Scaling behavior of topologically constrained polymer rings in a melt

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Abstract
Large scale molecular dynamics simulations on graphic processing units (GPUs) are employed to study the scaling behavior of ring polymers with various topological constraints in melts. Typical sizes of rings containing 31, 51 knots and catenanes made up of two unknotted rings scale like $N^{1/3}$ in the limit of large ring sizes $N$. This is consistent with the crumpled globule model and similar findings for unknotted rings. For small ring lengths knots occupy a significant fraction of the ring. The scaling of typical ring sizes for small $N$ thus depends on the particular knot type and the exponent is generally larger than 0.4.

Keywords: knots, molecular dynamics, GPU, ring melts, scaling behavior

(Some figures may appear in colour only in the online journal)

1. Introduction
Understanding the properties of ring polymer melts is one of the remaining major challenges in theoretical and experimental polymer physics [1–10]. The topic became even more popular when ring melts were proposed as a model for DNA organization in a cell nucleus [11]: Chromatin fibers are highly packed and occupy ‘territories’ [12] just like unconcatenated rings in melts [6–8, 13].

Unlike linear polymers, rings cannot change their topological constraints once they are created, as bond crossings are not allowed. Thus, their behavior differs substantially from open chains. In a melt of open polymers the typical size of a chain scales like $R_g \propto N^{1/2}$ [14] for large $N$, where $N$ stands for the number of monomers in the chain. In rings three different scaling regimes are present: For small chain lengths the radius of gyration scales with $R_g \propto N^{1/2}$, in an intermediate regime with $R_g \propto N^{2/5}$, while for long chain lengths a proportionality of $R_g \propto N^{1/3}$ [2, 3, 7, 8, 15–17] will be reached. This asymptotic regime is generally associated with the crumpled globule concept from Grosberg et al [18] which states that the polymer ring collapses to a sphere-like object with self-similar organization. It is essentially a compact, unknotted polymer fold which emerges due to topological constraints or during a polymer collapse.

Although knots are seldom considered in theoretical derivations of scaling laws they become abundant in polymers and DNA for long chain lengths [19, 20]. Even in relatively short proteins, knots have been reported [21–31] and also created artificially [32]. Topoisomerases are known to remove [33] or create [34] knots in DNA, which could otherwise inhibit transcription and replication. Viral DNA is known to be highly knotted inside capsids [35–39]. Artificial knots have been tied in single DNA molecules with optical tweezers and dynamics have been studied both experimentally [40] and with computer simulations [41]. Even though most of these examples are open chains and thus not knotted in a strict mathematical sense [42], where knots are only defined in closed curves, they nevertheless raise fundamental questions and challenge our understanding of topics as diverse as DNA ejection [43] and protein folding [44].

In this paper we aim to combine these two topics and investigate the scaling behavior of topologically constrained polymer rings. To this end we compare a melt of unconcatenated, unknotted rings with their knotted or concatenated counterparts.

In section 2 we describe the polymer model, simulation details, and the induced topological constraints. In section 3 we present our results for the scaling behavior and give a qualitative description of how knot sizes change for various chain lengths. Section 4 presents our conclusions.
2. Model and simulation techniques

We simulate 200 ring polymers at a density of \( \rho = 0.85 \sigma^{-3} \) in a simulation box with periodic boundary conditions. Chain lengths \( N \) vary from 100 monomers to up to 3200 monomers per polymer so the simulation box contains between 20 000 and 640 000 monomers. The temperature is set to \( T = 1.0 k_B \) and is controlled via a Langevin thermostat with a friction of \( \gamma = 640 \) monomers. The temperature is set to \( T = 109 \) MD steps and is controlled via a Langevin thermostat with a friction of \( \gamma = 10 \) monomers. We use the open source software HooMD blue [45] and simulate each system on a GeForce GTX480 graphics card.

For each system size \( 2 \cdot 10^6 \) MD steps with a time step of \( \Delta t = 0.01 \) are simulated. The polymer model is based on [7]:

\[
U_\text{har} (r_{ij}) = \begin{cases} 
4 \varepsilon \left[ (\sigma/r_{ij})^{12} - (\sigma/r_{ij})^6 \right] + \varepsilon, & r_{ij} < \sigma \\
0, & r_{ij} > \sigma
\end{cases}
\]

\[
U_\text{angle} (\theta_i) = \frac{1}{2} \zeta \alpha (\theta_i - \pi)^2,
\]

with \( k = 30 \varepsilon / \sigma^2 \), \( R_0 = 1.5 \sigma \), \( c = 1.5 \varepsilon \). In contrast to [7] we employ the harmonic potential implemented in HooMD. Nevertheless, we expect that the results are very similar to [7] as equation (3) is essentially the second order Taylor expansion of the angular potential used by [7]. Therefore, the entanglement length of this model system is expected to be around \( N_c \approx 28 \) [7, 46].

To investigate the influence of topology on the scaling of ring sizes in a melt we looked at various topologically constrained ring melts (see figure 1 for schematic drawings). We study unknotted rings (figure 1(a)), knotted rings with a trefoil (3_1) knot (figure 1(b)) and with a cinquefoil (5_1) knot (figure 1(c)), and concatenated rings (catenate) (figure 1(d)). The model we use does not allow for bond crossings so that the initial constraints will be present at all times. To confirm this, we calculate the Alexander polynomial [47] for each knotted ring every \( 10^6 \) MD steps. Additionally, we check that there are no bond crossings between the polymers via a primitive path analysis for all topologies [46]. To obtain the initial state we start with an already equilibrated configuration.

![Figure 1. Schematic drawings of the examined topologies: (a) unknotted, (b) trefoil (3_1), (c) cinquefoil (5_1), and (d) catenate.](image)

### Table 1. Exponents for the chain length dependency of the radius of gyration and the mid-to-mid radius obtained by fitting the function \( R^2 = a \cdot N^{2\nu} \) to the data points with \( N \leq 400 \) and \( R^2 = b \cdot N^{2\nu} \) for the region \( N \geq 800 \) as shown in figure 3(a).

| Topology   | \( 2\nu_1 \) | \( 2\nu_2 \) | \( 2\nu_1 \) | \( 2\nu_2 \) |
|------------|----------------|----------------|----------------|----------------|
| rings      | 0.779          | 0.689          | 0.740          | 0.679          |
| 3_1 knots  | 0.912          | 0.700          | 0.940          | 0.683          |
| 5_1 knots  | 0.966          | 0.706          | 1.050          | 0.699          |
| catenanes  | 0.809          | 0.711          | 0.762          | 0.707          |

For unconstrained rings the expected exponents are \( 2\nu_1 = 0.8 \) and \( 2\nu_2 = \frac{1}{2} \). Note that we only investigate the crossover region and that our rings are still not long enough to make definite statements about exponents in the asymptotic regime. In addition only three points are used to fit the corresponding power laws. Therefore, we refrain from providing an estimation of errors, and exponents are only shown to mark the crossover for the various topologies.

3. Results

To characterize the scaling behavior we calculate the squared radius of gyration \( \langle R^2 \rangle \) by averaging over all 200 ring polymers every \( 10^6 \) MD steps (see figure 2). Additionally, we monitor the squared mid-to-mid radius \( \langle R^2 \rangle \), by averaging over the...
Figure 3. (a) Scaling behavior of the squared radius of gyration for polymer rings with various topological constraints. (b) Scaling behavior of the squared mid-to-mid radius for polymer rings with various topological constraints. The error bars in both plots are smaller than the symbol size.

vector which connects the $i$th monomer to the $i + N/2$th monomer.

By plotting the average squared radius of gyration or the mid-to-mid radius against the chain length $N$ (see figure 3) we can obtain the scaling behavior by fitting a power law of the form $R^2(N) = a \cdot N^{2\nu}$. For all topologies we observe a scaling exponent compatible with $\nu_2 \approx 1/3$ as predicted by the crumpled globule model [18] (see table 1). For small systems, however, knots occupy a significant fraction of the polymer (see figure 4) resulting in a denser configuration with a smaller radius of gyration. This effect levels off (see figure 5) around the transition to the crumpled globule states (between 400 and 800 monomers). Hence, the effective exponent $\nu_1$ exceeds the predicted value of 0.4 for unconstrained rings.

in the scaling behavior between knotted and unknotted rings also carry over to dynamics. The small, denser knotted rings typically diffuse faster than their unknotted counterparts, but the differences vanish for large ring lengths. The catenanes behave very similar to the unconstrained rings, and the radius of gyration scales with the same exponent (see figure 3). Still, they are slightly larger than their unconstrained counterparts (see figure 5) for all ring sizes $N$. This is expected, as the catenanes have to stay in pairs of two and can thus not relax as easily as the unconstrained rings.

For knotted rings figure 5 suggests that the influence of the knot on the total size decreases as a function of $N$. Unfortunately, it is very difficult to determine sizes of knots in rings [6, 48] and our preliminary findings are not completely conclusive. To determine knot sizes we have followed a so called top-down approach [6]: We cut the chain at a random point and remove beads successively until the knot disappears. The remaining beads are essential and determine the knot size. However, if we cut inside the knot the analysis does not yield meaningful results. The closure may also lead to additional

\[^3\] It should be noted that our data only spans a bit more than a decade and exponents are typically obtained by fitting only three points.
distortions. By considering multiple random starting points and analyzing only the subset of data which yields consistent sizes for at least half of the starting points, we have determined the most likely knot size as 40 monomers for the trefoil knot and 51 monomers for the $5_1$ knot for ring size $N = 100$. For larger rings the most likely size is similar, but the distribution has a larger tail.

4. Conclusion

In conclusion, we have performed large scale molecular dynamics simulation on graphic processing units (GPUs) to study the scaling behavior of unknotted ring polymers, knotted rings with a trefoil ($3_1$) knot and with a cinquefoil ($5_1$) knot, and concatenated rings in a melt. For large $N$ the rings scale with roughly $N^{1/3}$ for all topological constraints, and the transition takes place at about the same ring sizes. These findings for large ring sizes are consistent with the crumpled globule model. For small ring lengths knots occupy a significant fraction of the ring. The scaling of typical ring sizes for small $N$ thus depends on the particular knot type and the exponent is generally larger than 0.4.

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