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

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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:

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

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

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Table I
Radius of Gyration and Static Scattering Form Factor of Gaussian Ring Chains

	BD[a]			theory		
N	$\langle s^2\rangle/b^2$	$S(x = 1)$	$S(x = 5)$	$\langle s^2\rangle/b^2$ [b]	$S(x = 1)$[c]	$S(x = 5)$[c]
6	0.492 ± 0.003	0.737 ± 0.001	0.297 ± 0.002	0.500	0.734	0.300
8	0.663 ± 0.009	0.728 ± 0.003	0.281 ± 0.003	0.667	0.730	0.281
11	0.914 ± 0.009	0.726 ± 0.002	0.269 ± 0.003	0.917	0.728	0.270
15	1.220 ± 0.009	0.731 ± 0.001	0.267 ± 0.003	1.215	0.726	0.264
20	1.62 ± 0.05	0.731 ± 0.007	0.264 ± 0.008	1.726	0.726	0.260

[a] BD, averaged over Brownian dynamics trajectories. [b] Computed from eq 3. [c] Computed from eq 4.

These parameters relate the properties of ring chains with those of linear chains with the same molecular weight. The preaveraged theory, when applied to Θ-condition solutions, gives the ratios[5,6] $q_\eta \simeq 0.66$ and $q_D = 3\pi/8 \simeq 1.18$, which are quite coincident with different experimental data[7-11] (a discussion on these experimental results will be provided immediately below).

An alternative way to calculate these properties, avoiding the preaveraging approximation, is computer simulation. In previous work, we have performed numerical calculations based on the Monte Carlo method for different models of flexible rings.[12] We have obtained results for q_D that are very close both to theoretical estimations and to experimental data, but this is not the case for q_η, whose simulation result is much lower ($q_\eta \sim 0.52$–0.60, depending on the model considered) than the other sets of results. This comparison does not invalidate the simulation, because the experimental data for the two ratios defined in eqs 1 and 2 must be considered with certain care. In fact, ideal thermodynamic conditions for a given polymer–solvent system occur at different temperatures depending on the topology (linear or cyclic, in our case) of the polymer, even for identical molecular weights.[7,11] This makes the experimental measurements of q_η and q_D in unperturbed conditions considerably difficult.

In this paper we have intended to confirm the Monte Carlo results (in which the rigid-body approximation was implicit) by computing Brownian dynamics trajectories of Gaussian rings with different number N of theoretical units, in unperturbed Θ conditions, with fluctuating hydrodynamic interactions. These simulations provide the transport properties D_t and $[\eta]$ without the preaveraging approximation. In addition, we can also obtain other dynamic properties from the simulations. These calculations have been previously accomplished for linear[13] and star-branched[14] chains but, as far as we know, they have not been previously attempted for ring polymers. The results for q_η and q_D are analyzed in the light of the comparison with experimental data that we performed earlier.[12] A comparison with recent renormalization group results[15] is also included.

2. Method

We have employed for this study of ring chains the iterative algorithm proposed by Ermak and McCammon[16] for polymers modeled as beads and springs with hydrodynamic interactions. The Rouse matrix **A** that describes the connectivity between chain units was defined for Gaussian rings by Bloomfield and Zimm.[2] Fluctuating hydrodynamic interactions are represented by a Rotne–Prager–Yamakawa tensor, with a friction size of the units in agreement with the choice of the parameter $h^* = 0.25$.[17] As in the case of linear and star chains studied before, the algorithm is numerically solved with an integration time step $\Delta t^* = 0.01$ (in the reduced units employed in our previous works), computing three independent trajectories of 40 000 steps each for the different rings considered. The algorithm begins with a closed conformation generated in a diamond lattice. The analysis of trajectories necessary for the calculation of properties is similar to that employed for linear[13] and star chains[14] and will be, in general, omitted, pointing out only the differences with respect to previous work, which will be described in the appropriate sections. We should only mention that the results presented in the different tables correspond to means and errors obtained from statistical deviations that have been calculated from the averages obtained over our three different trajectories, treated as independent data.

3. Results and Discussion

3.1. Equilibrium Averages. In Table I we collect the dimensions (mean quadratic radius of gyration) and the static structure factor (for two scattering angles) obtained for our Gaussian rings. The theoretical expressions corresponding to these averages are

$$\langle s^2\rangle = Nb^2/12 \tag{3}$$

for the radius of gyration, where b is the average distance between neighbor beads (equal to one, in reduced units), and

$$S(x) = \frac{1}{N^2}\sum_{i=1}^{N}\sum_{j=1}^{N}\exp\left(-\frac{2x\mu}{N}\right) \tag{4}$$

for the scattering structure factor, with

$$\mu = |i-j|(1-|i-j|/N) \tag{5}$$

The difference $|i - j|$ represents the smallest number of connections between neighbor units separating beads i and j. The values obtained from these theoretical expressions are also shown in Table I. It is readily observed that there is a very good agreement between theoretical and simulation results. This confirms the adequacy of our numerical procedures to reproduce the conformational properties of ring chains. From results corresponding to the radius of gyration of linear chains with the same number of units, it is easily feasible to compute the ratio $g = \langle s^2\rangle_{\mathrm{ring}}/\langle s^2\rangle_{\mathrm{linear}}$. For all the chains considered, we have found a value of this ratio very close to 0.5, the expected theoretical result.

3.2. Translational Diffusion Coefficient. Following the same scheme that we employed with linear and star chains, we have obtained the values of D_t from the quadratic displacements of the center of masses of the rings along the dynamic trajectories. The results computed this way are summarized in Table II, together with theoretical estimations derived from the preaveraging approximation and Monte Carlo results for rigid conformations, which constitute upper and lower bounds, respectively, for D_t. (Though in our previous paper[12] we reported a broad set of lower bound results, we include here some new values corresponding to chains with the number of units employed

Table II
Translational 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)

N	D_t^*					
	BD	MC	PT	LS(x = 1)	LS(x = 5)	ρ^a
6	0.43 ± 0.01	0.4040 ± 0.0002	0.446	0.42 ± 0.03	0.43 ± 0.05	1.18 ± 0.04
8	0.368 ± 0.006	0.3480 ± 0.0002	0.387	0.35 ± 0.01	0.41 ± 0.03	1.17 ± 0.04
11	0.306 ± 0.001	0.2948 ± 0.0004	0.331	0.303 ± 0.006	0.30 ± 0.01	1.14 ± 0.01
15	0.276 ± 0.003	0.2505 ± 0.0003	0.284	0.26 ± 0.01	0.26 ± 0.04	1.19 ± 0.02
20	0.228 ± 0.005	0.2156 ± 0.0005	0.247	0.222 ± 0.008	0.26 ± 0.02	1.13 ± 0.05

[a] Parameter obtained from BD trajectories.

Table III
Normal Mode Relaxation Times (in Reduced Units) for Gaussian Rings[a]

N	$(\tau_1')^{*b}$				$(\tau_2')^{*b}$	
	BD	PT	LS(x = 1)	LS(x = 5)	BD	PT
6	0.43 ± 0.01	0.421	0.40 ± 0.05	0.20 ± 0.08	0.174 ± 0.004	0.187
8	0.66 ± 0.01	0.619	0.62 ± 0.07	0.21 ± 0.09	0.248 ± 0.003	0.248
11	1.034 ± 0.009	0.968	0.96 ± 0.03	0.40 ± 0.02	0.407 ± 0.009	0.364
15	1.67 ± 0.02	1.515	0.72 ± 0.05	0.59 ± 0.07	0.576 ± 0.004	0.550
20	2.84 ± 0.03	2.307	2.76 ± 0.05	0.6 ± 0.1	0.92 ± 0.04	0.822

[a] BD, computed from the dynamic trajectories; PT, preaveraged theoretical estimations; LS, analysis of the scattering form factor. [b] Doubly degenerate values.

Table IV
Simulation to Preaveraged Theory Ratio, $[\eta]^{\rm sim}/[\eta]^{\rm PT}$, for Gaussian Rings[a]

N	BD	LB	UB
6	0.78 ± 0.01	0.73 ± 0.01	0.792 ± 0.001
8	0.76 ± 0.03	0.748 ± 0.005	0.783 ± 0.002
11	0.736 ± 0.005	0.746 ± 0.005	0.776 ± 0.004
15	0.68 ± 0.01	0.73 ± 0.02	0.774 ± 0.003
20	0.67 ± 0.02	0.69 ± 0.01	0.772 ± 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.

in the Brownian trajectories, both for rings and for linear chains.) We show also in this table the parameter ρ, the ratio of the radius of gyration to the hydrodynamic radius, calculated only from Brownian trajectories.

As it should be expected, dynamic simulation results lie between theoretical and Monte Carlo estimations. The simulation results do not show a definite trend toward one of the bounds, which could allow us to discern which of the two methods provides more exact values for D_t. Though the difference existing between their respective results amounts to ca. 10%, slightly greater than in linear chains, they are still very close to the uncertainty range inherent in the dynamic results.

Experimental data of ρ found in the literature for cyclic polymers of high molecular weight[7-10] show a certain dispersion (values have been reported in the range ρ = 1.00–1.15). Our simulation results do not have a clear behavior against N. Therefore, we have obtained an extrapolation to $N \rightarrow \infty$ just by computing the weighted average of the different results, which yields a value $\rho = 1.15 \pm 0.01$ in the upper limit of the experimental range. Although the broad distribution of experimental data precludes any rigorous conclusion, it seems clear that simulation results are closer to real data than the preaveraged theoretical estimation,[5,6,18] $\rho = (\pi/2)^{1/2} = 1.253$.

3.3. Relaxation Times. As we have mentioned in previous works for other structures,[13,14] theoretical estimations for the relaxation times of the internal normal movements can be calculated from the eigenvalues of the product **HA**, where **A** is the Rouse matrix and **H** is the preaveraged hydrodynamic interaction matrix calculated from the Rotne–Prager–Yamakawa tensor (see eqs 8–10 of the preceding paper; $\langle R_{ij}^2\rangle$ is now computed for rings as $\langle R_{ij}^2\rangle = \mu b^2$, with μ defined through eq 5). On the other hand, simulation results for these relaxation times can be extracted from normal coordinate correlation functions, computed along Brownian trajectories with fluctuating hydrodynamic interactions. Following the same treatment used for linear chains, we have defined normal coordinates from the analytical expression corresponding to the free-draining limit, which can be written for ring chains as[4]

$$\mathbf{q}_k(t) = \left(\frac{2}{N}\right)^{1/2} \sum_{j=1}^{N} \cos\left(\frac{2\pi kj}{N}\right) \mathbf{r}_j(t) \qquad (6)$$

where $\mathbf{r}_j(t)$ includes the coordinates of the jth bead in an internal reference frame (in our case, taking as origin the center of masses of the chain at every simulation step). Although these coordinates are not completely suitable when fluctuating hydrodynamic interaction is considered, preaveraged results and our previous studies on linear chains show that they represent a good approximation of real normal coordinates.

In Table III we show theoretical and simulation results for the relaxation times τ_k' for k = 1 and 2. The $N - 1$ relaxation times of a cyclic chain are doubly degenerate[2] (except the last one, $k = N - 1$, when N is even), a fact that is reproduced by our simulation results. It can be observed that simulation results are always slightly greater than theoretical ones. The same trend is also observed in linear and star-branched chains.

3.4. Dynamic Scattering Form Factor. We have also computed from our trajectories the dynamic scattering form factor $S(\mathbf{q},t)$. The analysis of this function for ring chains does not supply important differences with respect to linear or star chains. In Tables II and III we have summarized the diffusion coefficient and the first relaxation time obtained from $S(\mathbf{q},t)$ through a nonlinear least-squares fitting to a two-exponential sum, following the method proposed by Pecora. It can be seen that, for the smaller scattering angle, x = 1, the results are coincident, within their numerical uncertainties, with those computed directly from correlation functions along Brownian trajectories previously analyzed. However, for larger scattering angles, x = 5, the results from the fittings are clearly worse than those computed in a direct way,

Table V
Ratios of the Transport Properties of Rings to Linear Chains[a]

	q_D			q_η			
N	BD	MC	PT	BD	LB	UB	PT
6	1.39 ± 0.09	1.144 ± 0.002	1.173	0.57 ± 0.04	0.53 ± 0.02	0.547 ± 0.003	0.616
8	1.22 ± 0.07	1.152 ± 0.001	1.180	0.56 ± 0.05	0.539 ± 0.007	0.544 ± 0.003	0.616
11	1.18 ± 0.05	1.157 ± 0.002	1.187	0.55 ± 0.02	0.553 ± 0.008	0.543 ± 0.004	0.617
15	1.10 ± 0.06	1.159 ± 0.002	1.189	0.49 ± 0.02	0.55 ± 0.02	0.544 ± 0.005	0.620
20	1.14 ± 0.08	1.160 ± 0.003	1.192	0.49 ± 0.02	0.52 ± 0.01	0.546 ± 0.006	0.623

[a] Same notation as in Tables II and IV. PT, preaveraged theoretical results.

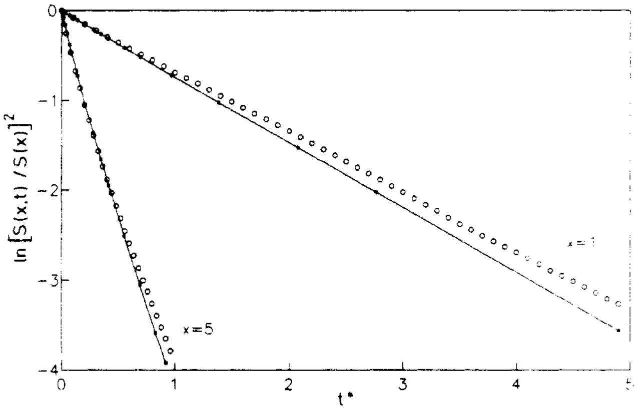

Figure 1. ln $[S(x,t)/S(x)]^2$ versus t for a ring chain of $N = 11$ with fluctuating HI: (○) results obtained from the trajectories; (*) theoretical estimations.

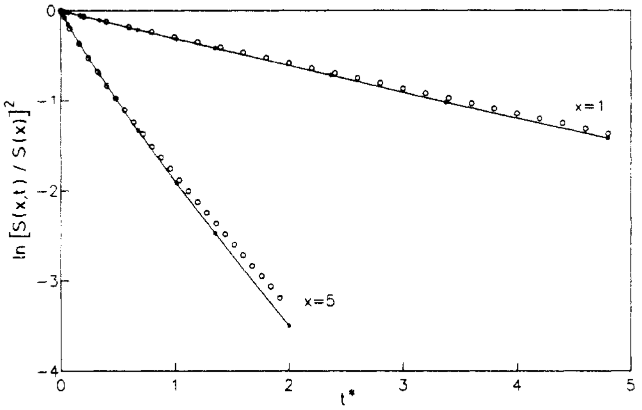

Figure 2. As Figure 1 but with $N = 20$.

especially in the case of τ_1'. This proves the necessity to introduce more terms in the Pecora expansion of $S(\mathbf{q},t)$ (eq 26 of ref 13). With these improvements, the fitting provides satisfactory results when one has a certain knowledge about the more significant preexponential coefficients, as we showed in the work on linear chains.

A direct comparison between simulated dynamic form factor (with fluctuating hydrodynamic interaction) and the preaveraged theoretical one, also provided by Pecora, is shown in Figures 1 and 2 for two of our rings. The differences between both types of results are very similar to those of linear chains but somewhat more pronounced than in star chains. Simulation results are slightly larger than theoretical ones, but the preaveraged method of Pecora seems to be essentially correct once more, even from a quantitative point of view.

3.5. Intrinsic Viscosity. In Table IV we show the values of $[\eta]$ (reduced with their corresponding preaveraged theoretical values), calculated from the different methods described in the preceding paper.[14] Dynamic simulation results computed from the stress correlation function (calculated from the dynamic trajectories), upper bounds from Monte Carlo simulations over rigid conformations (Zimm method[17]), and lower bounds from a different Monte Carlo simulation based on the variational method first proposed by Fixman[19,20] are included. It can be observed again that the ratios $[\eta]^{\mathrm{sim}}/[\eta]^{\mathrm{PT}}$ become progressively lower than one when the number of units of the ring increases. The effect is not so important as in star chains but is much more significant than in linear chains. We can therefore conclude that the theory with the preaveraging approximation provides worse estimations for intrinsic viscosities as the chain becomes more compact and more distorted from a linear structure.

From another point of view, the two sets of Monte Carlo simulations delimit also in cyclic chains a narrow range of values for $[\eta]$. The numerical procedure employed in the analysis of dynamic trajectories seems to underestimate the values of the intrinsic viscosity on some occasions, so that their values are sometimes smaller than the lower bound predictions, which seem to provide the best approximate estimations for longer chains, as occurs also for the linear and star structures.

3.6. Comparison with Linear Chains. In Table V, values are shown for the ratios q_D and q_η of transport properties of ring to linear chains with the same molecular weight (i.e., with the same number N of theoretical units).

The values of q_D just reflect our previous comments about D_t for the different structures considered. For the larger rings, the preaveraged theoretical estimations tend to slightly greater values than the simulation results, though the Brownian dynamics ratios have a significant numerical error, and the three sets of results are too close to one another to obtain more definitive conclusions.

Data for q_η are more interesting. Now, the theoretical estimations are clearly greater than the simulation results (the value $q_\eta = 0.66$ mentioned in the Introduction corresponds to chains of infinite molecular weight). However, the most important results correspond to the limiting values provided by the Monte Carlo simulations. Upper and lower bound ratios are now very close to each other. Even more, provided that neither of the two sets of results shows a clear tendency with N, an extrapolation of these results to high molecular weight can be obtained, at least as a first approximation, from their respective arithmetic averages, whose values are $q_\eta = 0.540 \pm 0.006$ for the lower bound and $q_\eta = 0.545 \pm 0.001$ for the upper bound (the latter result is coincident with that previously reported[12]). The results computed from dynamic simulations yield a somewhat lower extrapolation, but the numerical uncertainties associated with the calculation of $[\eta]$ are surely responsible for this discrepancy.

We can therefore conclude that our results confirm the considerations mentioned in the Introduction about the fortuitous similarity existing between the preaveraged theoretical results for q_η and the experimental data. A further clarification of this point may be provided by the calculation of q_η with excluded volume and its comparison with experimental data measured in good solvent conditions, both for linear and ring chains. These conditions are, from an experimental point of view, less restrictive than ideal Θ conditions and, consequently, they are free of the ambiguity inherent in the definition of q_η at the Θ point. Recent renormalization group calculations in the lowest order[15] predict $q_\eta = 0.486$ for Gaussian chains and $q_\eta = 0.561$ in the presence of excluded volume (the former value is much closer to our simulation results than the one provided by the preaveraged theory and is, again, in contradiction with some of the experimental data). Another alternative, discussed in previous work,[12] is to characterize the behavior at the Θ point by means of the Flory parameter Φ, which combines the viscosity and the radius of gyration in the form

$$[\eta] = \Phi \frac{6^{3/2}\langle s^2\rangle^{3/2}}{M} \qquad (7)$$

where M is the molecular weight of the polymer. The extrapolated results obtained for this parameter are $\Phi = (3.94 \pm 0.02) \times 10^{23}$ for the upper bound limit (very similar to the extrapolated result $\Phi = 4 \times 10^{23}$ reported earlier,[12] obtained with chains of different numbers of units), $\Phi = (3.8 \pm 0.1) \times 10^{23}$ for the lower bound limit, and $\Phi = (3.15 \pm 0.05) \times 10^{23}$ for the trajectories (this latter extrapolation biased again by numerical problems). Experimental data provide $\Phi = (3.4\text{–}4.1) \times 10^{23}$, while the preaveraged theory yields $\Phi = 5.23 \times 10^{23}$. Then, though the scattering shown by experimental data avoids a precise quantitative agreement, it can be concluded that the theoretical approximation clearly overestimates the intrinsic viscosity of ring chains.

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Ellipsometric Study of Binary Mixed Films of Poly(ethylene oxide) and Poly(methyl methacrylate) at the Air/Water Interface

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ABSTRACT: Binary mixtures of poly(ethylene oxide) (PEO) and poly(methyl methacrylate) (PMMA) spread at the air/water interface have been investigated by using ellipsometry and surface pressure measurements. From the surface pressure measurements both polymers were found to be compatible. This result correlates well with the compatibility of the blends of PEO and PMMA in the bulk state. Ellipsometry gave two quantities for the phase difference (Δ) between the parallel and perpendicular components of the reflected light and the azimuth (ψ) of the amplitude ratio for light polarized parallel and normal to the plane of incidence. The value of Δ was much more sensitive to the presence of polymers at the air/water interface as compared to the ψ value. The changes in Δ and δΔ between pure water and the water surface covered with polymers increased with an increase in the amount spread and approached a plateau value around the PMMA surface concentration of 1.7 mg/m^2 in the mixtures, irrespective of the mixed ratio. Their plateau values did not change if the surface concentration was further increased.

Introduction

The application of ellipsometry to polymer films and fatty acid monolayers spread at the air/water interface has recently been attempted to elucidate their interfacial conformation and surface structures.[1-12] Ellipsometry gives two quantities of the phase difference, Δ, and the azimuth, ψ, of the amplitude ratio for light polarized parallel and normal to the plane of incidence. Kawaguchi et al.[9,10] and Sauer et al.[12] especially have studied almost the same samples, and they reported similar results for the polymer concentration dependence of the changes in Δ between pure water and the water surface covered with polymers. From calculations of the thicknesses of the polymer layer spread as a film at the air/water interface it was found that a series of polymers of varying hydrophilicity preferred to dangle into the water phase rather than stick out of the air side, independent of the hydrophilicity and regardless of the difference in the thickness calculation methods.

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