Numerical Simulation of the Cyclization Dynamics for Flexible Chains with Excluded Volume

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ABSTRACT: Rate constants for the cyclization dynamics of flexible chains with excluded volume interactions have been evaluated through the analysis of Brownian dynamics trajectories. The results have been obtained through the calculation of the time-correlation function of the end-to-end vector and the subsequent application of the Wilemski and Fixman theory and, in an alternative way, from the exponents of single-exponential fits for the cyclization probability, which is directly evaluated from the trajectories. Differences between the numerical values obtained with these two different methods and with results obtained for unperturbed chains are analyzed. Existing theoretical predictions and experimental data are also considered and found in fair agreement with the simulation values. The most consistent description of experimental data in both θ and good solvent conditions corresponds to calculations where the standard theoretical approximations are eliminated.

Introduction

In previous work[1] (paper 1) we reported numerical results for the kinetics of diffusion-controlled cyclization processes, obtained from Brownian dynamics (BD) trajectories[2] of Gaussian (or bead and spring) linear chains. Rate constants were obtained by assuming a single-exponential behavior for $\Phi(\tau)$, the probability that two terminal groups remain active, i.e., do not react in the time interval τ. $\Phi(\tau)$ could be calculated as an average over the BD trajectories of the number of conformations for which the ends are at a distance higher than a given capture radius, R_0, at time t and have not yet approached at time $t + \tau$. In order to obtain these averages, we use an array variable containing counters for time intervals $\tau = 0, \Delta t, 2\Delta t, \ldots$, where Δt is the time-step interval used in the simulation, and once a given long trajectory has been generated, we check every trajectory step to know whether it corresponds to an open conformation. If this condition is met at a given time step t_o, we increase in one unit the counters from $\tau = 0$ to $\tau = t_o - t_c - 1$, where t_c denotes the last step before t_o where a closed conformation was found. $\Phi(\tau)$ is evaluated for the trajectory as the final values of all these counters, normalized to the value for $\tau = 0$.

The results were compared with calculations carried out by Perico and Cuniberti through the Wilemski and Fixman (WF) theory[4] applied to a bead and spring model.[5] Besides the Gaussian statistics for the equilibrium distribution of distances between units, implicit in the bead and spring model, this theory contains two important approximations: (a) Hydrodynamic interactions (HI) between the chain units are considered in their preaveraged form[6] (as in the standard Rouse–Zimm theory for the dynamics of dilute polymers[7]). (b) A sink operator is introduced so that the distribution function is spacially distorted as the time grows, and a specific form for this distortion is assumed (sink closure approximation). Our BD results in paper 1 pointed out significant discrepancies with the Perico and Cuniberti theoretical values, which increased dramatically when the ratio of capture radius to the statistical unit length, b, decreased, i.e., for stiffer chains. The origin of this disagreement is not clear since, in addition to the WF approximations, we should consider some necessary aspects of our simulations that somehow differ from the WF basic assumptions. Thus, the statistical ensemble of starting times in our simulations is composed only of the open chains, and we consider reversible cyclization processes. Moreover, our definition of cycled conformations is consistent with a Heaviside sink function, while WF theory (and Perico and Cuniberti) introduced a more complicated form for the sake of computational convenience.

In the present work, we investigate the cyclization process with BD trajectories generated for a model in which long-range interactions are added between nonneighboring units of the basic bead and spring chain to take into account excluded volume effects. These trajectories have been previously employed to check the model and calculate equilibrium[8] and dynamic properties.[9] In this case, we are not aware of previous quantitative results based on the WF theory, whose calculation implies knowledge of the time-correlation function of the end-to-end vector

$$\rho(\tau) = \langle \mathbf{R}(t)\cdot\mathbf{R}(t+\tau)\rangle / \langle R^2\rangle \qquad (1)$$

which cannot be exactly evaluated for excluded volume chains. (A qualitative discussion of excluded volume effects in k_1 was, however, included in the WF derivations.[5] More recently, scaling laws, based on the renormalization group theory, have been predicted[10] for the rate constant.) Therefore, a first step in the calculations consisted of obtaining $\rho(\tau)$ from our trajectories. Then we applied the WF method to evaluate the rate constants. As an alternative procedure, we have also obtained the rate constants from a direct evaluation of $\Phi(\tau)$ from our trajectories similar to that employed in paper 1. We have been able to analyze the influence of excluded volume effects according to these two different numerical methods and also make a comparison between our numerical values and theoretical predictions or existing data from photochemical experiments for flexible polymers in θ and good solvents.[11-16]

Methods

The chain model used in this work has been previously detailed.[8] Essentially, we consider a bead and spring model whose root-mean-square distance between neighboring units is b in the absence of long-range interactions and add an intramolecular potential between nonneighboring units to mimic excluded volume effects. This potential has a relatively soft form of the type $A_p e^{-\beta R_{ij}}$, with a cutoff at distance r_c, since harder potentials generate strong forces for overlapping situations that can distort the polymer dynamics unless one reduces drastically the size of

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the simulation time step. However, the trajectories obtained with this model and the same time step employed for unperturbed chains have been able to yield satisfactory results. Thus, the results for equilibrium properties and diffusion coefficients (calculated with preaveraged HI) are in good agreement with Monte Carlo evaluations for the alternative model in which the excluded volume is characterized by a hard-spheres potential of radius $0.56b$[8] for the following set of potential parameters, which is also used through this work: $A_p = 75.0$, $\beta = 4$, and $r_c = 0.512$, in reduced units, which will be described below.

The generation of trajectories was performed by means of an Ermak and McCammon algorithm, also described in earlier work.[2] For a given step characterized by a value of time, t, the coordinates of all the different chain units are calculated. This calculation requires obtaining the intramolecular forces defined by the model and the chain diffusion tensor (describing the fluctuating HI) which, in our first-order algorithm, depend on the relative positions between units at the end of the preceding step. We have also performed some calculations in which the HI are described in a preaveraged form[6] so that the diffusion tensor is constant along the trajectory, only depending on equilibrium averages of distances between the different units. In any case, the HI are gauged by parameter $h^* = (\pi/3)^{1/2}(\sigma/b)$, which is fixed at 0.25 in all our calculations. σ is the frictional radius of the unit. Once the unit coordinates are known in a given time step, we are able to evaluate the different properties of interest that are later averaged over the whole trajectory. In the present work, we need the averages for functions $\rho(\tau)$ and $\Phi(\tau)$, together with the values of $\langle R^2 \rangle$ previously reported for our model.[8] Typically, we generate trajectories composed of 40 000 steps. The final results for the properties are reported as means and statistical errors obtained with the sample formed by the values calculated in the different trajectories. All the results, when denoted by an asterisk, are given in reduced units with respect to the following basic values: k_BT, the Boltzmann factor, for energy, b for length, and ξ, the friction coefficient of a unit, for other frictional properties. The reduced rate constants can be converted to real units in inverse time through the relationship

$$k_1 = k_1^* k_B/[(12\pi^3)^{1/2}(\eta_0/T)h^* b^3] \quad (2)$$

where η_0 is the solvent viscosity. The time-step interval is set to our standard value $\Delta t^* = 0.01$.

The calculation of rate constants based on the WF method is accomplished by solving the integral equation[3,5,17]

$$k_1 = [\int_0^\infty (k(\tau)/k_\infty - 1) \exp(k_1\tau)\, d\tau]^{-1} \quad (3)$$

where

$$k(\tau) = \mathrm{erf}\,[z(\tau)] - (2/\pi^{1/2})z(\tau) \exp[-z^2(\tau)] \quad (4)$$

$$z(\tau) = \gamma_R[1 - \rho^2(\tau)]^{-1/2} \quad (5)$$

and

$$\gamma_R = (3/2)^{1/2}R_0/\langle R^2 \rangle^{1/2} \quad (6)$$

(k_∞ is $k(\tau)$ for $\tau \to \infty$).

WF developed this scheme for the bead and spring model (for which $\langle R^2 \rangle = (N-1)b^2$). However, using the boson representation for the position vectors of the units, they showed the validity of this procedure for chains with excluded volume effects.[4] In fact, they presented[5] a brief discussion of the excluded volume effect on k_1, based on qualitative arguments on the form of $\rho(\tau)$. In the present case, the numerical results for $\rho(\tau)$ obtained from the trajectories (together with the corresponding values of $\langle R^2 \rangle$) permit a numerical calculation of k_1. Thus, eq 3 is solved by following an iterative process similar to that described by Perico and Cuniberti,[3] starting with an initial rough estimation for k_1. The integral contained on the right-hand side of eq 3 is evaluated through a Gaussian quadrature.[18] We fix the upper limit so that a null value should be obtained for the last integration interval. ($\tau^* = 90$ is sufficient to this purpose in all the useful cases). Typically, a good convergence is found after a few iterations.

The accuracy of the results for $\rho(\tau)$ obtained from the trajectories can be checked in the case of unperturbed chains with preaveraged HI, since they can also be calculated from the following formula:[3,17]

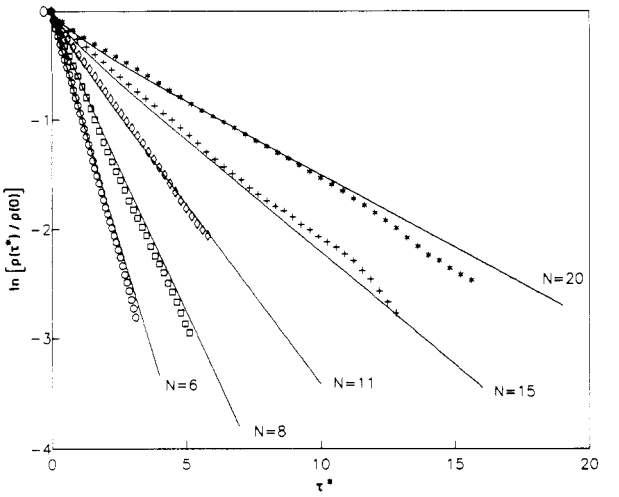

Figure 1. Time-correlation function of the end-to-end vector vs time (in reduced units) for unperturbed chains of varying lengths and preaveraged HI. The different points correspond to our BD results and the solid lines are obtained from eq 7.

$$\rho(\tau) = [1/(N-1)]\sum_{j=1}^{N-1}(Q_{Nj} - Q_{1j})^2/\lambda_j^F \exp[-(3k_BT/\xi b^2)\lambda_j\tau] \quad (7)$$

where Q_{ij} is component i of eigenvector j from the Rouse–Zimm hydrodynamic equation, while λ_j^F and λ_j are the corresponding eigenvalues in the absence or presence of HI. These quantities can be computed through standard numerical diagonalization techniques for given values of N and h^*. The results from eq 7 are compared with our BD values in Figure 1. The agreement between both sets of curves is satisfactory except for very long times (where the statistical noise of the BD values becomes high but these values are small so that they represent a low contribution in the calculation of k_1). In order to consider this long-time behavior in an adequate way, our BD estimations for $\rho(\tau)$ in reduced units are introduced in eqs 3–6 as a fitted curve of the biexponential form (in reduced units)

$$\rho(\tau^*) = A \exp(-B\tau^*) + (1 - A) \exp(-C\tau^*) \quad (8)$$

Although the first term typically contributes ~95% and contains the smallest exponent, a single-exponential fit is not accurate enough. The fitted parameters are given in Table I. According to eq 7, the long-time region of $\rho(\tau)$, governed by this first term, should be proportional to $\exp(-\tau/\tau_1)$, where τ_1 is the highest Rouse relaxation time. Table I also contains a column with values of $1/\tau_1$ (in reduced units) calculated from previously reported results.[2,9] A good agreement with the present values of B is observed in all cases (taking into account the associated statistical uncertainties). It should be noticed that the introduction of preaveraged HI has little effect on the fitted parameters or, consequently, on $\rho(\tau)$. This is hardy surprising since our previous calculations for the first and second relaxation times of the Rouse modes were also scarcely affected by this approximation.[2,9]

A further check of our numerical procedure to estimate rate constants with the WF method has been performed through a comparison of our results for k_1 for unperturbed chains and preaveraged HI (contained in Table II) with calculations of the same type where $\rho(\tau)$ is exactly calculated from eq 7. A good agreement is found for the different values of R_0/b and N.

However, we have found some disagreements between these results for k_1 and those obtained from our graphical estimations of the results for second-order rate constants reported by Perico and Cuniberti,[3] which were employed in the Discussion of paper 1 and are systematically higher by about 10–15%. The latter results were calculated with a slightly different value of h^* (corresponding to $\sigma/b = 0.25$), and moreover, they included approximate free-draining eigenvectors and other minor simplifications, but in any case, we expected a closer accordance with our estimations. Nevertheless, this discrepancy can be considered

Table I
Fitting Parameters for the Time Correlation Function $\rho(\tau)$ Obtained from Our BD Trajectories (Eq 8) for Different Models (Corresponding to Different Solving Conditions) and HI Treatments[a]

model	HI	N	A	B	$1/\tau^*$	C
θ	preaveraged	6	0.91 ± 0.07	0.8 ± 0.1	0.82	19 ± 13
		8	0.972 ± 0.009	0.60 ± 0.05	0.53	8 ± 1
		11	0.92 ± 0.02	0.33 ± 0.03	0.33	4 ± 1
		15	0.84 ± 0.01	0.19 ± 0.02	0.21	3 ± 1
		20	0.93 ± 0.01	0.148 ± 0.008	0.13	2.3 ± 0.4
θ	fluctuating	6	0.92 ± 0.07	0.83 ± 0.09	0.81 ± 0.03	15 ± 7
		8	0.969 ± 0.003	0.59 ± 0.04	0.53 ± 0.02	7.9 ± 0.3
		11	0.93 ± 0.02	0.32 ± 0.03	0.326 ± 0.005	4 ± 1
		15	0.88 ± 0.08	0.19 ± 0.02	0.198 ± 0.002	3 ± 1
		20	0.91 ± 0.03	0.14 ± 0.02	0.123 ± 0.004	3 ± 1
excluded volume	preaveraged	6	0.93 ± 0.02	0.63 ± 0.05	0.64 ± 0.01	9 ± 2
		8	0.958 ± 0.005	0.40 ± 0.02	0.37 ± 0.01	6.6 ± 0.7
		11	0.93 ± 0.02	0.21 ± 0.02	0.21 ± 0.01	3.7 ± 0.8
		15	0.91 ± 0.04	0.12 ± 0.02	0.130 ± 0.003	2.6 ± 0.7
		20	0.94 ± 0.02	0.08 ± 0.01	0.084 ± 0.002	2.0 ± 0.05
excluded volume	fluctuating	6	0.94 ± 0.02	0.70 ± 0.05	0.709 ± 0.005	6 ± 2
		8	0.7 ± 0.1	0.34 ± 0.06	0.42 ± 0.01	1.8 ± 0.7
		11	0.90 ± 0.02	0.22 ± 0.02	0.213 ± 0.04	2.3 ± 0.4
		15	0.92 ± 0.03	0.14 ± 0.01	0.139 ± 0.003	2.7 ± 0.7
		20	0.94 ± 0.02	0.09 ± 0.01	0.089 ± 0.002	2.8 ± 0.7

[a] Values of $1/\tau_1$ (in reduced units) previously obtained[2,9] are also included for comparison with B.

Table II
Rate Constants, $10k_1^*$, Obtained from $\rho(\tau)$ and the WF Method, for Unperturbed Chains, Different Values of N and R_0/b, and Different HI Treatments

		HI treatment	
R_0/b	N	preaveraged	fluctuating
1.0	6	4.3 ± 0.2	4.3 ± 0.1
	8	2.5 ± 0.2	2.5 ± 0.2
	11	1.3 ± 0.1	1.3 ± 0.1
	15	0.711 ± 0.004	0.70 ± 0.01
	20	0.46 ± 0.02	0.43 ± 0.04
0.50	6	2.2 ± 0.1	2.16 ± 0.03
	8	1.29 ± 0.06	1.3 ± 0.1
	11	0.70 ± 0.06	0.70 ± 0.03
	15	0.384 ± 0.006	0.384 ± 0.003
	20	0.26 ± 0.01	0.26 ± 0.02
0.25	6	1.09 ± 0.05	1.08 ± 0.02
	8	0.64 ± 0.03	0.66 ± 0.05
	11	0.36 ± 0.03	0.36 ± 0.02
	15	0.19 ± 0.01	0.198 ± 0.006
	20	0.13 ± 0.01	0.14 ± 0.02

as marginal when compared with the much higher differences found for results obtained with the different models and numerical methods, which will be analysed in next section.

Results and Discussion

Our results for k_1 obtained with $\rho(\tau)$ and the WF method for unperturbed chains with fluctuating HI are also contained in Table II. They are very close to the preaveraged results. All the results corresponding to the more direct calculations from $\Phi(\tau)$ for the same type of chains are included in Table III. The latter results were partially reported in paper 1, though we present here some values recalculated with higher precision and include new values coresponding to the case $R_0/b = 1$, in order to have at least two different values of R_0/b to compare with the excluded volume model (for which we have not been able to obtain values with $R_0/b = 0.25$, as will be explained below). The influence of the HI treatment is clearly more significant in this case, the preaveraged values being always higher than the ones corresponding to fluctuating HI, with increasing differences for decreasing values of the ratio R_0/b. It seems apparent that the main distortions in k_1 introduced with the preaveraging HI approximation are somehow obscured by the approximations included in the WF method.

Table III
Rate Constants, $10k_1^*$, Obtained from $\Phi(\tau)$, for Unperturbed Chains

		HI treatment	
R_0/b	N	preaveraged	fluctuating
1.0	6	6.1 ± 0.4	5.7 ± 0.4
	8	4.1 ± 0.2	3.4 ± 0.3
	11	2.0 ± 0.2	1.7 ± 0.2
	15	1.1 ± 0.2	1.1 ± 0.2
	20	0.65 ± 0.06	0.6 ± 0.18
0.50	6	2.27 ± 0.07	1.5 ± 0.2
	8	1.47 ± 0.04	1.12 ± 0.03
	11	0.8 ± 0.1	0.52 ± 0.03
	15	0.45 ± 0.07	0.26 ± 0.01
	20	0.27 ± 0.03	0.16 ± 0.01
0.25	6	0.81 ± 0.08	0.39 ± 0.03
	8	0.36 ± 0.05	0.25 ± 0.05
	11	0.27 ± 0.05	0.123 ± 0.0051
	15	0.117 ± 0.003	0.078 ± 0.003
	20	0.112 ± 0.003	0.067 ± 0.008

As discussed in paper 1, the results obtained through the WF method and those calculated from $\Phi(\tau)$ with preaveraged HI are in good agreement for $R_0/b = 0.5$, while the latter results are consistently smaller than the WF values for $R_0/b = 0.25$, i.e., for stiffer chains or smaller capture radius. Now we observe that the trend is inverted for $R_0/b = 1$ so that the smallest results are those obtained with the WF method. All these discrepancies can be attributed to effects of the sink closure and other approximations in the WF method or, as an alternative explanation for the highest values of R_0/b, to the assumption of reversible cyclizations in our method to compute $\Phi(\tau)$ from the trajectories. In fact, for the fairest comparison with the WF theory, we would need a theoretical expression for $k(\tau)$ derived with a symmetric choice of the sink function, instead of with the unsymmetric choice implicit in the use of eqs 3–6. Thus, for the harmonic spring model, k_1 depends somewhat on whether symmetric or unsymmetric choices for sink functions are made.[19-21]

We also present rate constants for excluded volume chains, calculated from the WF method (Table IV) or from our evaluation of $\Phi(\tau)$ (Table V) with the two alternative treatments for HI. A first comparison with the results for unperturbed chains reveals a clear decrease in k_1, due to the long-range interactions, in accordance with qualitative

Table IV
Rate Constants, $10k_1^*$, Obtained from $\rho(\tau)$ and the WF Method, for Excluded Volume Chains

		HI treatment	
R_0/b	N	preaveraged	fluctuating
1.0	6	3.2 ± 0.2	3.4 ± 0.1
	8	1.6 ± 0.2	1.7 ± 0.1
	11	0.74 ± 0.04	0.78 ± 0.04
	15	0.38 ± 0.003	0.41 ± 0.02
	20	0.22 ± 0.02	0.24 ± 0.01
0.50	6	1.71 ± 0.07	1.75 ± 0.03
	8	0.87 ± 0.03	0.84 ± 0.08
	11	0.42 ± 0.03	0.43 ± 0.03
	15	0.21 ± 0.02	0.23 ± 0.01
	20	0.126 ± 0.006	0.14 ± 0.01
0.25	6	0.87 ± 0.03	0.87 ± 0.02
	8	0.46 ± 0.02	0.41 ± 0.3
	11	0.22 ± 0.01	0.22 ± 0.02
	15	0.11 ± 0.01	0.120 ± 0.006
	20	0.067 ± 0.03	0.078 ± 0.02

Table V
Rate Constants, $10k_1^*$, Obtained from $\Phi(\tau)$, for Chains with Excluded Volume

		HI treatment	
R_0/b	N	preaveraged	fluctuating
1.0	6	4.5 ± 0.2	3.9 ± 0.2
	8	2.36 ± 0.04	2.0 ± 0.2
	11	1.0 ± 0.1	0.69 ± 0.04
	15	0.5 ± 0.1	0.3 ± 0.1
	20	0.26 ● 0.04	0.188 ± 0.04
0.50	6	1.43 ± 0.07	1.01 ± 0.07
	8	0.68 ± 0.03	0.48 ± 0.02
	11	0.33 ± 0.03	0.21 ± 0.07
	15	0.17 ± 0.03	0.08 ± 0.03
	20	0.10 ± 0.01	0.04 ± 0.01

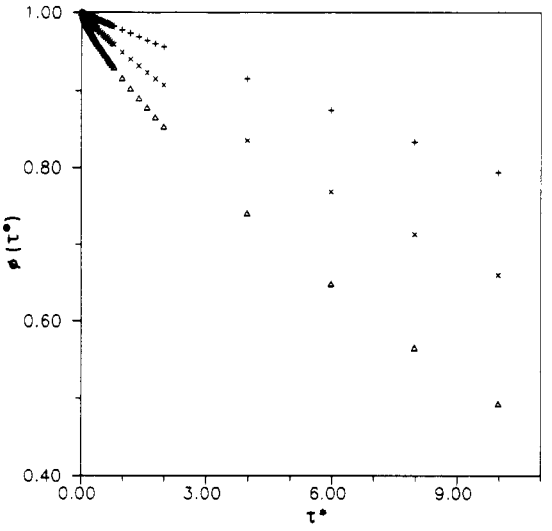

Figure 2. $\Phi(\tau)$ vs τ (in reduced units) from single trajectories of chains of 11 units (fluctuating HI), and R_0/b = 0.5, without (×) and with (+) intramolecular interactions, and with excluded volume and R_0/b = 1 (Δ).

predictions[5,10,12,17] and experimental data.[11,12,14] This implies slower decays for $\Phi(\tau)$ so that the time range required to obtain a cycled chain with R_0/b = 0.25 was found to be so wide that we could only detect a few cyclizations along the trajectories, making it impossible to report sufficiently accurate results for k_1. For the sake of illustration, the behavior of $\Phi(\tau)$ and its dependence on R_0/b and intramolecular interactions obtained from single trajectories of chains of 11 units with fluctuating HI are shown in Figure 2, while decay curves corresponding to R_0/b = 1 for chains with excluded volume, fluctuating HI, and different numbers of units are contained in Figure 3.

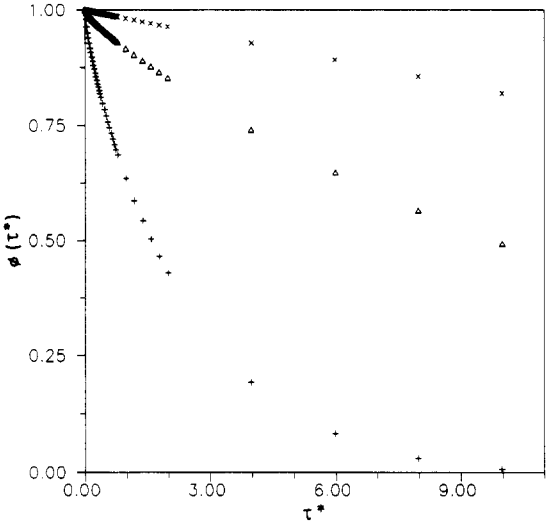

Figure 3. $\Phi(\tau)$ vs τ (in reduced units) obtained as in Figure 2, but for chains with excluded volume and N = 6 (+), 11 (Δ), and 20 (×), calculated with R_0/b = 1.

As in the case of unperturbed chains, we notice small differences between the results obtained for excluded volume chains with preaveraged or fluctuating HI and the WF method, but the preaveraged values of k_1 are consistently higher than those calculated with fluctuating HI when they are obtained from $\Phi(\tau)$, and the differences increase for decreasing values of R_0/b. The preaveraged results obtained with the WF method are higher than those calculated from $\Phi(\tau)$ (though they are still remarkably close to them) for R_0/b = 0.25, while the trend is inverted for R_0/b = 1, as also occurs for unperturbed chains. It should be remembered that the restrictions on equilibrium statistics, hydrodynamic treatment, and the unsymmetric choice of sink function used by WF, which lead to eqs 3–6, were employed to simplify the computational work. However, if the equilibrium distribution is non-Gaussian, it is not clear whether these equations are still valid, and their use with numerical values of $\rho(\tau)$ calculated with fluctuating HI can only be considered as an ad hoc approximation.

The suitability of the chosen value for the reduced time, Δt^* = 0.01, to adequately simulate different properties had been determined previously.[2,8,9] Notwithstanding, we have performed further checks in the present work. Thus, we have obtained the k_1 values from $\Phi(\tau)$ from trajectories for chains with excluded volume, employing smaller time steps in a few typical cases. We have verified that the results calculated with Δt^* = 0.005 are consistent with those shown in Table V for R_0/b = 1, N = 6 and 20, and for R_0/b = 0.5, N = 6. Adequate results are also obtained with the considerably shorter time step Δt^* = 0.002, for R_0/b = 0.5 and 1, N = 6. (The slow decays for N = 20 preclude a drastic reduction of Δt^* with this chain in the remaining cases.)

The effect of excluded volume interactions on k_1 (expressed in terms of ratios of results for excluded volume chains to those corresponding to the unperturbed model) does not change much with changing values of R_0/b or changing hydrodynamic treatments. (In fact, a slight increase of these effects with fluctuating HI or for smaller values of R_0/b can be observed, but the differences are of the order of typical statistical errors.) As a more interesting feature, it can be noted that the excluded volume effects are significantly higher in the values calculated from $\Phi(\tau)$ than in the results from $\rho(\tau)$ and the WF method.

As expected, the decrease in k_1 due to excluded volume is higher for longer chains. A quantitative analysis of this

tendency can be performed in terms of empirical scaling laws. However, the following analysis can only be considered as tentative, due to the statistical errors associated with the simulation values of k_1, and the relatively small chains for which the calculations were feasible.

We have performed log–log regression analysis of k_1 vs $N-1$ for the different cases shown in Tables II–V. This way, we have obtained the exponent γ, defined as

$$k_1 \sim (N-1)^{-\gamma} \tag{9}$$

The results vary for the different cases, but we can observe higher values of γ from values of k_1 calculated from $\Phi(\tau)$ than those calculated from $\rho(\tau)$ and the WF method. Preaveraged results give, in general, smaller exponents than the values obtained with fluctuating HI. Since all these effects can simply reflect deviations due to the numerical problems discussed above, we have performed a final estimation of γ as the mean over all the different values calculated for each model, giving equal weights to the results obtained with the two alternative calculations, based in $\rho(\tau)$ or $\Phi(\tau)$. This procedure yields $\gamma = 1.68 \pm 0.03$ and $\gamma = 2.1 \pm 0.1$ for unperturbed and excluded volume chains. The theoretical prediction for long unperturbed chains is $\gamma = 1.5$, consistent with the dependence on N of the equilibrium cyclization probability (evaluated as the end-to-end distance distribution function for small values of R, $F(0)$) and also with the relaxation times of the Rouse modes and the end-to-end vector time-correlation function. On the other hand, the results obtained by Perico and Cuniberti for finite bead and spring chains with preaveraged HI[3] were fitted with the exponent $\gamma = 1.43$.[12] Our results for the same model and treatment give $\gamma = 1.56$. This variety of values for γ shows its high sensitivity to numerical methods.

When excluded volume is introduced, the relaxation times for long chains are theoretically described as $\tau_k \sim N^{-3\nu}$, where ν is defined as a critical exponent value, $\nu = 0.588$. Nevertheless, the equilibrium cyclization probability follows a different behavior, $F(0) \sim N^{-\alpha}$, where an exponent higher than 3ν, $\alpha \simeq 1.95$, is predicted due to correlation hole effects.[10,12,22,23] It seems that our numerical values of γ are closer to α, favoring a description of k_1 through the equilibrium probability or a "mass action law", in accordance with recent work based on the renormalization group theory.[10] However, this conclusion should be considered with caution, since our values of γ are strongly conditioned by numerical procedures.

Finally, we should discuss our results in the light of existing data measured from spectroscopic decay experiments for end-capped flexible polymers in θ and good solvents (i.e., for unperturbed and excluded volume chains). The more systematically studied system polystyrene capped with pyrene (which exhibits photochemical decay due to intramolecular excimer formation) in cyclohexane (θ solvent) yields values of γ fluctuating around $\gamma = 1.5$. Thus, data that were initially reported to fit,[11,12] with $\gamma = 1.64$–1.68, have been later corrected by taking into account the experimental uncertainties so that they reproduce $\gamma = 1.43$, in agreement with the Perico and Cuniberti results.[3,12] This points out again that γ can be greatly affected by small changes in the numerical treatment. Once the factor η_0/T is discounted, a strong decrease of k_1 is observed for the same type of experimental data obtained with increasingly better solvents.[14] The data for polystyrene in toluene[11] (good solvent) were fitted[12] to $\gamma = 1.76$; i.e., an increase of 0.33 was found with respect to the result in θ conditions, slightly smaller than that obtained from our calculations. However, different results for γ have been obtained for other polymer–solvent systems. Thus, we can mention, as an illustrative instance, that $\gamma = 1.7$–1.9 has been found in a recent study of a particular type of polycarbonate chains in several solvents of varying qualities.[13]

A more direct analysis of the ratios of results for k_1 obtained in toluene to those obtained in cyclohexane for polystyrene chains of the same molecular weights (Table 3 of ref 11) can be directly contrasted with our results for excluded volume and unperturbed chains, though the experimental ratios have a somehow irregular dependence on N, caused by experimental error or polydispersity effects. At any rate, these ratios are ~ 0.3 in a wide region of intermediate molecular weights ($\bar{M}_n \simeq 3 \times 10^3$–$3 \times 10^4$), consistent with our results for a chain of 20 units, obtained directly from $\Phi(\tau)$, while the WF method would require longer chains to reproduce this ratio. Considering the center of this interval of molecular weights and employing the experimental relationship[3]

$$Nb^2 = 0.48 \times 10^{-16}\,\mathrm{M} \tag{10}$$

obtained from experimental determination of dimensions for unperturbed polystyrene chains, together with the commonly used[1,3] value of the capture radius, $R_0 = 5$ Å, we get a value of b of ~ 20 Å. We have verified that our results for k_1 for unperturbed chains, obtained from $\Phi(\tau)$ with fluctuating HI, and this value of b (according to the values shown in Table III and eq 2 with $h^* \simeq 0.25$ and $\eta_0/T \simeq 2 \times 10^{-5}$ poise/K) are roughly in quantitative agreement with the data for polystyrene in cyclohexane of ref 11. However, the unperturbed values of k_1 obtained with the WF method for unperturbed chains, namely, the Perico and Cuniberti results, are in better agreement with the data for $b = 60$ Å (when $R_0 = 5$ Å) but, in this case, a strong disagreement arises for the good solvent data, since the experimental excluded volume effects are much higher than those predicted with the WF method for chains with a small value of N or through corrections that only consider the chain expansion.[12] Therefore, the exclusion of approximations inherent to the WF method and to the standard HI treatment seems to be crucial to obtain a consistent reproduction of experimental rate constants measured in both θ and good solvent conditions. Notwithstanding, $b = 60$ Å is the result found when numerical values of hydrodynamic properties, obtained through the Rouse–Zimm theory,[6] are compared with experimental data.[3] (Though the preaveraged theory overestimates the viscosity by $\sim 15\%$ for long linear chains,[24,25] we do not believe that the present discrepancies can be solely explained with this argument.) We have not been able to calculate k_1 from $\Phi(\tau)$ with $b = 60$ Å, due to the drastic decrease of the rate constant for smaller values of R_0/b. However, it can be qualitatively predicted that the results should be considerably lower than those obtained with the WF method and, consequently, than the experimental data analyzed through this discussion, and closer to data obtained for polystyrene chains with anthracene end-caps in triplet–triplet annihilation experiments.[15,16] Nevertheless, these data show a nonexplained weak variation with molecular weight and solvent conditions, yielding an exponent γ close to 1 and small differences between the θ and good solvent conditions (compatible with chains of only a few units). From eq 10, and taking into account the molecular weight of the polystyrene repeating unit, $M_0 = 104$, one can intuitively argue that $b = 20$ Å corresponds to ~ 16 backbone bonds per statistical unit, which can be considered a small value for the moderate stiffness of polystyrene chains. On the other hand, $b = 60$ Å implies

a very high number of 144 backbone bonds per unit.

In summary, the excluded volume effects on the cyclization dynamics of flexible polymers, which are now qualitatively understood from the theoretical point of view, have been here reproduced through numerical simulation methods. These methods yield results fairly consistent with the experimental data when most standard approximations are suppressed in the procedure, though the adequate assignment of a statistical length for the units is found in disagreement with the value employed to reproduce hydrodynamic properties through the Rouse–Zimm theory. Only further progress in purely theoretical, numerical, and experimental work will be able to reconcile this and other minor remaining discrepancies.

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