

Structure and dynamics of ring polymers

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We study the equilibrium structure and dynamics of unconcatenated unknotted polymer rings in the melt. In accordance with earlier studies we find that rings in the melt are more compact than linear chains. We show that rings interpenetrate less and, perhaps as a result, diffuse faster than linear chains. Ring diffusion is faster for all ring sizes studied, the largest ring having numbers of monomers approximately ten times greater than the entanglement crossover of linear chains.

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I. INTRODUCTION

The dynamics of polymer melts and concentrated solutions is qualitatively different from that of simple liquids.¹ A unique feature of polymeric liquids is the strong dependence of transport coefficients on the degree of polymerization N . For linear polymers (the most extensively studied architecture) one finds two regimes. For chains shorter than a crossover chain length N_c the self-diffusion coefficient D scales as $D \sim N^{-1}$, whereas for longer chains the length dependence is much stronger and the self-diffusion coefficient scales as $D \sim N^{-2}$. The transition between these two regimes is attributed to the onset of entanglement effects, loosely interpreted as topological constraints on the motion of polymer molecules that originate from chain uncrossability.

A basis for the present understanding of the dynamics of linear polymers has been laid down by de Gennes,² and Doi and Edwards.³ In their theory the topological restrictions experienced by a given (probe) chain are replaced by an average constraint, a tube. The probe chain is assumed to move like a snake along the tube (hence the name reptation theory). This postulate leads to $D \sim N^{-2}$ scaling of the self-diffusion coefficient and to a number of other predictions, e.g., tracer diffusion, shear viscosity, etc. With some caveats, most of these predictions agree with experimental data.¹

A number of other theoretical approaches to the dynamics of entangled linear polymers have been proposed.⁴⁻¹⁰ Although most of these competing approaches are based on postulates that are very different from the tube assumption, at least some of them lead to results that are similar or even identical to the results of the reptation theory. Hence, these approaches also agree with experimental data.

It is, therefore, of great interest to study other polymer architecture, such as stars or rings. For these nonlinear architectures, predictions of different theories are, typically, very different. Thus such studies offer a chance to test the validity of different theoretical approaches. Indeed, one of the strongest arguments for the reptation theory comes from the fact that it predicts the dramatic slowing of star polymer relaxation relative to linear polymers,¹¹ which seems to have been seen experimentally.¹²

In this article we present a computer simulation study of the equilibrium structure and dynamics of unconcatenated,

unknotted polymer rings in the melt. The original motivation for this work was the fact that polymer rings (having no chain ends) cannot reptate in the original sense of the reptation theory. Slithering motions are possible only when rings adopt special “nonramified”¹³ configurations. Since these are highly unlikely the diffusion of ring polymers in ring matrices was argued to be exponentially slow.^{13,14} The main result of this study is that at least up to ring sizes about ten times larger than the entanglement crossover of linear chains ring diffusion is faster than diffusion of linear chains.

The paper is organized as follows. In Sec. II we present the model used in the computer simulation. In Secs. III and IV we present results pertaining to the ring equilibrium structure and ring dynamics, respectively. We conclude in Sec. V with a brief discussion of the results.

II. SIMULATION MODEL

We use a version of the bond fluctuation model¹⁵ proposed and investigated by Shaffer.¹⁶ The polymer beads (monomers) are placed on a simple cubic lattice. Only one bead may occupy a given lattice site at any given time. Three bond lengths are allowed: 1; $\sqrt{2}$; and $\sqrt{3}$ (we measure all distances in units of the lattice constant). Bond crossing is forbidden. The beads are moved on the lattice by attempting to displace a randomly selected monomer to one of its nearest-neighbor lattice sites. The move is accepted if it does not violate excluded volume constraints, no-bond-crossing constraints, or allowed bond lengths, and rejected if it does. $N \times n_{\text{pol}}$ of these attempted moves constitute one Monte Carlo time step (MCS) that is hereafter used as a time unit (N is the number of beads in a chain and n_{pol} is the number of polymers in the system).

A bead density of $\phi=0.5$ is used. A detailed analysis¹⁶⁻¹⁸ of the equilibrium structure and dynamics of linear chains has shown this density to correspond to melt density. In particular it has been found that at $\phi=0.5$ (a) the excluded volume interaction is screened; (b) there is a transition to entangled dynamics with the crossover chain length $N_c \approx 40$; and (c) the Rouse mode relaxation times τ_p depend on the mode index as $\tau_p \sim p^{-3}$. All these findings are qualitatively consistent with molecular dynamics simulations.¹⁹

TABLE I. Parameters and results of the simulation: degree of polymerization, N ; number of polymers in the simulation box, n_{pol} ; length of the cubic simulation box, L ; equilibration time, τ_{eq} ; simulation run time, τ_{run} ; radius of gyration, $\langle R_g^2 \rangle$; ring diameter, $\langle R_e^2 \rangle$; self-diffusion constant, D ; orientational relaxation time, τ_{ee} . All times are measured in Monte Carlo time steps (MCS), and all distances are in units of the lattice constant.

N	n_{pol}	L	τ_{eq}	τ_{run}	$\langle R_g^2 \rangle$	$\langle R_e^2 \rangle$	D	τ_{ee}
20	200	20	5×10^4	5×10^4	4.1	12.8	5.0×10^{-4}	1.0×10^3
100	40	20	1×10^6	1×10^6	18.7	53.8	7.1×10^{-5}	3.4×10^4
300	45	30	1×10^7	1×10^7	48.4	140.7	1.3×10^{-5}	3.6×10^5
500	64	40	1.8×10^7	6×10^7	73.8	212.4	5.8×10^{-6}	1.6×10^6

The most difficult problem in polymer ring simulations (and experiments) is avoiding self-knots and concatenations. To avoid them we generate the initial configurations by putting the rings on the lattice as highly compact, thin loops that are isolated from one another. To equilibrate these highly ordered initial configurations we run the simulation for more than 20 (smaller rings) and about 10 (500mers) orientational relaxation times before collecting the data (note that this requires some guessing as the relaxation time is estimated after data analysis).

Table I lists the main ring polymer simulation parameters and some of the results. For smaller rings we have performed six independent runs at each chain length. For 500mers we have performed two runs. We have also performed some simulations of linear polymer chains. The results from these runs are compared to the ring simulation results in the figures. Note however that most of the data points for linear chains are taken from Shaffer's papers.^{16,17}

III. EQUILIBRIUM STRUCTURE

To characterize the equilibrium structure of ring polymers we present results for the following quantities: the mean-square radius of gyration, $\langle R_g^2 \rangle$; the intra- and inter-chain monomer pair-correlation functions, $g_{\text{intra}}(r)$ and $g_{\text{inter}}(r)$; and finally, the polymer center-of-mass pair-correlation function, $g_{\text{cm}}(r)$.

For a given size N rings are smaller than linear chains (see Fig. 1). More precisely, the scaling exponent ν defined

through the relation $R_g \sim N^\nu$ has a value smaller than the linear chain value of $1/2$, $\nu=0.43$. This agrees with the theoretical prediction of Cates and Deutsch²⁰ and with the ring simulation of Müller, Wittmer, and Cates.²¹

Next, it can be seen from Fig. 2 that the ‘‘correlation hole’’ for rings is deeper and wider than that for linear chains. Furthermore, for rings the nearest neighbor of a given monomer belongs with greater probability to the same ring as that monomer, i.e., $g_{\text{intra}}(1) > g_{\text{inter}}(1)$ for rings, whereas for linear chains the opposite is true.

Finally, from a plot of the polymer center-of-mass pair-correlation function, $g_{\text{cm}}(r)$, we see that there is a smaller probability of finding neighboring rings separated by a distance comparable to R_g than there is for linear chains (see Fig. 3).

The main conclusion that we can draw from the investigation of the equilibrium structure of rings in the melt is that a given ring, because it is smaller and more compact than a linear chain of the same number of segments, excludes monomers from other rings more effectively. In other words, a ring has a harder ‘‘core’’ than a linear chain. As a result there is less intermolecular penetration in the melt of rings than in the melt of linear chains.

IV. DYNAMICS

We monitored several time correlation functions (e.g., the mean-square center of mass displacement and the ‘‘diameter vector’’ correlation function). Here we present only

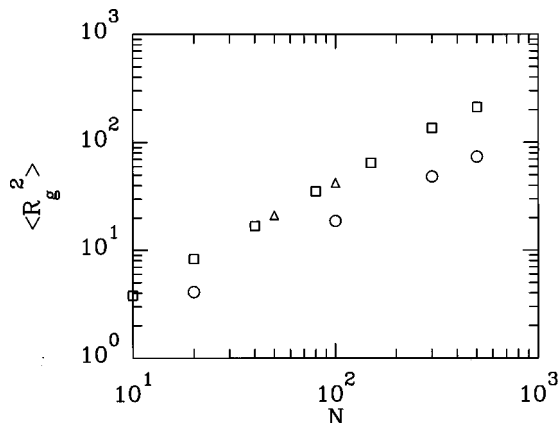


FIG. 1. Radius of gyration R_g vs polymer size N for ring and linear polymers. Circles: rings; triangles: linear chains, this work; squares: linear chains, data from Refs. 16 and 17. The observed scaling is $R_g \sim N^{0.43}$ for rings and $R_g \sim N^{0.5}$ for linear chains.

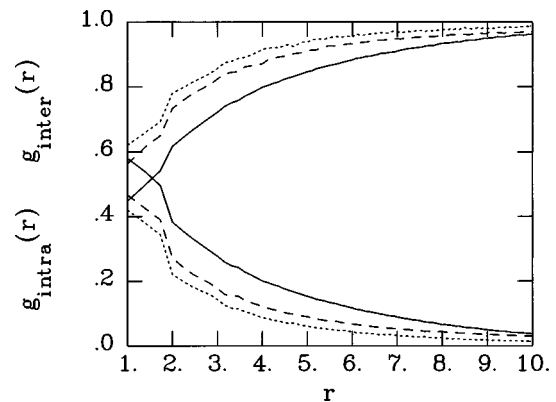


FIG. 2. Monomer pair-correlation functions $g_{\text{intra}}(r)$ and $g_{\text{inter}}(r)$ vs separation distance r for ring and linear polymers. Solid lines: 300mer rings; dashed lines: 300mer linear chains; dotted lines: 100mer linear chains. Note that 300mer rings and 100mer linear chains have comparable radii of gyration.

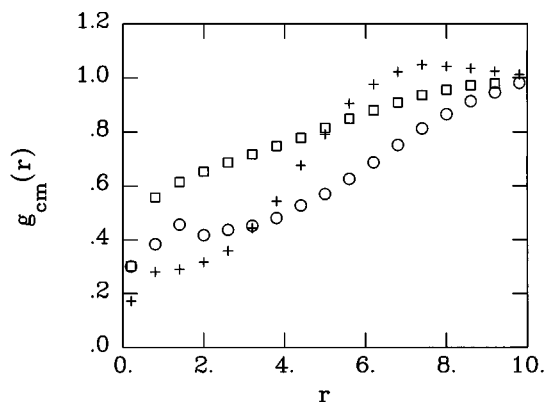


FIG. 3. Center-of-mass pair-correlation function $g_{cm}(r)$ plotted vs r for ring and linear polymers. Circles: 300mer rings; crosses: 100mer rings; squares: 100mer linear chains. Note that 300mer rings and 100mer linear chains have comparable radii of gyration.

data for the quantities that we have obtained from these correlation functions: center-of-mass self-diffusion coefficient and orientational relaxation time.

We calculate the center-of-mass self-diffusion coefficient from the long time asymptotics of the mean-square center-of-mass displacement. The results are presented in Fig. 4. The linear chain data show a transition between Rouse-like scaling $D \sim N^{-1}$ and entangled scaling $D \sim N^{-2}$ with the crossover chain length $N_c \approx 40$. The ring data do not show any transition. We see faster ring diffusion for all ring sizes investigated. For smaller rings (i.e., for $N \leq N_c$) this result agrees with the computer simulation of Müller *et al.* The fact that faster ring diffusion continues for sizes as large as ten crossover chain lengths for linear chains is the main result of the present study. Finally, we note that the power law fit of $N \geq 100$ data results in $D \sim N^{-1.55}$ scaling of the ring center-of-mass self-diffusion coefficient.

We obtain the orientational relaxation time from the “diameter vector” correlation function. The “diameter vector,” $\mathbf{R}_e(t)$, is a ring analog of the end-to-end vector used to define the single chain relaxation time for linear chains. We define $\mathbf{R}_e(t)$ as a vector joining two monomers on the same

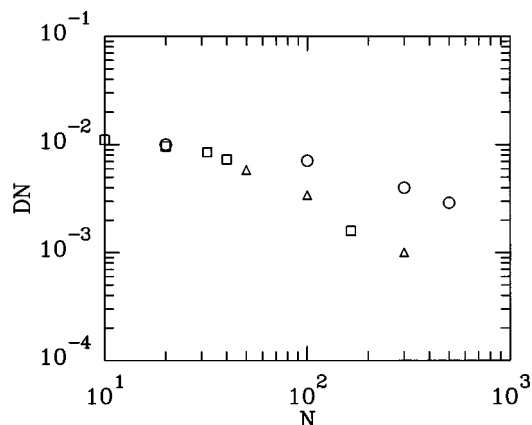


FIG. 4. Self-diffusion coefficient times degree of polymerization, DN , vs polymer size N for ring and linear polymers. Circles: rings; triangles: linear chains, this work; squares: linear chains, data from Refs. 16 and 17. The observed scaling is $DN \sim N^{-0.55}$ for rings and $DN \sim N^{-1}$ for linear chains.

chain that are separated by $N/2$ monomers. Next, the “diameter vector” correlation function is defined as $\langle \mathbf{R}_e(t) \mathbf{R}_e(0) \rangle$. For long times this correlation function decays exponentially. We define the asymptotic decay time as the orientational relaxation time, τ_{ee} .

The orientational relaxation time data are presented in Table I. Again, there is no hint of any transition to a different, slower dynamics. The power law fit of $N \geq 100$ data results in $\tau_{ee} \sim N^{2.4}$ scaling of the orientational relaxation time, in reasonable agreement with scaling found by Müller *et al.* for smaller rings (i.e., for $N \leq N_c$). This should be contrasted with $N^{3.4}$ scaling expected for entangled dynamics of linear chains.

V. DISCUSSION

The main result of this paper is that faster diffusion of rings (compared to linear chains of the same number of monomers) persists well beyond the entanglement crossover of linear chains: We do not see any hint of a transition to slower diffusion for $N=500$ whereas the entanglement crossover chain length for linear chains is $N_c \approx 40$.

In our opinion faster diffusion of rings in the melt originates from the more compact conformations of rings compared to those of linear chains. In particular we find that, due to the topological constraints of unknottedness and nonconcatenation, a given ring polymer is smaller and denser and therefore excludes monomers from other chains more effectively. This results in smaller interpenetration between different rings. We speculate that less intermolecular penetration leads to fewer entanglements (whatever their identity) and faster dynamics.

It is of great interest to understand whether observed faster ring diffusion constitutes a transient, finite N dependence or whether it is a truly asymptotic, large N result. This question is of course difficult to answer on the basis of the simulations alone. We may only note here that if there is a transition to a slower (entangled) dynamics then the crossover size for the bond fluctuation model of rings studied in this work is at least ten times larger than that for linear chains.

The final open question is the relation of the present study to the experimental results. Invariably, experiments find that the dynamics of rings in the melt is similar to that of linear chains. For example, McKenna *et al.*²² found that the molecular weight dependence of the viscosity of ring melts shows a similar transition to that of linear chains. Furthermore, they estimated that the crossover molecular weight of rings is just slightly higher than that of linear chains. The origin of this discrepancy between the simulations and experiments is unclear. We hope that the present work will stimulate more experimental studies of rings in the melt.

ACKNOWLEDGMENTS

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