The effect of topology on the conformations of ring polymers

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Abstract

The bond fluctuation method is used to simulate both non-concatenated entangled and interpenetrating melts of ring polymers. We find that the swelling of interpenetrating rings upon dilution follows the same laws as for linear chains. Knotting and linking probabilities of ring polymers in semi-dilute solution are analyzed using the HOMFLY polynomial. We find an exponential decay of the knotting probability of rings. The correlation length of the semi-dilute solution can be used to superimpose knotting data at different concentrations. A power law dependence $f_n \sim \phi R^2 \sim \phi^{0.77} N$ for the average number $f_n$ of linked rings per ring at concentrations larger than the overlap volume fraction of rings $\phi^*$ is determined from the simulation data. The fraction of non-concatenated rings displays an exponential decay $P_{OO} \sim \exp(-f_n)$, which indicates $f_n$ to provide the entropic effort for not forming concatenated conformations. Based upon this results we find four different regimes for the conformations of rings in melts that are separated by a critical lengths $N_{OO}$, $N_C$ and $N^*$. $N_{OO}$ describes the onset of the effect of non-concatenation below which topological effects are not important, $N_C$ is the cross-over between weak and strong compression of rings, and $N^*$ is defined by the cross-over from a non-concatenation contribution $f_n \sim \phi R^2$ to an overlap dominated concatenation contribution $f_n \sim \phi N^{1/2}$ at $N > N^*$. For $N_{OO} < N < N_C$, the scaling of ring sizes $R \sim N^{2/5}$ results from balancing non-concatenation with weak compression of rings. For $N_C < N < N^*$, non-concatenation and strong compression imply $R \sim N^{3/8}$. Our simulation data for non-interpenetrating rings up to $N = 1024$ are in good agreement with the prediction for weakly compressed rings.
I. INTRODUCTION

Even though ring polymers have an extremely simple structure similar to linear chains but without ends, there are still many unsolved questions concerning their properties in concentrated solutions or melts. The main reason for the difficulty to describe ring polymers lies in the fixed topological state of each individual ring and the topological interactions with overlapping molecules. The topology and classification of individual rings in terms of “knots” is a long standing problem in science ranging from early discussions on the nature of atoms [1] and mathematics [2] to applications in modern science [3]. This is an important point, since for polymers it is known, for instance, that the knot type affects swelling, collapse and average size of a ring polymer [4, 5].

Overlapping rings can also form permanently entwinned states or “links”. It was suggested that giant aggregates of such entwinned rings could form based on topological connectivity only, so called Olympic gels [6–8], which might allow to directly measure the entanglement contribution to elasticity. Simulations of melts of rings showed that topological interactions mutually compress the conformations of overlapping rings [9–13]. Cates and Deutsch (CD) conjectured that this compression might lead to a scaling of ring size \( R_g \sim N^{2/5} \) somewhere in between fully collapsed and ideal conformations [14]. Such a behavior is possible, since in melts, excluded volume interactions are typically screened and thus, topological constraints, which are often incorporated into the effects of excluded volume, become important. Therefore, the effect of topology, unlike the excluded volume effects in other situations, does not lead to a simplification or idealization of ring conformations, when bringing rings into overlap. The basic argument in the CD-model is that all overlapping rings which could interpenetrate in the absence of topological constraints are rejected from the volume of gyration of an individual ring in the case of non-interpenetration. The corresponding free energy effort is balanced by the free energy penalty arising from confining an ideal linear chain without taking into account topology. Recent simulation studies suggest that the conjecture of CD is only characteristic of an intermediate regime before the scaling of ring size crosses over to a compact state \( R_g \sim N^\nu \) with \( \nu \) close to 1/3 as summarized in Fig. 1 of Ref. [15]. A similar cross-over has been predicted recently [16] by proposing a model that needs to make assumptions on the nature of the knotting and the non-concatenation constraint that enter in the free energy of a polymer ring in melt.

It is the goal of the present work to clarify the assumptions made in the above works
concerning non-concatenation and knotting for a better understanding of the effect of topology onto the conformations of rings in melt. In the present work, we study both solutions of entangled non-concatenated rings and interpenetrating rings spanning the regime between dilute to melt concentrations using the bond fluctuation method. We analyze conformations in both types of ring-solutions and determine the linking and knotting probabilities as a function of concentration and degree of polymerization. These results are then combined with previous work on knotting of rings [4, 5] in order to estimate the conformations of on rings in melts of rings and linear chains.

II. SIMULATION METHODS AND SIMULATED SYSTEMS

We use the bond-fluctuation model (BFM) [17] to simulate solutions of ring polymers. This method was chosen, since it is known to reproduce conformational properties and dynamics of semi-dilute solutions [18] and polymer networks [19–21]. In this method, each monomer is represented by a cube occupying eight lattice sites on a cubic lattice. In the standard definition of this algorithm, the bonds between monomers are restricted to a set of 108 bond vectors which ensure cut-avoidance of polymer strands by checking for excluded volume. Monomer motion is modeled by random jumps to one of the six nearest lattice positions. A move is accepted, if the bonds connecting to the new position are still within the set of bond vectors and if no monomers overlap. All samples of the present study were created in simulation boxes with periodic boundary conditions. Athermal solvent is treated implicitly by empty lattice sites.

In the present work, we use this method to create solutions of non-concatenated rings. Additionally, we perform simulations where we allow for moves diagonal to the lattice axis. This switches off all entanglements, while excluded volume interactions are mainly unaffected. In consequence, the rings can interpenetrate each other to form concatenated conformations. In order to clarify the differences between both series of samples, we call them interpenetrating and non-interpenetrating throughout this work. In both cases, relaxation of the rings was monitored by the autocorrelation function of the vectors connecting opposite monomers of a ring. All samples were relaxed several relaxation times of the ring polymers. Afterward, chain conformations were analyzed from snapshots of the ring solutions from a very long simulation run. The error of the data points was computed by the total number of statistically independent conformations available.

For the analysis of topology, monomer motion in the interpenetrating samples was
slowly switched back to motion along the lattice axis in order to remove states in which pairs of bond vectors are intersecting each other. Then, rings were first simplified at conserved topology and regular projections of any pair of overlapping rings were determined as described in [22]. Finally, the Gauss code of the projection was computed and the types of knots and pairwise links formed were analyzed using the Skein-Template algorithm of Gouesbet et al. [23] based upon the HOMFLY-polynomial [24]. Note that in the present paper we restricted the analysis to permanent entanglements between pairs of rings. Brunnian links (permanent entanglements that cannot be detected by a pairwise analysis of rings) as for instance, the Borromean rings [2] cannot be detected by this approach. The data of previous work [25] shows that this simplification should affect the results of the present study by less than 5%, which is in the range of the accuracy of the individual data points.

We ran an array of different interpenetrating and non-interpenetrating samples with degrees of polymerization $N = 16, 32, 64, 128, 192, 256, 384, 512, 768,$ and $1024$ and polymer volume fractions of $\phi = 0.5, 0.375, 0.25, 0.1875, 0.125, 0.0625,$ and $0.03125$. The numbers of rings per sample varied from 512 to 4096 resulting in a simulation box size between $128^3$ to $512^3$ lattice sites.

### III. CONFORMATIONS OF RING POLYMERS

The conformations of ideal (no excluded volume and no entanglements) rings of $N$ segments are fully described by random walks that return to the origin. The situation is more complex for real ring polymers, since the fixed topological state of the molecules [5] and excluded volume affect the statistical properties of the ring conformations. However, the main properties of excluded volume for linear polymers are expected to be valid also for unknotted ring polymers [26], since the length at which knotting becomes important is typically large [4] as we also show in section IV.

Let us define the overlap volume fraction as the volume fraction of a polymer in its own radius of gyration in good solvent $R_g$ according to

$$\phi^* = \frac{N}{R_g^3}. \quad (\text{III.1})$$

At polymer volume fractions $\phi \gtrsim \phi^*$, both interpenetrating and non-interpenetrating rings mutually compress each other. For interpenetrating rings, compression is driven by screening of excluded volume effects and a corresponding change of the blob size $\xi$. For
non-interpenetrating rings topological interactions (exclusion of interpenetrating states) have to be taken into account. Let

\[ R_{g0} \approx bN^{\nu_0} \quad \text{for} \quad \phi \ll \phi^* \quad \text{(III.2)} \]

with \( \nu_0 \approx 0.587597(7) \) [27] denote the size of the swollen rings in good solvent and

\[ R_g \approx bN^\nu \quad \text{for} \quad \phi \gg \phi^* \quad \text{(III.3)} \]

is the size of rings in semi-dilute solution. Since the overlap-concentration is related to the onset of both excluded volume and pairwise topological effects, a scaling is expected according to

\[ \frac{R_g(\phi)}{R_{g0}} \sim f \left( \frac{\phi}{\phi^*} \right). \quad \text{(III.4)} \]

The asymptotic limits of the scaling function, \( f(y) \), can be obtained using Eqs.(III.1)-(III.3) as follows:

\[ f(y) = \begin{cases} 
1 & \text{for} \quad \phi \ll \phi^* \\
\frac{y^{1-\nu}}{y^{1-\nu_0}} & \text{for} \quad \phi \gg \phi^* 
\end{cases} \quad \text{(III.5)} \]

Different values for the exponent \( \nu \) are suggested in literature to describe the size \( R \approx bN^\nu \) of interpenetrating (\( \nu = 1/2 \)) or non-interpenetrating (\( \nu = 2/5, 1/3 \)) rings in melt [11, 14, 16]. Thus, we expect the following power laws, \( R \sim \phi^x \), for \( \phi \gg \phi^* \)

\[ R \sim \begin{cases} 
\phi^{-0.115} & \text{for} \quad \nu = 1/2 \\
\phi^{-0.25} & \text{for} \quad \nu = 2/5 \\
\phi^{-0.33} & \text{for} \quad \nu = 1/3 
\end{cases} \quad \text{(III.6)} \]

Here, the first case corresponds to interpenetrating rings and is equivalent with the behavior of linear chains in semi-dilute solutions [6]. The other two cases correspond to the two suggested regimes of the non-interpenetrating rings.

In Figure III.1, we present the simulation data both for interpenetrating rings and non-interpenetrating rings. The interpenetrating rings show an apparent exponent (dashed blue line) of \( x \approx -0.13 \) for \( \phi > \phi^* \), which is close to the above prediction. The data of non-interpenetrating rings (red line) show a clearly different exponent of \( x \approx -0.21 \), which agrees best with the prediction of CD [14] for the available molecular data. Based upon the data of Figure III.1 one might argue that this could be a continuous transition between fully swollen and fully compressed conformations. But this rather narrow regime as function of \( \phi/\phi^* \) stretches out to about one decade as function of \( N \). Furthermore, a stronger \( \phi \) dependence cannot be excluded for larger \( \phi/\phi^* \), as indicated by the data point for the largest rings at the highest concentration.
IV. KNOTTING AND LINKING PROBABILITIES

In this section, we investigate only interpenetrating solutions of rings. Self-entanglements of individual rings are discussed in terms of a knotting probability, $1 - P_O$, while concatenation with overlapping rings is analyzed by a linking probability, $1 - P_{OO}$. The complementary events are the probabilities of finding an unknotted conformation, $P_O$, or a ring that does not entrap any other ring, $P_{OO}$.

An exponential decrease of the appearance of unknotted conformations $P_O \sim \exp(-N/N_0)$ with a characteristic and model dependent “knotting length” $N_0$ was found in previous works [25, 28–32] and is a rigorous result for dilute lattice polygons [3]. This functional form was explained by the abundance of local knots formed within the range of a small number of bonds along the polymer as compared to knots that require the global ring conformation to be knotted. If short knots occur predominantly on a local
scale, the probability of finding no knot then requires that consecutively no small section of the molecule is knotted and thus the probability for finding an unknot is exponentially decreasing as function of $N$.

Above we showed that for freely interpenetrating rings the same scaling laws apply as for linear chains in semi-dilute solutions. In the following, we define the number of monomers per blob, $g$, therefore, as

$$g = \phi^{-1/(3\nu_0-1)}$$

(IV.1)

for simplicity. In the framework of the blob model, it is assumed that up to the size of the blob, the chains are merely mutually repelling each other. The blob itself plays thus the role of the basic monomer unit and the chain or ring on larger scale, composed of $N/g$ blobs, adopts conformations as in dense melts. If we combine this result with the above findings on knotting probability, we can postulate that the simulation data is expected to collapse onto a single curve, when plotting the probability of finding the “unknot” (an unknotted ring [2]), $P_O$, as function of the number of blobs $N/g$. This corresponds to assuming the chain as a tube of diameter $g^\nu$. Figure IV.1 demonstrates, that this rough estimate nearly leads to a full collapse of the data. The line is a least squares fit of all
data using
\[ P_O = \exp \left( -\frac{(N/g - a) N_0}{N} \right) \quad \text{(IV.2)} \]
similar to previous work \[3\]. The parameter \( a = 10 \pm 5 \) reflects a minimum required number of blobs to form a knot. We determine a knotting length \( N_0 = 1820 \pm 80 \) for the simulations of the present study. Note that \( N_0 \) depends strongly on excluded volume: for random walks one finds \( N_0 \approx 340 \) \[33, 34\], while for bead-spring rings with excluded volume one obtains, for instance \( N_0 \approx 8 \times 10^5 \) \[28\]. Our result is clearly larger than that for the random walk. This might be due to the incomplete screening of excluded volume on the length scale of individual monomers \[35\]. Since the knotting length is larger than the largest \( N \) of the present study, we do not expect significant effects of knotting on ring conformations for the non-interpenetrating samples as long as the rings remain swollen or close to ideal conformations. Note that there must be an additional small systematic decrease of \( P_O \) with increasing \( N \) after the above rescaling of \( N \) by \( N/g \) as visible in Figure IV.1. This is because blobs are soft objects allowing still for some residual knotting inside the blob. Furthermore, the case \( N/g = 1 \) can be taken as approximation of isolated self-avoiding walks that exhibit the above mentioned large knotting length. Both corrections lead to an additional systematic decrease of the fraction of unknotted rings at constant \( N/g \) for increasing \( N \).

Let us introduce the average number of concatenated rings (linked rings) per ring, \( f_n \). In order to estimate \( f_n \), we first neglect the effect of multiple concatenations between the same pair of rings (for instance, link \( 4 \) in the standard notation \[2\]) for sufficiently small \( N \) as supported by previous work \[25, 36\]. We now propose that the number of concatenations per ring is proportional to the minimal surface \( \sim R^2 \) spanned by the ring \[47\] as sketched in Figure IV.2. The number of rings in contact with the surface is proportional to the density \( \phi \) of the surrounding rings. Since for semi-dilute solutions all square sizes (blob and ring) scale as \( R^2 \sim \phi^{-0.23} N \) \[6, 37\], we can approximate
\[ f_n \sim \phi R^2 \sim \phi^{0.77} N \quad \text{(IV.3)} \]

With equation IV.3 we assume that a constant fraction of those ring conformations, that touch the shaded area in Figure IV.2, leads to a concatenated state. This assumption is reasonable for monodisperse melts, since because of \( N \gg R/b \) essentially all overlapping rings have the possibility to encircle the other ring independent of their relative position. This has been demonstrated by the rather constant linking probabilities of pairs of rings at distances \( < R \) in previous works \[25, 38\].
Figure IV.2: Model for estimating the average number of linked rings.

Figure IV.3: Average number of pairwise concatenations per ring. Error bars are below symbol size. Lines are theoretical estimates for $\phi = 1$.

The average number of concatenations per ring, $f_n$, is determined from the interpenetrating rings and shown in Figure IV.3. We find a good agreement with the prediction $\phi^{0.77}N$ of equation (IV.3) for $N > 100$ and a correction for small $N$ that is discussed below.

It is important to stress that the average number of entrapped rings per ring, $f_n$, grows
Figure IV.4: Probability $P_{OO}$ that a ring is not linked to any other rings as function of the average number of linked rings $\phi^{0.77}N$. Error bars are comparable to symbol size.

quicker with respect to $N$ and $\phi$ than the overlap number of rings, defined as

$$P = \phi R^3 / N \approx \phi^{1-3(\nu_0-1/2)(3\nu_0-1)} N^{1/2} \approx \phi^{0.65} N^{1/2}.$$  \hspace{1cm} (IV.4)

Nevertheless, we expect a cross-over to an overlap-dominated regime at a critical degree of polymerization $N^*$ at which

$$f_n \approx P.$$  \hspace{1cm} (IV.5)

Then, any ring will be concatenated with essentially all overlapping rings. Figure IV.3 indicates that this regime is not reached yet. Therefore, the degrees of polymerization in the present study are all below $N^*$ and we can conclude $N^* > 1024$.

In a previous work [39], an exponential decrease of $P_{OO}$ as function of $N$ was observed for rings formed in end-linked model networks. In Figure IV.4, we plot $P_{OO}$ as function of $\phi^{0.77}N$ and observe again a reasonable collapse of the data onto an exponential decay as function of $N$. The line in Figure IV.4 is a least squares fit to the data with $\phi = 0.5$ using an expression,

$$P_{OO} = \exp \left( - (N\phi^{0.77} - a)/N_{OO} \right),$$  \hspace{1cm} (IV.6)
similar to the one used for the non-knotting probability above. We find $a = 8.8 \pm 0.3$ and a linking length $N_{OO} = 23.5 \pm 0.1$ at $\phi = 1$ in good quantitative agreement with previous work [39].

Equation (IV.3) for $f_n$ can be improved by including the linking probability $1 - P_{OO}$ as shown in Figure IV.3 by the continuous line. Let us further introduce $\gamma$ as the constant of proportionality according to $f_n = \gamma \phi^{0.77} N (1 - P_{OO})$. From the simulation data in Figure IV.3 we obtain $\gamma = 0.034 \pm 0.001$. Thus, rings of roughly 50 monomers are needed at $\phi = 0.5$ to have an average of $f_n \approx 1$. For smaller rings, we do not expect a significant effect of topology onto ring conformations.

It is also instructive to approximate $P_{OO}$ by replacing $N\phi^{0.77}$ by $f_n/\gamma$. For large $f_n$ we obtain

$$P_{OO} \approx \exp (-f_n)$$

(IV.7)

up to a numerical coefficient of order unity. Thus, the number of unlinked ring conformations decreases roughly exponential with the average number of concatenations for sufficiently large $f_n$. This shows that we require a contribution of order $f_n$ to the free energy to describe the effect of non-concatenation.

Above we mentioned that we neglect Brunnian links. Besides the results of a previous work [25], the agreement between theoretical predictions (which ignores whatever type of linking may penetrate a ring) and our present data (based on pairwise linking) is a strong indication that restricting the analysis to pairwise linking is a reasonable approximation for the samples of the present study.

V. A FLORY THEORY OF RING CONFORMATIONS IN MELT

With the above results we have the missing data to discuss previous models [14, 16] to explain the scaling of the size of non-interpenetrating rings. In the former model [14], CD balance the entropy of confining an ideal ring with the loss of entropy caused by the exclusion of other polymers from the gyration volume. This can be expressed in a free energy of form[48]

$$F \approx N R^2 + \frac{R^3}{N}.$$  

(V.1)

The optimum size of a ring polymer is then given by

$$R \sim N^{2/5}.$$  

(V.2)
The second term is equivalent to assuming that all potentially overlapping rings share topological interactions with each other. Our data in Figure IV.3 show that this is only the case for molecular weights beyond the transition to the overlap dominated regime $N > N^*$ with $N^* > 10^3$. However, the available simulation studies [11, 40, 41], including the results of this work, see Fig.III.1, come to a different conclusion: the predicted exponent, $\nu = 2/5$ from the CD-model agrees better with the simulation data up to $N < 10^3$. For larger $N$, on the other hand, there are indications for a change in the scaling behavior towards $R \sim N^\nu$ with $\nu$ close to $1/3$ [15]. This is clearly surprising and we attempt to answer this point by a step-wise construction of an alternative Flory-ansatz for ring conformations in melt.

Moore and Grosberg [4] found that the effect of topology for large unknotted uncompressed rings can be expressed in terms of an additional excluded volume. This, in contrast to the native excluded volume, will not be screened in a melt of linear chains with melt degree of polymerization $> N^{1/2}$. Instead, the topological contribution stands out and is balanced by the elasticity of the ring. Let us consider an isolated ring in a melt of linear chains. This leads to a free energy of form

$$\frac{F}{kT} \approx \frac{R^2}{N} + \frac{N^2}{R^3},$$

(World V.3)

and to a swelling of the ring which is analog to linear chains or rings in good solvent

$$R \sim N^{3/5}.$$  

(World V.4)

Let us now return to a monodisperse melt of rings. By comparing the non-concatenated and the interpenetrating rings we conjecture that the expulsion of $f_n$ rings out of the volume of gyration of a given ring due to non-concatenation leads to a free energy contribution $\sim f_n \sim R^2$ for $N_{OO} < N < N^*$. This contribution dominates by far the elastic free energy of swelling in Equation (V.3) for large $N$. Note that the swelling term is appropriate to balance ring compression as long as ring size is not strongly compressed, since then, the $R$-tube confining the ring (see ref. [5] for a detailed discussion) is not yet compressed in length and width. Thus, for $N_{OO} < N \lesssim N_C$ below the crossover to strong compression at $N_C$, the free energy can be approximated by

$$\frac{F}{kT} \approx \frac{N}{R^2} + R^2 + \frac{N^2}{R^3}.  \quad \text{(V.5)}$$

Here, we formally introduced the entropy loss $N/R^2$ upon squeezing an ideal ring. This term is of minor importance and the free energy is controlled by balancing two merely
topological terms. This results in an optimal ring size of

\[ R \sim N^{2/5}. \]  

(V.6)

Note that our result for the \( \nu \)-exponent is formally equivalent to the result by Cates and Deutsch, but is obtained from a different estimate for non-concatenation for \( N < N^* \) and a topological contribution which prevents strong compression of rings at \( N < N_C \). According to the available data, for instance [42], it requires in melts at \( \phi = 0.5 \) an \( N > 512 \) to compensate the swelling of the rings due to incompletely screened excluded volume [35]. The above scaling of ring size is supported by simulation data of rings with moderate degree of polymerization [10, 42, 43] up to \( N \lesssim 10^3 \). We briefly note that dropping the topological excluded volume term in equation (V.5) leads to \( R \sim N^{1/4} \), a result that formally corresponds to ideal hyperbranched polymers and was found previously for non-concatenated rings in an array of obstacles [44].

Grosberg et al. [5] and Sakaue [16, 45] discussed, that the unknotting constraint leads to a free energy contribution that turns into \( \approx N^3/R^6 \) for a large compression of rings. This term results from the then dominating three body interactions among the monomers of the ring and can be pictured as a simultaneous compression in length and width of a the \( R \)-tube [5] that confines the ring. Such large compression is obtained above a critical \( N_C \) and adapting the third term of the free energy we have

\[ \frac{F}{kT} \approx \frac{N}{R^2} + R^2 + \frac{N^3}{R^6}. \]  

(V.7)

Again, the entropy loss upon squeezing a ring appears to be of minor importance for large \( N \). The equilibrium extension of compressed non-interpenetrating and unknotted rings with \( N_C < N < N^* \) is then given by

\[ R \sim N^{3/8}. \]  

(V.8)

A scaling of ring size with a power \(< 2/5 \) for large \( N > 10^3 \) is supported by computer simulation data as summarized, for instance, in Fig. 1 of Ref [15]. This suggest that \( N_C \approx 10^3 \) for the particular simulation models referenced in [15].

To the best of our knowledge, there is no data available for \( N \gg N^* \). For such large molecular weights, the non-concatenation contribution should be of the form as originally proposed by Cates and Deutsch [14], since then, all overlapping rings will be concatenated. Balancing this expression with the dominating non-knotting contribution for large \( N \) yields \( R \sim N^{4/9} \). It will be interesting to extend experimental or simulation
data beyond $N^*$ in order to test whether this proposed regime correctly describes the limiting behaviour for $N \to \infty$. Furthermore we have to mention that the available data suggests $N_C < N^*$ due to the observed change of the scaling behaviour of rings in melts. However, $N_C < N^*$ is not necessarily a universal result, since $N^*$ depends on overlap and the probability of trapping another ring, while $N_C$ is simply defined by the onset of significant compression of the rings. Finally, we would like to stress that the above Flory estimates have to be taken with care and that there is no guarantee that the above exponents can be considered as exact. But the general trend of whether compression becomes weaker or stronger in the particular regimes might be correctly reproduced.

Recently, Sakaue [16, 45] proposed an alternative model for the size of rings in melt. The non-concatenation condition was introduced similar to the original CD model, which is only correct for sufficiently large $N > N^*$ according to our simulation data. In contrast to the work of Sakaue, we find a well defined scaling regime for ring size and not a gradual transition from a power $1/2$ to $1/3$. Furthermore, our approach does not require to postulate that the topological length scale may be a function of the melt molecular weight. Since both models lead to quite similar predictions for rings size, it will be difficult to decide, which one might be more appropriate to describe conformations of rings in melt by discussing only the size of rings in monodisperse melts. However, the differences between both models should become most prominent in case of bimodal melts of rings, which is, therefore, the subject of ongoing research.

VI. SUMMARY

In the present work, we compared the conformations of non-concatenated entangled and interpenetrating disentangled melts of ring polymers. It was found that the swelling of interpenetrating rings upon dilution follows the same laws as for linear chains. Knotting and linking probabilities of ring polymers in semi-dilute solution were analyzed using the HOMFLY polynomial. We find an exponential decay of the non-knotting probability of rings. The correlation length of the semi-dilute solution can be used to superimpose knotting data at different concentrations. A power law dependence $f_n \sim \phi R^2 \sim \phi^{0.77} N$ for the average number $f_n$ of linked rings per ring at concentrations larger than the overlap volume fraction of rings $\phi^*$ is determined from simulation data. The fraction of non-concatenated rings displays an exponential decay $P_{OO} \sim \exp(-f_n)$, which indicates $f_n$ to provide the entropic effort for not forming concatenated conformations. For very
large overlap number $P$, it is expected that $f_n$ crosses over to $f_n \sim P \sim \phi N^{1/2}$. The cross-over defines a length scale $N^*\phi$ which turns out to be very large, at least $N^*>1024$. The exponential dependence of the non-linking probability as function of $N$ in penetrating rings indicates a minimal degree of polymerization $N_{OO}$, below which topology is unimportant. Furthermore, the available simulation data [15] indicate a degree of polymerization $N_C < N^*$ at which ring compression crosses over from weak at $N < N_C$ to strong $N > N_C$.

Based upon these observations we discuss Flory-type free energy models for the regimes separated by three cross-over degrees of polymerization, $N_{OO}$, $N_C$, and $N^*$. For intermediate degrees of polymerization $N_{OO} < N < N_C$ below significant compression of the rings, the scaling of ring conformations might result from balancing non-concatenation with the swelling term of ring topology. This leads to ring sizes $R \sim N^{2/5}$. For larger $N > N_C$ but still below the transition to the overlap dominated regime at $N^*$, significant compression of the rings can occur, where non-concatenation is now balanced by a free energy contribution upon strong compression $\approx N^3/R^6$, which implies $R \sim N^{3/8}$. This slight decrease of the exponent from $\approx 2/5$, towards a smaller value close to $1/3$ agrees with previous simulation results for larger rings [15]. Finally, for extremely long rings with $N > N^*$, a further change in the scaling behavior is expected. Here, all overlapping pairs of rings are concatenated and the scaling of $f_n \sim R^2$ turns over into the scaling of the Flory number, $f_n \sim R^3/N$, which may lead to ring size $R \sim N^{4/9}$ which is, however, rather speculative in view of lacking simulation data.

Even though a large part of the discussion is supported by the data presented in our work the major challenge is to fully explore the limiting regime of very large $N > N^*$ and to determine $N^*$. Furthermore, bidisperse blends of rings of different weight can serve as critical test to clarify differences between the model presented here and previous models [14, 16, 45] in literature.
VII. ACKNOWLEDGEMENT

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The properties of the minimal surface will be discussed in a forthcoming work [46].

For simplicity, we drop all (numerical) constants in this section.
Concatenation of rings
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Jakob Fischer
Jens-Uwe Sommer

\[ f_n = \gamma \varphi^{0.77} N \left(1-P_0\right) \]