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Monte Carlo Calculation of Hydrodynamic Properties of Linear and Cyclic Polymers in Good Solvents

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ABSTRACT: Using rigid-body Monte Carlo simulation coupled with rigorous treatment of hydrodynamic interaction, we have calculated translational coefficients and intrinsic viscosities of linear and cyclic polymers with excluded-volume interactions. We use two models: freely jointed chains with hard-sphere interactions and Gaussian chains with Lennard-Jones potential. Both models predict identical results in the practical limit of long chains. For linear polymers the calculated Flory parameters are $P = 5.3$ and $\Phi \times 10^{-23} = 1.9$, while their ratios to the values obtained in unperturbed conditions are $P/P_0 = 0.88$ and $\Phi/\Phi_0 = 0.76$. These values are found to be in quite good agreement with a variety of experimental data for linear polymers in good solvents. For cyclic polymers we obtain values for the cyclic-to-linear ratios, q_s, q_f, and q_η, which, interestingly, are very similar to those obtained for ideal conditions and are in agreement with experiments. The Flory parameters and their ratios for cyclic polymers are $P = 6.5$ and $\Phi \times 10^{-23} = 2.9$, with $P/P_0 = 0.90$ and $\Phi/\Phi_0 = 0.72$. These ratios are, within statistical uncertainty, practically identical with those of linear chains.

Introduction

In a previous paper,[1] the hydrodynamic properties of cyclic polymers at nearly ideal conditions were calculated by using the rigid-body treatment, which combines rigorous hydrodynamic procedures for rigid bodies with Monte Carlo simulation of chain conformations. As found earlier for linear[2] and star[3] polymers, this treatment produced an agreement between calculated and experimental properties that was generally much better than that obtained with less rigorous hydrodynamic treatments like those including preaveraging approximations.

In the present paper, we extend the previous work to study excluded-volume effects. In ref 1 we discussed the difficulty of establishing a common reference for the ideal behavior of cyclic and linear chains. Hopefully, there should not be such difficulties in the good-solvent behavior, where one would expect some kind of universality. Another motivation for the present work was the availability of various data for cyclic polystyrene in good solvents like toluene and tetrahydrofuran.[4,5] In order to evaluate the influence of excluded volume on ring-to-linear ratios of properties, we extend some previous results for linear chains with intramolecular interactions[3] and derived news results for another model. This enabled an additional analysis of the hydrodynamics of linear polymers in good solvents.

Theory and Models

The notation and definitions used here can be found in our previous article, which is hereafter referred to as paper I. The expressions contained there are denoted now as eq. I.xx.

The two basic models presented in paper I are used here with the modifications needed to represent excluded-volume effects. One of the models is the freely jointed (FJ) chain, either linear or cyclic, in which the elements are now regarded as hard spheres with diameter a. We set $a/b = 0.55$ (where b is the fixed bond length), which gives the typical value of the critical exponent of the radius of gyration, $a_r \simeq 0.6$. Conformations of the chain are produced by using the kink-jump method of Baumgärtner.[6] After a bead movement, excluded-volume interactions are tested; if the distance between the bead and any other in the chain is smaller than a, the new position is rejected, and the final position after that step coincides with the initial one. The working conditions in the simulation and other details are as in paper I.

The second model (GB–LJ) is a chain with Gaussian bonds of rms length b and Lennard-Jones interaction potential with parameters ϵ and σ. The proper choice of these parameters to represent the typical good-solvent behavior of linear chains was the object of a previous study.[7] Thus, we have chosen LJ parameters so that the asymptotic scaling laws expected for good-solvent conditions (i.e., with positive balance of binary intramolecular interactions) are already reached for finite values of N that can be conveniently handled in computational work. The exponent $a_r \simeq 0.6$ is obtained when $\sigma/b = 0.8$ and $\epsilon/kT = 0.1$. These are the parameters used in the present work. We recall that in paper I we used $\epsilon/kT = 0.3$ to represent the ideal behavior; this is the only difference between the simulations reported here and those in paper I, where all the details are described.

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Table I
Reduced Values of the Dimensionless Properties of Cyclic Chains and Cyclic-to-Linear Ratios

N	$\langle s^2\rangle^*$	f^*	$[\eta]^*$	P	$\Phi \times 10^{-23}$	q_s	q_f	q_η
Freely Jointed Rings (FJ)								
10	1.207 ± 0.006	0.974 ± 0.002	9.59 ± 0.06	6.82 ± 0.03	2.96 ± 0.04	0.577 ± 0.008	0.915 ± 0.007	0.652 ± 0.013
20	2.733 ± 0.013	1.443 ± 0.004	32.4 ± 0.3	6.72 ± 0.03	2.94 ± 0.05	0.557 ± 0.009	0.900 ± 0.007	0.609 ± 0.019
30	4.46 ± 0.03	1.835 ± 0.007	68.0 ± 0.7	6.69 ± 0.05	2.96 ± 0.06	0.551 ± 0.017	0.903 ± 0.013	0.61 ± 0.03
40	6.24 ± 0.04	2.155 ± 0.014	111 ± 2	6.64 ± 0.06	2.92 ± 0.08	0.552 ± 0.018	0.894 ± 0.012	0.60 ± 0.03
50	8.17 ± 0.12	2.457 ± 0.006	166 ± 2	6.61 ± 0.06	2.91 ± 0.09	0.54 ± 0.03	0.897 ± 0.005	0.60 ± 0.02
64	10.8 ± 0.2	2.825 ± 0.016	252 ± 6	6.61 ± 0.09	2.91 ± 0.15	0.53 ± 0.03	0.887 ± 0.013	0.58 ± 0.04
80	14.3 ± 0.2	3.247 ± 0.011	382 ± 3	6.61 ± 0.07	2.89 ± 0.08	0.57 ± 0.05	0.899 ± 0.009	0.61 ± 0.03
Gaussian Rings (GB–LJ)								
8	0.964 ± 0.007	0.829 ± 0.003	6.1 ± 0.6	6.50 ± 0.04	2.64 ± 0.05	0.555 ± 0.007	0.907 ± 0.004	0.598 ± 0.008
19	2.728 ± 0.010	1.387 ± 0.006	29.7 ± 0.4	6.46 ± 0.04	2.70 ± 0.05	0.542 ± 0.012	0.900 ± 0.004	0.594 ± 0.009
25	3.78 ± 0.03	1.626 ± 0.008	48.2 ± 0.8	6.44 ± 0.06	2.69 ± 0.08	0.551 ± 0.015	0.893 ± 0.006	0.586 ± 0.016
37	6.00 ± 0.03	2.058 ± 0.004	98.7 ± 1.2	6.46 ± 0.03	2.75 ± 0.05	0.55 ± 0.02	0.899 ± 0.004	0.598 ± 0.011
49	8.36 ± 0.09	2.241 ± 0.018	161 ± 5	6.44 ± 0.08	2.73 ± 0.13	0.529 ± 0.016	0.891 ± 0.009	0.58 ± 0.02
55	9.65 ± 0.16	2.60 ± 0.03	200 ± 7	6.45 ± 0.12	2.73 ± 0.16	0.54 ± 0.03	0.901 ± 0.012	0.60 ± 0.03
64	11.4 ± 0.3	2.83 ± 0.02	257 ± 7	6.46 ± 0.14	2.74 ± 0.18	0.53 ± 0.04	0.881 ± 0.012	0.54 ± 0.03

Table II
Reduced Values of the Dimensionless Properties of Linear Chains

N	$\langle s^2\rangle^*$	f^*	$[\eta]^*$	P	$\Phi \times 10^{-23}$
Freely Jointed Chains (FJ)					
10	2.092 ± 0.018	1.064 ± 0.006	14.7 ± 0.2	5.66 ± 0.05	1.99 ± 0.05
20	4.91 ± 0.06	1.603 ± 0.008	53.2 ± 1.2	5.56 ± 0.06	2.01 ± 0.08
30	8.1 ± 0.2	2.03 ± 0.02	111 ± 4	5.49 ± 0.12	1.97 ± 0.14
40	11.3 ± 0.3	2.410 ± 0.017	186 ± 5	5.52 ± 0.11	2.01 ± 0.13
50	15.0 ± 0.5	2.740 ± 0.008	276 ± 6	5.44 ± 0.11	1.95 ± 0.14
64	20.2 ± 0.9	3.18 ± 0.03	431 ± 16	5.45 ± 0.17	1.9 ± 0.2
80	25 ± 2	3.61 ± 0.03	623 ± 28	5.6 ± 0.3	2.0 ± 0.3
Gaussian Chains (GB–LJ)					
8	1.737 ± 0.011	0.914 ± 0.001	10.19 ± 0.04	5.34 ± 0.02	1.82 ± 0.02
19	5.03 ± 0.09	1.541 ± 0.002	50.01 ± 0.15	5.29 ± 0.05	1.82 ± 0.05
25	6.86 ± 0.14	1.821 ± 0.003	82.2 ± 0.8	5.35 ± 0.06	1.87 ± 0.08
37	10.9 ± 0.4	2.288 ± 0.005	165.1 ± 1.1	5.33 ± 0.11	1.88 ± 0.12
49	15.8 ± 0.5	2.717 ± 0.007	276.5 ± 0.9	5.26 ± 0.10	1.80 ± 0.09
55	17.7 ± 0.8	2.890 ± 0.008	333 ± 5	5.29 ± 0.13	1.83 ± 0.15
64	21.6 ± 1.0	3.21 ± 0.02	473 ± 13	5.32 ± 0.16	1.93 ± 0.19

In the presentation of results we shall use the following dimensionless forms for the mean-squared radius of gyration, translational friction coefficient, and intrinsic viscosity:

$$\langle s^2\rangle^* = \langle s^2\rangle / b^2 \qquad (1)$$

$$f_t^* = f_t / 6\pi\eta_0 b \qquad (2)$$

$$[\eta]^* = [\eta]M/N_A b^3 \qquad (3)$$

where η_0 is the viscosity of the solvent, M is the molecular weight of the polymer, and N_A is Avogadro's number. The cyclic-to-linear ratios for the three properties are defined as

$$q_s = \langle s^2\rangle_r / \langle s^2\rangle_l \qquad (4)$$

$$q_f = (f_t)_r / (f_t)_l \qquad (5)$$

$$q_\eta = [\eta]_r / [\eta]_l \qquad (6)$$

where subscripts r and l denoted, respectively, the ring and linear polymer.

Results

In Table I we present the values of the dimensionless radii of gyration, $\langle s^2\rangle^*$, translational friction coefficients, f^*, and intrinsic viscosities, $[\eta]^*$, defined in eqs 1–3, of the two models of cyclic chains with varying chain length, N. We also give the values of the Flory parameters, P and Φ, defined in eqs I.12 and I.13. A similar set of results for linear chains is presented in Table II. The cyclic-to-linear ratios, q_s, q_f, and q_η, defined in eqs I.1–I.3 were included in Table I.

A preliminary analysis of the simulation results was made in terms of scaling laws, which, for the dimensionless quantities, read

$$\langle s^2\rangle^* = C_s N^{2a_s} \qquad (7)$$

$$f^* = C_f N^{a_f} \qquad (8)$$

$$[\eta]^* = C_\eta N^{1+a_\eta} \qquad (9)$$

While for Θ conditions the values of the exponents so defined are $a_s = a_f = a_\eta = {}^1/_2$, the well-known mean-field theoretical values with excluded-volume effect are $a_s = a_f = {}^3/_5$ and $a_\eta = {}^4/_5$.

We carried out a fitting of our simulation results to eqs 7–9. Some examples are displayed in Figure 1. The fit was done as described in paper I, and the results are listed in Table III. These results indicate that the exponents of the scaling law are independent of the model. We note that in most cases the exponents obtained coincide within statistical error with the ones expected from theoretical predictions. (In some cases, we obtain exponents slightly higher than those predicted by theory, but these differences never exceed the statistical uncertainty intervals.) Although the exponents for linear chains may seem slightly higher than those for rings, the difference is not significant if one regards the statistical uncertainty.

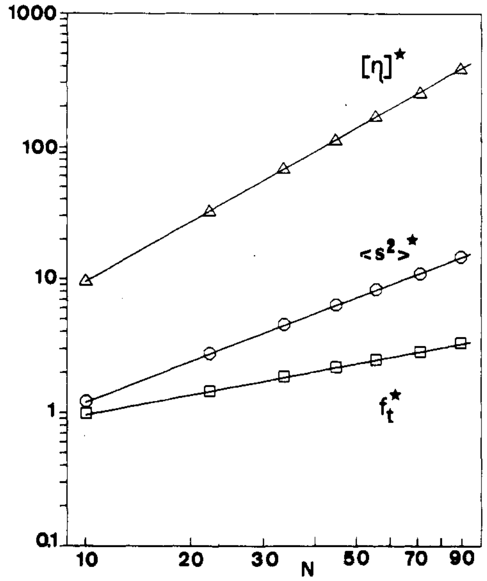

Figure 1. log–log plot of the reduced properties $\langle s^2\rangle^*$ (○), f^* (□), and $[\eta]^*$ (△) of FJ rings vs N. The straight lines are the fits to eqs 7–9, with the parameters in Table III.

Table III
Constants and Exponents in the Scaling Laws (Equations 7–9) of the Reduced Properties

	cyclic chains		linear chains	
	FJ	GB-LJ	FJ	GB-LJ
a_r	0.595 ± 0.004	0.590 ± 0.001	0.60 ± 0.01	0.61 ± 0.02
a_f	0.582 ± 0.003	0.592 ± 0.009	0.586 ± 0.005	0.591 ± 0.003
a_η	0.775 ± 0.008	0.79 ± 0.03	0.79 ± 0.03	0.811 ± 0.013
C_s	0.077 ± 0.002	0.084 ± 0.005	0.131 ± 0.010	0.134 ± 0.019
C_f	0.252 ± 0.003	0.242 ± 0.008	0.277 ± 0.005	0.271 ± 0.003
C_η	0.160 ± 0.005	0.154 ± 0.016	0.25 ± 0.02	0.240 ± 0.012

The values of P and Φ in Tables I and II were found to be practically independent of the chain length. Anyhow, they were treated as those of ideal rings in paper I, extrapolating to $N \to \infty$ in linear plots of the parameter vs $N^{-1/2}$. The extrapolations are presented in Figure 2. If we had assumed that the values are independent of N, the mean values obtained from P and Φ would have been within statistical error, practically the same as the extrapolated ones. The least-squares linear fits confirm that assuming values independent of N is an adequate approximation (both types of numerical treatments lead to extrapolated results with overlapping uncertainty ranges). A similar treatment was given to the N-dependent values of the q ratios. The limiting values are listed in Table IV. Combining the values of $\langle s^2\rangle$, f, and $[\eta]$ obtained in this work with those reported in paper I for ideal chains, we obtain the expansion factors (Table V)

$$\alpha_s^2 = \langle s^2\rangle / \langle s^2\rangle_0 \tag{10}$$

$$\alpha_f = f/f_0 \tag{11}$$

$$\alpha_\eta^3 = [\eta]/[\eta]_0 \tag{12}$$

The subscript 0 indicates ideal conditions. Obviously, the ratios are the same for the dimensionless properties. Furthermore, we obtain the ratios

$$P/P_0 = \alpha_f/\alpha_s^{1/2} \tag{13}$$

$$\Phi/\Phi_0 = \alpha_\eta^3/\alpha_s^{3/2} \tag{14}$$

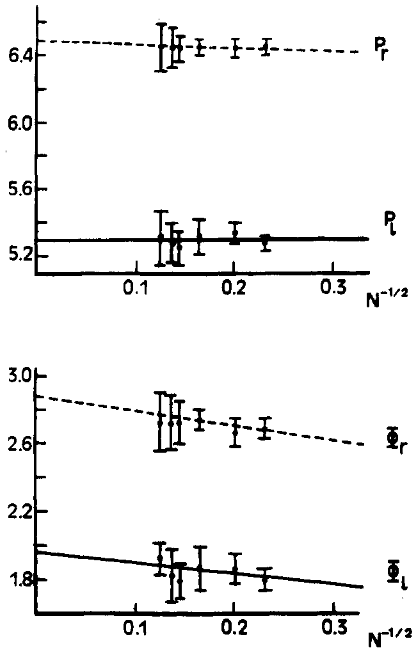

Figure 2. Extrapolations of P and Φ to $N \to \infty$ in linear plots vs $N^{-1/2}$. Data for cyclic (r) and linear (l) GB–LJ chains. The straight lines are least-square fits.

Table IV
Summary of the Limiting ($N \to \infty$) Values Obtained from Simulation

	FJ model	GB-LJ	mean
	Cyclic Chains		
P	6.48 ± 0.10	6.5 ± 0.2	6.5
Φ	2.86 ± 0.14	2.9 ± 0.3	2.9
q_s	0.54 ± 0.02	0.52 ± 0.03	0.53
q_f	0.894 ± 0.007	0.895 ± 0.011	0.89
q_η	0.60 ± 0.02	0.58 ± 0.03	0.59
	Linear Chains		
P	5.3 ± 0.2	5.3 ± 0.2	5.3
Φ	1.9 ± 0.2	1.9 ± 0.2	1.9

and the combination

$$\frac{\alpha_\eta^3}{\alpha_s^2\alpha_f} = \frac{\Phi}{\Phi_0}\frac{P_0}{P} \tag{15}$$

proposed by Freed et al.[8]

We have also analyzed the Flory–Scheraga–Mandelkern parameter, β, which may be helpful in the discussion of systems for which $\langle s^2\rangle$ data, and therefore P and Φ, are not available. The β parameter combines f and $[\eta]$:

$$\beta = \frac{([\eta]/100)^{1/3}M^{1/3}}{f/\eta_0} = \frac{(\Phi/100)^{1/3}}{P} \tag{16}$$

Comparison with Experimental Data for Linear Polymers. Experimental data are available for polystyrene in a variety of good solvents.[9–16] In Table VI we summarize data in tetrahydrofuran as well as in toluene and other aromatic solvents. Data for a rubbery, more flexible polymer, polyisoprene, in cyclohexane (good solvent) and 1,4-dioxane solvent are also included.[17–19] The theoretical results derived from our Monte Carlo simulations (means of the FJ and GB–LJ values) are presented for comparison. We can appreciate a good agreement between our theoretical results and experiental data for a_s and a_f exponents in Table VI. This agreement is better for polyisoprene in cyclohexane at 25 °C.[17,20] The a_η exponent shows different values for several experimental data, and our results of simulation for this exponent are

Table V
Expansion Factors for Cyclic and Linear Chains[a]

N	α_s^2	α_f	α_η^3	P/P_0	Φ/Φ_0	$\alpha_\eta^3/\alpha_s^2\alpha_f$
FJ Cyclic Chains						
10	1.31	1.10	1.32	0.96	0.87	0.91
20	1.56	1.16	1.55	0.93	0.80	0.86
30	1.72	1.21	1.75	0.92	0.78	0.85
40	1.79	1.22	1.82	0.91	0.77	0.85
50	1.92	1.25	1.98	0.90	0.75	0.83
64	1.98	1.28	2.10	0.91	0.75	0.82
80	2.10	1.32	2.26	0.90	0.74	0.82
GB–LJ Cyclic Chains						
8	1.46	1.14	1.45	0.98	0.95	0.97
19	1.73	1.22	1.78	0.97	0.92	0.95
25	1.83	1.23	1.84	0.96	0.89	0.93
37	1.94	1.27	2.05	0.95	0.88	0.93
49	2.05	1.29	2.20	0.93	0.83	0.89
55	2.07	1.31	2.25	0.93	0.83	0.89
64	2.19	1.32	2.27	0.92	0.81	0.88
FJ Linear Chains						
10	1.27	1.07	1.28	0.89	0.72	0.81
20	1.47	1.12	1.43	0.90	0.74	0.82
30	1.62	1.16	1.63	0.90	0.77	0.85
40	1.70	1.18	1.74	0.90	0.76	0.84
50	1.80	1.21	1.86	0.89	0.75	0.84
64	1.89	1.24	2.01	0.90	0.75	0.83
80	1.87	1.25	1.99	0.92	0.76	0.83
GB–LJ Linear Chains						
8	1.33	1.09	1.30	0.98	0.96	0.98
19	1.59	1.15	1.60	0.95	0.89	0.94
25	1.65	1.16	1.63	0.93	0.84	0.90
37	1.77	1.20	1.89	0.93	0.88	0.95
49	1.94	1.22	1.93	0.91	0.80	0.88
55	1.93	1.22	1.87	0.89	0.72	0.81
64	2.03	1.29	2.30	0.91	0.82	0.90

[a] The subscript zero indicates values for ideal chains.

also different in relation to the experimental ones. This situation is related to the fact that (contrary to what happens with models) the experimental values of the hydrodynamic exponents reach quite slowly the asymptotic limits and are therefore smaller than them even for moderately high molecular weights.

For the most relevant quantities in Table I, namely the Flory parameters P and Φ, the overall agreement between theory and experimental data is excellent for polyisoprene and polystyrene in aromatic solvents. The only exception is polystyrene in tetrahydrofuran. The differences between the behavior in this good solvent and the aromatic good solvents have been discussed elsewhere.[9,16]

With the theoretical results $P_0 = 6.0$ and $\Phi_0 = 2.5 \times 10^{23}$ derived in our previous work for unperturbed linear chains,[2] we obtain the values of P/P_0 and Φ/Φ_0 listed in Table VI. With the above-mentioned exception, the agreement is rather good. It should be mentioned that our results show a very weak dependence of Φ on N and yield well-defined limiting values for $N \rightarrow \infty$, so that the decrease with N observed for Φ and Φ/Φ_0 of polyisoprene in cyclohexane cannot be interpreted.

Comparison with Experimental Data for Cyclic Polymers. Unlike the situation for linear polymers in good solvents, data for cyclic polymers are not so abundant or systematic. Although polystyrene is again the most studied polymer, our literature search revealed the lack of a simultaneous characterization of dimensions and hydrodynamic properties of a set of polystyrene samples in a unique good solvent. Thus, while measurements of f and $[\eta]$ are available for polystyrene of moderately low molecular weight (M up to 3×10^5) in toluene[4,25,26] and tetrahydrofuran,[4,25,27] systematic data of $\langle s^2 \rangle$ vs M have been determined,[24] as far as we know, only in toluene for $M < 2 \times 10^4$. This makes it difficult to determine experimental values for the P and Φ parameter. We also analyze the Flory–Scheraga–Mandelkern parameter, β, as formulated in eq 16 of this paper.

From neutron-scattering data for polystyrene in toluene, Ragnetti et al.[24] obtained $a_r = 0.565$ and $q_s = 0.55$, in fair agreement with our results. The rather low M's in those measurements (1.2–1.9×10^4) make them less significant for the characterization of excluded-volume effects. Roovers[4] has reported translational (sedimentation) and viscosity data in toluene at 35 °C for M up to 4.4×10^5 and $\langle s^2 \rangle$ for a single sample of $M = 3.3 \times 10^5$. For the latter, using his power law result for $\langle s^2 \rangle$ in cyclohexane, we obtain $q_s = 0.52$, in good agreement with our result. Furthermore, interpolating with the power law equation for $[\eta]$ in toluene, we obtain $[\eta] = 61.3$ cm^3/g, which, along with $\langle s^2 \rangle = 2.5 \times 10^{-12}$ cm^2, yield $\Phi = 3.5 \times 10^{23}$. A similar estimation with Roovers sedimentation data gives, for the same sample, $P = 8$. As commented above, this comparison is not significant because it is based on data for a single sample. Roovers' results for the cyclic-to-linear ratios, including q_η, agree acceptably with our calculations.

Lutz, Strazielle, and co-workers[5,27] have studied polystyrene in tetrahydrofuran. f and $[\eta]$ have been reported for M up to 1.8×10^5, but $\langle s^2 \rangle$ is not available. The values of a_f, a_η, q_f, and q_η, listed in Table VII, deviate from the theoretical predictions more than the data in toluene. The situation could be due to the above-commented possible difference between the behaviors in tetrahydrofuran and good solvents.

The Flory–Scheraga–Mandelkern parameter, β, has been calculated for the various experimental data. The values obtained are listed in Table VII. We can observe the good agreement between the different experimental results and our theoretical result for this parameter. This agreement is excellent for polystyrene in toluene at 25 °C.

Other sets of data for polystyrene in toluene and tetrahydrofuran are those reported by Chinese workers.[25,26,28] They have presented viscosity and translational diffusion data that yield the values listed in Table VII.

Another cyclic polymer that has attracted much attention is poly(dimethylsiloxane), PDMS. Semlyen, Stepto, and co-workers[29,30] have reported conformational and hydrodynamic data for PMDS. Our values for the q ratios are in semiquantitative agreement with their results, which correspond to samples of quite low molecular weight which may be far from the long chain lengths at which asymptotic limits are reached and excluded-volume effects are well manifested. This is the reason for not extending the comparisons in Table VII to their data.

Excluded-Volume Effects in Linear and Cyclic Chains. Theoretical Aspects. Apart from the comparison of our results for rings with experimental data, which is particularly problematic due to the lack of systematic studies in good solvents, it is possible to analyze theoretically excluded-volume effects in ring polymers in comparison with those for linear polymers. A first look can be taken at the expansion factors, α_s, α_f, and α_η, listed in Table V.

Theoretical results for these factors should be discussed with care since, as shown by our results, they are slightly model-dependent. For both the FJ and GB–LJ models, the a's of rings are somewhat larger than those of linear chains, but the difference is small, of the order of a few percent only. This finding, in the case of α_s and α_f is in agreement with all previous work. In the case of α_η, there

Table VI
Summary of Experimental and Theoretical Results for Linear Polymers in Good Solvents

polymer	solvent (T, °C)	α_s	α_f	α_η	P	$\Phi \times 10^{23}$	P/P_0[a]	Φ/Φ_0[b]	$\alpha_\eta^3/\alpha_f\alpha_\psi^2$	refs
polystyrene	tetrahydrofuran (30)	0.57	0.56	0.70	5.9	2.2	0.98	0.86	0.88	9, 16
polystyrene	benzene	0.59	0.55		5.1	1.8	0.85	0.71	0.83	11–13
polystyrene	ethylbenzene (25)	0.59	0.56	0.56	4.8	1.8	0.80	0.71	0..89	9, 10, 16
polystyrene	toluene	0.59	0.58		5.2	2.0	0.87	0.78	0.90	14, 15, 19, 23
polyisoprene	cyclohexane (25)	0.61	0.61	0.74	5.1	*c*	0.85	*c*		17, 20
theoretical	(simulation)	0.61	0.59	0.80	5.3	1.9	0.88	0.76	0.87	this work

[a] $P_0 = 6.0$ for polystyrene in various Θ solvents;[21] $P_0 = 5.9$ for polyisoprene in 1,4-dioxane at 34.7 °C.[18] [b] $\Phi_0 = 2.55$ and 2.4 for polystyrene[22] and polyisoprene[20] in the same conditions. [c] $\Phi = 1.49–1.16$, decreasing with M.

Table VII
Summary of Experimental and Theoretical Results for Cyclic Polymers in Good Solvents

polymer	solvent (T, °C)	$M \times 10^{-4}$	α_s	α_f	α_η	q_s	q_f	q_η	$\beta \times 10^{-6}$	refs
polystyrene	toluene (22 ± 5)	1–2	0.565			0.55				24
polystyrene	toluene (25)	3–27			0.73		0.87	0.64[a]	2.20[a]	25, 26, 28
polystyrene	toluene (35)	1–44		0.55	0.67	0.52	0.85	0.56	1.92	3
polystyrene	THF (25)	1–18		0.52	0.72		0.90	0.72[a]	1.93	4, 27
polystyrene	THF (30)	0.4–27			0.68			0.66		25
theoretical	(simulation)		0.59	0.59	0.78	0.53	0.89	0.59	2.19	this work

[a] Average of values for several M's.

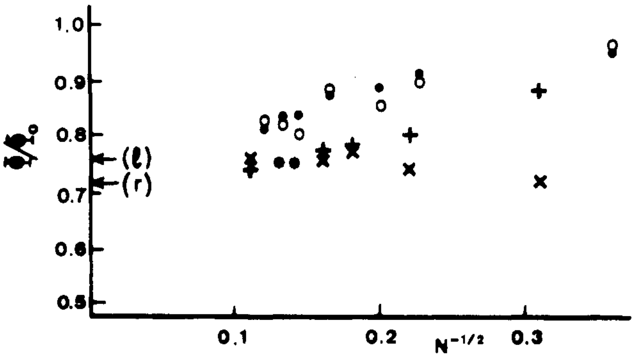

Figure 3. Ratios Φ/Φ_0 for the various N, for both linear and cyclic chains and both models: (●) cyclic, GB–LJ; (○) linear, GB–LJ; (+) cyclic, FJ; (×) linear, FJ. The arrows indicate the values obtained from the P's and Φ's listed in Table IV.

has been some controversy, summarized by Norisuye and Fujita[31] and attributed by Shimada and Yamakawa[32] to their incorrect calculation of α_η(l) of these authors. Our data support the thesis that $\alpha_\eta(\mathrm{r}) > \alpha_\eta(\mathrm{l})$.

Calculations based on renormalization-group theory have provided results that can be compared with our Monte Carlo data. In one of the first renormalization-group studies of excluded-volume effects on linear and cyclic chains, Prentis[33] obtained $q_s = 0.57$, while we obtain 0.53. More recently, Schaub et al.[34] have calculated $q_\eta = 0.56$ in the presence of both excluded-volume and hydrodynamic interaction. This is to be compared with our result, 0.59. The agreement between renormalization-group theory and Monte Carlo simulation is quite acceptable, mostly bearing in mind that the uncertainties in the latter are about ±0.03 and that the former has been carried out to the lowest order in ϵ.

From another point of view, there are significant differences in the excluded-volume effects on $\langle s^2 \rangle$, f, and $[\eta]$, which are reflected in the values of P and Φ. From our previous work[2,7] on linear chains (l) we take $P_0(\mathrm{l}) = 6.0$ and $\Phi_0(\mathrm{l}) = 2.5$, where the 10^{23} factor in Φ is omitted for the sake of brevity, and from the preceding paper, we take for rings $P_0(\mathrm{r}) = 7.2$ and $\Phi_0(\mathrm{r}) = 4.0$. Now, the results of this work are $P(\mathrm{l}) = 5.3$, $\Phi(\mathrm{l}) = 1.9$, $P(\mathrm{r}) = 6.5$, and $\Phi(\mathrm{r}) = 2.9$. Thus we obtain $P/P_0(\mathrm{l}) = 0.88$ and $\Phi/\Phi_0 = 0.76$, while for rings we calculate $P/P_0(\mathrm{r}) = 0.90$ and $\Phi/\Phi_0(\mathrm{r}) = 0.72$. The statistical error of these ratios can be estimated to be not less than 5%. Therefore, within this uncertainty the P/P_0 and Φ/Φ_0 ratios of linear and cyclic polymers are practically the same. Another dimensionless quantity is $\Phi P_0/\Phi_0 P$, as formulated in eq 15. We find 0.86 (l) and 0.80 (r). The statistical errors are larger in this combination, and we would not discard the possibility that this ratio were too the same for cyclic as for linear chains.

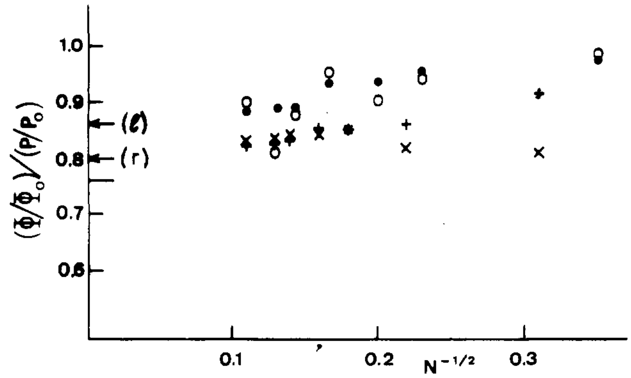

Figure 4. Same as in Figure 3 for the ratio $(\Phi/\Phi_0)/(P/P_0)$ proposed by Freed et al.[8]

There have been some discussions in the literature about the values of P/P_0 and Φ/Φ_0 of linear polymers. First, Wang et al.[35] obtained $P/P_0(\mathrm{l}) = 0.98$ and $\Phi/\Phi_0(\mathrm{l}) = 0.89$ from a renormalization-group calculation based on approximate, double-sum formulas for the hydrodynamic properties. Then, Rey et al.[3] presented a Monte Carlo calculation (GB–LJ model) including rigorously hydrodynamic interaction. If the N dependence of the ratios is neglected, averages close to the values of Wang et al. are obtained. However, as shown by our wider and more accurate set of data, there is a noticeable dependence on length, and the ratios must be obtained from extrapolation of the ratios or from extrapolated values of P and Φ. In this way, Rey et al.[3] obtained $P/P_0(\mathrm{l}) = 0.83$ or 0.85 and $\Phi/\Phi_0(\mathrm{l}) = 0.70$ or 0.76.

The N-dependent ratios Φ/Φ_0 for both linear and ring chains are displayed in Figure 3. For the P/P_0 ratios the situation is similar. Systematic curvature and/or numerical uncertainties prevent us from attempting extrapolations to $N \rightarrow \infty$ ($N^{-1/2} = 0$). However, Figure 3 shows clearly that (a) our results for the ratios obtained from the individual values of P and Φ are consistent with the length dependence of the ratios and (b) cyclic and ring chains have quite close values of the ratios that, on the average, we could estimate as $P/P_0 = 0.89$ and $\Phi/\Phi_0 = 0.74$. We hope that these estimates might be helpful in the analysis of experimental data.

Freed et al.[8] have recently questioned the universality of P/P_0 and Φ/Φ_0, due ot the finiteness of the hydrodynamic interaction strength. This is a problem that could be studied by using the methodology of this paper, varying the hydrodynamic interaction parameter, but this topic is out of the scope of our work. These authors propose that the ratio $\Phi P_0/\Phi_0 P$ is more nearly a universal function of excluded volume. Our N-dependent values for the two types of chains and models are displayed in Figure Although there is some model dependence, data for rings and linear chains are probably identical within simulation error. A value $\Phi P_0/\Phi_0 P = 0.84$ would represent well all the set of data, and considering that this quantity accumulates errors from many sources, it can be considered to be in good agreement with the values accepted by Freed et al.[8]

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