Geometrical complexity of conformations of ring polymers under topological constraints

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Abstract

One measure of geometrical complexity of a spatial curve is the number of crossings in a planar projection of the curve. For $N$-noded ring polymers with a fixed knot type, we evaluate numerically the average of the crossing number over some directions. We find that the average crossing number under the topological constraint are less than that of no topological constraint for large $N$. The decrease of the geometrical complexity is significant when the thickness of polymers is small. The simulation with or without a topological constraint also shows that the average crossing number and the average size of ring polymers are independent measures of conformational complexity.

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I. INTRODUCTION

Complexity of conformations of polymer chains should play an important role in the physics of polymers. Various dynamical or statistical properties of entangled polymers in solutions or melts should be related to the complexity of polymer chains as space curves. For instance, the reptation theory takes into account the entanglement complexity of polymer chains around a polymer by assuming the tube along it [1].

However, it is not trivial to investigate any aspect of the complexity of conformations of polymers directly through computer simulation. In fact, it is not clear how to express the entanglement complexity numerically for mutually entangled polymers. Furthermore, it is not known how the complexity of polymer conformations should depend on the property that polymer chains can not cross each other.

In this paper, we discuss the geometrical complexity of conformations of a ring polymer under some topological constraint. As a measure of geometrical complexity of a spatial curve, we consider the number of crossings in a planar projection of the curve, and take the average over some directions [2, 3]. Through computer simulation, we evaluate the average crossing number for \( N \)-noded ring polymers with fixed knots, and discuss their behaviors with respect to \( N \). We thus make it clear how the topological constraints can modify the geometrical complexity. Here we note that the condition that a ring polymer never cross with itself corresponds to a topological constraint on it, as far as its statistical properties are concerned. Furthermore, we plot the graphs of the mean square radius of gyration versus the average crossing number, for the SAPs with fixed knots. Then we find that the average crossing number and the mean-squared gyration radius behave independently under the topological constraints. It is thus suggested that the relation between the average sizes of ring polymers and the geometrical complexity of the conformations should be non-trivial.

Let us explain the average crossing number, more precisely. The *writhe* of a linear or ring polymer is defined by the average of the number of signed crossings appearing in a projection of the curve over all directions. As a simplified version of the writhe, Janse van Rensburg *et al.* introduced *the number of crossings* [2]. It is defined by the number of unsigned crossings in a projection. Then, *the average number of crossings* is defined by the number of crossings averaged over all possible projections. There are several numerical or theoretical studies on the average crossing number [4, 5, 6, 7].
The average crossing number is also related to ideal knots. For a knot, the ideal knot is given by its tightest geometric configuration [8, 9, 10]. Katritch et. al have obtained the average crossing number for the ideal knots up to 11 essential crossing numbers. The average crossing number should be useful for flexible DNA knots in thermal equilibrium [8]. Furthermore, it should also be useful for statistical or dynamical studies on knotted ring polymers [3, 11, 12].

II. METHODS OF SIMULATION

We consider self-avoiding polygons (SAPs) consisting of \( N \) rigid impenetrable cylinders of unit length and radius \( r \). There is no overlap allowed between any pair of non-adjacent cylindrical segments, while next-neighboring cylinders may overlap each other. We call them cylindrical SAPs, for short. A large number of cylindrical SAPs can be constructed by the cylindrical ring-dimerization method [13]. The method is based on the algorithm of ring dimerization [14], and useful for generating long SAPs systematically. In this paper, we have constructed \( M=10^4 \) samples of \( N \) cylindrical segments with radius \( r \), where \( N \) is from 20 to 1000 and \( r \) is from 0.0 to 0.07. We determine the number \( M_K \) of polygons with a knot \( K \), enumerating such polygons that have the same set of values of the two invariants: the determinant of the knot \( \Delta_K(−1) \) and the Vassiliev invariant \( v_2(K) \) of the second degree.

The mean value \( A \) of the average crossing number for a set of SAPs is defined by
\[
A = \frac{1}{M} \sum_{i=1}^{M} A_i
\]
Here, \( A_i \) denotes the average crossing number of the \( i \)th polygon. The mean value of the average crossing number for a set of the SAPs with a knot \( K \) is given by
\[
A_K = \frac{1}{M_K} \sum_{i=1}^{M_K} A_{K,i}
\]
where \( A_{K,i} \) denotes the average crossing number of the \( i \)th SAP having the knot \( K \). Thus, \( A \) is given by the average of \( A_K \)'s over all knots.

In the simulation, we have obtained the average crossing number \( A \) and \( A_K \)'s for the trivial and trefoil knots in the range of \( N \) from 20 to 1000. Here, we evaluate the average crossing number by taking the average over the \( x \), \( y \) and \( z \) directions.

The mean square radius of gyration \( R^2 \) for SAPs with \( N \) nodes is given by
\[
R^2 = \frac{1}{2N^2} \sum_{n,m=1}^{N} \langle (\vec{R}_n - \vec{R}_m)^2 \rangle
\]
Here \( \vec{R}_n \) is the position vector of the \( n \)th node, and the symbol \( \langle \cdot \rangle \) denotes the average over \( M \) polygons generated. For a knot \( K \), we define the mean square radius of gyration \( R^2_K \) for SAPs of the knot \( K \) by
\[
R^2_K = \frac{1}{M_K} \sum_{i=1}^{M_K} R^2_{K,i}
\]
Here, \( R^2_{K,i} \) denotes the mean square radius of gyration for the \( i \)th SAP in the \( M_K \) polygons of the knot.
In terms of $R^K_2$’s, $R^2$ is given by the average over all knots: $R^2 = \sum_K M_K R^K_2 / M$.

**III. AVERAGE CROSSING NUMBER UNDER A TOPOLOGICAL CONSTRAINT**

We now discuss the $N$ dependence of the average crossing number $A_K$ under the topological constraint of a knot $K$. The double-logarithmic graph of $A_K$ versus $N$ is given in Fig. 1 for the cylindrical SAPs of cylinder radius $r = 0.003$, for the trivial and trefoil knots. The graphs can be approximated by some straight lines in some large $N$ region.

Let us consider the ratio of $A_K$ to $A$ for the two knots. In Fig. 2, the ratio $A_K/A$ versus $N$ is plotted in a double logarithmic scale for the trivial and trefoil knots. The graph of the trivial knot has a concave curve: the ratio $A_{\text{triv}}/A$ is almost constant with respect to $N$ for small $N$ and then decreases with a larger gradient for large $N$. On the other hand, the graph of the trefoil knot suggests that $A_{\text{tre}}/A$ could be roughly approximated by a power of $N$ for some finite values of $N$.

In Fig. 2, the ratios $A_K/A$’s for the two knots become less than 1.0 when $N$ is large, i.e., the $A_K$’s are less than the average crossing number $A$ averaged over all knots for large $N$. Thus, the topological constraints make the conformations of ring polymers simpler with respect to the geometric complexity, when $N$ is large enough. The reduction of conformational complexity may be related to entropic repulsion arising from the topological constraints.

For the trivial knot, $A_{\text{triv}}/A$ is smaller than 1.0 in the whole range of $N$, while for the trefoil knot $A_{\text{tre}}/A$ is larger than 1.0 for $N < 200$, and smaller than 1.0 for $N > 300$. Thus, with respect to the average crossing number, the $N$-noded ring polymers with the trivial knot are less complex for any $N$ than those of no topological constraint, while those of the trefoil knot are more complex for small $N$ and less complex for large $N$ than those of no topological constraint.

The average crossing number of the trivial knot, $A_{\text{triv}}$, is smaller than that of the trefoil knot, $A_{\text{tre}}$, through the whole range of $N$. It suggests that the more complicated knot should have the larger value of the average crossing number, at least for finite $N$. The tendency is also seen in the data for the different values of $r$. As $N$ increases, however, the average crossing numbers $A_K$’s of the two knots gradually become close to each other and they become almost the same value when $N$ is very large.
The average crossing number $A_K$ of a knot $K$ have similar properties with the inverse of the mean-squared gyration radius $R^2_K$ of ring polymers with the knot $K$. In our previous work [13, 15], it is shown that for some random polygons and cylindrical SAPs, the double-logarithmic graph of the ratio $R^2_K/R^2$ versus $N$ is given by a downward convex curve and is larger than 1.0 for the trivial knot, while for the trefoil knot the graph is given by a straight line and the ratio $R^2_K/R^2$ is smaller than 1.0 for small $N$ and larger than 1.0 for large $N$.

We now consider possible asymptotic behaviors of the average crossing number. Let us review some known results on the large $N$ behavior of $N$-step self-avoiding walks (SAWs). The average crossing number can also be defined for SAWs, and we denote it by $A_{SAW}$. In Ref. [7], it is discussed that for asymptotically large $N$, the mean value $A_{SAW}$ of the average crossing number of self-avoiding walks (SAWs) is given by $A_{SAW}/N = a - b N^{1-2\nu}$ with some constants $a$ and $b$. Here $\nu$ is given by the exponent of the average size of SAWs. We also note that in Ref. [3], the large $N$ behavior of $A_{SAW}$ is approximated by a power of $N$, $A_{SAW} \sim N^{\mu_{SAW}}$, with the effective exponent: $\mu_{SAW} = 1.122 \pm 0.005$.

In order to illustrate some $r$ dependent properties of $A_K$, let us introduce an asymptotic expansion for the ratio $A_K/A$ versus $N$. Based on the asymptotic expansion of $A_{SAW}$ in Ref. [7], we assume the asymptotic expansion with respect to $N$ as follows: $A_K/N = a_K - b_K N^{1-2\nu_K}$ for any knot $K$. Here $a_K$ and $b_K$ are fitting parameters. From the simulations [13, 15], we may assume that $\nu_K = \nu$. For the ratio $A_K/A$, we thus have the following formula: $A_K/A = \alpha_K (1 - \beta_K N^{1-2\nu})$. Here, $\alpha_K$ and $\beta_K$ are fitting parameters corresponding to $a_K/a$ and $b_K/a_K - b/a$, respectively. We apply it to the data of $A_K/A$ of the $N$-noded SAPs with $N$ larger than some cut-off and for the different values of $r$.

Let us discuss the best estimates of $a_K/a$ plotted against cylinder radius $r$ in Fig. 3. When $r$ is small, the ratio $a_K/a$ becomes smaller than 1.0 both for the trivial and trefoil knots. This is consistent with the observation of Fig. 2 that the ratio $A_K/A$ for $r = 0.003$ decreases against $N$ and is smaller than 1.0 for large $N$. In Fig. 3, the ratio $a_K/a$ increases monotonically with respect to cylindrical radius $r$, and it becomes close to the value 1.0 at some large value of $r$. If the ratio $A_K/A$ becomes 1.0, then there is no topological effect on the average crossing number. On the other hand, if $A_K/A$ is less than 1.0, then it may be a consequence of the topological constraint. Thus, the behavior that the graph of $a_K/a$ versus $r$ increases up to 1.0 suggests that topological constraints on ring polymers make their conformations simpler for small $r$, while the topological effect becomes weak for large $r$.
Let us consider again the \( r \) dependence of \( A_K \) that the graph of \( a_K/a \) versus \( r \) increases upto 1.0 for the two knots, as shown in Fig. 3. A very similar behavior has also been observed for the case of the ratio \( R^2_K/R^2 \) of the mean squared gyration radii of the cylindrical SAPs with radius \( r \). In Refs. [13, 14], it has been shown for the cylindrical SAPs that a topological constraint on a ring polymer gives effective expansion to it, i.e., the ratio \( R^2_K/R^2 \) becomes larger than 1.0 for large \( N \). Furthermore, the effective expansion is significant when the cylinder radius \( r \) is small; the large \( N \) limit of \( R^2_K/R^2 \) decreases to 1.0 as \( r \) increases.

Summarizing the simulation results, we may conclude that the effect of topological constraints should be significant when the ring polymer is thin, both for the average crossing number \( A_K \) and the mean square radius of gyration \( R^2_K \).

**IV. THE MEAN SQUARED GYRATION RADIUS AND THE GEOMETRIC COMPLEXITY**

Let us discuss that the relation between the average crossing number and the average size of ring polymers should be nontrivial. In Fig. 4, the mean square radii of gyration \( R^2 \) and \( R^2_K \)’s are plotted against the average crossing numbers \( A \) and \( A_K \)’s in a double logarithmic scale for the cylindrical SAPs of \( r=0.003 \). The estimates of \( R^2 \) and \( R^2_K \)’s in Fig. 4 are different for any given value of the average crossing numbers. Thus, it follows that the mean-squared gyration radius and the average crossing number are independent quantities describing some geometric properties of conformations of ring polymers.

With the same average crossing number given, \( R^2_{\text{triv}} \) and \( R^2_{\text{tre}} \) are larger than \( R^2 \) for the cylindrical SAPs, as shown in Fig. 4. Thus, we may say that the topological constraints make the average sizes of ring polymers larger with respect to the average crossing number.

Among the \( R^2_K \)’s, \( R^2_{\text{triv}} \) is larger than \( R^2_{\text{tre}} \) in Fig. 4. It is thus suggested that the more complicated knot should have the smaller radius of gyration, as far as some finite values of \( A_K \)’s are concerned.

When the average crossing number is very large, the mean-squared gyration radius \( R^2 \) (or \( R^2_K \)) can be approximated by some power of \( A \) (or \( A_K \)): \( R^2 \sim A^\gamma \) for the average over all knots; \( R^2_K \sim A^{\gamma_K} \) for the trivial and trefoil knots. Applying the power law approximation to the data of \( N \geq 100 \), we obtain the following estimates of the effective exponents: \( \gamma = 0.860 \pm 0.001 \), \( \gamma_{\text{triv}} = 0.952 \pm 0.004 \) and \( \gamma_{\text{tre}} = 1.069 \pm 0.006 \). The graphs of Fig 4 suggests
that the effective exponent $\gamma_K$ should be independent of the knot type. Similar results are obtained also for the SAPs with the different values of $r$.

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FIG. 1: The average number of crossings with a knot type $K A_K$ versus $N$ for $r=0.003$. Numerical estimates of $A_K$ for $K=$ trivial and trefil knots are shown by closed triangles and squares, respectively.

FIG. 2: Double-logarithmic plots of the ratio $A_K/A$ versus $N$ for cylindrical SAPs with $r=0.003$. $A_{triv}/A$ and $A_{tre}/A$ are shown by closed triangles and squares, respectively.

FIG. 4: The mean-square radius of gyration $R^2_K$ versus the average number of crossings $A_K$ of cylindrical SAPs for $r=0.003$. Numerical estimates for $K=$ trivial knot, $3_1$ are shown by closed triangles and squares, respectively. Data of $R^2$ versus $A$ are shown by closed circles. $N$ are given by $51, 151$ and $100j+1$ for $j=1, \cdots, 10$.

FIG. 3: The ratio $a_K/a$ versus cylinder radius $r$ for cylindrical SAPs. The values of $a_{triv}/a$ and $a_{tre}/a$ are shown by closed triangles and squares, respectively.
Average Crossing Number

N: Number of nodes
Mean square radius of gyration vs. Average Crossing Number

- **ave**
- **triv**
- **tre**