Effective interactions of knotted ring polymers

Arturo Narros†, Angel J. Moreno†‡ and Christos N. Likos*
†Faculty of Physics, University of Vienna, Boltzmanngasse 5, A-1090 Vienna, Austria, ‡Centro de Física de Materiales, CSIC-UPV/EHU, Apartado 1072, E-20080 San Sebastián, Spain, and *Donostia International Physics Center, Paseo Manuel de Lardizabal 4, E-20018 San Sebastián, Spain

Abstract
In the present article, we review recent computational investigations on the properties of ring polymers in solution. In particular, we focus on effective interactions obtained by means of coarse-graining techniques. We discuss the relative importance of the self-avoidance and the topological contributions in the qualitative features of the effective potential. We extend our previous results on identical rings and determine the effective potential between dissimilar ring polymers of distinct topology and size. The results obtained reveal the dramatic effects of the specific topology on the effective interactions, and hence in the structural correlations, of polymeric systems.

Multiscale simulations is one of the most active and important fields in many areas of computational science [1,2]. They are an indispensable tool to obtain relevant information on a variety of physical systems at different length and time scales. They find wide applications, e.g. in biological systems [3,4], in the study of structural correlations [5] or as a means to improve simulation performance in combination with renormalization group theory [6]. Multiscale simulations of complex polymer systems involve the application of CG (coarse graining) techniques. CG amounts to the systematic extraction of the relevant information in order to simulate coarse-grained models, allowing the reduction of computational expense and bridging different length and time scales. This is particularly useful in polymers, which exhibit a rich and complex structure as well as relaxation processes extending over an extremely broad dynamic window. In the field of biophysics, DNA is an archetypical example of this complexity [7]. Basic biological process, such as DNA replication, involve a vast spectrum of length and time scales, arising from the long double-helix structure. Another relevant aspect of the macromolecular complexity is topology. This problem has generated increasing interest in the biophysical community over the last few years, since long biopolymers such as DNA are easily found in the knotted state [8–13]. Knotting is also possible for smaller systems such as proteins [14]. Given the importance of such systems and the role played in them by topology, it is pertinent to pay attention in CG techniques in which topology is an ingredient from the very outset.

The mathematical object that takes into account the interactions between coarse-grained particles is known as effective potential, \( V_{\text{eff}}(R) \) [15]. Here, \( R \) is the distance between two suitably chosen degrees of freedom, each one effectively describing the whole molecule. A typical and useful choice is to use the CMs (centres of mass) of the two considered macromolecules. The knowledge of \( V_{\text{eff}}(R) \) is a key goal of CG techniques. The effective potential allows extraction of the relevant information in order to simulate polymer solutions at least up to the overlap concentration, removing the irrelevant fast degrees of freedom, i.e. the fluctuations of the individual monomers. An illustrative example of the usefulness of CG is the fact that \( V_{\text{eff}}(R) \) is closely related to the second virial coefficient, \( B_2 \), of the solution. The temperature for which \( B_2 = 0 \) coincides with the so-called \( \Theta \) point, i.e. the temperature at which the dissolved polymers behave as ideal (Gaussian conformations). A considerable amount of work has been dedicated to the calculation of \( V_{\text{eff}}(R) \), combining different solvent quality and topological conditions, as for, e.g., linear polymers [16,17] or unknotted ring polymers [18,19]. The relevant determination of \( V_{\text{eff}}(R) \) allows prediction of, via the condition \( B_2 = 0 \), a decrease in the \( \Theta \)-temperature for ring polymers with respect to their linear counterparts. This has been confirmed experimentally [20,21].

One of the most striking effects of topology on the effective interactions is given by the so-called topological potential between two unknotted ring polymers, \( V_{\text{topo}}(R) \), which is a part of the total contribution to the effective potential \( V_{\text{eff}}(R) \). This topological interaction exists even for the ideal case of infinitely thin and non-interacting ring polymers, and it arises from the constraint that, as the two rings approach each other, any concatenation or link formation between them is forbidden. This topological constraint gives rise to a reduction in the number of available states, and thus of the total entropy. The resulting topological interaction was first considered in the pioneering work of Frank-Kamenetskii et al. [22], and has been investigated in detail in the work of Hirayama et al. [23] and of Bohn and Heermann [24]. There, the interdependence between topological interactions and those stemming from self-avoidance was discussed. Thus it was shown that \( V_{\text{topo}}(R) \) changes with the strength of the
excluded-volume parameter and it also depends on the degree of polymerization $N$ of the molecules.

The studies mentioned regard the case of simple circular (‘unknotted’) rings. To the best of our knowledge, the influence of the knottedness of the rings on the effective potential has only been considered in a study by us [25]. In that work, we derived, using MC (Monte Carlo) techniques, effective potentials between unknotted rings as well as between knotted rings with different topology. The study was restricted to the case of identical rings (i.e. both rings having the same topology and $N$). For moderate values of $N$, it was found that the strength of the effective potential grows with increasing complexity of the knot. In the present article, we extend the investigation reported in [25] and obtain effective potentials between pairs of dissimilar rings (distinct topologies and number of monomers). The results presented below provide new insights into the role of molecular size and topological constraints in the properties of ring polymers [18,19,23–25].

In our coarse-grained model for ring polymers, the relevant magnitudes are the distance between the CMs of the rings, $R$, and their average size characterized by the radius of gyration, $R_g$. We have calculated the effective interaction between two ring polymers and whose CMs are at a mutual distance $R$. The topologies of the two rings are denoted by $\tau_i$ and their degree of polymerization by $N_i$, with $i = A,B$. Thus we denote the effective potential between $A$ and $B$ as $V_{\text{eff}}(R;\tau_A,N_A,\tau_B,N_B)$. We consider the simplest ring topologies obtained by the torus-knot generator, i.e. the unknot (or trivial knot) $0_1$, the trefoil knot $3_1$ and the $5_1$ knot. These are very common in Nature, because they have the highest probability to be obtained from a long polymer [26]. Indeed, these topologies are very often found in circular DNA [10,27], under both dilute and semi-dilute conditions, as well as in proteins [14]. For completeness, we also introduce the notation $\tau = L$ to refer to common linear polymers. We use a model of tethered hard-spheres for the ring polymers, as described in [25]. The bounded character of the effective potential allows us to prevent accidental concatenation by bond-crossing [25]. Following the procedure described in [25], we have used the umbrella-sampling MC technique to generate configurations of the two rings at the whole relevant range of CM distances. This procedure allows us to obtain the radial distribution function $g(R)$ with high accuracy. The effective potential is then obtained as $V_{\text{eff}}(R) = -k_BT \ln g(R)$ [25], with $T$ the temperature, and $k_B$ Boltzmann’s constant.

The average radius of gyration $R_g$ of an isolated ring polymer in equilibrium depends on both the topology $\tau$ and the monomer number $N$ and it follows the law [28]:

$$R_g^2(\tau, N) \propto \begin{cases} N^{v_0} & N \leq N^*(\tau) \\ N^\alpha & N > N^*(\tau) \end{cases}$$

(1)

where $v_0 = 1/2$ and $\alpha \approx 3/5$ are the critical exponents of the random walk and the self-avoiding random walk respectively, and $N^*(\tau)$ is a topology- and model-dependent crossover value of $N$. Typically, $N^*(0_1) \approx 300$, for unknotted rings, whereas this value grows for more complicated knotted topologies. Owing to computational limitations, we have used relative short molecules, i.e. $N \in [15,200]$. When two rings interact with each other, the gyration radii are, in general, a function of their separation: $R_g^i = R_g^i = (R;\tau_A,N_A,\tau_B,N_B), i = A,B$. Obviously, for infinite separation, the latter is identical with the undisturbed gyration radius of an isolated ring (eqn 1). We thus introduce the notation:

$$R_g^i(R \to \infty; \tau_A, N_A, \tau_B, N_B) = R_g^i(\tau, N)$$

(2)

Accordingly, we also define a ‘swelling factor’, $\alpha_i$, as the relative change in the size of the ring with respect to its undisturbed size, $(R \to \infty)$ due to its interaction with the other ring when their CMs coincide ($R = 0$):

$$\alpha_i(\tau_A, N_A, \tau_B, N_B) = \frac{R_g^i(R = 0; \tau_A, N_A, \tau_B, N_B)}{R_g^i(0, \tau, N)}$$

(3)

In the following, the distance between the CMs of the two rings will be measured in units of the molecule-averaged infinite-separation radius of gyration:

$$\left\langle R_g^i \right\rangle = \frac{R_g^i(\tau_A, N_A) + R_g^i(\tau_B, N_B)}{2}$$

(4)

The effective potential $V_{\text{eff}}(R;L,N,\tau,L,N)$ between two linear polymers of $N$ monomers each has a characteristic Gaussian shape, a result arising both from on-lattice [16,24,29] and off-lattice simulations [25] under good solvent conditions. This behaviour can be rationalized by the fact that the monomer distribution around the CM is approximately Gaussian for a linear chain. For sufficiently long chains, the effective potential becomes a universal function of $R/L$, with high accuracy. The topological potential [22–24].

The specific molecular topology does not only alter the effective potential quantitatively. It also leads to qualitative differences. In particular, the effective potential $V_{\text{eff}}(R)$ for $0_1$-ring polymers does not show the Gaussian form found for their linear counterparts [23–25]. Its shape rather features a plateau at separations $R \leq 0.5L$, which is longer for small rings (reflecting an effective short-range attraction). This feature stems from the typical configurations of two unknotted rings at small mutual separation ($R \to 0$), in which one of the rings adopts an open conformation that facilitates penetration [25]. Similar features have been observed in the effective potential.
The effective potential for 01-rings is included for comparison (lower thin continuous line).

Figure 1 | The effective potential $V_{\text{eff}}(R)$ for identical ring polymers of 31 (continuous lines) and 51 (broken lines) topologies, and for different degrees of polymerization $N$

The different $N$ values are indicated in the key within parentheses. The effective interaction for 01-rings is included for comparison (lower thin continuous line).

Figure 2 | The effective potentials $V_{\text{eff}}(R;31,100,01,N)$ (continuous lines) and $V_{\text{eff}}(R;01,100,31,N)$ (broken lines)
The molecular sizes for the $B$ molecule are specified in the legend.

for amphiphilic dendrimers [32], giving rise to clustered structures under certain conditions [33].

Let us now discuss effective potentials for knotted rings, namely with 31- and 51-topologies. Figure 1 shows results for $V_{\text{eff}}(R;31,N,31,N)$ and $V_{\text{eff}}(R;51,N,51,N)$. As can be seen, the scaling regime has not been reached for either 31- or 51-rings for $N$ as large as 100, within the investigated range of polymerization degree $N \leq 200$, in contrast with the case of 01-topology, for which the effective potential already approaches a universal form for $N \approx 80$ [25]. Nevertheless, there is an apparent trend, especially for the 31-case, towards convergence to the universal form obtained for the 01-topology. For the smallest values of $N$, a strongly repulsive potential is found for both 31- and 51-topologies. This is an expected result since knotting yields smaller and thus denser molecules, giving rise to stronger self-avoidance effects. Such effects diminish for larger rings, in which the knot size becomes negligible in comparison with the overall size of the ring. Since $V_{\text{eff}}(R;51,N,51,N) > V_{\text{eff}}(R;31,N,31,N)$, we expect that the convergence to the scaling limit will be reached at smaller $N$ for 31-rings than for 51-rings. This guess is consistent with the observation that $N^\alpha(51) > N^\alpha(31)$ for the crossover (eqn 1) in the scaling behaviour of $R_{\gamma}^\alpha$.

New results for dissimilar rings, $V_{\text{eff}}(R;31,100,01,N)$ and $V_{\text{eff}}(R;01,100,31,N)$, are shown in Figure 2. For the cases of $V_{\text{eff}}(R;51,100,01,20)$ and $V_{\text{eff}}(R;31,100,01,50)$, there is no plateau or a minimum at $R = 0$, i.e. it becomes more repulsive the smaller the separation between CMs. A tentative explanation for this feature is that the large knotted ring has to open up in order to be penetrated by the small unknotted ring. However, this involves localization of the knot, which is entropically very unfavourable. In contrast, a plateau, and even a minimum at zero separation, are clearly visible for the case $V_{\text{eff}}(R;31,100,01,100)$. Inspection of the molecular conformations (Figure 3 shows a representative case), reveal that, in this case, the large unknotted ring adopts an open conformation and is penetrated by the small knotted ring, in analogy with the observation for two identical unknotted rings [25]. This feature is also reflected in the behaviour of the swelling factors, $\alpha_i, i = A,B$ defined in eqn (3). Thus we find $\alpha_i(31,100,01,100) \approx 1.57$, i.e. a swelling of the unknotted by almost 60%, to accommodate the 31-molecule, whereas the latter retains its size, $\alpha_i(31,100,01,100) \approx 1$. Interestingly, the swelling of the 01-ring is present in the whole range of $N$ for which the effective potential exhibits a plateau or a short-range attraction. Concomitantly, the knotted ring maintains its size in the former range of $N$. Indeed, interpenetration facilitated by swelling of the knotted ring is entropically unfavourable, since it would involve localization of the knot (see also above). Since the 01-ring is already big enough, no strong swelling of the latter is necessary at full interpenetration. For instance, we find $\alpha_i(01,100,31,20) \approx 1.17$ and $\alpha_i(01,100,31,50) \approx 1$ for the unknotted and knotted ring respectively. Finally, owing to the high penalty for knotted rings to swell, penetration of large unknotted rings by small knotted rings is more favourable than penetration of large knotted rings by small unknotted rings. Hence the effective potential $V_{\text{eff}}(R;01,100,31,N)$ is weaker than its counterpart $V_{\text{eff}}(R;31,100,01,N)$.

It is pertinent to ask what is the contribution of the topological interaction to the total effective potential. For 01-rings, it has been shown that the topological contribution amounts to less than 10% of the full interaction potential [23,24]. Despite its rather small magnitude, the topological contribution has the particular feature of showing an attractive part at small distances, in contrast with the monotonic repulsive contribution that arises from self-avoidance. The interplay of both contributions brings about a plateau, and even a minimum at $R = 0$ for the full $V_{\text{eff}}(R;01,N,01,100)$ [25]. With regard to the cases examined in the present article, we find that, for small identical knotted rings, the effect of the topological potential is even smaller, since the steric crowding caused by the knots dominates the effective interaction. However, as $N$ grows, $V_{\text{eff}}(R;\tau,\tau,N,\tau,N)$ seems to converge to a form independent of the topology, i.e.
the relative importance of the topological and self-avoidance terms will approach the one discussed for the $0_1$-case. For dissimilar rings, the topological contribution to $V_{\text{eff}}(R)$ seems to be even less important: when the large ring is the knotted one, there is no plateau in $V_{\text{eff}}(R)$ and, in the opposite case, the weak swelling of the large unknotted ring is sufficient to explain the existence of the plateau on the basis of excluded-volume interactions alone (A. Narros, A.J. Moreno and C.N. Likos, unpublished work).

We have put forward a concise review of previously derived results for the effective interaction between identical ring polymers in good solvent. Moreover, we have extended this work to derive effective interactions between dissimilar rings, of different sizes and topologies. We have assigned salient characteristics of the derived potentials to the relative swelling of the rings at small separation. A short-range attraction in the effective potential is found when the large ring is the unknotted one, whereas a monotonic repulsion is observed in the opposite case. The obtained results suggest that the topological contribution to the effective potential is less important for knotted rings than for unknotted ones.

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