

Size and Dynamics of Ring Polymers under Different Topological Constraints

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 Electronic Supplementary Information

Abstract The impact of ring polymer length N and the influence of interchain and intrachain interactions on the size and dynamic behaviors of ring polymers, including the structural relaxation time τ_R and self-diffusion coefficient D , remain poorly understood at present due to a lack of systematic studies with relatively large N values. This work addressed this issue by applying dynamic Monte Carlo simulations with independently tuned interchain and intrachain interactions to investigate the size and dynamics of the ring melts with chain lengths over a wide range of $0.2N_e \leq N \leq 80N_e$ (N_e is the entanglement length of corresponding linear chains) under different topological constraints, including all-crossing and inter-crossing systems. We found that it was inappropriate to treat the unknotting constraint free energy of the ring chains in the melts as the free energy contributed by the excluded volume interactions of polymers in a good solvent. Scaling exponents of 2.5 and 1.5 reflecting the N -dependence of τ_R were obtained for long ring chains in non-crossing and intra-crossing systems, respectively, suggesting that the ring chains behaved as individual clusters and exhibited Zimm-like dynamics in intra-crossing systems. A single scaling exponent of -2 reflecting the N -dependence of D was obtained for ring chains in non-crossing and intra-crossing systems, indicating that the intrachain constraints affected only the value of D , and had little influence on the scaling relationship between D and N . Furthermore, the extended Stokes-Einstein relation broke down for the ring chains in the non-crossing and intra-crossing systems because the structural relaxation and translational diffusion were decoupled for the short ring systems, while both the translational diffusion and rotational relaxations, as well as diffusion at short and long time scales, were decoupled for long ring systems.

Keywords Ring polymer; Topological constraint; Extended Stokes-Einstein relation; Monte Carlo simulation

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INTRODUCTION

The lack of chain ends in ring polymers results in ring polymer melts and solutions or materials containing ring polymers that exhibit a series of unique properties.^[1] For example, the closed-loop structures of ring polymer chains that do not entangle like linear and branched polymers produce anomalous power law dependences on the polymer length for the mean-squared radius of gyration $\langle R_g^2 \rangle$ ^[2–9] and various dynamic behaviors.^[10,11] Moreover, advancements in synthesis and characterization techniques increasingly enable the design and fabrication of highly purified ring polymer melts with tailored molecular weights.^[12] Meanwhile, ring polymers play a pivotal role in biological processes.^[13] In addition, small concentrations of ring polymers in linear polymer melts have been demonstrated to

offer good potential for examining the topological effects and fundamental dynamic behaviors of polymer systems.^[14] As a result, ring polymers have been studied extensively experimentally,^[6,14–18] theoretically,^[2,3,7,8,19–22] and *via* computer simulations.^[3–5,9,10,23–29] However, the mechanisms responsible for the unique properties of ring polymer systems are still not well understood.^[30–32]

As early as 1986, the free energy F of ring chains in melts was defined as follows:^[2]

$$\frac{F}{k_B T} \approx \frac{R^3}{N} + \frac{N}{R^2} \quad (1)$$

where k_B denotes the Boltzmann constant, T is temperature, and R and N are the radius and length of the polymer ring, respectively. Here, the first term on the right side represents the interchain constraint contribution resulting from interchain topological interactions, and the second term on the right is the intrachain constraint contribution resulting from intrachain topological interactions, and represents the free energy required to force a Gaussian chain polymer into a region of size R . The N -dependence of R can be obtained from Eq. (1) when

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$dF/dR=0$, yielding a power law relationship $R \propto N^\nu$ for which the scaling exponent $\nu = 2/5$ was established. Subsequently, Suzuki *et al.*^[3] and Sakaue^[7,8] revised the above theoretical framework for relatively large values of N , and obtained a value of $\nu = 1/3$, which was supported by the results of computer simulations.^[3–5] Furthermore, Lang *et al.*^[19] evaluated the free energy of an isolated ring in a melt of linear chains to deduce the following expression for ring chains with moderate lengths in melts:

$$\frac{F}{k_B T} \approx \frac{N}{R^2} + R^2 + \frac{N^2}{R^3} \quad (2)$$

where the three terms from left to right on the right side represent the intrachain constraint contribution presented with respect to Eq. (1), the interchain constraint contribution, and the unknotting constraint contribution, respectively. These researchers applied the standard minimization process to Eq. (2), and obtained a value of $\nu = 2/5$ for ring chains with moderate lengths in melts. For simplicity, the contribution of the unknotting constraint was treated as an excluded volume effect for a polymer in a good solvent. The analogy between the unknotting constraint effect and excluded volume effect was demonstrated earlier by Moore and Grosberg^[33] as valid for a single ring. Nonetheless, for ring chains in melts, the validity of the analogy warranted further investigation. Furthermore, they predicted that $\nu = 3/8$ for large ring chains ($N > 1000$) and even $\nu = 4/9$ for ring chains with $N \gg 1000$, i.e., where the value of ν initially increased first and then decreased with increasing N .^[19]

The structural relaxation time, or rotational correlation time τ_R , of ring chains in melts have also been systematically investigated. Based on the lattice tree model,^[34] Rubinstein *et al.*,^[34] Cates and Deutsch,^[2] and Nechaev *et al.*^[35] found that the only difference between the configurations of a ring chain and a linear chain in a fixed network is in the geometry of the contours, and this yielded a consistent power law N -dependence of τ_R as $\tau_R \propto N^3$ with a scaling exponent $\mu_R=3$ for both systems. However, Obukhov *et al.*^[36] obtained $\mu_R=2.5$ theoretically. Subsequently, Rubinstein *et al.*^[37] obtained $\mu_R=2.5$ theoretically as well. In addition, the results of molecular dynamics (MD) studies obtained by Halverson *et al.*^[10] and Tsalikis *et al.*^[28,38] predicted a value of $\mu_R=2$. Nonetheless, the simulation results of Halverson *et al.*^[10] included only 3 data points for values of N greater than $10N_e$, where N_e is the entanglement length of the linear polymer system, while those of Tsalikis *et al.*^[28,38] included only 2 data points in this scale regime. Therefore, obtaining a better understanding of the scaling relation between τ_R and N for ring polymers requires systematic studies involving longer ring chains.

The diffusion behavior of ring polymers in melts represents another very important issue, and several different physical models have been proposed. However, the different assumptions applied for building and implementing these models lead to various scaling relationships reflecting the N -dependence of the self-diffusion coefficient D . Theoretically, Cates and Deutsch^[2] established the relationship $D \propto N^{-2}$ with a scaling exponent of $\mu_D=-2$ based on the lattice tree model, Grosberg *et al.*^[39] obtained $\mu_D=-1.9$ based on an annealed tree model, and Rubinstein *et al.*^[22] obtained $\mu_D=-5/3$ based on fractal loopy globules (FLGs) formed from topological constraints acting on ring polymers. Experimentally, Gooßen

et al.^[18] obtained $D \propto N^{-2}$ for N approaching $10N_e$. Based on computer simulations, Tsalikis *et al.*^[28,38] demonstrated that μ_D gradually decreases from -1.2 to -2 as N increases from $0.2N_e$ to $10N_e$. However, Halverson *et al.*^[10] obtained the relationship $D \propto N^{-5/3}$ for N values up to $57N_e$. Accordingly, the N -dependencies of D obtained from theories, experiments, and computer simulations differ considerably. This is particularly problematic for the results of simulations owing to their reliance on the use of different chain models and different means by which the crucial parameter of ring topology is controlled. Therefore, a thorough investigation with well-defined ring topologies under different chain length regimes is crucial for clarifying the scaling relation between D and N for ring polymers.

The effects of ring topology are particularly prominent when evaluating the relationship between the product $D\tau_R$ and N for ring polymers in melts. For example, Halverson *et al.*^[10] attributed decoupling between the structural relaxation and the translational diffusion of ring polymers in melts to ring-ring threadings. Lee and Jung^[30] applied Monte Carlo (MC) simulations to ring polymer melts with a fixed chain length and demonstrated that the value of $D\tau_R$ decreases as the probability for which two neighboring rings reside in a threading configuration increases. This behavior was argued to be evidence for the breakdown of the Stokes-Einstein (SE) relation. In a recent study,^[40] we obtained the relationship $D\tau_R \propto N$ for a short tracer ring in linear chain melts, and the relationship was denoted as the extended SE relation. However, we note that the influences of interchain and intrachain interactions on this extended SE relation have never been investigated directly for ring chains in melts.

The present work addresses the above-discussed issues by investigating the size and dynamics of ring polymer in melts by means of dynamic MC simulations with the bond fluctuation model, which provides superior computational efficiency relative to bead-spring MD simulations.^[41,42] The applied method enables interchain and intrachain interactions to be tuned independently by controlling topological interactions via the manipulation of bond crossings. Accordingly, we investigate the impacts of interchain and intrachain interactions on τ_R and D in ring chain melts with chain lengths over a wide range of $0.2N_e \leq N \leq 80N_e$. Moreover, we elucidate the molecular mechanisms responsible for the breakdown of the extended SE relation for ring chain systems. The remainder of this paper is organized as follows. The following section presents the applied simulation methodology. In the Results and Discussion, the simulation results were discussed for four aspects, followed by the overall conclusions that were drawn from these results, which are presented in the conclusions.

SIMULATION METHODOLOGY

The simulated systems were composed of N_R ring polymer chains, where each chain consisted of N monomers ($6 \leq N \leq 2400$) placed at random on a simple cubic lattice. The lattice-based polymer chain system was simulated in a cubic box of dimension L_{box} with periodic boundary conditions. Finite system size effect was avoided by setting $L_{\text{box}} > 3\langle R_g^2 \rangle^{1/2}$ for the respective ring polymer chains. Some results obtained for two

ring polymer systems with different L_{box} values greater than $3\langle R_g^2 \rangle^{1/2}$ were found to be in close agreement. The value of L_{box} was further set to maintain the total fractional occupancy of the simulation box at a monomer density of $\rho=0.5$, which ensured that the simulation results pertained to bulk systems.^[42–44]

The lattice-based MC simulation reproduced polymer system dynamics from the application of local movements to only single monomers and consisted of no non-physical and non-local movements (e.g., reptation, crankshaft rotation, wedge flipping). Therefore, the MC simulation time is mapped directly onto a physical time scale.^[44–46] An individual monomer in a lattice system is selected at random, and an attempt is made to move the monomer to one of its six nearest neighbors. An attempted move is accepted if it does not violate the following three constraints: (1) excluded volume constraint, which is implemented by allowing only a single monomer to occupy one lattice site simultaneously; (2) chain connectivity constraint, which is enforced by restricting the length of the bond connecting two neighboring monomers to the set of values $\{1, \sqrt{2}, \sqrt{3}\}$; (3) chain uncrossability constraint, which is maintained by forbidding the mid-points of the bonds to intersect. All lengths are reported herein as dimensionless values, given as a product of the lattice spacing. The simulation process involves attempting to move each monomer in each polymer at each step of the simulation. Therefore, a single MC step consists of $N_R \times N$ attempted monomer movements. The number of Monte Carlo steps were regarded as time in this study.

Self-knots and concatenations between ring polymer chains were avoided by arranging all initial ring polymer chain configurations by double folding, and then placing the rings on the lattice as highly compact thin loops that are isolated from one another. In addition, the applied simulation scheme enables chain uncrossability to be arbitrarily controlled by turning the chain uncrossability constraint on or off for all movements, or selectively for the intrachain or interchain movements only. This yields the four systems shown in Fig. 1, including (a) a non-crossing system (i.e., a real system), where constraint (3) always remains in force, (b) an all-crossing system, where constraint (3) is never applied (i.e., the chains are allowed to cross through each other freely), (c) an inter-crossing system, where constraint (3) is always applied for the intrachain movements, but is never applied for the interchain movements, and (d) the intra-crossing system, where constraint (3) is always applied for interchain movements, but is never applied for intrachain movements.

It was assumed that τ_R can be approximately defined according to the nominal structural relaxation time t_{eq} required for the polymer system to fully equilibrate, which was evaluated according to the following autocorrelation function $C_{\text{dd}}(t)$ of the diametrical vector $\mathbf{d}(t)$ at time t and $\mathbf{d}(0)$ at $t=0$.

$$C_{\text{dd}}(t) = \frac{\langle \mathbf{d}(t) \cdot \mathbf{d}(0) \rangle}{\langle \mathbf{d}^2(0) \rangle} \quad (3)$$

where $\mathbf{d}(t) = \mathbf{R}_{i+N/2}(t) - \mathbf{R}_i(t)$, and is calculated for each monomer i ($1 \leq i \leq N/2$) to $i + N/2$, and $\langle \cdot \rangle$ represents the ensemble average over all available conformations of ring polymer chains. Normally, the rotational correlation time is the time when C_{dd} decreases to less than or equal to e^{-1} . However, ring polymer

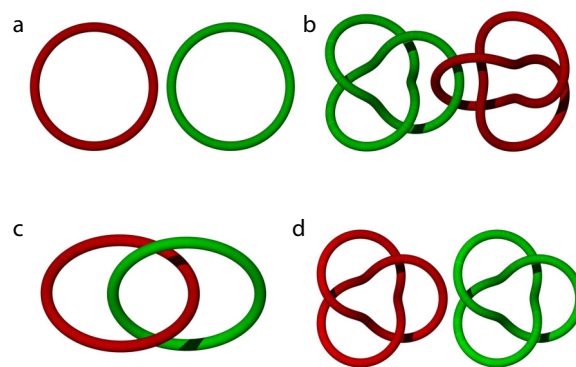


Fig. 1 Schematics illustrating the ring polymer chain systems employed in the present study: (a) non-crossing system; (b) all-crossing system; (c) inter-crossing system; (d) intra-crossing system.

chains, in particular, long ring polymer chains, do not exhibit a C_{dd} decay that satisfies this exponential relaxation (see Fig. S1 in the electronic supplementary information, ESI). Therefore, τ_R was computed by numerically integrating $C_{\text{dd}}(t)$ from zero to infinity as follows:

$$\tau_R = \int_0^\infty C_{\text{dd}}(t) dt \quad (4)$$

To ensure that the ring polymer chains were distributed evenly in space, all simulations actually employed a longer equilibration time of $t_{\text{eq}} \geq 5\tau_R$. After system equilibration, simulations were conducted for a time $t_{\text{run}} \geq 5\tau_R$, during which pertinent data was collected. All data reported herein were averages obtained over 4 independent simulations. The mean-squared bond length $\langle b^2 \rangle \approx 2.04$, the average characteristic ratio $C_\infty \approx 1.17$, and the entanglement length $N_e \approx 30$ were obtained for the corresponding linear chain by the primitive path analysis.^[44,46] The applied simulation parameters and main results are listed in Tables S1 and S2 in ESI, respectively. The physical quantities monitored for characterizing the dynamic properties of the ring polymers are given in detail in the following discussion.

The mean-square displacement (MSD) $g_3(t)$ was calculated for the center-of-mass $\mathbf{R}_{\text{cm}}$ of the ring polymer chains as follows:

$$g_3(t) = \langle |\mathbf{R}_{\text{cm}}(t) - \mathbf{R}_{\text{cm}}(0)|^2 \rangle \quad (5)$$

Therefore, the corresponding value of D can be obtained from $g_3(t)$ using the Einstein formula as follows:

$$D = \lim_{t \rightarrow \infty} \frac{g_3(t)}{6t} \quad (6)$$

Despite the adoption of a simulation runtime of $t_{\text{run}} \geq 5t_{\text{eq}}$, the non-crossing and intra-crossing systems with the largest values of N ($1000 \leq N \leq 2400$) did not reach the fully diffusive regime (see Fig. S2 in ESI). Therefore, the extrapolation method proposed by Yang *et al.*^[47] was employed to calculate D for the above systems. Additional details regarding the simulations are given in ESI (Figs. S3 and S4 in ESI). Based on D , the translational diffusion time τ_D can be obtained over a long time scale as follows:^[10]

$$\tau_D = \frac{\langle R_g^2 \rangle}{6D} \quad (7)$$

However, the longer ring polymer chains underwent sub-

stantial internal rearrangements much faster than their rate of translational diffusion relative to their size. Thus, we also calculate a new translational time τ_{D1} based on the translational motion over a shorter time scale as follows:

$$g_3(\tau_{D1}) = \langle R_g^2 \rangle \quad (8)$$

where τ_{D1} is the time t when $g_3(t) = \langle R_g^2 \rangle$ and may differ somewhat from τ_D , and in this study $\langle R_g^2 \rangle$ is the mean-square radius of gyration of ring polymer chains.

RESULTS AND DISCUSSION

Mean-squared Radius of Gyration

We first analyze the N -dependence of $\langle R_g^2 \rangle$, for ring polymers in the all-crossing and inter-crossing systems, and thereby obtain the value of ν by linear fitting to $\langle R_g^2 \rangle$ with respect to N versus N on a log-log scale in Fig. 2(a). The results indicate that $\nu=0.5$ for ring polymers in the all-crossing systems, which is consistent with the results of Brown *et al.*^[45] while $\nu=0.53$ for the inter-crossing systems. However, the free energy for ring chains in inter-crossing systems can be written as:

$$\frac{F}{k_B T} \approx \frac{R^2}{N} + \frac{N^2}{R^3} \quad (9)$$

where R^2/N represents the entropic contribution to the free energy^[37] and N^2/R^3 is the contribution of intrachain interactions, which Lang *et al.*^[19] treated as the contribution of an excluded volume effect for a polymer in a good solvent. Then we obtained $\nu=0.6$, which was larger than the simulation results shown in Fig. 2(a). Moreover, we analyzed the $\langle R_g^2 \rangle/N$ versus N on a log-log scale results obtained for tracer rings in a linear melt matrix, where the length of the linear chains in the melt was 100. Here, the free energy of the tracer ring consists of the contribution from the elasticity of the ring and the unknotted topological contribution, which is similar to the case of ring chains in inter-crossing systems. We further note that the value of ν obtained for tracer rings is also less than 0.6. These results suggest the intrachain interactions of ring polymers in melts are weaker than the excluded volume interactions of linear chains in a good solvent.^[7,8,19,48,49] Therefore, the standard simplification of treating them as equivalent can lead to inaccurate results.

We also analyzed the N -dependence of $\langle R_g^2 \rangle$ for ring polymers in non-crossing and intra-crossing systems, and the plots of $\langle R_g^2 \rangle/N$ versus N on a log-log scale are presented in Fig. 2(b). Similar to the effects of intrachain interactions observed in Fig. 2(a), the results in Fig. 2(b) demonstrated that interchain interactions will also affect both $\langle R_g^2 \rangle$ and ν . We first noted that the value of ν obtained for short rings ($N < N_e \approx 30$) in the non-crossing and intra-crossing systems agreed well with the value obtained for ideal chains (*i.e.*, $\nu=0.5$). Accordingly, we can conclude that topological effects are not obvious for short ring chains, as has been discussed previously. However, ν is observed to decrease with increasing N , where $\nu=0.4$ for ring polymers with medium lengths in non-crossing systems, which agrees well with the theoretical results of Cates and Deutsch^[2] and those of Lang *et al.*^[19] A value of $\nu=0.375$ was then observed at larger N , which was consistent with the theoretical results obtained by Lang *et al.*^[19] for the

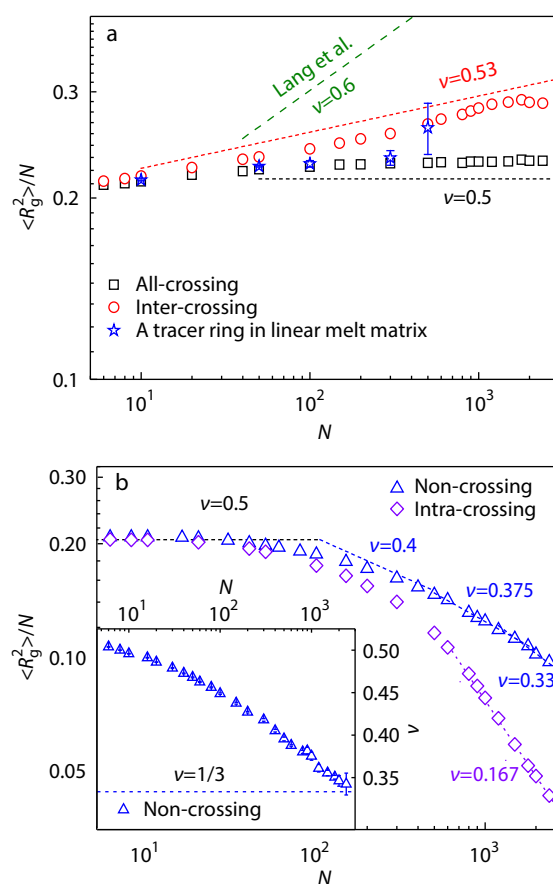


Fig. 2 Plots of the mean-squared radius of gyration ($\langle R_g^2 \rangle$) divided by N versus N (a) for all-crossing systems, inter-crossing systems, and tracer rings in a melt of linear chains, (b) for non-crossing systems and intra-crossing systems, where the inset of (b) shows the ν versus N for ring chains in non-crossing systems.

long rings. Finally, $\nu=0.33$ (*i.e.*, $\nu \approx 1/3$) was obtained for the very long ring chains (*i.e.*, $N > 1000$). The non-monotonic behavior of ν predicted by Lang *et al.*^[19] was not observed in our simulations; however, our results agreed with previously reported theoretical and simulation results.^[3–5,7,8] The decrease in ν is shown in the inset of Fig. 2(b) more clearly. Similarly, ν decreased rapidly with increasing N for the ring polymers in the intra-crossing systems, and decreased to a very low value of 0.167 (*i.e.*, $\nu \approx 1/6$) at relatively large values of N because of the rapid increase of topological interactions between chains with increasing N .

To understand the above viewpoints, we calculated the monomer density $\rho(r)$ as a function of the distance r from the center-of-mass of the ring to each monomer for ring polymers with $N=1000$ and $N=2000$ in the four different topological systems, and the results are presented in Fig. 3. The results indicate the following. (1) A value of $\rho(0) \approx 0.25$ is obtained for ring polymers in non-crossing systems, and $\rho(0)$ is independent of N for the large ring systems considered, the threshold of N was about 800, as shown in Fig. S5 in ESI. These results indicate that each ring polymer in the melt has a core region, which impedes penetration by neighboring ring polymers. These conclusions agree with the results of Suzuki *et al.*^[3] and Halverson *et al.*^[4] (2) Values of $\rho(0) \approx 0.4$ and

$\rho(0) \approx 0.5$ are respectively obtained for ring polymers in the intra-crossing systems with $N=1000$ and $N=2000$. Here, the value obtained for the $N=2000$ system approaches the averaged total monomer density of the system, and the values are distinctly larger than that of the non-crossing systems, which explains why the size of the ring polymers in the intra-crossing systems was much smaller than that in the non-crossing systems. These results indicate that ring polymers are even less likely to be penetrated by neighboring rings in intra-crossing systems than in non-crossing systems. (3) For the case where ring polymers can cross each other in inter-crossing (with intrachain topological constraints) and all-crossing (without intrachain topological constraints) systems, the values of $\rho(r)$ are close, and $\rho(r)$ decreases more slowly with increasing r and the values of $\rho(0)$ are much smaller in comparison to that observed in non-crossing and intra-crossing systems. These results indicate that the ring polymers in these systems can penetrate each other easily. Accordingly, the interchain topological constraint clearly preserves core regions in ring melts, which enforces segregation between the individual ring polymers. In addition, the inset of Fig. 3 indicates that the values of $\rho(r)$ obtained for a ring polymer with $N=1000$ in a good solvent without excluded volume (EV) effects are generally much greater than those obtained with EV effects. These results confirm that intrachain topological constraints have little influence on the structure of ring polymers in melts, and treating intrachain interactions as EV interactions is inappropriate for polymers in melts.

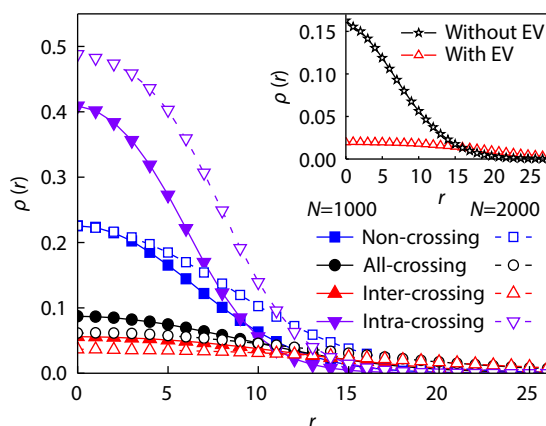


Fig. 3 Variations in the monomer density $\rho(r)$ profile of a single ring in melts with $N=1000$ and $N=2000$ versus the distance r from the center-of-mass of the ring to each monomer. The inset shows the variations in $\rho(r)$ obtained for a ring polymer with $N=1000$ in a good solvent with excluded volume (EV) and without EV. Note that the monomer densities of all ring chains in these systems were set to 0.5.

Relaxation Time

The values of τ_R/N^2 obtained for ring polymer chains in all-crossing, inter-crossing, non-crossing, and intra-crossing systems are plotted on a log-log scale in Fig. 4 with respect to N . These results demonstrate that intrachain and interchain interactions influence the structural relaxation time in different ways. For ring polymer chains in all-crossing and inter-crossing systems, we find that the scaling relation is $\tau_R \propto N^{2.0}$, where the value $\mu_R=2.0$ is consistent with the predictions of the Rouse model.^[50] The same scaling relation is obtained for ring chains in

non-crossing systems when the chain lengths are relatively short ($N < 10N_e$), which agrees with the MD simulation results of Halverson *et al.*^[10] and Tsallikis *et al.*^[28,38] However, $\tau_R \propto N^{2.5}$ when the chain length is relatively long ($N > 10N_e$), which agrees with the predictions of Obukhov *et al.*^[36] and Rubinstein *et al.*^[37] It should also be noted that this scaling exponent is much smaller than the value of $\mu_R=3.4$ obtained for linear chains in entangled polymer melts, which indicates that the application of topological constraints to ring polymer chains hinders their structural relaxation, but the influence is weaker than that of their linear counterparts. It is also interesting that the value of $\mu_R=1.5$ obtained for ring chains in intra-crossing systems deviates significantly from the prediction of the Rouse model (*i.e.*, $\mu_R=2.0$). However, $\mu_R=1.5$ is consistent with the prediction of the Zimm model,^[51] which indicates that the ring chains compress each other and random coil segments of a ring chain move cooperatively due to interchain topological constraints. Restraint reptation for the ring chains in the intra-crossing systems no longer existed, and each ring preferred to adopt a collapsed conformation and behaved like an individual cluster.

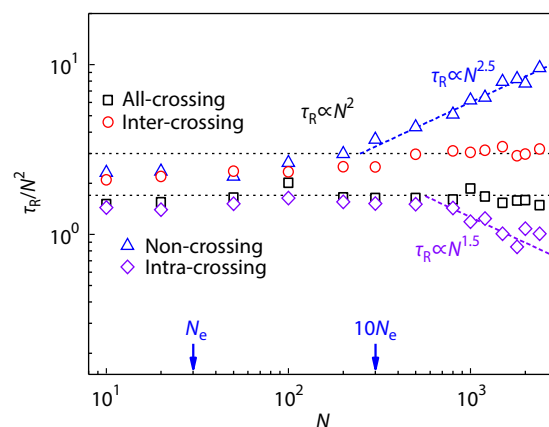


Fig. 4 Structural relaxation time τ_R divided by N^2 versus N for ring polymer chains in all-crossing, inter-crossing, non-crossing, and intra-crossing systems.

Diffusion Behavior

The values of $g_3(t)$ obtained from Eq. (5) for ring polymer chains with $N=1000$ in all-crossing, inter-crossing, non-crossing, and intra-crossing systems are plotted on a log-log scale in Fig. 5 with respect to t/τ_R . The results obtained for ring polymer chains in all-crossing and inter-crossing systems conform to the relation $g_3(t) \propto t$ for $t/\tau_R > 0.1$, which is indicative of simple Brownian diffusion. In contrast, the polymer chains in non-crossing and intra-crossing systems exhibit scaling exponents that increase gradually over the range of increasing t/τ_R . For example, the scaling exponent observed for intra-crossing systems increased from approximately 0.5 in the range of $0.01\tau_R < t < 0.1\tau_R$ to approximately 0.75 in the range of $0.1\tau_R < t < \tau_R$, and increased further to 0.8 with further increase of t/τ_R . Accordingly, these systems deviated from strictly Brownian diffusion even for simulation times as long as $10\tau_R$. It is worth noting that the $g_3(t)$ of the ring chains in the inter-crossing systems was smaller than those in the all-crossing systems for the same t , as shown in Fig. S6 in ESI.

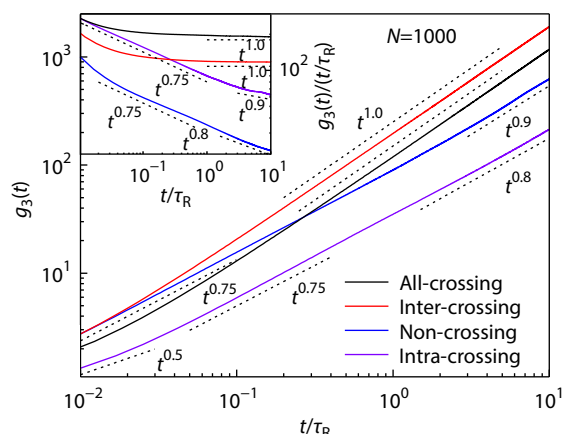


Fig. 5 The mean-square displacements $g_3(t)$ as a function of reduced time of ring polymers with $N=1000$ in different systems. The inset shows $g_3(t)/t$ versus t/τ_R .

The values of D obtained from Eq. (6) for ring polymer chains in all-crossing, inter-crossing, non-crossing, and intra-crossing systems are plotted on a log-log scale according to the product DN in Fig. 6 with respect to N . The results obtained for ring chains in all-crossing and inter-crossing systems present a scaling relation of $D \propto N^{-1}$, where $\mu_D = -1.0$. The fact that these results are in accord with the Rouse model suggests that the diffusion of ring chains without interchain constraints is well described by Rouse dynamics. Meanwhile, μ_D becomes increasingly negative for non-crossing systems with increasing chain length, and approaches a value of -2.0 for long chains. This finding agrees with the limited MD simulation (only 2 data points for $N > 10N_e$) results obtained by Tsilikis *et al.*^[28,38] the experimental results of Gooßen *et al.*^[18] and the theoretical predictions of Mei *et al.*^[52] However, the limited MD simulation (only 3 data points for $N > 10N_e$) results presented by Halverson *et al.*^[10] obtained $\mu_D = -2.3$ and the results obtained by Rubinstein *et al.*^[22] based on FLGs predicted $\mu_D = -1.67$ (i.e., $-5/3$). The scaling exponent observed for polymer rings in intra-crossing systems is the same as that obtained for non-crossing systems, but the intra-crossing systems diffuse more rapidly, which can be attributed to the cooperative motion of ring chains induced by interchain topological constraints discussed above with respect to the structural relaxation behavior of these systems. These findings indicate that the diffusion of ring polymer chains is mainly determined by interchain constraints, but these intrachain constraints affect only the value of D , and have little influence on the scaling relationship between D and N .

Extended Stokes-Einstein Relation

The impact of intrachain and interchain constraints on the extended SE relation of the ring polymer systems can be evaluated according to the product $D\tau_R$ obtained relative to N (i.e., $D\tau_R/N$) for ring polymer chains in all-crossing, inter-crossing, non-crossing, and intra-crossing systems, which are plotted in Fig. 7 with respect to N . The results clearly demonstrate that intrachain and interchain constraints also have a significant influence on the extended SE relation of ring chains in melts. Here, the extended SE relation (i.e., $D\tau_R \propto N$) is observed to hold well for ring chains in all-crossing and inter-crossing systems. In

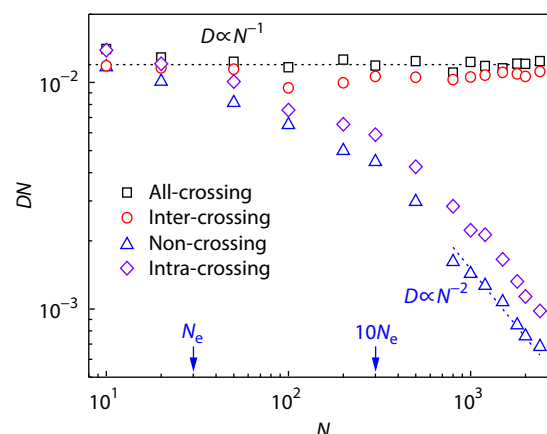


Fig. 6 Plots of the product of the self-diffusion coefficient D and N versus N for ring polymers in all-crossing, inter-crossing, non-crossing, and intra-crossing systems.

contrast, the scaling exponent decreases gradually with increasing N for ring chains in non-crossing and intra-crossing systems, and an explicit breakdown of the extended SE relation is observed at sufficiently large values of N . In fact, the scaling exponents observed for non-crossing and intra-crossing systems respectively decrease to 0.5 and -0.5 at N values on the order of 1000 or greater. This significant violation of the extended SE relation in the non-crossing and intra-crossing systems suggests that the diffusion of the ring polymers under these topological constraints has become decoupled from their structural relaxation at large values of N .

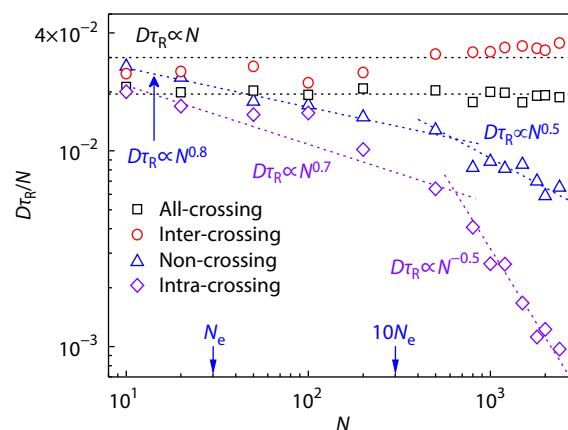


Fig. 7 Examination of the extended SE relation (i.e., $D\tau_R \propto N$) based on plots of $D\tau_R/N$ versus N for ring polymers in all-crossing, inter-crossing, non-crossing, and intra-crossing systems.

The origin for the breakdown of the extended SE relation can be clarified based on the plots of the characteristic relaxation times τ_D , τ_{D1} , and τ_R relative to N^2 for ring chains in non-crossing and intra-crossing systems, which are respectively presented in Figs. 8(a) and 8(b) versus N on a log-log scale. We first note that $\tau_D > \tau_{D1} > \tau_R$ for both systems, and nearly all plots exhibit inflection points at some value of N where the scaling factors change distinctly. At relatively short chain lengths, both systems present scaling exponents reflecting

the N -dependence of τ_D and τ_{D1} of 2.2, while the exponent for τ_R is 2. These findings reveal that the translational diffusion and rotational relaxation of the non-crossing and intra-crossing systems with relatively short chain lengths are decoupled, which results in the breakdown of the extended SE relation. For long chains, the exponent reflecting the N -dependence of τ_D for non-crossing systems increases to 2.7, while the exponents for τ_{D1} and τ_R increase to 2.5, which is more clearly shown in the inset of Fig. 8(a). These results demonstrate that the translational diffusion and rotational relaxation of non-crossing systems are coupled on a short time scale, but decoupled over a long time scale, which results in the breakdown of the extended SE relation. For intra-crossing systems (Fig. 8b), the N -dependence of τ_D presents no inflection point, and the exponent remains 2.2 for all values of N considered. However, in contrast to what was observed for non-crossing systems, the scaling exponents reflecting the N -dependence of τ_{D1} and τ_R for intra-crossing systems with relatively long chain lengths decrease to 2 and 1.5, respectively. Clearly, the translational motion of ring chains is confined significantly by the interchain constraints over long time scales, resulting in reduced translational diffusion. However, the effects of the interchain constraints are negligible over short time scales, leading to freely translational diffusion. Meanwhile, the ring chains undergo rotational relaxation via cluster-like motions (see Fig. 4). Therefore, both the translational diffusion and ro-

tational relaxation of intra-crossing systems, as well as the diffusion observed at short and long time scales, are decoupled, which collectively contribute toward the significant violation of the extended SE relation observed herein.

CONCLUSIONS

The present work addressed the influence of interchain and intrachain interactions on the size and unique dynamic behaviors of ring polymers by applying dynamic MC simulations with independently tuned the interchain and intrachain interactions with chain lengths over a wide range of $0.2N_e \leq N \leq 80N_e$. The main results of this work can be given as follows. (1) The standard approach of treating the unknotting constraint contribution to the free energy of ring chains in melts as the free energy contributed by the excluded volume interactions of polymers in a good solvent is inappropriate. (2) Both the structural relaxation and translational diffusion properties of the simulated ring chains in all-crossing and inter-crossing systems agree well with the predictions of the Rouse model. (3) The scaling exponent μ_R reflecting the N -dependence of the relaxation time is found to be 2.0 for short ring chains and 2.5 for long ring chains in non-crossing systems. This latter value is significantly greater than those calculated by Halverson *et al.*^[10] and Tsalikis *et al.*^[28,38] based on only a very limited number of data points with $N > 10N_e$. Accordingly, the results indicate that topological constraints hinder the structural relaxation of ring polymer chains. In addition, a value of $\mu_R = 1.5$ was obtained for long ring chains in intra-crossing systems, suggesting that the ring chains behave as individual clusters and exhibit Zimm-like dynamics. (4) The scaling exponent μ_D was found to be -1 for ring chains in all-crossing and inter-crossing systems, while μ_D approaches -2 for long ring chains in non-crossing and intra-crossing systems. These values are in agreement with the experimental results of Gooßen *et al.*^[18] and the theoretical predictions of Mei *et al.*^[52] However, these values are greater than the value of $\mu_D = -2.3$ obtained from the limited simulation results presented by Halverson *et al.*^[10] and are less than the value of $\mu_D = -1.67$ (*i.e.*, $5/3$) obtained from the theoretical results of Rubinstein *et al.*^[22] These findings demonstrate that intrachain constraints affect only the value of D , and have little effect on the scaling relationship between D and N . (5) The extended SE relation breaks down for ring chains in non-crossing and intra-crossing systems. This arises for both systems because the translational diffusion and rotational relaxation are decoupled when the chain length is relatively short, and the translational diffusion and rotational relaxation are decoupled on long time scales for non-crossing systems with relatively long chain lengths. Accordingly, these results contribute toward a better understanding of the mechanisms producing the unique dynamic behaviors of ring polymers.

NOTES

The authors declare no competing financial interest.



Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://doi.org/>

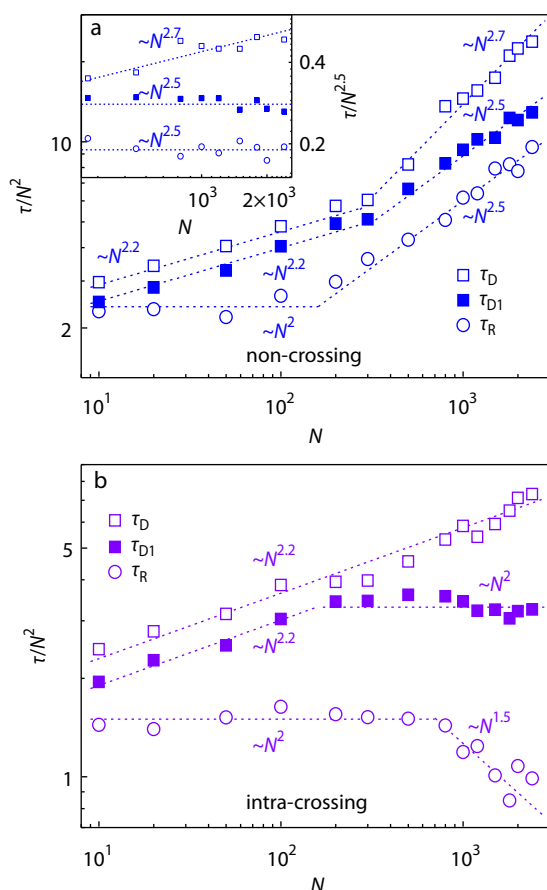


Fig. 8 Plots of relaxation times τ_D , τ_{D1} , and τ_R relative to N^2 versus N for (a) non-crossing systems, where the results obtained at large N are presented in the inset, and (b) intra-crossing systems.

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