Brownian Dynamics of Nonlinear Gaussian Chains with Fluctuating Hydrodynamic Interactions. 1. Star Chains

Antonio Rey and Juan J. Freire*

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

Jose Garcia de la Torre

Departamento de Quimica Fisica, Facultad de Ciencias Quimicas y Matematicas, Universidad de Murcia, 30071 Murcia, Spain

ABSTRACT: A Brownian dynamics simulation has been employed to obtain transport and dynamic properties of Gaussian star chains with fluctuating hydrodynamic interactions. The results obtained for diffusion coefficient, relaxation times, and dynamic scattering function are compared with values calculated from the preaveraged Rouse–Zimm theory, finding relatively small differences between both sets of results, in agreement with previous work performed for linear chains. Simulation values for the intrinsic viscosity are, on the other hand, significantly lower than preaveraged theoretical predictions. This conclusion is fully confirmed by upper and lower bounds of this property computed by means of equilibrium Monte Carlo simulations.

1. Introduction

The study of polymers with nonlinear structures is not as much developed as that of linear chains. Although the existence of branching points in the chemical sequence of a macromolecule is a usual consequence of certain polymerization techniques, a systematic study of this kind of polymer has not been accomplished until recently, attributing the observed deviations from the physical behavior of linear chains to possible branched structures, without further explanation.[1]

A special class of branched polymers is constituted by the star polymers, in which F linear homopolymers are chemically attached to a seed or center unit. The diameter of this center is typically much smaller than the whole extension of the polymer. In recent years, star polymers have become a focus of interest, from both theoretical[2-7] and experimental[8-11] points of view. The theoretical investigations have been mainly focused on the calculation of their shape dimensions, not only in ideal Θ conditions but also in good solvent or excluded volume conditions. However, studies related with transport or dynamic properties are not so well represented, and they are usually based in a series of approximations, which very often include the preaveraging of hydrodynamic interactions (HI).[12]

These approximations can be avoided when computer simulations are employed. Thus, the application of the Zimm method[13] to Gaussian chains through a Monte Carlo simulation over supposedly rigid conformations, treated individually and avoiding the orientational preaverage of HI, yields bound values for the intrinsic viscosity and the translational diffusion coefficient. Some calculations employing this method have shown a significant difference between theoretical results (including the preaveraging approximation) and simulation values.[14,15]

For purely dynamic properties (relaxation times, dynamic scattering form factor) a dynamic type of simulation is required. Recently, a molecular dynamics simulation has been employed to study certain relaxation processes appearing in star chains.[16] However, this work is mainly concerned with the different scaling laws derived from the blob model,[6] neglecting hydrodynamic interactions.

In previous work,[17] we made use of a Brownian dynamics (BD) simulation algorithm[18] to obtain transport and dynamic properties of Gaussian linear chains. In those simulations we considered HI in a rigorous, i.e., fluctuating, form. Fixman has also employed similar (though considerably more specialized) algorithms for the study of linear chains.[19]

In this paper we present results obtained from Brownian dynamics trajectories for Gaussian star chains. This model is not fully suitable for these polymers, because it does not take into account the effects due to the presence of the star central core, whose influence can be important when the number of branches is high, even for considerably high molecular weight polymers. Since the introduction of these effects, however, complicates both the model and the simulation algorithm, they have been neglected in this paper, so that our interest is only aimed at the influence of topology (i.e., the arrangement of beads) on the different nonequilibrium properties. This influence had been previously investigated by employing simpler methods that disregard fluctuating hydrodynamic interactions or were reduced to the consideration of equilibrium and transport properties through Monte Carlo rigid-chain simulations. To the best of our knowledge, this is the first time that a rigorous treatment of HI is incorporated in a dynamic simulation procedure to obtain nonequilibrium properties of nonlinear flexible polymer chains.

2. Methods

The numerical procedures followed in this paper for the generation and analysis of trajectories are essentially the same that were employed in the study of linear chains.[17] They are based on the first-order algorithm originally proposed by Ermak and McCammon.[18]

We model the star polymer molecules as bead and spring chains composed of F equal branches (or arms), with m_b identical beads per arm. The total number of units composing the model is, therefore, $N = m_b F + 1$. The intramolecular spring and bead force exerted by the neighbors of bead j in a chain that obeys Gaussian statistics

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* To whom correspondence should be addressed.

is given by

$$\mathbf{F}_j = (3k_BT/b^2)\mathbf{AR} \tag{1}$$

where k_BT is the Boltzmann factor, b is the bead statistical length, $\mathbf{R}$ contains the position vectors of the different units, $\mathbf{r}_j$, and $\mathbf{A}$ is the Rouse connectivity matrix, whose form for a star was established by Zimm and Kilb.[12]

Configurational-dependent hydrodynamic interactions are introduced through a diffusion tensor $\mathbf{D}$, depending on the relative positions between pairs of bonds, $\mathbf{R}_{ij}$. The strength of these interactions is gauged by the parameter

$$h^* = (3/\pi)^{1/2}(\sigma/b) \tag{2}$$

where σ is the Stokes radius of the units. We use a Rotne-Prager-Yamakawa tensor, which takes into account the finite size of the units and the possibility of overlapping between them. For the parameter h^* we have set the value $h^* = 0.25$, convenient to describe the hydrodynamic behavior of Gaussian chains.[13]

For the initial conformation that constitutes the starting point for the iterative algorithm we employ a cubic lattice whose occupancy (face centers, vertices, or edge centers) depends on the number of arms of the model. This lattice ensures a symmetric initial arrangement of units in the central core. Of course, off-lattice positions are allowed in the consecutive steps that constitute the dynamic trajectory.

Both in this procedure and in the forthcoming analysis of the trajectories we employ scaled or reduced quantities based on the following units: ξ for friction coefficients, b for lengths and k_BT for energy. Therefore, $\xi b^2/(k_BT)$ is the basic unit for time and $N_A\xi b^2/(M\eta_0)$ for intrinsic viscosity. ($\xi = 6\pi\eta_0\sigma$ is the friction coefficient of one unit, η_0 being the solvent viscosity, N_A the Avogadro number, and M the polymer molecular weight.)

We have generated three different trajectories of 40 000 steps with $\Delta t^* = 0.01$ (the asterisk means reduced units) for each type of star, starting from different initial conformations. Our final results are presented in the different tables as arithmetic means and statistical errors (obtained from their standard deviations) of the averages computed over these three samples, treated as independent data.

3. Results and Discussion

3.1. Equilibrium Averages. As a test of the simulation algorithm, when applied to Gaussian star chains, we have first calculated the dimensions (radius of gyration of the star and end-to-end quadratic distance of the branches) and the static light scattering form factor from the generated trajectories. The theoretical expressions for these quantities usually found in the literature[20,21] correspond to the asymptotic limit $m_b \rightarrow \infty$ and yield poor results for our stars. However, more adequate expressions can be derived starting with the original definition of these properties

$$\langle s^2 \rangle = \frac{1}{N^2}\sum_i^N\sum_{j>i}^N \langle R_{ij}^2 \rangle \tag{3}$$

$$S(x) = \frac{1}{N^2}\sum_i\sum_j \exp\left(-\frac{q^2}{6}\langle R_{ij}^2 \rangle\right) \tag{4}$$

where q is the modulus of the scattering vector and $x = q^2\langle s^2 \rangle$. $\langle R_{ij}^2 \rangle$, the quadratic average distance between two units in the Gaussian star, is given by

$$\langle R_{ij}^2 \rangle = |i_b - j_b|b^2 \tag{5}$$

Table I
Theoretical and BD Simulation Results for the Dimensions of Gaussian Regular Stars (in Reduced Units)

F	m_b	$\langle R^2 \rangle^*_{\text{branch}}{}^a$	$\langle s^2 \rangle^*_{\text{BD}}$	$\langle s^2 \rangle^*_{\text{theor}}{}^b$	g
6	1	1.014 ± 0.004	0.739 ± 0.002	0.735	0.643
	2	2.01 ± 0.01	1.207 ± 0.006	1.207	0.560
	3	2.94 ± 0.02	1.61 ± 0.01	1.662	0.526
	4	4.01 ± 0.06	2.12 ± 0.04	2.112	0.508
8	1	1.013 ± 0.007	0.794 ± 0.006	0.790	0.533
	2	1.99 ± 0.02	1.26 ± 0.01	1.273	0.451
	3	2.97 ± 0.01	1.72 ± 0.02	1.741	0.419
12	1	1.014 ± 0.008	0.855 ± 0.008	0.852	0.396
	2	1.988 ± 0.003	1.335 ± 0.002	1.357	0.326
	3	2.95 ± 0.02	1.79 ± 0.01	1.823	0.296

^{a} The theoretical value equals m_b and is proportional to the molecular weight of each branch. ^{b} Computed from eq 7.

Table II
Theoretical and BD Simulation Results for the Static Scattering Form Factor $S(x)$ for Two Values of the Scattering Angle

		BD		theory^a	
	m_b	$x = 1$	$x = 5$	$x = 1$	$x = 5$
6	1	0.726 ± 0.001	0.285 ± 0.001	0.727	0.285
	2	0.727 ± 0.001	0.268 ± 0.001	0.726	0.267
	3	0.733 ± 0.002	0.272 ± 0.003	0.726	0.263
	4	0.727 ± 0.004	0.261 ± 0.006	0.726	0.263
8	1	0.724 ± 0.002	0.265 ± 0.002	0.724	0.264
	2	0.728 ± 0.002	0.257 ± 0.003	0.724	0.252
	3	0.729 ± 0.002	0.254 ± 0.001	0.725	0.251
12	1	0.722 ± 0.002	0.242 ± 0.003	0.722	0.241
	2	0.726 ± 0.001	0.241 ± 0.001	0.725	0.240
	3	0.733 ± 0.001	0.245 ± 0.001	0.723	0.239

^{a} Computed from eq 8.

for two beads at the same branch, and

$$\langle R_{ij}^2 \rangle = |i_b + j_b|b^2 \tag{6}$$

if the beads are in different branches (index numbers i and j run independently for each branch, from 1 at the attached end to m_b at the free end). Taking into account the number of terms with the same value of $\langle R_{ij}^2 \rangle$, we can easily evaluate the sums in eqs 3 and 4. We have arrived at

$$\langle s^2 \rangle = \frac{b^2}{N^2}\left\{ m_b F\left[1 + \frac{(m_b + 4)(m_b - 1)}{6}\right] + m_b^2\frac{m_b + 1}{2}F(F - 1)\right\} \tag{7}$$

for the radius of gyration and

$$S(x) = \frac{1}{N} + \frac{F}{N^2}\sum_{j=1}^{m_b}2(m_b - j + 1)\exp\left(-\frac{x}{6\langle s^2 \rangle}j\right) + \frac{F(F-1)}{N^2}\sum_{j=1}^{2m_b-1}\min(j, 2m_b - j)\exp\left[-\frac{x}{6\langle s^2 \rangle}(j + 1)\right] \tag{8}$$

for the static form factor. These results are reduced to those of a linear chain when $F = 1$ ($m_b = N - 1$) or $F = 2$ ($m_b = (N - 1)/2$) are considered and lead to the expressions usually employed in experimental work concerning high molecular weight linear or star polymers when $m_b \rightarrow \infty$.

The results obtained from these equations and the numerical averages calculated over the steps of the Brownian trajectories, together with their estimated errors, are shown in Tables I and II. It can be observed that our simulation results give an adequate reproduction of the theoretical predictions. This confirms the validity of our numerical procedures. In Table I we have also included

Table III
Diffusion Coefficient (in Reduced Units) Obtained from Brownian Trajectories (BD), Monte Carlo Simulations on Rigid Conformations (MC), Preaveraged Theoretical Expressions (PT), and Scattering Form Factor Analysis (LS)

| F | N | $D_t{}^*$ | | | | ρ^a |
		BD	MC	PT	LS($x = 1$)	
6	7	0.365 ± 0.008	0.3441 ± 0.0005	0.374	0.35 ± 0.01	1.22 ± 0.02
	13	0.274 ± 0.003	0.2537 ± 0.0002	0.283	0.25 ± 0.01	1.18 ± 0.02
	19	0.233 ± 0.004	0.2104 ± 0.0002	0.237	0.230 ± 0.008	1.15 ± 0.02
	25	0.201 ± 0.002	0.1836 ± 0.0001	0.209	0.194 ± 0.004	1.15 ± 0.02
	∞					1.07 ± 0.03
8	9	0.330 ± 0.003	0.3119 ± 0.0003	0.344	0.327 ± 0.007	1.15 ± 0.02
	17	0.249 ± 0.001	0.2309 ± 0.0001	0.261	0.246 ± 0.004	1.09 ± 0.01
	25	0.210 ± 0.004	0.1918 ± 0.0001	0.219	0.205 ± 0.003	1.07 ± 0.03
	∞					0.97 ± 0.04
12	13	0.2899 ± 0.0006	0.2751 ± 0.0002	0.310	0.281 ± 0.008	1.05 ± 0.01
	25	0.227 ± 0.004	0.2051 ± 0.0002	0.237	0.220 ± 0.009	1.03 ± 0.01
	37	0.203 ± 0.006	0.1708 ± 0.0001	0.199	0.143 ± 0.003	1.05 ± 0.03
	∞					1.041 ± 0.003[b]

^{a} Parameter obtained from BD trajectories. ^{b} Extrapolation obtained as arithmetic mean.

the theoretical estimations of g, the ratio corresponding to a star and a linear chain of the same molecular weight, $g = \langle s^2 \rangle_{\text{star}} / \langle s^2 \rangle_{\text{linear}}$. Obviously, the values included in the table tend to the well-known limit $g = (3F - 2)/F^2$, corresponding to infinite molecular weight.

3.2. Translational Diffusion Coefficient. There are two possibilities to obtain D_t from our Brownian trajectories. The first one, previously used by Fixman,[22] involves the calculation of a velocity correlation function and its integration over all possible values of time. This method is rather complicated but permits isolation of the contribution D_1 in $D_t = D_0 - D_1$ due to the presence of fluctuating HI (the term D_0 can be obtained exactly without making use of the preaveraging approximation). The second method, much simpler, requires the calculation of the quadratic displacement of the center of masses position vector. A fitting of this function against time yields directly the global value of D_t.

Since previous Monte Carlo simulations both for linear and for star Gaussian chains showed that the differences between diffusion coefficients computed with and without preaveraging are quite small,[15] we have calculated this magnitude through the second, simpler method, assuming that the detailed conclusions obtained through the more elaborate study of Fixman for linear chains are also applicable to the star chains. Our results for D_t are summarized, in reduced units, in Table III, together with Monte Carlo simulation results calculated with the Zimm method and also with preaveraged theoretical estimations. We can see that the dynamic simulation results lie between preaveraged and Monte Carlo data. This is an expected result, since these two sets of results must correspond to upper and lower bounds, respectively, for D_t.[23,24]

The comparison between our results and experimental data can be performed through the parameter ρ, defined as the ratio between the radius of gyration and the hydrodynamic radius, i.e.

$$\rho = \frac{6\pi\eta_0 D_t}{k_B T} \langle s^2 \rangle^{1/2} = \frac{D_t{}^*(\langle s^2 \rangle^*)^{1/2}}{\sigma/b} \quad (9)$$

The values for ρ that we have obtained from Brownian trajectories are also included in Table III, together with tentative extrapolations to $N \to \infty$. These extrapolated values can be directly compared with experimental data measured from well-characterized star polymers of high molecular weight. We have found in the literature[9,10] the data $\rho = 0.927$ for $F = 6$ and $\rho = 0.810$–0.895 for stars with $F = 12$ branches, smaller than our simulation values. The existing differences can be attributed to the simplicity of

the Gaussian model, which is unable to reproduce properly the compact central core in star chains, whose influence may be important even for relatively high molecular weights when the number of branches is not too small. A highly packed central core should significantly increase the radius of gyration, while its influence in the hydrodynamic radius should be considerably smaller. Monte Carlo simulations based on the Zimm method were obtained in previous work also for star chains with intramolecular interactions represented by means of a Lennard-Jones potential between nonneighbor units.[25] These calculations can mimic the effect of the central core for highly armed stars of relatively high molecular weight and, in fact, yield values for ρ in good agreement with the experimental data. Since we can show now that differences between the rigorous simulation results and their lower bounds represented by the Zimm type calculations are always small for Gaussian chains, the validity of the results obtained with the intramolecular potential is validated from the theoretical point of view.

3.3. Internal Modes. Relaxation times, τ_k', which describe in an approximate way the internal normal modes $k = 1, ..., N - 1$ of star chains, can be calculated very easily, in the scheme of preaveraged Rouse–Zimm theory, from the eigenvalues of the matrix product **HA**. **A** is the Rouse matrix mentioned above and **H** is the preaveraged HI matrix. In our case, **H** is defined from the preaveraged Rotne–Prager–Yamakawa tensor and, therefore, is calculated as[19]

$$H_{ii} = 1 \quad (10a)$$

$$H_{ij} = \text{erf}(y) - \frac{1 - e^{-y^2}}{\pi^{1/2} y} \quad (10b)$$

with

$$y = \frac{\pi}{3^{1/2}} bh^* \langle R_{ij}{}^{-1} \rangle \quad (11)$$

$\langle R_{ij}{}^{-1} \rangle$ is the mean reciprocal distance between units i and j. For chains that obey Gaussian statistics it can be obtained as

$$\langle R_{ij}{}^{-1} \rangle = (6/\pi)^{1/2} \langle R_{ij}{}^2 \rangle^{-1/2} \quad (12)$$

and the quadratic averages are $\langle R_{ij}{}^2 \rangle = \mu_{ij} b^2$, where μ_{ij} is the number of springs connecting units i and j along the chain contour (eqs 5 and 6).

The corresponding eigenvectors of **HA** represent the normal coordinates of the chains. Normal coordinates depend very weakly on HI and, consequently, the eigen-

Table IV
Normal Mode Relaxation Times (in Reduced Units) for Gaussian Stars[a]

F	N	$(\tau_1')^{*b}$			$(\tau_2')^{*c}$	
		BD	PT	LS($x = 1$)	BD	PT
6	7	0.439 ± 0.004	0.440	0.43 ± 0.06	0.074 ± 0.001	0.0789
	13	0.98 ± 0.02	0.944	0.90 ± 0.04	0.240 ± 0.001	0.242
	19	1.64 ± 0.04	1.574	1.6 ± 0.3	0.405 ± 0.007	0.384
	25	2.43 ± 0.04	2.305	2.15 ± 0.04	0.618 ± 0.007	0.582
8	9	0.445 ± 0.006	0.440	0.45 ± 0.04	0.058 ± 0.001	0.0619
	17	0.97 ± 0.01	0.944	0.8 ± 0.2	0.238 ± 0.008	0.232
	25	1.64 ± 0.02	1.574	1.7 ± 0.1	0.402 ± 0.004	0.378
12	13	0.467 ± 0.006	0.440	0.49 ± 0.09	0.038 ± 0.001	0.0433
	25	0.963 ± 0.009	0.944	1.0 ± 0.3	0.241 ± 0.002	0.220
	37	1.72 ± 0.03	1.574	1.6 ± 0.5	0.395 ± 0.001	0.348

[a] BD, computed from the dynamic trajectories; PT, preaveraged theoretical estimations from the Rouse–Zimm eigenvalues; LS, scattering form factor analysis. [b] ($F - 1$)-fold degenerate values. [c] No degenerate values.

vectors of **HA** constitute a valid description for them, even when fluctuating HI are considered.

The correlation function of these normal coordinates computed over the Brownian trajectories yields, therefore, appropriate relaxation times for the normal modes. These relaxation times have been computed following a numerical procedure similar to that previously employed with linear chains;[17] that is, we have performed a least-squares fitting of the normalized correlation function to a straight line over the range of times where a linear dependence is found (in a first- and second-derivative numerical analysis) and obtained estimations of $(-1/\tau_k')$ from the slope values. (In the study of linear chains, however, we obtained the relaxation times for the Rouse normal coordinates—i.e., the eigenvalues of **A**—while preaveraged values were calculated from eigenvalues of **HA**, calculated from a matrix **H** defined from the Oseen tensor. Nevertheless, these differences in definitions should cause only marginal differences in the final results of properties.)

The results for the theoretical values (i.e., the eigenvalues of **HA**) and the simulation relaxation times are contained in Table IV. It can be observed that, although both sets of results are quite similar to each other, the relaxation times obtained with fluctuating HI are slightly but systematically greater than their theoretical estimations for the longest chains. This conclusion was also found in the case of linear chains.[17] Moreover, the first relaxation time and, in general, the relaxation times with odd index k are ($F - 1$)-fold degenerate and depend on m_b, but not on F, as previously predicted by the preaveraged theory. This fact, together with the important quantitative difference existing between the values of τ_1' and τ_2' in all the cases under study, makes the longest relaxation time always much more relevant than the remaining τ_k' in the description of the low-frequency dynamic properties of star polymers.

3.4. Dynamic Scattering Form Factor. The analysis of trajectories necessary to calculate the dynamic scattering form factor $S(\mathbf{q},t)$ of Gaussian stars is completely identical with that carried out for linear chains. We have obtained the time correlation function of $e^{-i\mathbf{q}\cdot\mathbf{r}_i(t)}$, where $\mathbf{q}$ is the scattering vector and $\mathbf{r}_i(t)$ is the position vector of unit i, obtained in the trajectory for time t (see eq 14 in ref 17). With respect to theoretical predictions, the preaveraged formula given by Pecora[26]

$$S(q,t) = \frac{1}{N^2}\sum_{i=1}^{N}\sum_{j=1}^{N}\exp\left[-\frac{1}{6}q^2\sum_{k=1}^{N}b^2\mu_k^{-1}(Q_{ik}^2 + Q_{jk}^2 - 2Q_{ik}Q_{jk}e^{-t/\tau_k})\right] \quad (13)$$

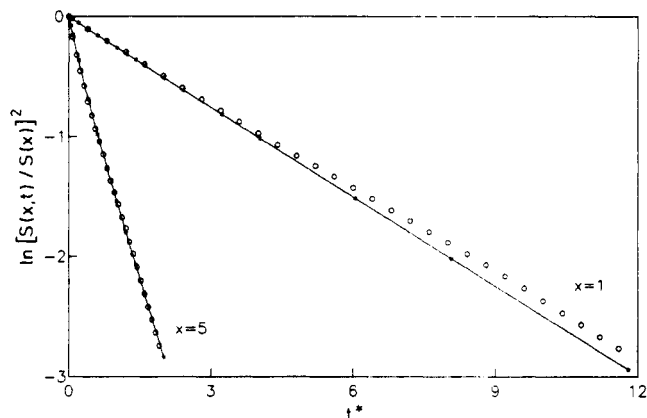where μ_k is the kth eigenvalue of matrix **A** and Q_{ij} is an

Figure 1. ln $[S(x,t)/S(x)]^2$ versus t for a star chain of $F = 8$ and $N = 25$ with fluctuating HI: (O) Results obtained from the trajectories; (—) theoretical estimations from eq 13.
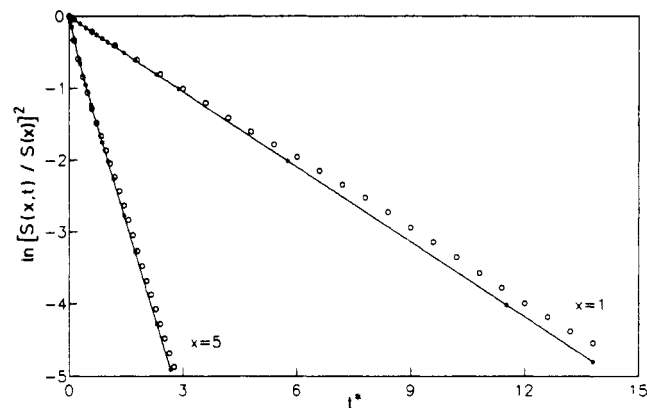

Figure 2. As Figure 1 but with $F = 12$ and $N = 25$.

element of the transform matrix whose columns contain the eigenvectors of **HA**, is of general validity and does not depend on the topology of the Gaussian chain.

A direct comparison between the preaveraged theoretical values and the simulation results (obtained with fluctuating HI) for $S(\mathbf{q},t)$ is shown in Figures 1 and 2. It can be noticed that there is a good agreement between both types of results. The small differences existing for $x = 1$ (the preaveraged results seem to show a systematic downward deviation) are even less pronounced than those observed for linear chains.[17] This fact confirms the validity of the Pecora procedure in the calculation of $S(\mathbf{q},t)$ for different structures, in spite of the preaveraging approximation contained in his method.

This conclusion is also supported by a fitting analysis of the form factor, from which the translational diffusion coefficient and the first relaxation time can be extracted

Table V
Simulation to Preaveraged Theory Ratio, $[\eta]^{sim}/[\eta]^{PT}$, for Gaussian Star Chains

F	N	BD	LB	UB
6	7	0.773 ± 0.009	0.791 ± 0.005	0.821 ± 0.005
	13	0.779 ± 0.007	0.749 ± 0.007	0.784 ± 0.002
	19	0.68 ± 0.02	0.718 ± 0.002	0.768 ± 0.002
	25	0.708 ± 0.005	0.697 ± 0.001	0.760 ± 0.002
8	9	0.75 ± 0.03	0.745 ± 0.006	0.779 ± 0.003
	17	0.702 ± 0.002	0.688 ± 0.005	0.735 ± 0.002
	25	0.681 ± 0.001	0.659 ± 0.003	0.719 ± 0.003
12	13	0.676 ± 0.008	0.672 ± 0.008	0.708 ± 0.002
	25	0.62 ± 0.01	0.599 ± 0.002	0.659 ± 0.002
	37	0.541 ± 0.006	0.565 ± 0.003	0.641 ± 0.002

a BD, simulation results computed from BD trajectories; LB, lower bounds obtained from MC simulations based on the variational method proposed by Fixman; UB, upper bounds obtained from MC simulations on rigid conformations.

when the scattering angle is small enough. According to Pecora, $S(\mathbf{q},t)$ can be expanded as

$$S(q,t) = S_0(x) \exp(-q^2 D_t t) + S_2(x) \exp[-(q^2 D_t + 2/\tau_1')t] + \ldots \quad (14)$$

The results for D_t and τ_1' obtained this way (from values for $S(x,t)$ with $x = 1$ computed from our trajectories) have been collected in Tables III and IV. Considering the uncertainty ranges (the numerical noise present in $S(x,t)$ makes the nonlinear fitting procedure difficult), a good agreement is found between these results and those directly computed from the study of correlation functions of the normal modes obtained from our trajectories, described above in the section on the analysis of internal modes.

3.5. Intrinsic Viscosity. The effects of preaveraged HI are very remarkable when this approximation is applied to the calculation of the intrinsic viscosity of star chains. In previous works, we have checked the approximate preaveraged results with Monte Carlo simulations on rigid conformations.[15,25] It was observed that the theoretical results are considerably higher than the simulation ones, even though these latter results represent upper limits for $[\eta]$.[24] This misfunction of the preaveraged theory is confirmed when introducing experimental data through the parameter

$$\Phi = \frac{[\eta]M}{6^{3/2}\langle S^2 \rangle^{3/2}} \quad (15)$$

Some experimental data taken from the literature[9,10] give $\Phi = 5.2 \times 10^{23}$ for $F = 6$ and $\Phi = 7.1 \times 10^{23}$ for $F = 12$, corresponding to unperturbed high molecular weight star chains. From Monte Carlo simulations we obtained extrapolations of this parameter to $N \rightarrow \infty$ of $\Phi = (4.9 \pm 0.2) \times 10^{23}$ for $F = 6$ and $\Phi = (7.6 \pm 0.8) \times 10^{23}$ for $F = 12$, both for the Gaussian model.[15] Nevertheless, the preaveraged theory yields the extrapolations[27] $\Phi = 6.65 \times 10^{23}$ for $F = 6$ and $\Phi = 12.7 \times 10^{23}$ for $F = 12$.

The calculation of intrinsic viscosity from our Brownian trajectories requires a complex numerical procedure, which includes the integration of a stress correlation function.[28] To avoid the problems implicit in this integration,[29] we have followed a method recently proposed by Fixman[19,22] based on the calculation of the ratio between stress correlation functions computed with fluctuating and preaveraged HI (an analytical expression for the latter function is formulated in terms of the eigenvalues of **HA**). The details of the procedure that we have followed are given elsewhere.[30] In Table V we collect the ratios between intrinsic viscosities calculated from simulation (MC and BD) and the theoretical preaveraged results. In the fourth

column of this table are also included the values that we have obtained by employing an alternative MC simulation. This simulation has been performed[31] through a variational method proposed by Fixman[24] that provides lower bounds for $[\eta]$. It is interesting to notice the trend followed by the results in the table. The greater is the number of units per arm, the lower is the ratio $[\eta]^{sim}/[\eta]^{PT}$, showing that the preaveraging approximation supplies rather poor estimations for the intrinsic viscosity in star chains with a not very small number of units.

One can also observe in Table V how the results obtained from the upper and lower bound MC simulations bracket a quite narrow range (the difference between them is ca. 5–10% of the dynamic simulation results) for the intrinsic viscosity. Taking into account that the computer time required for these simulations is considerably lower than that consumed by BD simulations, the bound calculations provide a much simpler method to obtain estimations of $[\eta]$ of much better accuracy than those provided by preaveraged theory. This accuracy seems to be especially remarkable for the lower bounds obtained with Fixman's variational method, very close in most cases to the results calculated from Brownian trajectories (we even have cases in which these latter results are smaller than the lower bound values, because of the higher uncertainties inherent in the cumbersome dynamic simulations).

Finally, we point out the very different way in which fluctuating HI affects the stress correlation function, the internal mode correlation function, and the dynamic scattering form factor (which can be also considered as a time correlation function). The small differences (see Table IV) existing between relaxation times with fluctuating and preaveraged HI, which reflect quite reduced differences in the corresponding internal mode relaxation functions, produce small discrepancies in the dynamic scattering factor, which depends on these times in a sophisticated way (according to the preaveraged theory, eq 14). This is not the case, however, with the stress correlation function involved in the calculation of intrinsic viscosity. This function is very easily described from the relaxation times when preaveraging is employed, but fluctuating HI modifies deeply the theoretical dependence,[30] actually yielding strong disagreements between theory and real results for $[\eta]$. In fact, the preaveraged intrinsic viscosity can be obtained as[20]

$$[\eta] = \frac{RT}{M\eta_0} \sum_{j=1}^{N-1} \tau_j'/2 \quad (16)$$

but this formula is unable to provide the actual results for fluctuating HI, even if the relaxation times obtained from correlation functions of the normal modes (i.e., the dynamic simulation results contained in Table IV) are introduced.

References and Notes

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Brownian Dynamics of Nonlinear Gaussian Chains with Fluctuating Hydrodynamic Interactions. 2. Rings

Antonio Rey and Juan J. Freire*

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

Jose Garcia de la Torre

Departamento de Quimica Fisica, Facultad de Ciencias Quimicas y Matematicas, Universidad de Murcia, 30071 Murcia, Spain

ABSTRACT: Static, dynamic, and transport properties of Gaussian ring polymers are computed by means of Brownian dynamic simulation with fluctuating hydrodynamic interactions. The comparison of these results with values provided by preaveraged Rouse–Zimm theory leads to a variety of conclusions for the different properties investigated. A certain controversy is raised when ratios q_D and q_η of the properties of cyclic to linear polymers with the same molecular weight are considered. Although experimental data seem to confirm the validity of preaveraged theory, our simulations, together with Monte Carlo calculations that provide upper and lower bounds for transport properties, show a different behavior, reinforced by the values obtained for the Flory parameter Φ and their simultaneous comparison with the data.

1. Introduction

The study of cyclic polymers has an important role in the field of theoretical developments related to macromolecular behavior. Translational symmetry and the lack of end groups in ring chains yield important simplifications in some treatments, making problems easier to treat than in linear chains. Nevertheless, the deficiencies present in old experimental techniques of synthesis and characterization for these rings suppressed in part the practical interest of the theoretical approaches, which could even be considered just as mathematical exercises of scarce application.

Recently, this situation has considerably changed. The improvement of experimental techniques allows nowadays both synthesis and accurate characterization of different classes of ring polymers.[1] This fact makes necessary a further theoretical development to try to explain the reactions that yield to the creation of cyclic structures and the equilibrium and dynamic behavior of ring polymers, both with well-differentiated characteristics when compared with those corresponding to linear chains with the same molecular weight.

Most of the analytical expressions derived for the calculation of dynamic and transport properties of flexible cyclic chains are based on the Rouse–Zimm bead–spring model, which includes an equilibrium preaveraging of hydrodynamic interactions.[2] Even later developments suitable for more general models[3] and refinements over the Gaussian chain model[4] have maintained this approximation. From these theories, the calculation of the translational diffusion coefficient and the intrinsic viscosity of rings is relatively simple.

To check the validity of theory through comparison with experimental data, two adimensional parameters are often introduced:

$$q_D = (D_t)_{\text{ring}}/(D_t)_{\text{linear}} \tag{1}$$

$$q_\eta = [\eta]_{\text{ring}}/[\eta]_{\text{linear}} \tag{2}$$

* To whom correspondence should be addressed.