Macromolecules **1980,** *13,* 699-704

An Evaluation of Rotational Isomeric State Model Calculations of Hydrocarbon Chains, with and without Excluded Volume

Mitchell A. Winnik*

Erindale College and Lash Miller Laboratories, Department of Chemistry, University of Toronto, Toronto, Canada M5S 1A1

David Rigby and R. F. T. Stepto*

Department of Polymer and Fibre Science, University of Manchester Institute of Technology, P.O. Box 88, Manchester, England M60 1QD

Bernard Lemaire*

Centre de Recherches Paul Pascal, Domaine Universitaire, 33405 Talence Cedex, France.
Received November 14, 1979

ABSTRACT: Various properties of hydrocarbon chains are calculated with the use of three different variants of the rotational isomeric state model: lattice chains, unperturbed chains, and off-lattice chains with excluded volume. The properties examined are $\langle r^2 \rangle$, $\langle s^2 \rangle$, $\langle r \rangle$, and $\langle r^{-6} \rangle$. It is found that lower and inverse moments of r are more sensitive to excluded volume effects than $\langle r^2 \rangle$.

The rotational isomeric state [RIS] model has been used by many research groups to calculate the configurational properties of hydrocarbon chains. It has been applied to chains as short as decane as well as to polyethylene.[1-5] A variety of experimental properties of hydrocarbon chains and their derivatives have been simulated with the use of this model, including vectorial properties like the dipole moments of α,ω-dibromoalkanes[2] and tensorial properties like the depolarization ratios from Rayleigh light scattering studies of alkanes and their solutions.[3] It has been applied to the cyclization probability of *n*-alkanes and their derivatives[4] and to calculating the mean-squared end-to-end length $\langle r^2 \rangle$ and its temperature dependence for polyethylene,[1] to the diffusion constants for alkanes,[5] and more recently to the form of the scattering function for neutron diffraction from alkanes and polyethylene.[6] The model is so widely accepted that in many ways we have learned to think in its language and in terms of its assumptions in viewing any property of alkanes.

Nonetheless, applications of the RIS model to hydrocarbon chains have not been without controversy. As it is a semiempirical model, there have been questions about the correct parameters to use. Different mathematical methods have been employed to carry out calculations based upon the model. Each has required further simplifying assumptions.

Various research groups have expressed different opinions of how realistic were each set of assumptions. These competing points of view have coexisted for many years because there are relatively few properties of hydrocarbon chains that have been calculated with complimentary sets of assumptions in order to assess their quantitative differences.

Within the context of realistic RIS models of hydrocarbon chains, the two extremes are (self-avoiding) lattice chains, which confine the chain and its substituents to the vertices of a diamond lattice, and off-lattice unperturbed chains. The latter permit the ∠CCC bond angle to be set at 112°, the value found in the crystalline state of simple alkanes, whereas the former distort this angle to 109.5°. Markov chains can take account of local or proximate interactions. For hydrocarbon chains these are almost always interactions over successive pairs of bonds so that the destabilization associated with pairs of gauche rotamers of the opposite sense—the pentane effect[8]—can be included in the parameterization of the model. Nonlocal interactions[9] are neglected. These are treated as part of the excluded volume problem which is assumed to be unimportant for chains of less than several hundred atoms.

Diamond lattice chains have the advantage that they permit one to include nonlocal interactions into the RIS model. In principle one could use this power to assess their contribution to the excluded volume effect. Aside from ∠CCC bond angle distortion, the structure imposed upon a hydrocarbon chain [e.g., 120° rotational angles] is very similar to that incorporated into off-lattice models of these molecules. Few would deny that the most realistic of all the variations on the RIS model would be off-lattice chains which took account of remote interactions. So far the amount of computer time necessary to carry out computations for such chains has precluded wide-spread use of this model.

Elegant mathematical methods have been developed for investigating unperturbed chains. The matrix multiplication method, developed by Volkenstein,[10a] Lifson,[10b] and Nagai,[10c] and widely applied by Flory,[1] permits one to compute exactly any property of an unperturbed chain which can be expressed in the proper mathematical format. While mathematically sophisticated, these calculations are often economical in computer time. This is the method most frequently applied to hydrocarbon chains.

There are properties of molecules not yet amenable to being expressed in the form of (a vector) × (a matrix) × (a vector), where × means the direct product. These properties cannot be evaluated by the matrix multiplication method. Monte-Carlo methods are often used in these and other instances to estimate chain properties from a random sample of chain molecules grown by a computer. Monte-Carlo methods have been applied to unperturbed chains,[6,11] to diamond lattice chains,[3a,4,12] and even to off-lattice chains with remote interactions included.[4a,13] As the sophistication of the model increases, the expense in computer time increases. Monte-Carlo estimates are tinged with a mathematical uncertainty which can only set limits to the numerical value of the property of interest. Of course the variance of the estimate goes to zero as the sample of chains becomes infinitely large. Practical considerations, however, such as available computer time, make their imposition. Each calculation represents a compromise among factors such as the sophistication of the model, the required precision, and the cost of the calculation.

We felt it would be particularly worthwhile to examine certain properties of hydrocarbon chains in light of each

0024-9297/80/2213-0699$01.00/0

of these variations of the RIS model. Beginning with commonly accepted parameters for the RIS model of alkanes, we have calculated the mean-squared end-to-end length $\langle r^2\rangle$ and the mean-squared radius of gyration $\langle s^2\rangle$ for a wide variety of often used secondary assumptions. In addition and within the limits of time and finances available to us, we have carried out comparison Monte-Carlo calculations for off-lattice chains, taking full account of both local and nonlocal interactions.

Mathematical Methods and Parameters

Matrix multiplication calculations were carried out as described by Flory. Diamond lattice chains were examined by a Monte-Carlo technique, previously described,[12] which consisted of growing independent samples of 100 000–300 000 chains of length up to and including 225 bonds. Off-lattice chains were examined by two methods. Chains of up to 14 bonds were enumerated exactly and chain properties computed from this ensemble. For longer chains, a Metropolis sampling technique, related to that of Lal and Stepto[15] for tetrahedral lattice chains, was used. A new configuration was generated by changing randomly the conformational angles of a sequence of up to four-chain bonds. The position of the sequence in the chain was also chosen randomly. An algorithm was devised for circumventing the accumulation of rounding errors which can arise[13b] with off-lattice chains as a result of the repetitious computation of new coordinates for skeletal atoms. It was often necessary to generate several million configurations for proper convergence of the estimate. One way of ascertaining whether a Monte-Carlo calculation includes a large enough sample to give a proper estimate of $\langle r^2\rangle$ or $\langle s^2\rangle$ is to estimate values of $\langle r_0{}^2\rangle$ or $\langle s_0{}^2\rangle$ where remote interactions are neglected and which can be enumerated exactly by matrix multiplication methods. These estimates were calculated for all chain lengths reported in the tables. Estimates of $\langle r_0{}^2\rangle$ and $\langle s_0{}^2\rangle$ agreed with their exact values within 1–2% in all cases.

Our parameterization of the RIS model is similar to that described by Flory. The CC bond length is chosen to be 1.53 Å. The ∠CCC bond angle is taken to be 112° except in the diamond lattice versions where it is set at 109.5°. Rotational angles of 0°,±120° are used in all calculations.

Two of the most critical parameters introduced into the RIS model of alkanes are E_σ, the gauche-trans energy difference, and E_ω, the additional destabilization due to successive gauche bonds of the opposite sense ($g^\pm g^\mp$). Experimental values of the former appear to be converging around 600 cal/mol in the liquid phase.[17] This value of E_σ was used in all computations.

Flory has argued that a value of $E_\sigma + E_\omega$ of ca. 2500 cal/mol is necessary to account for the experimental properties of polyethylene at 140 °C. At that temperature the statistical weight of a $g^\pm g^\mp$ sequence $\sigma\omega = \exp[-(E_\sigma + E_\omega)/RT]$ is ca. 0.05. At lower temperatures this sequence is less important to chain properties and its statistical weight is much smaller. In consequence, one often simplifies RIS calculations by assigning the $g^\pm g^\mp$ sequence zero probability, i.e., $E_\omega = \infty$, $\omega = 0$. We have carried out computations with the use of the values of 1900 cal/mol and ∞ for E_ω in order to assess their effect on the various forms of the RIS model.

Nonlocal interactions are considered in different ways in each model. In unperturbed chain models they are ignored; excluded volume is neglected. In diamond lattice models, second neighbor hard sphere exclusion is invoked for all carbons. Thus, no carbons are able to approach one another by less than 3 Å, and $g^\pm g^\mp$ sequences are forbidden ($E_\omega = \infty$). In the off-lattice Monte-Carlo calculations, $g^\pm g^\mp$ sequences are permitted at a cost of E_ω = 1900 cal/mol. Nonlocal hard sphere repulsions are invoked to accomodate excluded volume effects. The effect of the radius of this hard sphere on chain properties was examined. In one set of calculations, chain properties were estimated for chains in which remote carbons could approach to as close as 3.0 Å. In a second set of calculations, the hard sphere repulsion distance was relaxed to 2.7 Å. The former value is probably more realistic.

Results and Discussion

Table I contains values of the mean-squared end-to-end length, expressed as $\langle r^2\rangle/n^2$ and $\langle r_0{}^2\rangle/nl^2$, for chains of up to 225 bonds. Tetrahedral variations (∠CCC = 109.5°) of the RIS model are grouped in the four left-hand columns. The more realistic variations (∠CCC = 112°) are found in the six columns on the right. The letters "ev" at the head of the column indicate that excluded volume has been introduced into the calculation in the form of hard sphere repulsions as discussed above. Results with Professor Flory's model (with E_σ = 600 cal/mol) are found in columns 6 (25°) and 9 (140°). Results from the "most realistic" model, off-lattice RIS chains incorporating excluded volume, are found in columns 7 (25°) and 10 (140°).

Corresponding calculations of the mean-squared radius of gyration, expressed as $\langle s^2/nl^2\rangle$ and $\langle s_0{}^2/nl^2\rangle$, are found in Table II.

For unperturbed chains (columns 2 and 3 as well as 5 and 6), one sees that only very small differences arise in values of $\langle r^2\rangle$ or $\langle s^2\rangle$ at room temperature due to the choice of E_ω = 1900 cal/mol and ∞. At 25° the statistical weight of a $g^\pm g^\mp$ sequence is 1.55% for E_ω = 1900 cal/mol and of course zero for $E_\omega = \infty$. The former probability is small; nonetheless for a sufficiently long chain, a single such sequence can lower the end-to-end separation of a fairly extended chain. Chain properties dependent upon higher moments of r would be particularly sensitive to these conformations. At room temperature chains $\langle r^2\rangle$ and $\langle s^2\rangle$ vary only by 2% at 30 bonds for these two choices of E_ω and by 3% at 200 bonds. Since experimental techniques are unlikely to achieve precision better than 5% in measures related to chain properties, simulations of chain properties are unlikely to be affected by the choice of E_ω as long as it is taken to be sufficiently large (≥1900 cal/mol).

Changes in the ∠CCC bond angle from 112 to 109.5° have somewhat more important effects on $\langle r^2\rangle$ and $\langle s^2\rangle$, and the magnitude of the change increases with chain length. For decane the predicted values of $\langle r^2\rangle$ differ by 6% and of $\langle s^2\rangle$, by 5%. For hexatriacontane, predicted values of $\langle r^2\rangle$ differ by nearly 9% and of $\langle s^2\rangle$, by 7%. At 200 bonds, values of both $\langle r^2\rangle$ and $\langle s^2\rangle$ are 10% smaller from calculations employing tetrahedral bond angles than those using ∠CCC = 112°. These changes are quite a bit larger than those found (~3%) for the fully extended chains. For many purposes, the differences of ≤10% found from these different parameters are unimportant, particularly when other features of diamond lattice calculations offer important advantages to that kind of calculation. Of course, if it is desired to evaluate only characteristic ratios of unperturbed chains, most of the effects of bond angle choice can be alleviated by taking the ratios[14] $\langle r_0{}^2\rangle/(nl^2(1 + \cos\theta)/(1 - \cos\theta))$ and $\langle s_0{}^2\rangle/(nl^2(1 + \cos\theta)/(1 - \cos\theta))$, where θ is the supplement of the valence angle. As the chain length increases, such ratios become more characteristic of the hindrance to free rotation, and in the present cases, the effects of choice of valence angle are reduced, for chains of 200 bonds, to 0.4 and 0.2%, respectively, on the bases of $\langle r_0{}^2\rangle$ and $\langle s_0{}^2\rangle$.

Table I
Mean-Squared End-to-End Distance of Hydrocarbon Chains Calculated for Various Models[a] [$\langle r^2\rangle/nl^2$ and $\langle r_0^2\rangle/nl^2$]

	tetrahedral lattice chains, ∠CCC = 109.5°				off-lattice chains, ∠CCC = 112.0°					
no. of bonds	$E_\omega = \infty$[b] (ev[d])	∞[c]	1900[c]	all trans[c]	∞[c]	1900[c]	1900[b] (ev[d])	all trans[c]	1900[c] (140 °C)	1900[b] (ev[d]) (140 °C)
1										
2	1.33	1.33	1.33	1.33	1.38	1.38	1.37	1.38	1.38	1.37
3	1.74	1.74	1.74	2.11	1.81	1.80	1.80	2.17	1.74	1.74
4	2.18	2.18	2.18	2.66	2.28	2.27	2.27	2.75	2.18	2.18
5	2.56	2.56	2.55	3.40	2.68	2.67	2.67	3.50	2.55	2.54
6	2.91	2.92	2.90	4.00	3.07	3.05	3.05	4.12	2.88	2.88
7	3.23	3.24	3.22	4.71	3.41	3.39	3.39	4.86	3.18	3.19
8	3.53	3.54	3.51	5.33	3.73	3.71	3.71	5.50	3.46	3.47
9	3.80	3.81	3.78	6.04	4.03	4.00	4.00	6.22	3.70	3.71
10	4.04	4.05	4.02	6.67	4.30	4.26	4.26	6.87	3.92	3.94
11	4.26	4.28	4.24	7.36	4.55	4.50	4.50	7.59	4.12	4.15
12	4.47	4.49	4.44	8.00	4.77	4.72	4.72	8.25	4.31	4.34
13	4.65	4.67	4.62	8.69	4.98	4.93	4.93	8.96	4.47	4.51
14	4.83	4.85	4.79	9.33	5.18	5.16	5.16	9.62	4.62	4.71
15	4.99	5.01	4.94	10.02	5.35	5.29	5.31	10.33	4.76	4.85
16	5.14	5.15	5.08	10.67	5.52	5.45	5.51	11.00	4.89	5.00
17	5.27	5.29	5.21	11.35	5.67	5.59	5.65	11.70	5.00	5.11
18	5.40	5.41	5.33	12.00	5.81	5.73	5.79	12.37	5.11	5.24
19	5.52	5.53	5.44	12.68	5.94	5.86	5.93	13.08	5.20	5.35
20	5.63	5.63	5.55	13.33	6.07	5.97	6.06	13.75	5.29	5.50
21	5.73	5.73	5.64	14.02	6.18	6.08	6.17	14.45	5.37	5.57
22	5.83	5.83	5.73	14.67	6.29	6.18	6.28	15.12	5.45	5.67
23	5.92	5.91	5.81	15.35	6.38	6.28	6.41	15.82	5.52	5.75
24	6.00	5.99	5.89	16.00	6.48	6.37	6.46	16.50	5.59	5.81
25	6.08	6.07	5.96	16.68	6.56	6.45	6.60	17.20	5.65	5.92
26	6.16	6.14	6.03	17.33	6.64	6.53	6.72	17.87	5.70	6.01
27	6.24	6.20	6.09	18.00	6.72	6.60	6.76	18.57	5.76	6.09
28	6.31	6.26	6.15	18.67	6.79	6.67	6.87	19.21	5.81	6.16
29	6.38	6.32	6.20	19.35	6.86	6.73	6.98	19.94	5.85	
30	6.45	6.38	6.25	20.00	6.92	6.79	7.02	20.62	5.90	6.26
35	6.73	6.61	6.47	23.35	7.19	7.04		24.06	6.08	
40	6.97	6.78	6.64	26.67	7.39	7.24	7.62	27.49	6.22	6.79
47	7.77	6.92	6.77	30.01	7.56	7.39		30.94	6.32	
50	7.34	7.03	6.87	33.34	7.69	7.52	8.01	34.37	6.41	7.14
60	7.63	7.19	7.03	40.01	7.88	7.70	8.49[e]	41.24	6.54	7.43[e]
70	7.88	7.31	7.14	46.68	8.02	7.83		48.11	6.63	
80	8.06	7.40	7.22	53.35	8.13	7.93		54.98	6.70	
90	8.22	7.47	7.29	60.02	8.21	8.01		61.86	6.76	
100	8.38	7.52	7.34	66.69	8.27	8.07	9.27[e]	68.73	6.80	8.28[e]
125	8.69	7.62	7.44	83.36	8.38	8.18		85.92	6.88	
150	8.99	7.69	7.50	100.03	8.47	8.26		103.1	6.93	
175	9.26	7.74	7.54	116.71	8.53	8.31		120.3	6.97	
200	9.53	7.77	7.58	133.38	8.57	8.35		137.4	7.00	
225	9.77	7.80	7.60	150.05	8.60	8.38		154.6	7.02	

[a] E_g = 600 cal/mol; E_ω = 1900 cal/mol or ∞. [b] Monte-Carlo calculation. [c] Matrix multiplication calculation. [d] Excluded volume considered: Chains are self-avoiding with cut-off distances between centers of remote CH_2 groups taken to be 3.0 Å. [e] Excluded volume considered: Chains are self-avoiding with cut-off distances between centers of remote CH_2 groups taken to be 2.7 Å.

The excluded volume effect is usually discussed in terms of an expansion parameter $\alpha^2{}_{r^2} = \langle r^2\rangle/\langle r_0^2\rangle$ which describes the extent to which model chains have their mean dimensions expanded due to the inclusion of nonlocal nonbonded interactions into the computation. Our calculations permit us to examine the magnitude of α for lattice chains at 25° and for off-lattice chains (∠CCC = 112°) at both 25 and 140°. We have in most cases computed $\langle r^2\rangle$ and $\langle s^2\rangle$ for off-lattice chains for hard core repulsion distances of both 2.7 and 3.0 Å in order to assess the effects of small changes in this distance on the magnitude of the excluded volume effect. Our calculations also permit us to examine another expansion parameter $\alpha^2{}_{s^2} = \langle s^2\rangle/\langle s_0^2\rangle$ for these chains. These data are collected in Table III and Figure 1.

At normally accessible temperatures, nonlocal nonbonding repulsions make only small contributions to $\langle r^2\rangle$ and $\langle s^2\rangle$ for short chains. Both α_{r^2} and α_{s^2} are less than 2% for chains of fewer than 20 carbons and less than 5% for room-temperature chains of fewer than 40 carbons. Consequently neutron diffraction studies of hexatriacontane (35 bonds)[16c] at room temperature would be unlikely to be sensitive to the very small excluded volume effect predicted in Figure 1.

Values of α_{r^2} and α_{s^2} are sensitive to both the temperature and the model used to calculate chain properties. For off-lattice chains—the most realistic variant of the RIS model—the excluded volume effect is significantly more important at 140° than at 25°. As the temperature is increased, the chains become more compact, and correspondingly more sensitive to nonlocal nonbonding interactions. For $\langle s^2\rangle$, $\alpha^2{}_{s^2}$ approaches 10% for 60-bond chains at 140° and 17% for 100-bond chains. Neutron diffraction studies of fractionated low molecular weight polyethylene

Table II
Mean-Squared Radius of Gyration of Hydrocarbon Chains Calculated for Various Models[a] [$\langle s^2\rangle/nl^2$ and $\langle s_0{}^2\rangle/nl^2$]

	tetrahedral lattice chains, ∠CCC = 109.5°				off-lattice chains, ∠CCC = 112.0°					
no. of bonds	$E_\omega = \infty$[b] (ev[d])	∞[c]	1900[c]	all trans[c]	∞[c]	1900[c]	1900[b] (ev[d])	all trans[c]	1900[c] (140 °C)	1900[b] (ev[d]) (140 °C)
1	0.250	0.250	0.250	0.250	0.250	0.250		0.250	0.250	
2	0.259	0.259	0.259	0.259	0.264	0.264		0.264	0.264	
3	0.282	0.285	0.255	0.305	0.293	0.293		0.312	0.289	
4	0.314	0.317	0.317	0.353	0.327	0.327	0.324	0.362	0.320	0.318
5	0.346	0.349	0.348	0.405	0.361	0.361	0.358	0.417	0.351	0.349
6	0.377	0.380	0.379	0.458	0.395	0.394	0.392	0.471	0.381	0.379
7	0.407	0.410	0.409	0.512	0.427	0.426	0.424	0.527	0.410	0.408
8	0.436	0.439	0.437	0.566	0.459	0.457	0.455	0.582	0.437	0.436
9	0.464	0.467	0.465	0.620	0.488	0.486	0.485	0.637	0.463	0.463
10	0.491	0.493	0.490	0.675	0.517	0.514	0.513	0.695	0.488	0.488
11	0.516	0.518	0.515	0.730	0.544	0.541	0.540	0.752	0.511	0.512
12	0.540	0.542	0.539	0.785	0.570	0.566	0.566	0.808	0.533	0.534
13	0.563	0.565	0.561	0.840	0.595	0.571	0.590	0.865	0.554	0.556
14	0.584	0.587	0.582	0.895	0.619	0.614	0.614	0.922	0.573	0.577
15	0.605	0.607	0.602	0.950	0.641	0.636	0.634	0.979	0.592	0.596
16	0.625	0.627	0.621	1.005	0.663	0.657	0.658	1.036	0.610	0.616
17	0.644	0.646	0.640	1.060	0.683	0.677	0.679	1.093	0.627	0.633
18	0.661	0.664	0.657	1.116	0.703	0.679	0.699	1.150	0.643	0.651
19	0.679	0.681	0.674	1.170	0.722	0.715	0.718	1.207	0.658	0.667
20	0.696	0.697	0.690	1.226	0.749	0.733	0.737	1.264	0.672	0.687
21	0.712	0.713	0.705	1.282	0.757	0.749	0.755	1.321	0.686	0.701
22	0.727	0.728	0.720	1.337	0.774	0.765	0.771	1.378	0.699	0.716
23	0.742	0.742	0.733	1.393	0.790	0.781	0.791	1.435	0.712	0.730
24	0.756	0.756	0.747	1.448	0.805	0.796	0.802	1.492	0.724	0.742
25	0.770	0.769	0.759	1.503	0.820	0.810	0.821	1.550	0.735	0.758
26	0.783	0.781	0.772	1.559	0.834	0.824	0.839	1.607	0.746	0.771
27	0.796	0.794	0.783	1.614	0.848	0.837	0.850	1.664	0.757	0.783
28	0.809	0.805	0.795	1.780	0.861	0.850	0.865	1.721	0.767	0.796
29	0.820	0.816	0.805	1.725	0.873	0.862	0.881	1.778	0.776	
30	0.833	0.827	0.816	1.781	0.885	0.874	0.892	1.835	0.786	0.818
35	0.886	0.875	0.862	2.05	0.940	0.926		2.12	0.826	
40	0.933	0.915	0.901	2.33	0.985	0.970	1.005	2.41	0.860	0.915
45	0.973	0.949	0.933	2.61	1.024	1.007		2.69	0.889	
50	1.01	0.978	0.961	2.89	1.057	1.039	1.088	2.98	0.913	0.983
60	1.07	1.025	1.006	3.44	1.111	1.091	1.171[e]	3.55	0.951	1.047[e]
70	1.13	1.062	1.051	4.00	1.153	1.131		4.13	0.981	
80	1.17	1.091	1.068	4.55	1.187	1.163		4.70	1.004	
90	1.21	1.114	1.091	5.11	1.214	1.189		5.27	1.023	
100	1.24	1.133	1.109	5.67	1.237	1.210	1.354[e]	5.84	1.039	1.216[e]
125	1.31	1.170	1.144	7.05	1.279	1.251		7.27	1.069	
150	1.37	1.195	1.168	8.44	1.309	1.279		8.71	1.088	
175	1.42	1.214	1.186	9.83	1.331	1.300		10.14	1.102	
200	1.47	1.228	1.199	11.22	1.348	1.316		11.57	1.114	
225	1.52	1.240	1.210	12.61	1.362	1.329		13.00	1.123	

[a] E_g = 600 cal/mol; E_ω = 1900 cal/mol or ∞. [b] Monte-Carlo calculation. [c] Matrix multiplication calculation. [d] Excluded volume considered: Chains are self-avoiding with cut-off distances between centers of remote CH_2 groups taken to be 3.0 Å. [e] Excluded volume considered: Chains are self-avoiding with cut-off distances between centers of remote CH_2 groups taken to be 2.7 Å.

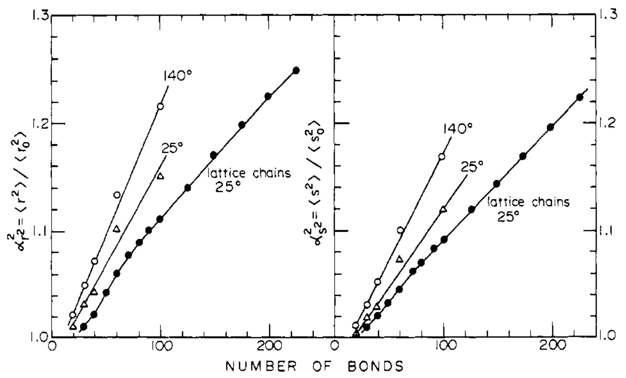

Figure 1. The expansion factors $\alpha^2_{r^2}$ and $\alpha^2_{s^2}$ comparing excluded volume to "unperturbed" chains for two different models: (●) diamond lattice chains for 25 °C; (△) off-lattice chains at 25 °C; (○) off-lattice chains at 140 °C.

should be capable of providing measurements from which α_{s^2} can be calculated, thus permitting the parameters of the off-lattice calculation to be tested.

Lattice chains with second neighbor exclusions are significantly less sensitive to remote nonbonding repulsions than off-lattice chains. The origin of this difference is not immediately obvious. It derives from structural features of the lattice imposed upon bond angles, together with the absence of $g^{\pm}g^{\mp}$ sequences in the present lattice chains. By comparison, these sequences are permitted (with low probability) in the off-lattice chains. They make important contributions to very compact chain conformations and become increasingly important at high temperatures.

Mean end-to-end distances $\langle r\rangle$ computed for off-lattice polymethylene chains are collected in Table IV. These values have been calculated for remote hard sphere repulsion distances of 3.0 and 0 Å. Calculations without

Table III
Effect of the Hard Sphere Repulsion Radius on the Magnitude of the Excluded Volume Effect

no. of bonds	hard sphere radius 3.0 Å 298 K	hard sphere radius 3.0 Å 413 K	hard sphere radius 2.7 Å 298 K	hard sphere radius 2.7 Å 413 K
		$\alpha^2{}_{r^2} = \langle r^2\rangle/\langle r_0{}^2\rangle$		
10	1.00	1.00	1.00	1.00
20	1.02	1.04	1.01	1.02
30	1.03	1.06	1.03	1.05
40	1.05	1.09	1.04	1.07
50	1.07	1.11		
60			1.10	1.14
100			1.15	1.22
		$\alpha^2{}_{s^2} = \langle s^2\rangle/\langle s_0{}^2\rangle$		
10	1.00	1.00	1.00	1.00
20	1.01	1.02	1.00	1.01
30	1.02	1.04	1.02	1.03
40	1.04	1.06	1.03	1.05
50	1.05	1.08		
60			1.07	1.10
100			1.12	1.17

Table IV
Mean End-to-End Distances for Off-Lattice Chains;[a] with $\langle r\rangle$ and without $\langle r_0\rangle$ Account of Excluded Volume[b]

no. of bonds	$\langle r\rangle$, Å 298 K	$\langle r\rangle$, Å 413 K	$\langle r_0\rangle$, Å 298 K	$\langle r_0\rangle$, Å 413 K
5	5.56	5.42		
6	6.50	6.32		
7	7.41	7.17		
8	8.28	7.98	8.26	7.97
9	9.09	8.75	9.09	8.73
10	9.88	9.49	9.88	9.46
11	10.64	10.19	10.63	10.15
12	11.37	10.87	11.36	10.82
13	12.07	11.52	12.06	11.45
14	12.75	12.15		
15	13.4	12.8	13.4	12.6
16	14.1	13.4	14.0	13.2
17	14.7	13.9	14.6	13.7
18	15.3	14.5	15.2	14.3
19	15.9	15.0	15.7	14.7
20	16.4 (16.4)[c]	15.6 (15.5)[c]	16.2	15.2
21	17.0	16.1	16.8	15.7
33	17.5	16.6	17.3	16.2
23	18.1	17.1	17.8	16.6
24	18.5	17.5	18.2	17.0
25	19.1	18.0	18.8	17.5
26	19.6	18.5	19.3	17.9
37	20.0	18.9	19.7	18.3
28	20.5	19.4	20.2	18.8
29	21.0		20.6	19.1
30	21.4 (21.4)[c]	20.2 (20.1)[c]	20.9	19.4
40	25.6 (25.4)[c]	24.1 (23.9)[c]	24.6	22.9
50	29.2	27.5		
60	32.8[c]	30.6[c]		
100	44.0[c]	41.6[c]		

[a] Off-lattice exact enumeration for chains of 14 or fewer bonds; Monte-Carlo calculations for longer chains. E_σ = 600 cal/mol, E_ω = 1900 cal/mol, ∠CCC = 112°, $\phi_t = 0°$, $\phi_{g^\pm} = 120°$, l = 1.53 Å. [b] $\langle r\rangle$ calculated with a hard sphere repulsion distance of 3.0 Å between carbons separated by more than four bonds. [c] The hard sphere distance chosen to be 2.7 Å.

remote interactions give rise to "unperturbed dimensions" of the chain, and these are here represented by $\langle r_0\rangle$. For the chain lengths considered, an increase in the temperature causes decreases in both $\langle r\rangle$ and $\langle r_0\rangle$. The former are not very sensitive to the particular choices of hard sphere radii.

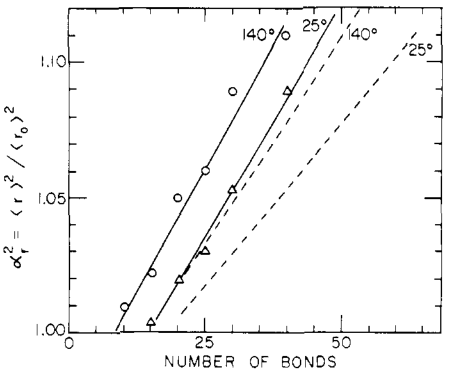

Figure 2. The expansion factor α_r^2 of the mean end-to-end distance r for off-lattice chains: (○) 140 °C, (△) 25 °C; the two dashed lines are the corresponding values of $\alpha^2{}_{r^2}$ at these temperatures.

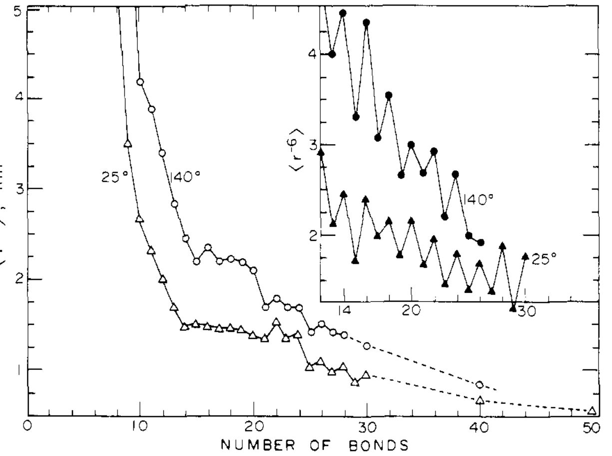

Figure 3. Values of $\langle r^{-6}\rangle$ in nm^{-6} [10^6 Å^{-6}] for off-lattice chains. The open circles and triangles refer to calculations made with the use of a 3.0 Å radius hard sphere repulsive potential for remote interactions. The insert (●, ▲) refers to a 2.7 Å radius hard sphere repulsion.

In order to compare the sensitivity of $\langle r\rangle$, the first moment of r, with that of the second moment $\langle r^2\rangle$, we have chosen to define an expansion parameter

$$\alpha_r = \langle r\rangle/\langle r_0\rangle$$

End-to-end distances enter into α_r^2 with the same exponent as they enter into $\alpha^2{}_{r^2}$ via $\langle r^2\rangle$. Values of $\alpha^2{}_{r^2}$ for polymethylene chains of up to 40 bonds are plotted in Figure 2. Two features of this plot are important. First α_r^2, like $\alpha^2{}_{r^2}$, is more important at higher temperatures. Second, the magnitude of α_r^2 at each temperature is significantly larger than that of $\alpha^2{}_{r^2}$. The excluded volume effect appears to be more important for lower moments of $\langle r\rangle$, symptomatic of uneven expansion of the chain.[18]

As higher moments of r are particularly sensitive to chains of large end-to-end distance, inverse moments of r should be sensitive to compact configurations of the chain. Inverse moments of the end-to-end distance are important to many physical properties of chain molecules. $\langle r^{-1}\rangle$ plays an important role in determining the diffusion coefficient of polymers.[5] $\langle r^{-3}\rangle$ enters into descriptions of dipolar interactions.[19] The negative sixth moment $\langle r^{-6}\rangle$ appears in descriptions of electronic energy transfer [Förster dipole–dipole mechanism] between chromophores attached to the ends of a polymer chain.[20] Because $\langle r^{-6}\rangle$ is in principle an experimentally accessible quantity through fluorescence energy transfer experiments, we have used exact enumeration (less than 15 bonds) and Monte-Carlo methods to calculate these quantities. The results are shown in Figure 3.

Values of $\langle r^{-6}\rangle$ are very sensitive to the choice of remote hard sphere repulsion radius. Large values of $\langle r^{-6}\rangle$ imply short end-to-end distances. A 2.7-Å excluded volume radius lets the chain ends approach closer than does a 3.0-Å radius. Once the chains are longer than 20 bonds in the former case, and longer than 14 bonds in the latter, $\langle r^{-6}\rangle$ changes only slowly with chain length. It is worth noting that an apparently large relative change in $\langle r^{-6}\rangle$ corresponds to a much smaller change in r (e.g., a change from $\langle r^{-6}\rangle = 2$ to 1 nm^{-6} corresponds to a change of $r = 9$ to 10 Å).

One interesting feature in the $\langle r^{-6}\rangle$ calculation is the apparent odd–even oscillations that occur with the 2.7 Å excluded volume radius. While we can estimate error bars in the Monte-Carlo calculation of $\langle r^{-6}\rangle$ (ca. 2% at $n = 20$ and 30), this average is exceedingly sensitive to the presence of chains with their ends in proximity. Very small fluctuations in distances of closest approach can lead to the odd–even oscillations seen in the insert in Figure 3.

Our RIS model off-lattice chains differ from diamond lattice chains only in the choice of the ∠CCC bond angle; the chains retain many characteristics of lattice chains. In addition, inverse moments of r are very sensitive to the end-to-end distance of chains with their ends in proximity. One might anticipate that $\langle r^{-6}\rangle$ would be sensitive to conformational constraints similar to those experienced in chain cyclization. It is well known that tetrahedral lattice chains form closed loops only for even-membered rings. Thus, there is a "trivial" explanation for an odd–even alternating effect, persisting to long chain length, for properties of lattice chains related to end-to-end cyclization.

A final comment is in order about the applicability of the RIS model to calculations of large inverse moments of r. These models assume fixed bond lengths and neglect bond angle vibrations and torsional librations of the dihedral angles. One normally assumes these will not have much effect. In end-to-end cyclization of real polymers, especially short and medium length hydrocarbon chains,[21] certain configurations are involved which are prohibited for RIS model chains. It may therefore be necessary to employ more sophisticated models[22-25] to account for properties of chains with their ends in proximity.

Acknowledgment. M.A.W. would like to acknowledge the gracious hospitality of the CRPP, Talence, France, during his sabbatical stay.

References and Notes

(1) P. J. Flory, "Statistical Mechanics of Chain Molecules", Interscience, New York, 1969.

(2) W. J. Leonard, R. L. Jernigan, and P. J. Flory, *J. Chem. Phys.*, **35**, 644 (1961).

(3) (a) R. P. Smith and E. M. Mortensen, *J. Chem. Phys.*, **35**, 714 (1961); (b) C. Clement and P. Bothorel, *J. Chim. Phys., Phys.-Chim. Biol.*, **61**, 878, 1068, 1262 (1964); (c) K. Nagai, *J. Chem. Phys.*, **47**, 4690 (1967); (d) G. D. Patterson and P. J. Flory, *J. Chem. Soc., Faraday Trans. 2*, **68**, 1098 (1972); (e) P. Bothorel and G. Fourche, *ibid.*, **69**, 441 (1973).

(4) (a) M. Sisido, *Macromolecules*, **4**, 737 (1971); (b) M. A. Winnik, R. E. Trueman, G. Jackowski, D. S. Saunders, and S. G. Whittington, *J. Am. Chem. Soc.*, **96**, 4843 (1974); (c) D. S. Saunders and M. A. Winnik, *Macromolecules*, **11**, 18, 25 (1978).

(5) (a) I. J. Mokrys, D. Rigby, and R. F. T. Stepto, *Ber. Bunsenges. Phys. Chem.*, **83**, 446 (1979); (b) J. J. Friere and A. Horta, *J. Chem. Phys.*, **65**, 2860, 2867, 4049 (1976).

(6) D. Y. Yoon and P. J. Flory, *J. Chem. Phys.*, **69**, 2536 (1978).

(7) J. L. Hill and R. F. T. Stepto, *Trans. Faraday Soc.*, **67**, 3202 (1971).

(8) W. J. Taylor, *J. Chem. Phys.*, **16**, 257 (1948).

(9) In this paper "local" interactions are those which occur between substituents separated by four or fewer C–C bonds. These include the pentane effect. Interactions due to the close approach of groups separated by more than four C–C bonds are called "nonlocal" interactions. The excluded volume effect is associated with the sum of all nonlocal interactions in a polymer, as compounded by solvent effects. Neglect of excluded volume in a model calculation corresponds to a measurement in a Θ solvent. Hard sphere remote repulsive interactions correspond to an athermal solvent.

(10) (a) M. V. Volkenstein, *J. Polym. Sci.*, **29**, 441 (1958); (b) S. Lifson, *J. Chem. Phys.*, **29**, 80 (1958); **30**, 964 (1958); (c) K. Nagai, *ibid.*, **31**, 1169 (1959).

(11) (a) G. G. Lowry, Ed., "Markov Chains and Monte Carlo Calculations in Polymer Science", Marcel Dekker, New York, 1970; (b) M. Fixman and R. Alben, *J. Chem. Phys.*, **58**, 1553 (1973); (c) M. Fixman, *ibid.*, **58**, 1559 (1973); (d) D. Y. Yoon and P. J. Flory, *ibid.*, **61**, 5367 (1974).

(12) (a) P. Bothorel, *J. Chim. Phys., Phys.-Chim. Biol.*, **71**, 1133 (1974); (b) K. Suzuki and Y. Nakata, *Bull. Chem. Soc. Jpn.*, **43**, 1006 (1970).

(13) (a) M. Lal and D. Spencer, *Mol. Phys.*, **22**, 649 (1971); (b) S. D. Stellman and P. J. Gans, *Macromolecules*, **5**, 516 (1972); (c) M. Kumbar and S. Windwer, *ibid.*, **7**, 624 (1974); (d) M. Sisido and K. Shimada, *J. Am. Chem. Soc.*, **99**, 7785 (1977).

(14) (a) G. Fourche and B. Lemaire, *J. Chim. Phys., Phys.-Chim. Biol.*, **7-8**, 1170 (1970); (b) B. Lemaire and G. Fourche, *J. Polym. Sci., Part A-2*, **9**, 961 (1971); (c) B. Lemaire, F. Fourche, and E. Sanchez, *J. Polym. Sci., Polym. Phys. Ed.*, **12**, 417 (1974).

(15) M. Lal and R. F. T. Stepto, *J. Polym. Sci., Polym. Symp.*, **61**, 401 (1977).

(16) (a) P. Wollar and E. W. Garbisch, *J. Am. Chem. Soc.*, **94**, 5310 (1972); (b) I. Harada, H. Takeuchi, M. Sakakibara, H. Matsuura, and T. Shimanouchi, *Bull. Chem. Soc. Jpn.*, **50**, 102 (1977); (c) M. Dettenmaier, *J. Chem. Phys.*, **68**, 2319 (1978), and ref 5.

(17) See M. B. Huglin and R. F. T. Stepto, *Makromol. Chem.*, **132**, 225 (1970).

(18) H. Yamakawa, "Modern Theory of Polymer Solutions", Harper and Row, New York, 1971.

(19) H. M. McConnell and R. E. Robertson, *J. Chem. Phys.*, **29**, 1361 (1958).

(20) J. B. Birks, "Photophysics of Aromatic Molecules", Wiley, New York, 1970, pp 567 ff.

(21) G. M. Bennett, *Trans. Farady Soc.*, **37**, 794 (1941).

(22) A. Baram and W. M. Gelbart, *J. Chem. Phys.*, **66**, 4666 (1977).

(23) R. Cook and M. Moon, *Macromolecules*, **11**, 1054 (1978).

(24) J. Freire and M. Fixman, *J. Chem. Phys.*, **69**, 634 (1978).

(25) M. L. Mansfield, *J. Chem. Phys.*, in press.