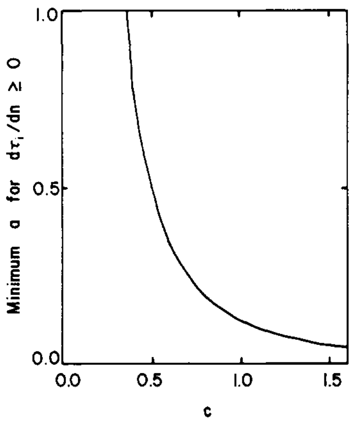

Figure 12. Limiting behavior for a specified by eq 44.

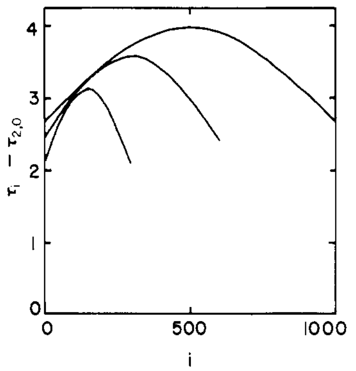

Figure 13. Chains with Gaussian τ_i calculated from eq 43 with $a = {}^1/_5$, $c = 0.79$, and $K = 1$.

for σ and ω also yield a straight line when $[(\alpha_s{}^5 - \alpha_s{}^3)/n^{1/2}]_\infty{}^{2/5}$ is plotted vs. K. However, the slope of this line depends on the values used for σ and ω.

An equivalent assumption concerning identification of the asymptotic limit for $(\alpha_s{}^5 - \alpha_s{}^3)/n^{1/2}$ in Figure 8 permits formulation of a relationship between K and z, the conventional parameter used in excluded-volume studies. With $[(\alpha_s{}^5 - \alpha_s{}^3)/n^{1/2}]_\infty = 1.67z/n^{1/2}$,[21] for example, the relationship obtained for polymethylene at 25 °C via Figure 11 is

$$K = (8.35z/n^{1/2})^{2/5} \qquad (42)$$

Figure 9 depicts the average number of bonds in a sequence of trans placements for chains containing 10^4 bonds. This term increases continuously with α_s. While $\langle n_t \rangle$ remains small for small expansions, it can become enormous at large expansions. It is unlikely that $\langle n_t \rangle$ for real perturbed polymethylene chains behaves in the manner predicted by the model at large α_s. The procedure used to produce perturbed chains does not account for all configurations whose $(n - 2)$-order a priori probability is increased by long-range interactions. At high α_s it should produce too large a bias toward chains whose trans placements occur in long sequences.

The general approach described here for computation of configuration-dependent properties of perturbed chains can be implemented by means other than assuming parabolic behavior for τ_i. For example, τ_i might be represented by a Gaussian centered at bond ${}^1/_2(n + 1)$. If eq 36 describes $\tau_{(n+1)/2}$, all $\mathrm{d}\tau_i/\mathrm{d}n$ are to be nonnegative, and the half-width of the Gaussian is cn, where c is a constant, then

$$\tau_i = \tau_{2,0} + Kn^a \exp\{-[(n + 1 - 2i)/2cn]^2\} \qquad (43)$$

$$a \geq (n + 1 - 2i)(2i - 1)(2c^2n^2)^{-1} \qquad (44)$$

The minimum a is depicted as a function of c in Figure 12. If c is 0.79, a can be no smaller than 0.20. Gaussian curves constructed using $a = 0.20$, $c = 0.79$, and $K = 1$ are depicted in Figure 13. The behavior of τ_i in this figure is not dramatically different from that seen in Figure 6.

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