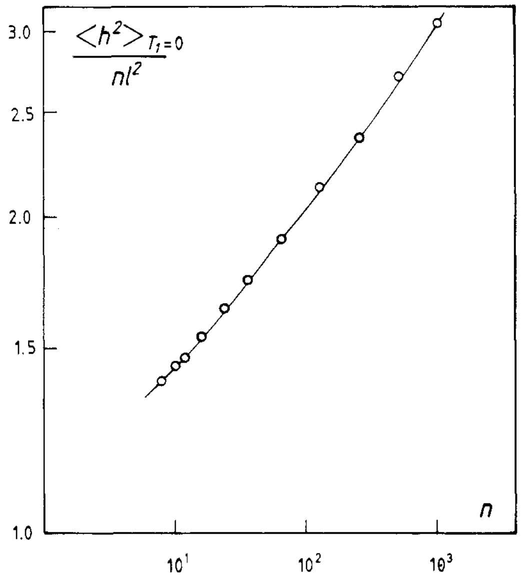

Figure 7. Double-logarithmic plot of $\langle h^2\rangle/(nl^2)$ vs. n if $T_1 = 0$.

end-to-end distance. This quantity was evaluated by Monte Carlo methods for some values of n and plotted against n in a double-logarithmic fit (Figure 7).

As can be seen, the ratio $\langle h^2\rangle/(nl^2)$ diverges, thus indicating that polymer chains at the state of vanishing binary interactions are not pseudoideal. The shape of the curve suggests that it may become linear for $n \rightarrow \infty$. If so, the asymptotic relation $\langle h^2\rangle \sim n^\gamma$ is obeyed. A rough estimation of the slope of the nearly linear part of the curve ($n > 150$) gives $\gamma = 1.17$. This value nearly equals the exponent obtained for hard-sphere chains (1.18).

Table III gives a brief summary of the characteristic data of chains on a simple cubic latice with repulsive and various attractive forces.

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Monte Carlo Calculations for Linear Chains and Star Polymers with Intramolecular Interactions. 3. Dimensions and Hydrodynamic Properties in Good Solvent Conditions

Antonio Rey and Juan J. Freire*

Departamento de Quimica Fisica, Facultad de Ciencias Quimicas, Universidad Complutense, 28040 Madrid, Spain

José Garcia de la Torre

Departamento de Quimica Fisica, Facultad de Ciencias Quimicas y Matemáticas, Universidad de Murcia, 30001 Murcia, Spain. Received June 30, 1986

ABSTRACT: The dimensions and reduced hydrodynamic properties of linear and several types of star polymers with differing numbers of units, N, have been calculated by averaging over samples of Monte Carlo simulated conformations, using a chain model that considers Gaussian distribution of distances between neighboring units and a Lennard-Jones (LJ) potential to describe the intramolecular interactions. The LJ parameters have been set so that they are able to reproduce the good solvent conditions. The hydrodynamic parameters P, Φ, and β have been calculated together with the ratios g, h, and g' of the properties of the star chains to those of linear chains with the same values of N. Extrapolation to high molecular weights has been performed, and the estimates have been analyzed and compared with previously reported theoretical and experimental results. Our values are extended to stars with many arms for which previous theoretical calculations are not available, and they can be considered to be in good agreement with the experimental data.

Introduction

The study of the dimensions and hydrodynamic properties of flexible polymers in solution has attracted much attention recently from both theoretical and experimental points of view. The influence of the solvent quality (and temperature) on the dimensions of linear chains has been investigated in the "good solvent region", in unperturbed or Θ conditions, and also in the case of systems with temperature below the Θ point.[1-3] The measurement and prediction of the hydrodynamic properties of linear flexible polymers in all these regions have been the goal of many studies,[1-7] while the basis of the theoretical treatment of these properties has been revised and improved.[8-10] Moreover, the recent synthesis of well-characterized samples of starlike polymers with a high number, $F > 6$, of uniform arms, by Roovers et al., has caused an increasing interest in the understanding of the properties of these particular molecules. Thus, these systems have been the object of many experimental[11-14] and theoretical[15,16] investigations, as well as detailed numerical calculations.[17-23]

In previous work we have performed theoretical calculations for the dimensions[24] and hydrodynamic properties[25]

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of a chain model for flexible polymers that includes intramolecular interactions through a Lennard-Jones (LJ) potential. The potential tries to mimic the balance between the real intramolecular interactions in the polymer and the polymer–solvent interactions, allowing us to study different temperature–solvent conditions. Our calculations are based in a Monte Carlo generation of conformations (which are considered as instantaneously rigid bodies for the evaluation of hydrodynamic properties[8]). We have already reported the variation of dimensions with temperature for linear chains and obtained results for dimensions and hydrodynamic properties of linear and star chains (with different values of F) with the LJ parameters that best reproduce the unperturbed conditions.

In this paper we report the results obtained in the good solvent limit and perform the corresponding analysis and comparison with other theoretical values and experimental data. In the light of the new results and the simultaneous comparison of theoretical and experimental values in good and unperturbed conditions, we include a general discussion of the influence of solvent conditions on the conformational properties of linear and star chains.

Methods and Results

Our chain model consists of $N + 1$ units (Gaussian subchains) placed so that the distance between neighboring units follows a Gaussian distribution. Nonneighboring units interact through the LJ potential. Therefore, the statistical weight corresponding to the total intramolecular interaction energy in a given generated conformation is given by

$$w = \exp\{-\sum_{i}^{N+1} \sum_{j}^{N+1} 4(\epsilon/k_BT)[(\sigma/r_{ij})^{12} - (\sigma/r_{ij})^6]\} \quad (1)$$

where the sum extends over all nonneighboring pairs of different units i and j. The reduced energetic parameter ϵ/k_BT is a function of temperature, while σ and r_{ij} are the LJ diameter and the distance between i and j (that we express in units relative to the statistical segment length, or mean distance between neighboring units, b).

The analysis of our results for the mean quadratic radius of gyration of linear chains suggests that a value of $\sigma/b = 0.8$ is adequate to reproduce a realistic expansion of the chains employing a number of units that can be reasonably handled in numerical computations.[24] With this value of σ/b fixed, we have obtained results for different choices of ϵ/k_BT and N. The fitting of the results for a given temperature to the scaling law

$$\langle S^2 \rangle \propto N^{2\nu} \quad (2)$$

has yielded the values $\nu = 0.6$ for $\epsilon/k_BT = 0.1$ and $\nu = 0.5$ for $\epsilon/k_BT = 0.3$ corresponding to the good solvent and the unperturbed conditions, respectively. The latter choice of ϵ/k_BT was employed in our previously reported calculations.[24,25] Here, we will analyze the results for $\epsilon/k_BT = 0.1$, which should be equivalent to those associated with chain models that reproduce the excluded volume effect (as the self-avoiding chains).

The hydrodynamic properties have been obtained through the method (first proposed by Zimm)[8] of averaging over the values calculated for rigid conformations. We treat these "rigid" structures through a version of the Kirkwood–Riseman theory that makes use of a nonpreaveraged tensor for the hydrodynamic interaction between friction elements and follows a numerical algorithm previously summarized.[26] The translational friction of each element (unit), ξ, is obtained from

$$h^* = \xi/[(12\pi^3)^{1/2}\eta_0 b] \quad (3)$$

where η_0 is the solvent viscosity, by using $h^* = 0.25$. This value is very near to the theoretical result for a Gaussian coil and has been used in our previous calculations with this model and also with Gaussian chains.[27]

Other details or references on the rationale of the model, the Monte Carlo method used for generating conformations (based on the application of the Metropolis criterion for accepting new conformations, changing a part of the chain by a step), and the validity of the rigid-body algorithm can be found in ref 24 and 25, together with the practical calculation of $\langle S^2 \rangle$ and the hydrodynamic properties (formulas employed, numerical considerations, etc.). It should be noted that we use eight samples, each one with a different seed number, to initiate the stochastic process. For the calculation of dimensions we generate 25000 conformations per sample. For hydrodynamic properties we generate 750–4000 conformations per sample and evaluate the properties of about 10% of these conformations.[25] The number of evaluations (which is about our limit of computational capability) is enough for these properties with distributions considerably narrower than those of the radius of gyration.[26]

The hydrodynamic properties are obtained in terms of the dimensionless coefficients

$$f_t^* = f_t/6\pi\eta_0 b \quad (4)$$

for translational friction, while for viscosity we use

$$[\eta]^* = [\eta]M/N_A b^3 \quad (5)$$

where M is the polymer molecular weight and N_A is Avogadro's number. In combination with $\langle S^2 \rangle$, we analyze also the parameters

$$P = f_t/6^{1/2}\eta_0\langle S^2 \rangle^{1/2} \quad (6)$$

$$\rho = \langle S^2 \rangle^{1/2}/(f_t/6\pi\eta_0) \quad (7)$$

$$\Phi = [\eta]M/6^{3/2}\langle S^2 \rangle^{3/2} \quad (8)$$

and when translation and viscosity are combined

$$\beta = (M[\eta]/100)^{1/3}\eta_0/f_t \quad (9)$$

Moreover, the results for stars are discussed in terms of the ratios

$$g = \langle S^2 \rangle_b/\langle S^2 \rangle_l \quad (10)$$

$$h = (f_t)_b/(f_t)_l \quad (11)$$

and

$$g' = [\eta]_b/[\eta]_l \quad (12)$$

where subscripts b and l represent a branched and a linear chain with the same molecular weight (or value of N).

In Table I we present our results obtained for $\langle S^2 \rangle$, f_t^*, and $[\eta]^*$ for chains of different types and number of units. (The values of $\langle S^2 \rangle$ for linear chains are graphically reported in ref 24.) We also show the values of the ratios g, h, and g'. From the combined results for dimensions and hydrodynamic properties we have evaluated the parameters P, Φ, ρ, and β, which we show in Table II. The values of these parameters corresponding to each given type of polymer and different choices of N have been introduced in linear regression analysis vs. $N^{-1/2}$ (taking into account numerical uncertainties) in order to predict the extrapolated behavior to high molecular weights. The extrapolated results are also included in Table II. The choice of this dependence is based in the $N^{-1/2}$ dependence that one should expect for P and Φ in the limit of high molecular weights according to the simpler verions of the Kirkwood–Riseman theory.[8] In the cases for which the

Table I
Monte Carlo Results for Different Properties of Linear and Star Chains with a LJ Intramolecular Potential ($\epsilon/k_BT = 0.1$; $\sigma/b = 0.8$)

F	$N+1$	$\langle S^2\rangle$	f_t^*	$[\eta]^*$	g	h	g'
2	19	4.98 ± 0.02	1.462 ± 0.003	42.6 ± 0.6			
2	25	6.83 ± 0.04	1.689 ± 0.04	71.9 ± 0.7			
2	37	10.9 ± 0.1	2.14 ± 0.01	140 ± 4			
2	49	15.4 ± 0.2	2.53 ± 0.02	230 ± 9			
2	55	17.7 ± 0.2	2.77 ± 0.03	305 ± 14			
6	19	2.54 ± 0.04	1.305 ± 0.002	25.6 ± 0.1	0.51 ± 0.01	0.915 ± 0.003	0.60 ± 0.01
6	37	5.22 ± 0.02	1.928 ± 0.009	82 ± 1	0.48 ± 0.03	0.901 ± 0.009	0.59 ± 0.02
6	49	7.06 ± 0.01	2.30 ± 0.02	138 ± 5	0.46 ± 0.05	0.91 ± 0.02	0.60 ± 0.05
12	25	2.26 ± 0.01	1.404 ± 0.006	29.2 ± 0.4	0.331 ± 0.003	0.831 ± 0.006	0.41 ± 0.01
12	37	3.31 ± 0.01	1.74 ± 0.01	55.5 ± 1	0.30 ± 0.02	0.813 ± 0.008	0.40 ± 0.02
12	49	4.39 ± 0.01	2.04 ± 0.01	89 ± 2	0.28 ± 0.03	0.81 ± 0.01	0.39 ± 0.02
18	19	1.57 ± 0.01	1.185 ± 0.002	17.0 ± 0.1	0.315 ± 0.002	0.831 ± 0.003	0.40 ± 0.01
18	37	2.64 ± 0.01	1.62 ± 0.01	43.6 ± 0.9	0.24 ± 0.01	0.757 ± 0.008	0.31 ± 0.02
18	55	3.84 ± 0.01	2.03 ± 0.02	85 ± 2	0.217 ± 0.003	0.73 ± 0.02	0.28 ± 0.02

Table II
Hydrodynamic Parameters Obtained from the Values Contained in Table I, Including Extrapolations to the High Molecular Weight Limit

F	$N+1$	P	$10^{-23}\Phi$	ρ	$10^{-6}\beta$	P_{EV}/P_Θ	Φ_{EV}/Φ_Θ
2	19	5.04 ± 0.02	1.57 ± 0.03	1.53 ± 0.01	2.31 ± 0.02	0.98	0.92
2	25	4.97 ± 0.03	1.65 ± 0.03	1.55 ± 0.01	2.38 ± 0.03	0.96	0.97
2	37	4.99 ± 0.05	1.59 ± 0.07	1.54 ± 0.01	2.34 ± 0.06	0.94	0.88
2	49	4.96 ± 0.07	1.56 ± 0.09	1.55 ± 0.02	2.34 ± 0.08	0.90	0.76
2	55	5.07 ± 0.08	1.7 ± 0.1	1.52 ± 0.03	2.35 ± 0.08	0.91	0.83
2	∞	5.01 ± 0.02[a]	1.61 ± 0.02[a]	1.54 ± 0.01[a]	2.33 ± 0.02[a]	0.85[b]	0.70[b]
2	∞	4.9 ± 0.1	1.75 ± 0.14	1.56 ± 0.03		0.83[b]	0.76[b]
6	19	6.30 ± 0.06	2.59 ± 0.07	1.22 ± 0.01	2.18 ± 0.04	0.97	0.95
6	37	6.49 ± 0.04	2.82 ± 0.05	1.19 ± 0.01	2.18 ± 0.03	0.97	0.93
6	49	6.66 ± 0.06	3.0 ± 0.1	1.16 ± 0.01	2.17 ± 0.05	0.96	0.92
6	∞	7.1 ± 0.2	3.5 ± 0.2	1.06 ± 0.03	2.18 ± 0.01[a]	0.96[b]	0.90[b]
12	25	7.19 ± 0.05	3.52 ± 0.07	1.07 ± 0.01	2.12 ± 0.03	1.00	0.99
12	37	7.36 ± 0.05	3.78 ± 0.09	1.05 ± 0.01	2.12 ± 0.03	0.98	0.94
12	49	7.49 ± 0.05	4.0 ± 0.1	1.03 ± 0.01	2.11 ± 0.03	0.99	1.01
12	∞	8.20 ± 0.06	5.1 ± 0.1	0.92 ± 0.01	2.12 ± 0.01[a]	0.95[b]	0.93[b]
18	19	7.28 ± 0.02	3.55 ± 0.03	1.06 ± 0.01	2.09 ± 0.01	1.00	0.99
18	37	7.68 ± 0.06	4.2 ± 0.1	1.00 ± 0.01	2.10 ± 0.03	0.98	0.97
18	55	7.97 ± 0.09	4.6 ± 0.1	0.97 ± 0.01	2.09 ± 0.04	0.99	0.96
18	∞	8.8 ± 0.1	5.9 ± 0.1	0.86 ± 0.01	2.09 ± 0.01[a]	0.97[b]	0.94[b]
rigid sphere		9.93	9.23	0.774	2.12		

[a] Estimation of the extrapolated value as an arithmetic mean (low correlation in the linear regression analysis). [b] Ratio from the corresponding extrapolated values. When not otherwise indicated, the extrapolated values correspond to a linear regression analysis vs. $N^{-1/2}$. See text.

statistical correlations of linear dependences are low, so that the parameters seem to oscillate without a clearly defined pattern, we estimate the extrapolated results as simple arithmetic means over the different values of N. These results are also shown in Table II together with their statistical deviations. This procedure is applied to β (which does not change much with varying chain lengths) and also to the other parameters in the case of linear chains (where we find higher uncertainties). In the latter case tentative extrapolations assuming the $N^{-1/2}$ dependence are also tried, and the results are included in Table II. Moreover, we have plotted in Figure 1 the values of P and Φ for different linear chains in order to give a better idea of the trends and uncertainties involved in these particular cases.

We have performed a similar regression analysis for the ratios g, h, and g' vs. N^{-1} in order to obtain the estimates in the long-chain limit. The extrapolated values for F = 6, 12, and 18 can be found in Table III, together with the results obtained for both unperturbed conditions[24,25] and the simpler Gaussian model[27] and values previously reported by other authors for lattice[19,23] and off-lattice[22] chain models that take into account intramolecular interactions. Experimental data measured in good and Θ solvents are also included. The influence of finite size effects on the performance of these extrapolations was analyzed in ref 24 and 25 for the unperturbed-state values. The differences inherent to the presently studied good solvent limit with respect to those effects will be discussed below.

Discussion

The results obtained for the parameters in the case of linear chains (Table II, F = 2) deserve some specific comments. First, it can be observed that the extrapolations of P, Φ, and ρ to the high molecular weight limit ($N^{-1/2}$ = 0) are more problematic than in the case of star polymers (β changes very little with varying N). In fact, the correlation coefficients of the numerical fittings to a straight line are consistently closer to unity as F increases, while the variation with N for linear chains is blurred by statistical oscillations, as shown graphically in Figure 1. This can be attributed to the narrowing of the distribution of intramolecular distances in highly branched chains due to the reduction in the number of available conformations. Thus, finite size effects and statistical uncertainties pre-

Table III
High Molecular Weight Extrapolations of Ratios g, h, and g' from our Results in Table I together with Other Theoretical and Experimental Results

		g			h			g'		
	ref	$F = 6$	$F = 12$	$F = 18$	$F = 6$	$F = 12$	$F = 18$	$F = 6$	$F = 12$	$F = 18$
$\epsilon/k_BT = 0.1$	a	0.44 ± 0.01	0.233 ± 0.005	0.168 ± 0.001	0.892 ± 0.009	0.785 ± 0.007	0.682 ± 0.001	0.584 ± 0.008	0.373 ± 0.005	0.2207 ± 0.0002
$\epsilon/k_BT = 0.3$	24, 25	0.49 ± 0.03	0.33 ± 0.02	0.212 ± 0.003	0.89 ± 0.02	0.82 ± 0.03	0.73 ± 0.02	0.59 ± 0.03	0.39 ± 0.06	0.28 ± 0.04
Gaussian chain	20, 27	0.444	0.236	0.160	0.86 ± 0.01	0.75 ± 0.01	0.66 ± 0.01	0.58 ± 0.02	0.38 ± 0.03	0.24 ± 0.03
lattice	17[b,c]	0.45								
(good solvent)	19[b]	0.44	0.24							
	23	0.43 ± 0.01								
Zimm (good solvent)	22	0.45 ± 0.02			0.887 ± 0.10			0.563 ± 0.020		
exptl[d]	12		0.24	0.20		0.70	0.68		0.35	0.26
(good solvent)	13		0.32[e]	0.19		0.73[e]	0.58			
	14			0.17			0.52			0.22
exptl[d]	11	0.46	0.33							
(Θ solvent)	12		0.28	0.23		0.81	0.76		0.41	0.35
	13		0.28[e]	0.23		0.75[e]	0.71			
	14									0.31
	29							0.63		
	30				0.89					
lattice	18	0.52	0.35							
(Θ solvent)	19[b]	0.50	0.31							

[a] Present work. [b] Estimates from graphic results. [c] From the results for $\Phi_{EV} = 0.2$ (see text). [d] Obtained with different polymers and molecular weights. [e] Data corresponding to the highest molecular weight.

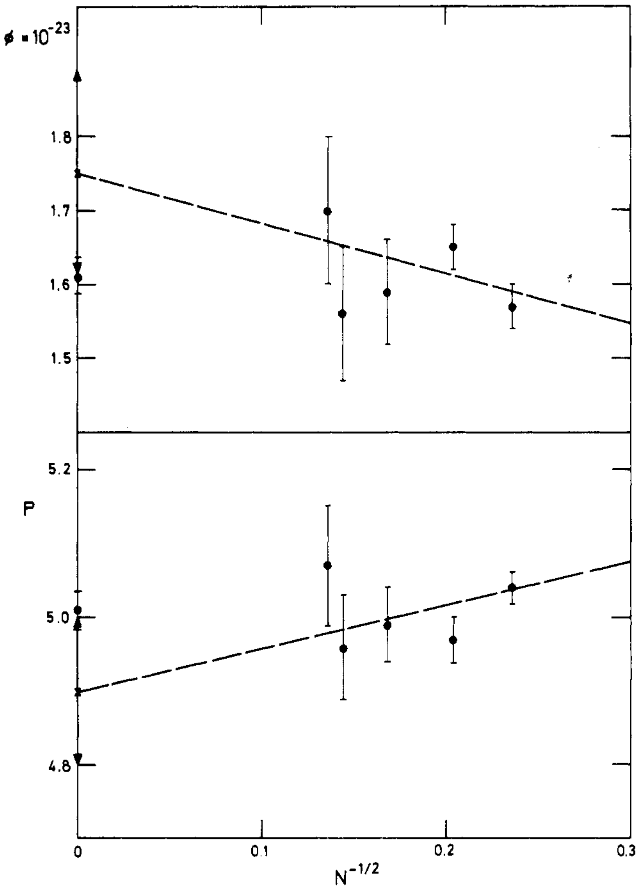

Figure 1. Results for P and Φ vs. $N^{-1/2}$ together with their long-chain estimations. Dots and error bars correspond to the results and their arithmetic means (the latter as long-chain limits). Crosses and arrows correspond to the extrapolated values and their uncertainties in linear regression fittings (---).

clude a very accurate estimation of these parameters for linear chains, since it is not easy to decide whether the linear regression vs. $N^{-1/2}$ or the arithmetic mean gives a better estimation of the long-chain limit (see Table II). At any rate, it should be emphasized that the direct and extrapolated results for the hydrodynamic parameters obtained in the excluded volume region are significantly smaller than those calculated in the unperturbed-state region.[25] Whether P and Φ should reach universal values for high molecular weight polymers in good solvents is still a controversial point.[2] A recent renormalization group study performed by Wang, Douglas, and Freed[7] indicates that the ratio between the values of P in the excluded volume (EV) and the unperturbed state (Θ) regions tends to $P_{EV}/P_{\Theta} = 0.98$, while it predicts that $\Phi_{EV}/\Phi_{\Theta} = 0.886$. Their results for Φ seem to agree with scattered but consistently disposed experimental data (see Figure 2 of ref 7), though these theoretical limits are based on hydrodynamic treatments that employ simplified double-sum formulas.[28] Our estimations yield smaller ratios with a more significant difference for P (we find $P_{EV}/P_{\Theta} = 0.94$ and $\Phi_{EV}/\Phi_{\Theta} = 0.87$ from the arithmetic mean of the ratios corresponding to different values of N for our LJ chains, while still smaller values are calculated from the ratio between extrapolated results; see Table II).

A reason for these discrepancies can be attributed to the fact that (as stated before) the values of N used in this work may only mimic the intermediate region of molecular weights with respect to the description of those parameters so that the extrapolated results should be considered (at least for linear chains) as tentative values. However, we believe that this is not the general case since better results for high molecular weights can be obtained for other properties less affected by these finite size effects. As to parameter β, we find that the extrapolated result is slightly higher than that obtained for Gaussian chains[27] or LJ chains[25] in the Θ region. The variation of this parameter with N and solvent conditions is, nevertheless, modest, and therefore we believe that our value can be confidently used to obtain molecular weights from combined diffusion and viscosity measurements of linear flexible polymers in a good solvent.

For the star chains, the parameters P and Φ shown in Table II increase with increasing F to be closer to the rigid-sphere limit. The ratios P_{EV}/P_{Θ} and Φ_{EV}/Φ_{Θ} increase slightly for higher numbers of arms, though they are in all cases within the range 0.9–1.0. We have tried to confirm these predictions from experimental data for g, h, and g' measured in Θ and good solvents[12–14] for $F = 12$ and 18 but, unfortunately, the different values available yield a more scattered range of these ratios, within the limits 0.9–1.1. β decreases as F increases, and for $F > 6$ it reaches the rigid-sphere value.

The analysis of the extrapolated ratios g, h, and g' contained in Table III can be performed in several different ways. First, it should be stated that, though a small additional contribution due to finite size effects may be included in the uncertainty ranges in some cases, the extrapolations seem to be more sound than those for the parameters P and Φ. It should also be considered that the results presented here are free of the ambiguities inherent to the values previously reported for the Θ region.[24,25] There, the extrapolations were aimed to suppress the dependence with N exhibited by the results for polymers composed of a small number of units while retaining the repulsion between units close to the center of the star polymer, whose influence is supposed to disappear only for very long (perhaps unrealistic) arms. The agreement between our extrapolations and the experimental data seems to confirm that, at least from the practical point of view of reproducing data for realistic polymer samples in their unperturbed state, the central core repulsions should persist even in the long-chain limit. In this respect, we should mention that the lattice simulations performed for considerably longer chains in the unperturbed state by Mazur and McCrackin[17,18] and Kolinski and Sikorski[19] confirm the presence of this core effect (see Table III). Of course, our present results in the good solvent limit describe long intramolecular steric effects in all the regions of the chain. Then the arms tend to be in expanded conformations, independent of their lengths and, consequently, the central core influence is extrapolated in a smoother way. Another interesting point is to verify the scaling law proposed by Daoud and Cotton,[15] $g \propto F^{-4/5}$. Our extrapolated results for $F = 6$, 12, and 18 yield $g \propto F^{-0.88\pm0.03}$ with a good correlation in the fitting and, consequently, they can be considered to be in reasonable agreement with the theoretical prediction.

The comparison between our values in the good and unperturbed[24,25] solvent conditions reveals that the ratios are consistently smaller for good solvents, and this trend increases for highly branched stars. The same conclusion can be reached by direct comparison of experimental data obtained in both solvent conditions[11–14,29,30] (Table III). Our results for $F = 6$ are in good agreement with those calculated by Zimm[21,22] by means of an algorithm similar to ours for the calculation of hydrodynamic properties, using a simple hard-sphere potential to describe the excluded volume effect and a symmetric arrangement of units to describe the central core repulsion. The Zimm results, however, do not show many differences with respect to values that he obtains when the excluded volume effect is removed (perhaps as a consequence of the uncertainties and the low number of arms investigated). Our values of g for $F = 6$ and 12 are also in good agreement with the good solvent limit results from the lattice calculations of Kolinski and Sikorski,[19] and the result for $F = 6$ is also similar to the value reported by Mazur and McCrackin[17] for their excluded volume parameter choice $\Phi_{\mathrm{EV}} = 0.2$ and to that recently reported by Whittington et al.[23] (also from lattice computations). An important feature, also discussed by Zimm[22] and Whittington et al.,[23] is the very small difference between the values of the ratios corresponding to a chain in the good solvent conditions and a Gaussian chain, i.e., a chain without intramolecular interactions or core effects. In our case this striking similarity extends to all of the types of chains and properties studied (g, h, and g', $F = 6$, 12, and 18). Therefore, the experimental decrease in the ratios observed on going from Θ to good solvent conditions should be mainly attributed to the effect of the nonhomogeneous expansion in the central part of the chain in the Θ state and may eventually vanish for very high (perhaps unrealistic) molecular weights. Although the significant finite size effects in our model constitute a difficulty in performing some of the extrapolations to the high molecular weight limit, our results point out that the model is able to mimic the core expansion in the unperturbed state and, moreover, reproduce the features exhibited by the experimental values in both solvent regions (within the sometimes wide interval of variations of the scattered data).

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