Influence of topology on effective potentials: coarse-graining ring polymers

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We employ computer simulations and integral equation technique theories to perform coarse-graining of self-avoiding ring polymers with different knottedness and to derive effective interaction potentials between the centers of mass of these macromolecular entities. Different microscopic models for the monomer-monomer interactions and bonding are employed, bringing about an insensitivity of the effective interactions on the microscopic details and a convergence to a universal form for sufficiently long molecules. The pair effective interactions are shown to be accurate up to within the semidilute regime with additional, many-body forces becoming increasingly important as the polymer concentration grows. The dramatic effects of topological constraints in the form of interaction potentials are brought forward and critically discussed.

I. Introduction

The interplay between topology and the natural sciences is one of the most fascinating realms of research, with interest ranging from pure and applied mathematics all the way to materials science and biology. In this work, we focus on one particular aspect of topology, namely on the problem of knots, which finds a concrete physical realization in the field of polymer science. The simplest operation that modifies the topology of a linear polymer chain results by connecting together its two ends, thereby creating a ring or cyclic polymer, and corresponding to the so-called 0-knot or trivial knot, a situation which we will also describe as an unknotted ring polymer. DNA is the most common example of an unknotted ring; however, synthetic ring polymers display very complex knotted configurations, and the probability of obtaining a knotted ring polymer tends to unity when the number of monomers in the ring goes to infinity. A recently-developed synthesis technique allows for a production of a large number of unknotted rings, but it has the drawback of producing highly polydispersed cyclic polymers.

Mathematical work on knots is very rich and we mention here just a key aspect of it, pertaining to the classification of knots and the effort to find efficient topological invariants that characterize them; a universal topological invariant providing a one-to-one correspondence to each type of knot is still lacking. The Alexander polynomial Δ(s) provides a possibility to characterize knottedness but, unfortunately, topologically different knots can share the same Δ(s). In biologically-motivated work, there exist experimental investigations of DNA pertaining to the mechanisms of obtaining knotted DNA through the influence of topoenzymes. The relationship between the speed of migration and topology of DNA molecules has been studied in ref. 10. Since the presence of knots in a cyclic macromolecule can be viewed as a self-entanglement phenomenon, it has clear consequences in its self-reptation dynamics and acts as an inhibitor to the ‘unzipping’ of DNA, i.e., to its separation into two isolated, cyclic strands. Virnau et al. have recently carried out an analysis of knotted structures in the Protein Data Bank, discovering 241 complex knots and putting forward a hypothesis on the relationship between knottedness and protein function.

In physics, work on ring polymers has mainly concentrated on two complementary aspects. Isolated rings (at the infinite dilution limit) have been studied by theory and simulation, focusing on the question of the dependence of the polymer size on the degree of polymerization N. The infinite-dilution gyration radius, $R_g$, has been found to scale with N as a power-law, featuring the Flory exponent of self-avoiding linear chains, $R_g \sim N^{0.83}$, even in the absence of self-avoidance. This is a clear manifestation of the effects of the topological constraint, namely that the knottedness of the ring cannot be altered even though the random walk can intersect itself. At the other end of the concentration spectrum, melts of unknotted ring polymers have attracted quite a bit of attention. There, it is expected that entanglement effects between rings (concatenations) will have a drastic effect on the dynamics, since they are permanent (contrary to the case of entanglements between linear chains). On-lattice simulation work has focused on the size, structure and self-diffusion of ring melts, whilst recent experimental investigations revealed a novel power-law stress relaxation in entangled ring polymers.

A broad field of research that has remained hitherto unexplored pertains to the question of bridging the length- and time-scales of the problem by performing accurate coarse-graining approaches to switch from a language that employs individual monomers to one that replaces the ring by a suitably-chosen effective degree of freedom. This modern and very fruitful approach to describe polymer solutions both in the dilute and the semidilute regimes is well-established by now and has found successful application for polymer chains, star polymers, dendrimers, star-shaped polyelectrolytes and block copolymers. For example, this approach has led to the determination of the equilibrium and glassy phase diagrams of star polymer solutions, and to a discovery of a host of novel arrested states in

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mixtures of the same homopolymer additives. Depending on the molecular architecture, the terminal monomer, the central monomer or the center of mass of the molecule can be chosen as effective coordinates, whose interaction is described by a suitably derived effective potential $V_{\text{eff}}(R)$, $R$ denoting their mutual separation. Ring polymers are prime candidates to examine the effects of topology on $V_{\text{eff}}(R)$, by comparing either to the corresponding quantity for linear chains or among effective interactions between rings of different knottedness. Moreover, accurate effective potentials open the way for an economical description of their structure and thermodynamics.

In this work, we apply off-lattice simulation and related numerical techniques to coarse-grain ring polymers of three different degrees of knottedness, namely, in Conway’s notation, the $0_1$-knot, the $3_1$-knot and the $5_1$-knot. We derive the effective potentials between their centers of mass, establishing rings as a novel kind of ultrasoft colloid with tunable softness. We further examine the robustness of the effective pair potentials on concentration and the deformations of the ring sizes with density, providing evidence for the role and effects of many-body interactions at increasing densities.

II. The models

From the theoretical point of view, topological constraints are difficult to include in the Hamiltonian. Therefore, an appropriate tool to study this subject is computer simulations. Here, one can construct ring polymers of the desired topology (type of knot) in the first place, and then ascertain that the model and/or the simulation moves applied are such that both the intra-ring and the inter-ring topological constraints are conserved throughout the simulation. Whereas, the former refer to the type of knot, the latter pertain to the absence of concatenations. We have performed off-lattice Monte-Carlo (MC) simulations to calculate the effective potential, $V_{\text{eff}}(R)$, for two fully flexible rings (i.e., at the limit of infinite dilution) in athermal solvent conditions, $R$ being the distance between their centers of mass. By construction, $V_{\text{eff}}(R)$ is a pair potential; questions on its applicability for finite concentrations $\rho$ of polymer rings will be discussed in another section. We employed, for comparison, two different models for the monomer-monomer interactions and bondedness, as described below.

Model I – Here, the monomers are modelled as hard spheres (HS) of diameter $d$ and the connections among them by threads of maximal surface-to-surface extension $\delta d$ ($\delta > 0$), as in ref. 38. Accordingly, the monomer-monomer interaction $V_{\text{mm}}(r)$ and the bonding interaction $V_{\text{bond}}(r)$, where $r$ is the distance between the monomer centers, reads as:

$$V_{\text{mm}}(r) = \begin{cases} \infty & \text{for } \frac{r}{d} < 1 \\ 0 & \text{for } \frac{r}{d} > 1 \end{cases}$$

acting among all monomers and

$$V_{\text{bond}}(r) = \begin{cases} \infty & \text{for } \frac{r}{\delta d} < 1 \\ 0 & \text{for } 1 < \frac{r}{\delta} < 1 + \delta \\ \infty & \text{for } \frac{r}{\delta} > 1 + \delta \end{cases}$$

for connected ones. We set $d = 1$ in what follows and we prevent crossing of the bonds and thus conservation of topological constraints by setting $\delta = 0.2 < (\sqrt{2} - 1)$ and choosing the Monte Carlo displacement step to be less than $\delta$. We have explicitly checked the avoidance of spurious concatenations by creating a pair of concatenated rings, pulling each of them with opposite forces and verifying that they never disentangle, no matter how strong the applied force is.

Model II – Alternatively, we employ a soft-sphere model for the monomer-monomer interactions and also a soft bonding potential, which reads as:

$$V_{\text{mm}}(r) = \begin{cases} \infty & \text{for } \frac{r}{\delta h} < 1 \\ 4e \left[ \left( \frac{\sigma}{\sigma} \right)^{16} - 9c^{-16} + 8c^{-18} \left( \frac{\sigma}{\sigma} \right)^2 \right] & \text{for } \frac{h}{c} < \frac{r}{\delta c} < 1 \\ 0 & \text{for } \frac{r}{\delta c} > 1 \end{cases}$$

for all monomers and

$$V_{\text{bond}}(r) = \begin{cases} \infty & \text{for } \frac{r}{\delta h} < 1 \\ 4e \left( \frac{\sigma}{\sigma} \right)^{22} & \text{for } 1 < \frac{r}{\delta h} < \frac{\xi}{h} \\ \infty & \text{for } \frac{r}{\delta h} > \frac{\xi}{h} \end{cases}$$

for bonded ones. We set $\sigma = \varepsilon = 1$ and we choose the values $h = 0.843$, $\xi = 1.147$, and $c = 1.15$ for the remaining parameters. In this way, the maximum bond extension is $\xi - h = 0.304$, thus we prevent crossing by choosing a Monte Carlo step less than this number. The potential of eqn (3) is purely repulsive and does not show local minima within the interaction range. The used quadratic correction guarantees continuity of potential and forces at the cutoff distance. The sum of $V_{\text{mm}}(r)$ and $V_{\text{bond}}(r)$ yields an effective potential between connected monomers with a deep minimum at $r = 0.955$, which guarantees chain uncrossability. As for Model I, we also checked the preservation of topology in Model II by pulling two concatenated rings away from each other and verifying that they remained linked to one another.

III. Effective pair potentials: Monte Carlo simulations

We apply Monte Carlo (MC) simulations of both models above to measure the probability $G(R)$ of finding the centers of mass of the rings at separation $R$, then deriving the effective pair potential from it as:

$$\beta V_{\text{eff}}(R) = -\ln G(R)$$

where $\beta = (k_B T)^{-1}$, with Boltzmann’s constant $k_B$ and the absolute temperature $T$. Since the range of interactions should be finite (of the order of the infinite-dilution gyration radius $R_g,0$ of the rings), we do not need statistics for very long distances, where $V_{\text{eff}}(R) \rightarrow 0$. However, for short distances, $R \leq R_{g,0}$, the entropic repulsion between molecules can be strong and the statistics very poor. To overcome this technical difficulty, we have used the
same umbrella-sampling technique employed by Mladek et al. in ref. 39. We have included in our MC simulations a combination of rigid translations (less than the MC step, defined as the attempt to move one monomer) and small rotations on some MC steps to explore the phase space faster. The production run is started after \(5 \times 10^5\) MC steps for equilibrating. Statistics over \(10^3\) and \(10^4\) MC steps for small and big molecules, respectively, is sufficient to reach good-quality results.

Results obtained from Model I above and for unknotted rings, are shown in Fig. 1, where a comparison with linear chains is also provided. In the inset of Fig. 1, we show the effective interaction potential between linear chains obtained by our model, which fully conform to the previously-obtained results by Louis and co-workers, obtained by on-lattice simulations of long chains. Indeed, for the linear polymer, we obtain for \(V_{\text{eff}}(R)\) a Gaussian-shaped curve, whose amplitude decreases with \(N\) and seems to be converging on some universal value. For the highest simulated \(N\), \(N = 100\), our result for \(\beta V_{\text{eff}}(R = 0) \equiv 2.4\) is somewhat higher than the corresponding one from the lattice model, but this is caused by the continuum vs. discrete natures of the two models; we believe that at sufficiently high values of \(N\), the universal amplitude \(\beta V_{\text{eff}}(R = 0) \equiv 1.87\) found in refs 23 and 24 will be recovered.

Turning our attention to the main plot of Fig. 1, and in comparison with the inset, we immediately see the influence of the simplest topological operation on chains, i.e., of connecting their two free ends together, on the effective interaction between the centers of mass. As expected, the range of the potential is set by the molecule size: at about \(R \approx 3 R_g,0\), \(V_{\text{eff}}(R)\) has decayed to zero, as for the linear chains. Moreover, as \(N\) grows, the amplitude \(\beta V_{\text{eff}}(R = 0)\) decreases, since larger rings have more free space available for interpenetration. However, both the shape and the amplitude of the ring effective potentials are dramatically different than those of chains. At small separations, \(R \lesssim 0.5 R_g,0\), there is a local attraction for small \(N\), which turns into a flat region as soon as the scaling limit is reached, for which \(V_{\text{eff}}(R)\) reaches a universal form. This limit appears to already be there for \(N \gtrsim 70\) for the ring-topology, whilst one needs much larger \(N\)-values for chains on the lattice.

Both the flat region and the higher amplitude, \(V_{\text{eff}}(R = 0) \equiv 6 k_B T\), can be understood by considering the typical conformations between rings as soon as their inter-center separations become small enough. As can be seen in the snapshot shown in Fig. 2, two rings bring their centers of mass into coincidence by a mechanism in which one ring ‘opens up’, the other ‘shrinks’ in one direction and penetrates the first. The loss of entropy caused by such an arrangement is clearly higher than the one needed for two linear chains to bring their centers of mass on top of each other, since the chains can still explore phase space more efficiently due to the freedom of their untied ends. This inter-penetrating configuration is the most common one for all distances \(R \lesssim 0.5 R_g,0\), so that the typical cost it has on the free energy can be roughly estimated by a Flory theory, in which a polymer is confined to a spherical cavity of radius \(R_g,0/2\) (the precise shape of the cavity being immaterial for a scaling argument). Indeed, the resulting free energy cost turns out to be of the order of \(10k_B T\), in agreement with the aforementioned value of

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**Fig. 1** Main plot: effective pair interaction potentials \(V_{\text{eff}}(R)\) between the centers of mass of two unknotted and unconcatenated ring polymers, consisting of the hard-sphere monomers connected with threads, as described in eqn (1) and (2), and obtained by umbrella-sampling Monte Carlo simulations. Results are shown for six different degrees of polymerization \(N\), as indicated in the legends. Distances are scaled with the gyration radius of the rings at infinite dilution, \(R_g,0\). Inset: the same quantity for linear chains and for three different values of the degree of polymerization.

**Fig. 2** A simulation snapshot of two \(N = 50\), self-avoiding ring polymers, whose monomers are modeled by eqn (1) and (2), and at a configuration for which the distance between the centers of mass vanishes. The position of the common center of mass is denoted by the black sphere. Beads and threads connecting them are not drawn to scale.

**Fig. 3** The same as Fig. 2, but for a distance \(R = 2 R_g,0\) between the centers of mass, which are denoted by the two black spheres.
the amplitude of the interaction. Since this is the typical configuration for the whole range $\leq 0.5 R_{g,0}$, the effective potential $\beta V_{\text{eff}}(R)$ is flat there. For larger separations, rings do not necessarily have to penetrate, as shown exemplarily in Fig. 3, and $\beta V_{\text{eff}}(R)$ decreases again. The presence of the local minimum (for lower $N$-values) or the flat region (at the scaling limit) for $\beta V_{\text{eff}}(R)$ at and around $R = 0$ are by no means minor curiosities: as shown by means of analytical arguments and simulation in refs 40 and 41, this feature causes the Fourier transform of $\beta V_{\text{eff}}(R)$ to contain negative components, leading to the formation of clusters at sufficiently concentrated fluid phases, which order into crystals at even higher densities. Whether this scenario applies to ring polymers is an issue that will be discussed in the following section.

The effective potential would be of little use if it were not robust with respect to changes in the microscopic details of the model; after all, the very sense of coarse-graining is to eliminate the latter and replace the ring with a single, ‘soft colloid’, without having to worry about the specific chemistry of the polymer, as long as the solvent is athermal. To check this, we have repeated the MC simulations employing Model II above, and in the main plot of Fig. 4 we show representative results to compare them with those from Model I. We indeed see that the shape of the obtained effective potential is very similar between the two models for fixed degrees of polymerization $N$; in fact, to a very high degree of accuracy, $V_{\text{eff}}(R)$ from Model II is just a scaled version of its counterpart from Model I, with a factor of roughly 1.2. In the inset of Fig. 4 we show the scaling of the ring size with $N$, confirming the validity of the Flory scaling, and lending further corroboration to the soundness of the simulation method employed.

The hitherto presented results pertain to the trivial ring topology, also called a 0-knot. Since any solution of rings will also contain chains as well as other types of knots, it is pertinent to consider also the effective interactions among those. We have constructed initial configurations of self-avoiding rings with the $3_1$- and $5_1$-knotted topologies by using the parametrization: $x = [2 + \cos(qf/p)]\cos\phi$; $y = [2 + \cos(qf/p)]\sin\phi$; $z = \sin(qf/p)$ on the surface of a torus, with $(p, q) = (2, 3)$ and $(p, q) = (2, 5)$ for the $3_1$- and $5_1$-knots, respectively. Thereafter, we calculated, following the methods presented above, all of the interaction potentials between them. For the sake of economy, we show in Fig. 5 only the effective interactions between species of the same topology. We find big differences between ring and linear molecules; not only the height, also the shape of the curve changes, from an approximately Gaussian to a non-Gaussian potential. It can be clearly seen that the presence of knots has a double effect on $V_{\text{eff}}(R)$: on the one hand, the amplitude of the interaction grows with the complexity of the knot; on the other, the flatness around $R = 0$ is lost and the potential now decreases monotonically as $R$ grows. Once again, these results bring about the essential role of topological constraints, since all simulated rings are identical at the microscopic level.

**IV. Finite concentrations: molecular dynamics simulations**

Any coarse-graining procedure of complex (macro)molecules inadvertently generates not only an effective pair potential but also many-body interactions, which make their presence visible as the concentration grows. The physically relevant question is how strong these are and from which concentration do they begin to have tangible effects on the structure and thermodynamics of the system? To address this question for the system at hand, we have followed the strategy, also applied in refs 24 and 38, of performing two types of simulations, both for a range of increasing densities: in the first, coarse-grained type, rings are
modeled as soft colloids (point particles) interacting by the previously-derived \( V_{\text{eff}}(R) \). In the second, full monomer-resolved simulations of the rings at the same concentration are carried out. Each type of simulation yields, e.g., the radial distribution function \( g_{\text{rad}}(R) \) between the centers and a comparison between the results offers information on the validity of the pair potential. Evidently, the monomer-resolved simulation yields the true correlation functions, whilst the effective simulation provides, in general, only an approximation. We use the interactions of Model II and limit ourselves to knot-free rings only.42

The monomer-resolved simulations were carried out as follows. For the initial configurations of the rings, we constructed \( M \) polygons of \( N \) monomers, of perimeter \( \approx N\sigma \), and set the bonds to form a connected ring. In this way, knotting was avoided. Random orientations were assigned to the rings. Concatenation was avoided by initially placing the centers-of-mass of the rings on single-occupied nodes of a cubic lattice with spacing much larger than \( N\sigma \). Thus, we started from a large simulation cell in dilute conditions \( (pD_{b,0} \ll 1) \), with \( p \) the number density of rings and \( D_{b,0} = 2R_{g,0} \) the diameter of gyration at infinite dilution.

Starting from this initial dilute density, we performed molecular dynamics (MD) simulations at several target densities. The transition between two consecutive target densities was achieved through a slow compression procedure, by rescaling the simulation cell by a factor of 0.99 every 2000 time steps, up to a total reduction of the original cell size by about 15%. This slow compression, together with the properties of the microscopic potentials results in exclusion of accidental concatenations. Once the new target density was achieved, we performed a long equilibration run before the production run. For the latter, no drift was observed in thermodynamic quantities and average radii of gyration. The selected target densities covered a range from high dilution to many times the overlap density (see below). All simulations were performed at temperature \( k_{B}T = \varepsilon \). We investigated rings of \( N = 20 \) and 50 monomers. The simulation cell contained, respectively, \( M = 2400 \) and 1600 rings. We performed averages to obtain the correlation function \( g_{\text{rad}}(R) \) and also the concentration-dependent radius of gyration \( R_{g}(\rho) \). The latter is a very important quantity, since it is known, e.g., from linear chains, that polymers shrink as concentration grows beyond its overlap value, due to screening of the excluded volume interactions.

For the effective fluid simulation, we performed MD simulations of point particles interacting via \( V_{\text{eff}}(R) \) derived using Model II, also at temperature \( k_{B}T = \varepsilon \). We thereby employed ultrasoft particles, with the same number \( M \) and the same cell size as those used in the monomer-resolved MD simulations. The particles were randomly placed in the simulation box, and a long equilibration run was performed before the production run. The equilibration runs, both for the real rings and the effective fluids, were performed under periodic velocity rescaling. Production runs were microcanonical. The duration of the equilibration and production MD runs was typically between \( 2 \times 10^6 \) and \( 10 \times 10^6 \) time steps. Equations of motion were integrated in the velocity Verlet scheme, with a typical time step of \( \Delta t = 2 \times 10^{-3} \). Static observables (see below) were typically averaged over 1000 equispaced configurations.

Results for the center-of-mass correlation functions are shown in Fig. 6, where we have scaled the densities with the value of the overlap concentration, \( \rho^* \) (for the determination of the latter, see inset of Fig. 7 and the discussion below). Excellent agreement between the monomer-resolved and the effective-fluid simulations is obtained for densities as high as four times the overlap density; however, small discrepancies exist at low values of \( R \), which become clearly visible at the two higher concentrations shown there. In particular, the effective fluid simulations yield accumulation of particles ‘on top of each other’, corresponding to the clustering scenario mentioned above, characteristic of potentials containing negative Fourier components.40,41

**Fig. 6** A comparison of the radial distribution functions between the centers of mass of unknotted ring polymers, as obtained by monomer-resolved simulations (■) and by effective simulations (–) via the infinite-dilution effective pair potential \( V_{\text{eff}}(R) \). The ring densities \( \rho \) are scaled over the overlap density \( \rho^* \) (for a definition of the latter see the inset of Fig. 7) and their values are indicated in the legend.

**Fig. 7** Main plot: the density-dependent, effective pair potential \( U(R,\rho) \) that reproduces the structure obtained by the monomer-resolved simulations of ring polymers. The curves are shown for the same ratios \( \rho\rho^* \) as Fig. 6 and color-coded in the same fashion. Inset: the dependence of the radius of gyration \( R_{g} \) of self-avoiding rings on the concentration of the solution. The arrow indicates the density for which \( R_{g} \) starts deviating (by \( \approx 1\% \)) from its infinite dilution value, \( R_{g,0} \) and serves to define the overlap density \( \rho^* \).
Although this would imply that several rings share a common center of mass, the monomer-resolved simulations do not reproduce this effect. Here, the obtained radial distribution functions \( g_{\text{cm}}(R) \), instead of a local maximum, show a local minimum at \( R = 0 \). This feature is characteristic of pair interactions with fully positive Fourier spectra. Evidently, many-body effects, most likely related to the deformation of the rings, come into play and cause deviations of the correlation functions of the system from those predicted by the coarse-grained procedure, at least for short distances; coarse-graining is, however, quite accurate for larger values of \( R \).

The definition of the overlap concentration \( \rho^* \) is rather ambiguous for polymers, since it is typically determined by the relation \( \rho^* D^3 \sim 1 \), where \( D \) is some characteristic length scale of the molecule. Depending on whether one uses the gyration radius or diameter, the end-to-end distance or the hydrodynamic radius, quite disparate estimates can be obtained, differing by as much as one order of magnitude. Here, we are anticipating that the many-body forces should arise from deformation and shrinking of the rings, therefore we aim at a definition of \( \rho^* \) that takes this physical process into account. It is reasonable that as long as no significant overlaps between rings occur in a concentrated solution, each molecule should maintain the size it possesses at infinite dilution. In the inset of Fig. 7, we show the ratio \( R_c/R_{g,0} \) of rings with various numbers of monomers \( N \), plotted against the dimensionless density \( \rho D_{g,0}^2 \). The characteristic shrinking of the rings can be seen to set in from the value \( \rho D_{g,0}^2 = 0.2 \) onwards. This density for which \( R_c \) deviates by \( \approx 1\% \) from \( R_{g,0} \), serves as the definition of the overlap density.

The combined effects of all many-body forces can be incorporated in a density-dependent, effective pair interaction \( U(R,\rho) \), which is constructed in such a way that it reproduces the correlation function \( g_{\text{cm}}(R) \) at the given density. In view of the fact that this interaction is expected to be very soft, we followed the procedure put forward in ref. 24 and applied an iterative hypernetted-chain inversion procedure on the functions \( g_{\text{cm}}(R) \) obtained by the monomer-resolved simulations to obtain the sought-for quantity \( U(R,\rho) \); evidently, \( U(R,\rho \rightarrow 0) = V_{\text{eff}}(R) \). Results for the so-obtained quantity \( U(R,\rho) \) are shown in the main plot of Fig. 7. In full consistency with the definition of \( \rho^* \), we see that \( U(R,\rho) \) is, within numerical error, indistinguishable from its infinite-dilution counterpart, \( V_{\text{eff}}(R) \), up to more than twice the overlap concentration. As density grows, discrepancies become more pronounced and, in particular, \( U(R,\rho) \) grows more repulsive and is deprived of the property of ‘flatness’ around \( R = 0 \). Instead, it is monotonically decreasing with \( R \), a feature akin to the infinite-dilution potentials of linear chains or knotted rings, as presented above. Concomitantly, the full Fourier spectrum of \( U(R,\rho) \) becomes positive and the clustering property is lost, so that \( g_{\text{cm}}(R) \) shows a local minimum at the origin.

The development of increasing effective repulsions at higher polymer concentrations is a feature that has also been seen for linear polymer solutions in the semidilute regime.\(^{24}\) For rings, the phenomenon is even more pronounced. Since it is setting-in almost exactly at the point where the rings start to shrink, we argue that its physical origin lies at precisely the deformation of the rings, which causes an increase in the local monomer concentration around the center of mass and thus imposes an increasingly high penalty on full overlaps between the centers. In this sense, adding some stiffness to the rings, which acts as an inhibitor to shrinking, should help in carrying the validity of the infinite-dilution effective interaction \( V_{\text{eff}}(R) \) deeper into the semidilute regime and thus bringing about the phenomenon of clustering. Preliminary results from our work show that this is indeed the case and their presentation will be the subject of a future publication.

V. Conclusions

We have presented an approach for coarse-graining ring polymers by tracing out their microscopic degrees of freedom and representing them as ultrasoft colloids that can fully overlap. Real solutions of cyclic polymers are not only mixtures of chains and rings of different knottedness but, in addition, they are characterized by considerable polydispersities in their degrees of polymerization. Our work is the first step in the direction of a full and realistic coarse-graining of such complex fluids and results pertaining to interactions between rings of different sizes and topologies will be presented elsewhere. From the fundamental point of view, our work brings forward the tremendous influence that topology can have on physics without the slightest change in the underlying microscopic interactions, an effect that has been detected in various expressions in other fields of physics but it has not been sufficiently explored within soft matter science. Changes in the polymer architecture, such as, e.g., the formation of star polymers with \( f \) arms, have been looked upon but there, there is a well-defined limit (\( f = 2 \)), for which stars reduce again to linear chains. For the case of rings, the differences are truly irreducible.

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