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Equilibrium Properties of Flexible Polymer Chains

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ABSTRACT: The effect of bond rotational angle fluctuations on the equilibrium properties of a macromolecule is considered by introducing rotational angle flexibility into the configurational statistics methods of Flory. The development of distribution functions for flexible chains by Monte Carlo generation is also discussed. The results of the study show that flexibility causes a decrease in the characteristic ratio and an accelerated decay of the end-bond correlation function from that obtained with the strict RIS model. Additionally, for polyethylene the flexible model gives better agreement with independent estimates of the g^+ and g^+g^- energies when it is fitted to the experimentally determined characteristic ratio and its temperature coefficient at 140 °C.

I. Introduction

The rotational isomeric state (RIS) model is widely used to compute equilibrium values of conformationally dependent properties of chain molecules,[1] and attempts have also been made to extend the model to dynamic properties.[2,3] In justifying the rotational isomeric model as a realistic representation of a polymer molecule, it is generally agreed that the bond-stretching and -bending vibrations are small and rapid and thus have little effect on configurational properties. The validity of these assumptions will not be addressed here in detail.[4] The restriction of the bond internal rotational angles to several discrete values is a more severe approximation.

The question of flexibility in the rotational angles has been addressed by several workers. Fixman and coworkers[5,6] have introduced fluctuations into the bond rotational angles in order to obtain smooth distribution functions for short chains. Helfand[7] has pointed to the importance of flexibility in enhancing the likelihood of certain internal rotations by allowing the chain tails to pick up some of the strain associated with the rotation. Recent Brownian dynamical simulations by Fixman[8] and Helfand[9] using realistic rotational angle potentials have shed more light on the importance of flexibility in dynamic processes. In a recent note[10] we found that the introduction of a small amount of flexibility into the rotational angles of a model RIS chain gives rise to a broad distribution of possible end-to-end distances for a single 10-bond configuration, and these results have been extended analytically by Mansfield.[11] In the work presented here we focus on the effect of rotational angle flexibility on general equilibrium properties of simple polymethylene-type polymer systems, with particular attention to the mean-squared end-to-end distance, the end-bond correlation,[12] and the probability distribution function of the end-to-end distance.

In the next section we introduce flexibility in the rotational angle into the configurational statistics methods of Flory.[1] In section III the development of distribution functions for flexible chains by Monte Carlo generation is discussed. Section IV reports the results of this study, and section V offers a discussion of some related points.

II. Theory

In this section we show how flexibility in the bond rotational angles can easily be introduced into the configurational statistics methods of Flory.[1,13] The quantities of interest are the characteristic ratio $C_n = \langle R^2 \rangle / n$ and the end-bond correlation $\gamma_n = \langle \mathbf{b}_1 \cdot \mathbf{b}_n \rangle = \langle \cos (\zeta_{1,n}) \rangle$, where we have assumed bond vectors $\mathbf{b}_i$ of unit length and $\zeta_{1,n}$ is the angle between the first and last bonds. Both of these quantities (and most others we might be interested in) involve the evaluation of vector products between different reference frames attached to each bond. In order to evaluate the product $\mathbf{b}_i \cdot \mathbf{b}_j$ we must express the vector $\mathbf{b}_j$ in the ith frame. This may be accomplished by using a transformation matrix $\boldsymbol{T}_i$ which has the form

$$T_i = \begin{pmatrix} \cos \theta_i & \sin \theta_i & 0 \\ \sin \theta_i \cos \phi_i & -\cos \theta_i \cos \phi_i & \sin \phi_i \\ \sin \theta_i \sin \phi_i & -\cos \theta_i \sin \phi_i & -\cos \phi_i \end{pmatrix} \quad (1)$$

We use the reference-frame definitions of Flory[1] so that θ_i is the complement of the bond angle between bonds i and $i + 1$ and ϕ_i is the rotational angle of bond i, the value for a trans state being zero. By successive application of $\boldsymbol{T}_i$ we can write

$$\mathbf{b}_i \cdot \mathbf{b}_j = \mathbf{b}_i^{\mathrm{t}} (\boldsymbol{T}_i ... \boldsymbol{T}_{j-1}) \mathbf{b}_j \quad (2)$$

where the product of transformation matrices brings $\mathbf{b}_j$ into the reference frame of $\mathbf{b}_i$ and $\mathbf{b}_i^{\mathrm{t}}$ is the transpose of $\mathbf{b}_i$.

For polymethylene the rotational isomeric state model restricts ϕ_i to only three values, corresponding to a trans (t) and two gauche (g^+, g^-) states. In our flexible model we remove this restriction and let the value of each ϕ_i be governed by a simple quadratic energy relation

$$E(\phi_i) = E(\phi_i^0 + \delta\phi_i) = E(\phi_i^0) + \frac{(\delta\phi_i)^2}{2\delta_\phi^{\,2}} kT \quad (3)$$

where ϕ_i^0 is the RIS closest to ϕ_i, $\delta\phi_i$ is the deviation of ϕ_i from ϕ_i^0, and δ_ϕ is the root-mean-square fluctuation in ϕ_i. Thus we can think of the rotational angles in our model chain as oscillating in potential wells about the RIS angles for each bond. Note that in eq 3 the energy of a fluctuation is independent of the states of neighboring bonds. This does not interfere with the treatment of the interdependence of the rotational isomeric states via the statistical weight matrix but rather neglects the interdependence of the fluctuations. Inspection of models suggests that this approximation will be most serious for the gauche plus–gauche minus configuration, where the energy of fluctuations in adjacent rotational angles will be appreciably coupled. However, the weight of these configurations is small. The coupling of fluctuations for other rotational angle pairs should be much less.[14]

Thus in computing the average value of a quantity such as $\langle \mathbf{b}_i \cdot \mathbf{b}_j \rangle$, we need to average over both the possible RIS configurations and the fluctuations about each RIS. Since the fluctuations are independent, this second average can be done first and only involves computing the average value of the transformation matrix due to fluctuations, $\langle \mathbf{T} \rangle_{\mathrm{f}}$, where

$$\langle T \rangle_{\mathrm{f}} = \begin{pmatrix} \cos \theta & \sin \theta & 0 \\ \sin \theta \langle \cos \phi \rangle_{\mathrm{f}} & -\cos \theta \langle \cos \phi \rangle_{\mathrm{f}} & \langle \sin \phi \rangle_{\mathrm{f}} \\ \sin \theta \langle \sin \phi \rangle_{\mathrm{f}} & -\cos \theta \langle \sin \phi \rangle_{\mathrm{f}} & -\langle \cos \phi \rangle_{\mathrm{f}} \end{pmatrix} (4)$$

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The averages $\langle\ \rangle_f$ are taken with weight $\exp(-\delta\phi^2/2\delta_\phi^2)$, and the subscripts from eq 1 have been dropped in view of the symmetry of the polymethylene chain. The averages in eq 4 can be calculated as

$$\langle \cos \phi \rangle = \int_{-\infty}^{+\infty} \cos (\phi_0 + \delta\phi) \exp(-\delta\phi^2/2\delta_\phi^2)\, d(\delta\phi) \Big/ \int_{-\infty}^{+\infty} \exp(-\delta\phi^2/2\delta_\phi^2)\, d(\delta\phi) = \cos \phi_0 \exp(-\delta_\phi^2/2) \qquad (5)$$

and similarly

$$\langle \sin \phi \rangle = \sin \phi_0 \exp(-\delta_\phi^2/2) \qquad (6)$$

The factor $\exp(-\delta_\phi^2/2)$ is the same as the term developed by Freire and Fixman[6] to add fluctuations to the moment-generating Fixman–Skolnick[5] recursion relations.

Use of the preaveraged transformation matrix, eq 4, with expressions such as eq 2 allows for the calculation of chain properties with rotational angle flexibility.

III. Monte Carlo Chain Generation

In order to probe the form of the distribution function for chains with rotational angle flexibility, we used Monte Carlo methods to generate model chains of n bonds. A two-step process was employed.

First, a strict three-state RIS chain was generated by the Monte Carlo techniques of Fixman and Alben.[15] Briefly, if we let α_i represent the conformation of the ith bond and restrict our model to a simple chain with three rotational states [trans ($\alpha = 1$), gauche plus ($\alpha = 2$), and gauche minus ($\alpha = 3$)], then the probability of a configuration specified by the set $\{\alpha\}$ of which there are $n - 2$ members for an n-bond chain is given by

$$f\{\alpha\} = \frac{u(\alpha_2) U(\alpha_2, \alpha_3) ... U(\alpha_{n-2}, \alpha_{n-1})}{\mathbf{u} \cdot \mathbf{U}^{n-3} \cdot \mathbf{q}^{t}} \qquad (7)$$

where the $U(\alpha_i, \alpha_{i+1})$ are elements of the statistical weight matrix

$$U = \begin{pmatrix} 1 & \sigma & \sigma \\ 1 & \sigma & \sigma\omega \\ 1 & \sigma\omega & \sigma \end{pmatrix} \qquad (8)$$

as introduced by Flory.[1] The elements of the matrix are developed from the Boltzmann factor for the energy of a state relative to the trans state. As can be seen, g^+g^- and g^-g^+ effects have been accounted for. The values of σ and ω are taken as 0.54 and 0.088, which, along with chain bond angles of 112°, reproduce fairly well the dependence on n of the characteristic ratio of polymethylene and its temperature coefficient at 140 °C. The vectors $\mathbf{u} = (1 \quad \sigma \quad \sigma)$ and $\mathbf{q} = (1 \quad 1 \quad 1)$ in eq 7 take care of end effects.

Following Fixman and Alben, we express $f\{\alpha\}$ as a product of conditional probabilities

$$f\{\alpha\} = p(\alpha_2) f_3^{c}(\alpha_2|\alpha_3) ... f_{n-1}^{c}(\alpha_{n-2}|\alpha_{n-1}) \qquad (9)$$

where $f_i^{c}(\alpha_{i-1}|\alpha_i)$ is the probability that bond i is in state α_i, given that bond $i - 1$ is in state α_{i-1}, and $p(\alpha_2)$ is the term which accounts for bond 2 and is clearly equal to the appropriate element of $\mathbf{u}$. It follows that

$$f_i^{c}(\alpha_{i-1}|\alpha_i) = \frac{U(\alpha_{i-1}, \alpha_i) [\mathbf{U}^{n-i-1}\mathbf{q}]_{\alpha_i}}{[\mathbf{U}^{n-i} \cdot \mathbf{q}]_{\alpha_{i-1}}} \qquad (10)$$

where $[\ ]_{\alpha_i}$ means the α_ith element of the vector in brackets. With these conditional probabilities the strict three-state conformation of each bond of an n-bond chain can be assigned sequentially by usual Monte Carlo means.

Once the configuration has been generated, deviations are introduced into each rotational angle. The deviations are picked by a Monte Carlo method such that the probability of a given deviation is given by

$$P(\delta\phi_i) = \frac{1}{\delta_\phi (2\pi)^{1/2}} \exp(-\tfrac{1}{2}(\delta\phi_i)^2/\delta_\phi^2) \qquad (11)$$

where $\delta\phi_i$ is the deviation (both positive and negative values are possible) to be added to ϕ_i^0, the three-state rotational angle. The root-mean-square deviation, δ_ϕ, is picked to determine the degree of flexibility.

Thus we generate "flexible" chains with continuous bond rotational angle possibilities. For each chain length n, 100 000 chains were generated in this manner. The square of the end-to-end distance was calculated for each chain both before and after the addition of fluctuations and tabulated so that distribution functions could be determined. In addition, the characteristic ratio and end-bond correlation were calculated for each chain length n, allowing for a check against the values obtained by the analytical means described in section II. Agreement for C_n with $\delta_\phi = 15°$ was within 0.9% for the longest chains ($n = 100$) and much better for short chains (less than 0.4% for $n \leq 20$). Values of γ_n obtained by Monte Carlo averaging agreed to within ±0.002 with the calculated results.

IV. Results

A. Analytic Calculations. Calculations were carried out by using the preaveraged transformation matrix of eq 4 along with standard formulas developed by Flory (ref 1, eq IV-16, IV-29, IV-44, and related expressions) to compute the characteristic ratio, C_n, and end-bond correlation, γ_n, for chains of length n. The limiting characteristic ratio C_∞ was also computed. Standard RIS parameters $\sigma = 0.54$ and $\omega = 0.088$ were used in all calculations along with chain bond angles of 112° and unit bond lengths. The "proper" value of δ_ϕ for polymethylene can be approximated from energy contour maps for butane and pentane to be in the region of 10–20°.[1] The curvature about the potential minimum is somewhat greater for a gauche state than for a trans state and this difference could easily be incorporated into our model if desired. For the purpose of these illustrative examples we have used a single value δ_ϕ, thus ignoring these differences. Tables I and II display the calculated values of C_n and γ_n for three different δ_ϕ, along with those values at $\delta_\phi = 0°$, the strict RIS results. We remark that our results for $\delta_\phi = 15°$ agree to at least five decimal places with those obtained by Freire and Fixman,[6] who used a different formalism.

Clearly the effect of flexibility upon C_n is to shorten or compress the average chain end-to-end distance. This point is graphically illustrated in Figure 1, where the difference in C_n from the value for the strict three-state model is plotted vs. $1/n$ for root-mean-square flexibilities of 5–30°. To further illustrate this point, we plot in Figure 2 C_∞ vs. the root-mean-square flexibility. Notice that C_∞ passes smoothly toward the freely rotating chain value of 2.1980 as δ_ϕ becomes larger.

As Table II shows, coupled with a compacting of the chains, there is a loss of correlation between the ends of the chain as δ_ϕ increases. The decay of γ_n with n, for n greater than 4, can be fit quite well with a simple exponential form, $\gamma_n = A \exp(-bn)$. A summary of the fitting parameters is given in Table III. For very short chains ($n = 3$ and 4) γ_n varies significantly from the exponential form, and, in fact, γ_3 is less than γ_4 for stiff chains. This mimics the irregular behavior of the dipole moments in

Table I
Dependence of the Characteristic Ratio, C_n, upon the Chain Length, n, for Various Flexibility Parameters δ_ϕ

n	C_n			
	$\delta_\phi = 0°$	$\delta_\phi = 10°$	$\delta_\phi = 15°$	$\delta_\phi = 20°$
3	1.7198	1.7179	1.7155	1.7123
4	2.1512	2.1442	2.1356	2.1239
5	2.5044	2.4927	2.4784	2.4589
6	2.8277	2.8107	2.7900	2.7617
7	3.1213	3.0986	3.0709	3.0333
8	3.3831	3.3546	3.3200	3.2731
9	3.6194	3.5851	3.5435	3.4873
10	3.8320	3.7920	3.7435	3.6782
12	4.1975	4.1465	4.0848	4.0022
16	4.7460	4.6753	4.5905	4.4776
20	5.1281	5.0415	4.9379	4.8011
25	5.4604	5.3584	5.2369	5.0773
30	5.6924	5.5788	5.4440	5.2677
40	5.9895	5.8604	5.7078	5.5094
50	6.1696	6.0308	5.8673	5.6553
60	6.2899	6.1446	5.9737	5.7526
80	6.4403	6.2869	6.1068	5.8743
100	6.5305	6.3723	6.1867	5.9473
∞	6.8916	6.7138	6.5061	6.2393

Table II
Dependence of the End-Bond Correlations, γ_n, upon the Chain Length, n, for Various Flexibility Parameters δ_ϕ

n	γ_n			
	$\delta_\phi = 0°$	$\delta_\phi = 10°$	$\delta_\phi = 15°$	$\delta_\phi = 20°$
3	0.3304	0.3276	0.3240	0.3192
4	0.3438	0.3382	0.3313	0.3219
5	0.2544	0.2994	0.2434	0.2352
6	0.2145	0.2090	0.2024	0.1935
7	0.1788	0.1733	0.1666	0.1576
8	0.1472	0.1419	0.1356	0.1272
9	0.1221	0.1170	0.1110	0.1031
10	0.1011	0.0963	0.0908	0.0836
12	0.0692	0.0653	0.0607	0.0548
16	0.0325	0.0300	0.0271	0.0236
20	0.0153	0.0138	0.0121	0.0102
25	0.0059	0.0052	0.0044	0.0035
30	0.0023	0.0020	0.0016	0.0012
40	0.0003	0.0003	0.0002	0.0001
50	0.0001	0.0000	0.0000	0.0000

Table III
Fits of the End-Bond Correlation, γ_n, to the Form Ae^{-bn} for Various Flexibility Parameters δ_ϕ

δ_ϕ, deg	A	b
0	0.6653	0.1887
5	0.6632	0.1887
10	0.6731	0.1997
15	0.6750	0.2009
20	0.6833	0.2104
25	0.6943	0.2225
30	0.7053	0.2369

Table IV
Limiting Characteristic Ratio, C_∞, as Calculated from Our Flexible Model, σ^f, and E_g^f [a]

δ_ϕ, deg	C_∞	σ^f	E_g^f, cal/mol
0	6.8916	0.540 00	506.0
5	6.8461	0.548 25	493.5
10	6.7138	0.573 72	456.2
15	6.5061	0.618 72	394.2
20	6.2393	0.687 80	307.3
25	5.9322	0.789 11	194.5
30	5.6028	0.938 50	52.1

[a] The flexibility parameter δ_ϕ is fit by the strict RIS model by using statistical weight σ^f, the statistical weight ω being kept at 0.088. From σ^f the fitted energy of the gauche state E_g^f is calculated at 140 °C.

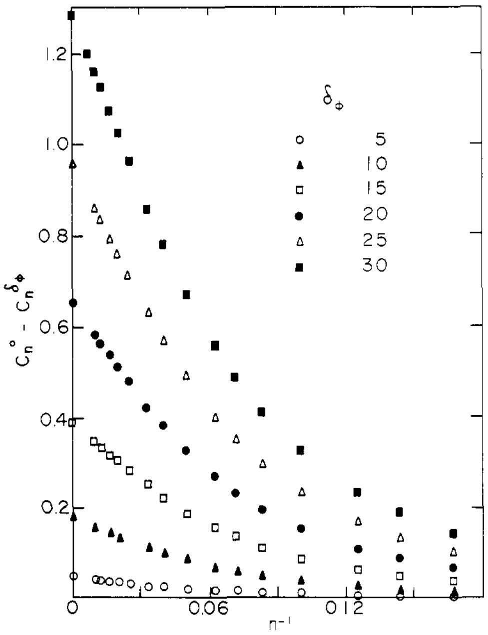

Figure 1. $C_n^0 - C_n^{\delta\phi}$ vs. $1/n$ for δ_ϕ = 5, 10, 15, 20, 25, and 30°. C_n^0 is the characteristic ratio for the strict three-state model, $C_n^{\delta\phi}$ is the characteristic ratio calculated with the flexibility parameter δ_ϕ, and n is the chain length.

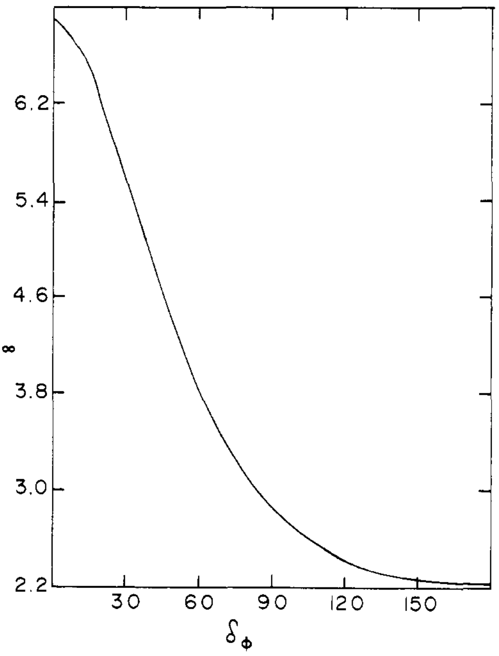

Figure 2. Limiting characteristic ratio C_∞ vs. the flexibility parameter δ_ϕ. The limiting value for large δ_ϕ is 2.1980, the value of C_∞ for the freely rotating chain.

short-chain α,ω-dibromo-n-alkanes, $Br(CH_2)_nBr$, observed by Hayman and Eliezer,[16] or in perfluoroalkanes, $H(CF_2)_nH$, as reported by Bates.[17]

To explore further the significance of rotational angle flexibility, we have taken the characteristic ratio results for various δ_ϕ and fit them to the strict three-state model by fixing ω at 0.088 and varying σ until the value of C_∞ for the flexible chain could be reproduced with the strict (δ_ϕ = 0°) RIS formulas. This results in a fair fit (within 1 or 2%) for all chain lengths ($n > 6$) for both C_n and γ_n. Table IV summarizes the results of this study. Notice that as δ_ϕ increases, larger σ are necessary, corresponding to significantly lower effective well depths for the gauche state. Thus, assuming a 15° root-mean-square fluctuation in the rotational angle of a system where E_g is 506.0 cal/mol above E_t, a strict three-state fit to "experimental" data would yield an E_g of 394.2 cal/mol, a difference of 111.8 cal/mol or over 20%. It is also significant to note that the same fitted σ reproduces equally well the C_n and γ_n data for a flexible system. This result lends credence to the work of Bates and Stockmayer,[17] who used dipole moment data for short-chain perfluoroalkanes to fit energy parameters to a finite-state model and then used these parameters to calculate solution and melt viscosities from the predicted characteristic ratio. This approach of fitting energy parameters from one set of data for the purposes of predicting considerably different types of information clearly relies heavily on the model used and appears to be valid in this case.

B. Distribution Functions. Monte Carlo generation of chains with flexible rotational angles was undertaken to examine the nature of the distribution function of the square of the end-to-end distance, $F(R^2)$. As described in section III, 100 000 chains of length n, with n varying from 3 to 100, were generated by using a root-mean-square flexibility parameter δ_ϕ equal to 15°. The square of the end-to-end distance, R^2, both with and without flexibility was tabulated by dividing it by the square of the maximum end-to-end distance

$$R_{\max}^2 = \tfrac{1}{2}[n^2(1 + \cos\theta) + (1 - \cos\theta)\sin^2(n\pi/2)] \quad (12)$$

where θ, the complement of the bond angle, is taken as 68°. The ratios $X^2 = R^2/R_{\max}^2$ were recorded on separate zero-to-one grids with spacings of 0.01. The resulting normalized distributions, $F(X^2)$, for flexible and strict RIS chains are related to $P(X)$, the distribution of the scaled end-to-end vector, by

$$F(X^2) = 2\pi XP(X) \quad (13)$$

Since our interest is only in the general features of the flexible and strict RIS distributions, we will use the more easily obtainable $F(X^2)$ in our discussions.

For rigid three-state chains the number of configurations goes as 3^{n-2}, which suggests the order of 5.9 × 10^4 different end-to-end distances for a 12-bond chain and presumably a nearly continuous distribution. However, configurational symmetries reduce this number markedly, and this, along with geometrical considerations, yields a very jagged distribution function, a situation which is usually averaged away in one manner or another. As first demonstrated by Freire and Fixman,[6] the more physically reasonable model with rotational angle fluctuations accomplishes this smoothing in a direct way since, as shown previously,[10] the range of end-to-end distances for a single conformation is great when flexibility is added.

Figure 3 shows the distribution functions for several short chains. The solid spikes represent the strict RIS model while the continuous curve connects the flexible-chain results, the grid size being 0.01 unit. Even for very short chains the flexible distribution is reasonably smooth over the possible values of X^2. Thus smooth distributions for short chains are not features which must be artificially averaged in but rather can be regarded as essential features of the model when flexibility is added. For longer chains both the strict RIS and flexible chains give reasonably smooth distributions on the grid size used, the flexible distribution being shifted slightly to smaller X^2.

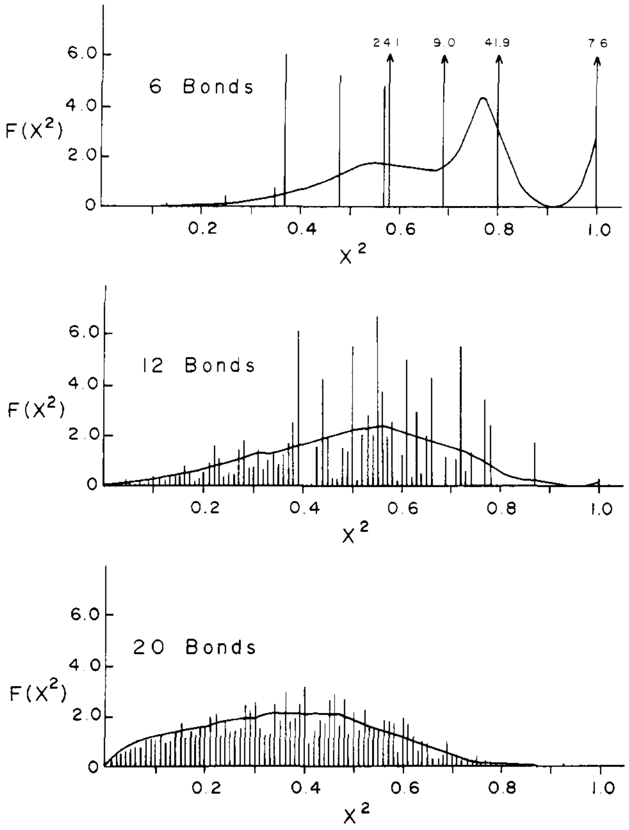

Figure 3. Comparison of the normalized distribution functions, $F(X^2)$, for the strict RIS model (spikes) and the flexible model (smooth curve, δ_ϕ = 15°) for chains of 6, 12, and 20 bonds. The ordinate is expressed as $X^2 = R^2/R^2_{\max}$, where $R_{\max}$ is the end-to-end distance of the all-trans configuration.

Table V
Best Fits for $F(X^2)$ to the Form $CX \exp[-aX^2 - (bX^2)^s]$ for Chains of Length n with a Rotational Angle Flexibility Factor δ_ϕ = 15°

n	a	b	s
8	−4.83	1.44	4.93
9	−6.06	1.65	4.04
10	−5.28	1.67	3.93
12	−3.89	1.64	4.26
16	−1.96	1.66	4.62
20	−0.34	1.69	4.96
30	+0.23	1.86	4.84

Limited attempts were made to fit the flexible-chain distribution to the functional form suggested by Fixman[5,6] for $P(X)$, namely, $P(X) \propto \exp(-aX^2 - (bX^2)^s)$. Thus attempts were made to fit our $F(X^2)$ data as

$$F(X^2) = CXe^{-aX^2-(bX^2)^s} \quad (14)$$

where s was found by Freire and Fixman to be best taken as 5. The parameters a, b, and s obtained for the best fits (good to about 10%) for several chain lengths n are given in Table V. Additionally, a direct comparison was made between the distribution function obtained by Freire and Fixman[6] for a 10-bond chain with a rotational angle flexibility parameter δ_ϕ = 15° and our Monte Carlo generated distribution function for the same chain. Agreement is within 10% for the points given by Freire and Fixman, their distribution function being somewhat greater in magnitude than ours at $R/R_{\max}$ values of 0.6 and 0.8.

V. Discussion

Let us examine more closely the effect of adding flexibility to the three-state model with an eye toward whether the flexible model better represents experimental results. For δ_ϕ = 15° the decrease in C_∞ is only about 5.5% for σ = 0.54 and ω = 0.088 but becomes markedly larger as σ decreases, rising to 13.1% for σ = 0.10. This can be understood by considering the flexibility will tend only to shorten the distance between atom n and n + 3 if their central bond is in a trans configuration, a situation whose probability is enhanced by small σ. For the case where $\sigma = 0$, C_∞ for the strict RIS chain is infinite, while C_∞ for a chain with rotational angle flexibility does not diverge, $C_\infty = 128.289$ for $\delta_\phi = 15°$. Though the differences at $\sigma = 0.54$ are small, our fits of σ to the flexible (and thus more realistic) data show that large errors in experimental determinations of E_g can be made if data are fit to a strict RIS model. Since for most calculations E_g and thus σ are used merely as parameters, little difficulty arises in studies such as the Bates–Stockmayer work mentioned earlier. However, one other point is worth mentioning along these lines. The parameters $\sigma = 0.54$ and $\omega = 0.088$ are often used because they reproduce the dependence of C_n on n appropriate to polymethylene at 140 °C. Also for $\sigma = 0.54$, $E_g = 506$ cal/mol, in good agreement with independent experimental determinations which place E_g at 500 ± 100 cal/mol for liquid n-alkanes. However, to reproduce the dependence of C_n on n using the more reasonable model for polymethylene with rotational angle flexibility $\delta_\phi = 15°$, a σ of 0.473 corresponding to $E_g = 615$ cal/mol is needed. This is somewhat outside the experimentally determined range and though a slightly lower δ_ϕ would put E_g into the range, it would still be at the upper limits of it.

Experimental estimates for polymethylene of C_∞ and its temperature coefficient at 140 °C are 6.7 ± 0.3 and $-0.0011 \pm 0.0001°$, respectively.[1] Using the best estimate of the gauche rotational angle of 112.5°, bond angles of 112°, and a temperature of 140 °C, one finds for the strict RIS model that $E_g = 322$ cal/mol ($\sigma = 0.68$) and $E_{g^+g^-} = 1410$ cal/mol ($\omega = 0.18$) best fit these values.[18] Where flexibility is added with $\delta_\phi = 15°$ the best fits occur for $E_g = 420$ cal/mol and $E_{g^+g^-} = 1475$ cal/mol. This increase in E_g with the addition of flexibility is particularly important for it brings the value into much closer agreement with experimental measurements.

Lastly the magnitude of the effect of flexibility in a backbone bond angle can be calculated in a fashion similar to that in section II. If we let $\delta\theta$ be the root-mean-square fluctuation in the bond angle, then averaging the chain bond angle over a Gaussian distribution of fluctuations can be accounted for by the insertion of a $\exp(-\delta_\theta^2/2)$ term preceding the $\sin\theta$ and $\cos\theta$ terms in the transformation matrix. The effect of this is relatively small since δ_θ is small; a δ_θ of 3° causes a reduction in C_∞ of about 0.66%. It can also be noted that symmetrical fluctuations in the bond length will have no effect on C_n, though asymmetrical fluctuations which would affect C_n could be introduced with little difficulty.

In this paper we have demonstrated the effect on equilibrium chain properties of flexibility in the rotational angles of the RIS polymer model. The situation with nonequilibrium dynamic properties is not so clear. The recent work of Fixman[8] and Helfand[9] suggests rotational angle flexibility is essential to an understanding of dynamic properties and may be acting in a coupled and complicated way to relieve the stress of chain motions which would be unallowed in a strict three-state model. It seems likely that bond-bending and -stretching flexibility may also contribute[4,9] and that a detailed backbone potential may be necessary to study dynamic processes.

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(12) We note that there is an absence in the literature of studies on the end-bond correlation, $\langle \mathbf{b}_i \cdot \mathbf{b}_n \rangle$, except with reference to dipole moments (see ref 1). An exception to this is the work of Baram and Gelbart (Baram, A.; Gelbart, W. M. *J. Chem. Phys.* **1977**, *66*, 617), who have looked at angular correlations between bond vectors interior to a large chain. These correlations are independent of chain length if the segments being considered are sufficiently distant from the chain ends. The data presented in this paper differ from the above-mentioned work in that angular correlations between the chain ends are considered, clearly a property which depends upon chain length.
(13) The essence of what will be described here was developed previously by Freire and Fixman[6] for a different formalism. See also ref 14.
(14) Tanaka (Tanaka, G., private communication) had developed a formalism for dealing with coupled fluctuations but the approach is relatively intractable computationally.
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