Influence of topological constraints on the statics and dynamics of ring polymers

Scott Brown, Tim Lenczycki, and Grzegorz Szamel
Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523
(Received 13 July 2000; published 16 April 2001)

We report a computer simulation study of the influence of topological constraints on the statics and dynamics of single ring polymers and ring polymers in the melt. We show that single rings have identical static and dynamic scaling behavior regardless of the presence of topological constraints. For rings in the melt we find that the scaling behavior is significantly influenced by the presence of topological constraints.

DOI: 10.1103/PhysRevE.63.052801 PACS number(s): 61.25.Hq, 66.10.−x, 66.90.+r

I. INTRODUCTION

Recently, there have been several computational studies exploring the influence of topological constraints on the structure of ring polymers. It has been found [1–3] that unknotted, unconcatenated ring polymers in the melt are smaller than their linear chain counterparts, with observed radius of gyration scaling exponent ν, $R_g \sim N^{\nu}$, in the range of $\nu=0.4$ to $\nu=0.42$.

This value roughly agrees with scaling arguments [4] based on a Flory-like approach to topological constraints. A more recent study [5] suggests that the *observed* exponents are due to crossover (finite N) effects and that asymptotically (in the $N\rightarrow\infty$ limit) rings behave similar to compact lattice animals with $\nu=1/3$. Obviously, more work is needed to elucidate this issue.

In a different study [6] the size of isolated unknotted rings with no excluded volume was investigated. It was claimed that the scaling exponent shows approach to the self-avoiding random walk (SAW) value, in agreement with an analytical argument [7] that topological constraints lead to the same scaling as excluded volume interactions.

The purpose of this Brief Report is to contrast the influence of topological constraints on the structure and dynamics of isolated ring polymers with that of ring polymers in the melt. The main result is that, whereas topological interactions (i.e., constraints that prevent different bonds from passing through one another; note that these are separate from excluded volume interactions) have only a mild quantitative influence on the structure and dynamics of isolated ring polymers [8], they profoundly affect those of ring polymers in the melt.

In our study we use a modified version of the original bond fluctuation model [9] proposed by Shaffer [10,11]. In this model the topological interaction can be turned on and off by controlling bond crossing. The computational advantage of Shaffer's model is a relatively low crossover chain length for linear chains, $N_c \approx 40$, which allows one to simulate chains with relatively large N/N_c.

II. ISOLATED RING POLYMERS

We use two measures of the average size of our ring polymers: the mean-square radius of gyration R_g^2 and the

TABLE I. Relevant simulation parameters and results for isolated rings: degree of polymerization N; number of polymers in simulation box n_{ring}; number of independent trajectories n_{traj}; size of simulation box L; equilibration time τ_{eq}; run time τ_{run}; mean-square radius of gyration R_g^2; mean-square ring diameter R_e^2; self-diffusion coefficient D; orientational relaxation time τ_{ee}. Time is measured in Monte Carlo time steps (MCS), and distance in units of the lattice constant.

N	n_{ring}	n_{traj}	L	τ_{eq}	τ_{run}	R_g^2	R_e^2	D	τ_{ee}
					Crossing				
10	1	400	40	2×10^4	2×10^4	2.24	7.21	4.6×10^{-3}	1.1×10^2
20	1	200	40	2×10^4	2×10^4	4.86	15.6	2.2×10^{-3}	3.1×10^2
40	1	100	40	8×10^4	8×10^4	10.8	35.0	1.1×10^{-3}	1.6×10^3
100	1	135	50	4×10^5	4×10^5	31.2	101	4.5×10^{-4}	1.0×10^3
300	1	40	60	1×10^6	5×10^6	113	368	1.6×10^{-4}	1.0×10^5
500	1	64	100	4×10^6	2×10^7	204	661	9.1×10^{-5}	3.2×10^5
					Noncrossing				
10	1	400	40	2×10^4	2×10^4	2.27	7.37	4.1×10^{-3}	72
20	1	200	40	2×10^4	2×10^4	4.96	16.1	2.0×10^{-3}	3.9×10^2
40	1	100	40	8×10^4	8×10^4	11.0	35.7	1.0×10^{-3}	2.0×10^3
100	1	135	50	4×10^5	4×10^5	32.1	104	4.2×10^{-4}	1.4×10^4
300	1	40	60	1×10^6	5×10^6	116	379	1.4×10^{-4}	1.6×10^5
500	1	64	100	4×10^6	2×10^7	210	683	8.4×10^{-5}	4.0×10^5

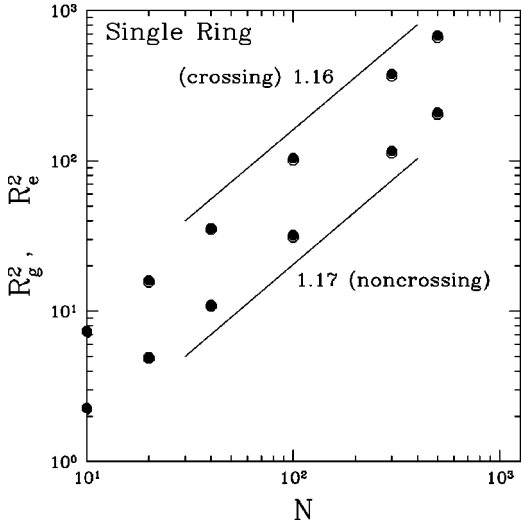

FIG. 1. Mean-square radius of gyration R_g^2 and mean-square diameter vector R_e^2 versus degree of polymerization N for single rings. Open circles: crossing rings; filled circles: noncrossing rings. For the crossing rings the upper solid line shows the fit $R_{g,e}^2 \sim N^{1.16}$. For the noncrossing rings the lower solid line is a fit showing the scaling law $R_{g,e}^2 \sim N^{1.17}$.

mean-square ring diameter R_e^2. R_e is the distance between bead n and bead $n+N/2$ in a ring.

Results and parameters for all simulation runs of single rings are given Table I. Fits for crossing and noncrossing isolated rings (see Fig. 1) yield scaling relationships $R_g^2 \sim N^{1.16}$ and $R_e^2 \sim N^{1.17}$, respectively. Off-lattice simulations by Baumgärtner [12] of a single unknotted ring polymer find the scaling $N^{1.18}$ for both R_e^2 and R_g^2, whereas an on-lattice study [13] finds $R_e^2 \sim N^{1.18}$ and $R_g^2 \sim N^{1.19}$.

Recent simulations by Deutsch [6] of rings with no excluded volume find a scaling relationship for larger rings of

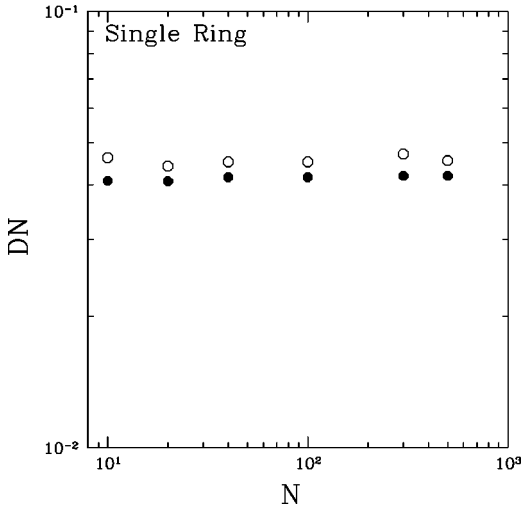

FIG. 2. Center-of-mass self-diffusion coefficient times degree of polymerization DN versus degree of polymerization N for single rings. Open circles: crossing rings; filled circles: noncrossing rings. DN is independent of N indicating the Rouse-like scaling $D \sim N^{-1}$.

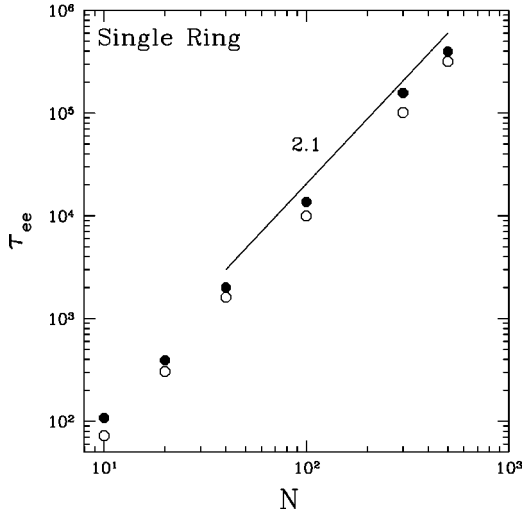

FIG. 3. Orientational relaxation time τ_{ee} versus degree of polymerization N for single rings. Open circles: crossing rings; filled circles: noncrossing rings. The solid line indicates the fit $\tau_{ee} \sim N^{2.1}$.

$R_g^2 \sim N^{1.17}$. It is argued that the topological interaction alone is sufficient to produce SAW scaling for large rings. We see no significant difference in the scaling exponents for our single rings in either the crossing or noncrossing systems; however, noncrossing rings are systematically larger: topological interactions produce an increase of the excluded volume as argued in Ref. [7].

Dynamics is monitored through the center-of-mass mean-square displacement $\langle (\mathbf{R}_{\text{c.m.}}(t) - \mathbf{R}_{\text{c.m.}}(0))^2 \rangle$, and the diameter vector autocorrelation function $C_{ee} = \langle \mathbf{R}_e(t) \cdot \mathbf{R}_e(0) \rangle$. From the mean-square displacement we obtain a center-of-mass self-diffusion coefficient D, and from the decay of the diameter vector autocorrelation function we obtain an orientational relaxation time τ_{ee}.

In Fig. 2 we show self-diffusion data for single rings. DN is roughly independent of N for both crossing and noncrossing simulations, indicating the Rouse-like scaling $D \sim N^{-1}$. Furthermore, we find that both the crossing and noncrossing cases exhibit an identical scaling of $\tau_{ee} \sim N^{2.1}$, see Fig. 3. This is consistent with the previous simulations of isolated rings on the lattice by Skolnick and Kolinski [14] in which they report $\tau_{ee} \sim N^{2.1}$. We find then that the dynamics of isolated rings occurs on similar time scales regardless of the presence of topological constraints in the system.

III. RINGS IN THE MELT

Results and parameters for the melt simulation runs are shown in Table II. For rings in the melt we find that by removing the constraint of nonconcatenation we recover Gaussian statistics. For crossing rings in the melt the radius of gyration scales as $R_g^2 \sim N$ (shown in Fig. 4), whereas for noncrossing rings we find $R_g^2 \sim N^{0.83}$. Thus the topological interactions have quite a significant effect on the average size of rings in the melt.

Shown in Fig. 5 is the center-of-mass pair-correlation function for crossing and noncrossing 100mer rings in the

TABLE II. Relevant simulation parameters and results for rings in the melt ($\phi=0.5$): degree of polymerization N; number of polymers in simulation box n_{ring}; number of independent trajectories n_{traj}; size of simulation box L; equilibration time τ_{eq}; run time τ_{run}; mean-square radius of gyration R_g^2; mean-square ring diameter R_e^2; self-diffusion coefficient D; orientational relaxation time τ_{ee}.

N	n_{ring}	n_{traj}	L	τ_{eq}	τ_{run}	R_g^2	R_e^2	D	τ_{ee}
					Crossing				
10	400	6	20	2.5×10^4	2.5×10^4	2.13	6.74	1.4×10^{-3}	1.8×10^2
20	200	6	20	2.5×10^4	2.5×10^4	4.37	13.6	6.8×10^{-4}	7.5×10^2
40	100	6	20	5×10^4	1×10^5	8.88	27.9	3.3×10^{-4}	2.9×10^3
100	135	6	30	1×10^6	1×10^6	22.5	70.3	1.3×10^{-4}	1.9×10^4
300	45	3	30	5×10^6	1×10^7	68.8	212	4.1×10^{-5}	1.8×10^5
500	64	2	40	6×10^6	2.5×10^7	114	350	2.4×10^{-5}	5.0×10^5
					Noncrossing				
10	400	6	20	2.5×10^4	2.5×10^4	2.1	6.6	1.1×10^{-3}	2.2×10^2
20	200	6	20	5×10^4	5×10^4	4.1	12.8	5.1×10^{-4}	1.0×10^3
40	100	6	20	5×10^4	1×10^5	8.1	24.5	2.2×10^{-4}	4.0×10^3
100	135	6	30	1×10^6	1×10^6	18.7	55.3	7.0×10^{-5}	3.0×10^4
150	90	6	30	2.5×10^6	2.5×10^6	26.8	78.3	3.8×10^{-5}	7.2×10^4
200	160	3	30	5×10^6	5×10^6	34.4	100	2.6×10^{-5}	1.5×10^5
300	45	6	30	1×10^7	1×10^7	48.4	140	1.3×10^{-5}	4.2×10^5
500	64	3	40	1.8×10^7	1×10^8	73.8	210	6.0×10^{-6}	1.5×10^6
800	40	4	40	1.9×10^7	2×10^8	105	297	2.7×10^{-6}	4.9×10^6

melt. The absence of the topological constraints frees the crossing rings to explore more extended conformations. The average result is a more open ring structure which allows ring centers of mass to approach closer to one another, as can be seen in Fig. 5.

For self-diffusion of rings in the melt (Fig. 6) we also find quite different behavior between crossing and noncrossing rings. Noncrossing rings in the melt exhibit an approach to a scaling for the self-diffusion coefficient of $D\sim N^{-1.59}$. For crossing rings we observe a Rouse-like scaling of the self-diffusion coefficient $D\sim N^{-1}$ for all ring sizes simulated. Furthermore, we find that relaxation occurs on different time scales (Fig. 7). The crossing rings follow a scaling of $\tau_{ee}\sim N^{2.0}$, and the noncrossing rings scale with a stronger N dependence $\tau_{ee}\sim N^{2.5}$.

It is clear that the constraint of nonconcatenation has significant consequences for dense many-chain systems of ring polymers. This is in contrast to the single-chain systems,

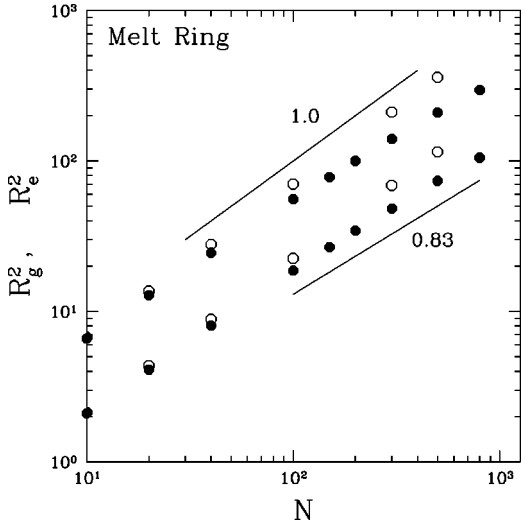

FIG. 4. Mean-square radius of gyration R_g^2 and mean-square diameter vector R_e^2 versus degree of polymerization N for rings in the melt. Open circles: crossing rings; filled circles: noncrossing rings. For the crossing rings the (upper) solid line shows the ideal (Gaussian) scaling fit $R_{g,e}^2\sim N^{1.0}$. For the noncrossing rings the (lower) solid line is a fit showing the collapsed scaling $R_{g,e}^2\sim N^{0.83}$.

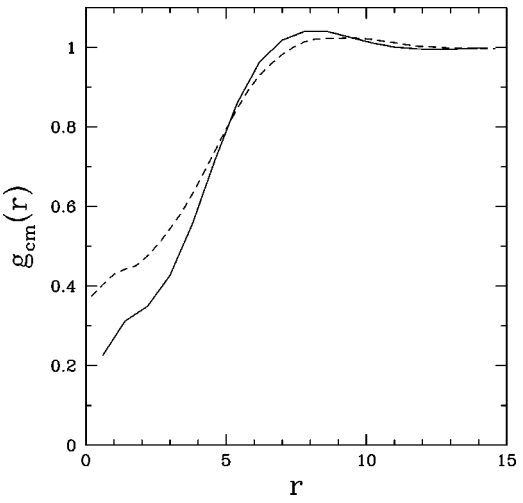

FIG. 5. Center-of-mass pair-correlation function $g_{\text{c.m.}}(r)$ versus distance r for 100mer rings in the melt. Dashed line: crossing 100mer rings; solid line: noncrossing 100mer rings.

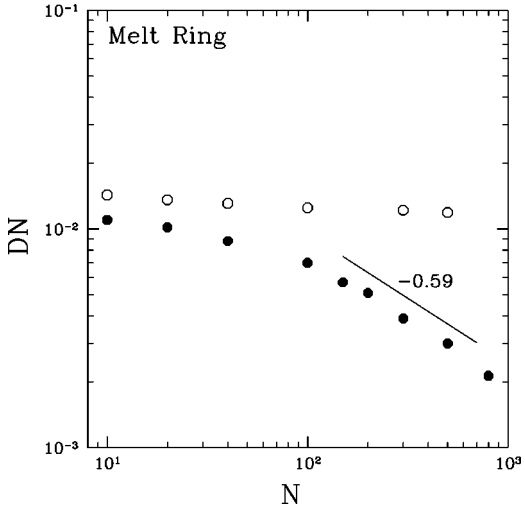

FIG. 6. Center-of-mass self-diffusion coefficient times degree of polymerization DN versus degree of polymerization N for rings in the melt. Open circles: crossing rings; filled circles: noncrossing rings. For the crossing rings DN is independent of N; whereas the noncrossing rings undergo a transition to a scaling $DN \sim N^{-0.59}$.

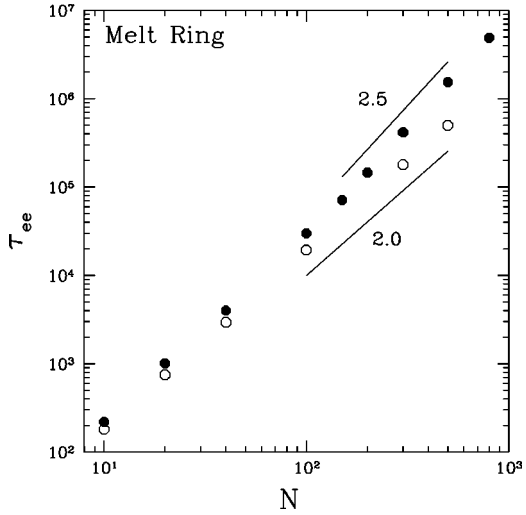

FIG. 7. Orientational relaxation time τ_{ee} versus degree of polymerization N for rings in the melt. Open circles: crossing rings; filled circles: noncrossing rings. The upper solid line indicates the noncrossing fit $\tau_{ee} \sim N^{2.5}$, and the lower solid line indicates the crossing fit $\tau_{ee} \sim N^{2.0}$.

where the constraint of unknottedness was seen to have little effect.

IV. CONCLUSION

In conclusion, we find that for isolated ring polymers the presence or absence of the topological interactions does not seem to affect, *qualitatively*, either static or dynamic properties: scaling exponents do not change. In contrast, topological interactions do matter in the melt state. The absence of topological constraints leads to Gaussian scaling of the ring polymer size with the degree of polymerization $R_g^2 \sim N$, whereas their presence results in much more compact conformations in the melt with $R_g^2 \sim N^{0.83}$ scaling.

As with linear polymers in this model [10], topological interactions influence the melt dynamics more than the statics: crossing rings obey Rouse-like scaling of the self-diffusion coefficient $D \sim N^{-1}$, whereas for the noncrossing rings we get approximately $D \sim N^{-1.59}$. The relaxation times for the crossing and noncrossing rings scale as $\tau_{ee} \sim N^{2.0}$ and $\tau_{ee} \sim N^{2.5}$, respectively.

ACKNOWLEDGMENT

This work was partially supported by NSF Grant No. CHE-9624596.

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