Geometrical complexity of conformations of ring polymers under topological constraints

Miyuki K. Shimamura
Department of Physics, Faculty of Science and Graduate School of Humanities and Sciences, Ochanomizu University, 2-1-1 Ohtsuka, Bunkyo-ku, Tokyo 112-8610, Japan

Tetsuo Deguchi
Department of Physics, Faculty of Science, Ochanomizu University, 2-1-1 Ohtsuka, Bunkyo-ku, Tokyo 112-8610, Japan
(Received 25 November 2002; revised manuscript received 16 October 2003; published 24 December 2003)

One measure of geometrical complexity of a spatial curve is the average of the number of crossings appearing in its planar projection. The mean number of crossings averaged over some directions have been numerically evaluated for *N*-noded ring polymers with a fixed knot type. When *N* is large, the average crossing number of ring polymers under the topological constraint is smaller than that of no topological constraint. The decrease of the geometrical complexity is significant when the thickness of polymers is small. It is also suggested from the simulation that the relation between the average crossing number and the average size of ring polymers should depend on whether they are under a topological constraint or not.

DOI: 10.1103/PhysRevE.68.061108 PACS number(s): 05.40.Fb, 36.20.−r, 61.41.+e

I. INTRODUCTION

Complexity of conformations of polymer chains should play an important role in the physics of polymers [1]. However, it is not trivial how one can 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 cannot cross each other.

In this paper, we discuss the geometrical complexity of conformations of a ring polymer under a 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 as some functions of *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 crosses itself corresponds to a topological constraint on it, as far as its statistical properties are concerned. Furthermore, we discuss the relation between the average crossing number and the mean-squared gyration radius. Simulation results suggest that it should depend on topological constraints and should be nontrivial.

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 averaged 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 [4–7].

The average crossing number is also related to ideal knots. For a knot, the ideal knot is given by its tightest geometric configuration [8–10]. 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 [5,11,12].

The paper is organized as follows. In Sec. II, we briefly explain some aspects of simulation methods. We consider self-avoiding polygons consisting of *N* cylindrical segments in our simulation. In Sec. III, we show simulation results of the average crossing number of cylindrical self-avoiding polygons with fixed knots. We discuss some finite-size behaviors as well as asymptotic behaviors. It seems that asymptotic behaviors of the average crossing number for Self-avoiding polygons (SAPs) with fixed knots have not been discussed yet. Furthermore, we plot the graphs of the mean-square radius of gyration versus the average crossing number, for the SAPs with fixed knots.

II. METHODS OF SIMULATION

We consider SAPs consisting of *N* rigid impenetrable cylinders of unit length and radius *r*. There is no overlap allowed between any pair of nonadjacent cylindrical segments, while 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 $\Delta_K(-1)$ [15] and the Vassiliev invariant $v_2(K)$ of the second degree [16].

TABLE I. The determinant of a knot K and the Vassiliev invariant $v_2(K)$.

Knot K	$\lvert\Delta_K(-1)\rvert$	v_2
Trivial	1	0
Trefoil	3	-12
Figure-eight	5	12

The values of the invariants for some typical knots are given in Table I.

The mean value A of the average crossing number for a set of SAPs is defined by $A=\Sigma_{i=1}^{M}A_i/M$. Here, A_i denotes the average crossing number of the ith polygon. The mean value of the average crossing number for a set of the SAPs with a knot K is given by $A_K=\Sigma_{i=1}^{M_K}A_{K,i}/M_K$, where $A_{K,i}$ denotes the average crossing number of the ith SAP having the knot K. Thus, A is nothing but 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, trefoil, and figure-eight 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. Furthermore, we note that the number of M_K depends not only on the knot type, but also on the step number N [13,17]. When the knot type K is complicated, M_K can be very small. By taking into account the fact, we express statistical errors of data points explicitly by error bars which correspond to standard deviations.

The mean-square radius of gyration R^2 for SAPs with N nodes is given by $R^2=\Sigma_{n,m=1}^{N}\langle(\vec{R}_n-\vec{R}_m)^2\rangle/2N^2$. Here $\vec{R}_n$ is the position vector of the nth 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_K^2 for SAPs of the knot K by $R_K^2=\Sigma_{i=1}^{M_K}R_{K,i}^2/M_K$ [18,19]. Here, $R_{K,i}^2$ denotes the mean-square radius of gyration for the i th SAP in the M_K polygons of the knot K. In terms of R_K^2's, R^2 is given by the average over all knots: $R^2=\Sigma_K M_K R_K^2/M$.

III. SIMULATION RESULTS OF THE AVERAGE CROSSING NUMBER UNDER A TOPOLOGICAL CONSTRAINT

A. Finite-size behaviors of the average crossing number A_K

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 $r=0.003$, where K is given by the trivial, trefoil, and figure-eight knots. The graph can be approximated by a power of N such as $A_K \propto N^{\nu_{\mathrm{eff}}^K}$, when N is large enough. Here the symbol ν_{eff}^K denotes the effective exponent for the knot type K. Applying the power law approximation to the data of $N\geqslant 100$, we obtain the following estimates of the effective exponents: $\nu_{\mathrm{eff}}^{triv}=1.134\pm0.004$, $\nu_{\mathrm{eff}}^{tre}=1.070\pm0.005$, $\nu_{\mathrm{eff}}^{fig}=1.057\pm0.013$.

Let us consider the ratio of A_K to A for the trivial and trefoil knots. The ratio A_K/A versus N is plotted in Fig. 2

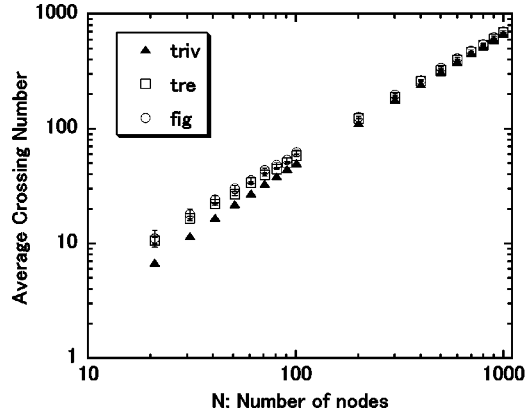

FIG. 1. The average number of crossings with a knot type K A_K vs N for $r=0.003$. Numerical estimates of A_K for $K=$trivial, trefoil, and figure-eight knots are shown by closed triangles, open squares, and circles, respectively.

with a double-logarithmic scale for the two knots. For the trivial knot, the graph has a concave curve: the ratio A_{triv}/A is almost constant with respect to N for small N and then decreases with a larger gradient for large N. The ratio A_{triv}/A is smaller than 1.0 in the whole range of N. It follows that in terms of the average crossing number, the N-noded ring polymers with the trivial knot are less complex than those of no topological constraint, for any N. For the trefoil knot, the graph of A_{tre}/A versus N can be roughly approximated by a negative power of N for some finite values of N. The ratio A_{tre}/A is larger than 1.0 for $N<200$, and smaller than 1.0 for $N>300$. Thus, the SAPs of the trefoil knot are more complex for small N and less complex for large N than those of no topological constraint.

It is remarkable in Fig. 2 that both of the ratios A_K/A's for the two knots become less than 1.0 when N is large. The A_K's are less than the average crossing number A that is averaged over all knots, when N is large. Here we recall that A corresponds to the average crossing number of the SAPs under no topological constraint, while A_K denotes the average crossing number of the SAPs with the fixed knot type K. Thus, it is suggested from Fig. 2 that topological constraints should make the conformations of ring polymers simpler

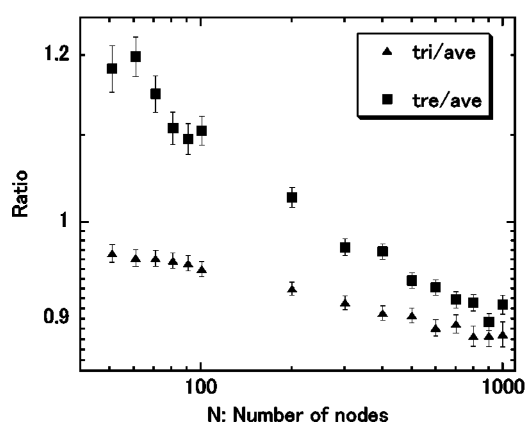

FIG. 2. Double-logarithmic plots of the ratio A_K/A vs N for cylindrical SAPs with $r=0.003$. A_{triv}/A and A_{tre}/A are shown by closed triangles and squares, respectively.

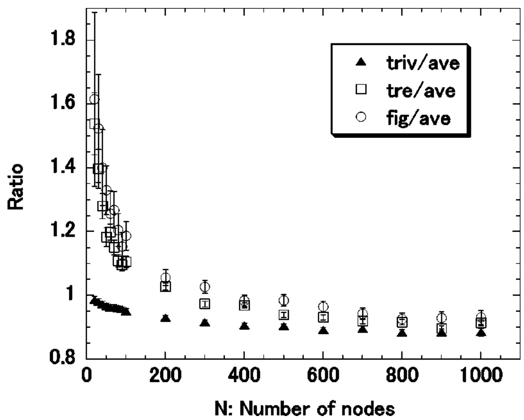

FIG. 3. Graph of the ratio A_K/A vs N for cylindrical SAPs with $r=0.003$ in linear scale. A_{triv}/A, A_{tre}/A, and A_{fig}/A are shown by closed triangles, open squares, and circles, respectively.

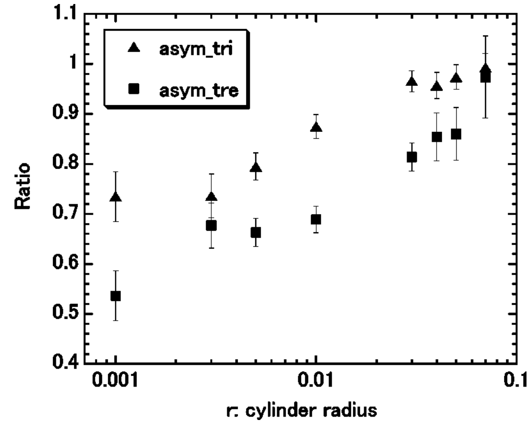

FIG. 4. The ratio a_K/a vs cylinder radius r for cylindrical SAPs. The values of a_{triv}/a and a_{tre}/a are shown by closed triangles and squares, respectively.

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.

The ratio A_K/A versus N is plotted in a linear scale for the three knots in Fig. 3. Here we find some finite-size behaviors clearly. The average crossing number of the trivial knot, A_{triv}, is smaller than that of the trefoil or figure-eight knots, A_{tre}, and A_{fig}, through the whole range of the plot, $N \leqslant 1000$. It is thus suggested that the more complicated knot should have the larger value of the average crossing number, for the case of finite N. The tendency is also seen in the data for the different values of cylinder radius r. As N increases, however, the average crossing numbers A_K's of the three knots gradually become close to each other. When N is very large, they become almost constant with respect to N, as shown in Fig. 3. The flatness of the graph of A_K/A versus N for large N suggests that the ratio A_K/A should be independent of N when N is asymptotically large.

The average crossing number A_K of a knot K have some similar finite-size behaviors in common with the mean-squared gyration radius R_K^2 of SAPs with the knot K. In some previous work [18,19], it is shown that for random polygons and cylindrical SAPs, the double-logarithmic graph of the ratio R_K^2/R^2 versus N is given by a downward convex curve, and the ratio 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_K^2/R^2 is smaller than 1.0 for small N and larger than 1.0 for large N. To be precise, the ratios A_K/A and $(R_K^2/R^2)^{-1}$ have the same decreasing behaviors as N increases, particularly at around $N=300$, for the trivial and trefoil knots.

B. Asymptotic behaviors of the average crossing number A_K

We now discuss possible asymptotic behaviors of the average crossing number. Let us review some known results on the large N behavior of N-step 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 SAWs is given by $A_{\mathrm{SAW}}/N=a-bN^{1-2\nu}$ with some constants a and b. Here ν 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, $A_{\mathrm{SAW}} \sim N^{\mu_{SAW}}$, 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. Taking the analogy with the simulation results on R_K^2/R^2 [18,19], we may assume that $\nu_K=\nu$ also for the average crossing number A_K. We thus have the formula of the ratio A_K/A in the following: $A_K/A = \alpha_K(1-\beta_K N^{1-2\nu})$. Here, α_K and β_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. 4. 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 Figs. 2 and 3 that the ratio A_K/A for $r=0.003$ decreases against N and is smaller than 1.0 for large N. In Fig. 4, 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 obvious 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. The fact that the ratio a_K/a is smaller than 1.0 when r is small shows that the effect of topological constraints on ring polymers is large for small r. From the fact that r increases up to 1.0 when r is large, it follows that the topological effect decreases when radius r is large.

Let us consider again the r dependence of A_K that the graph of a_K/a versus r increases up to 1.0 for the two knots, as shown in Fig. 4. A very similar behavior has also been observed for the case of the ratio R_K^2/R^2 of the mean-squared

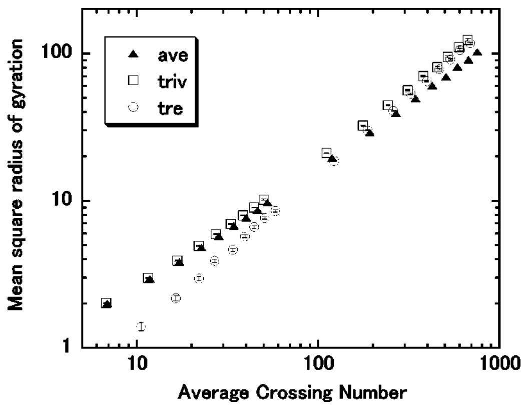

FIG. 5. The mean-square radius of gyration R_K^2 vs the average number of crossings A_K of cylindrical SAPs for $r=0.003$. Numerical estimates for K=trivial knot, 3_1 are shown by open squares and circles, respectively. Data of R^2 versus A are shown by closed triangles. N are given by 51, 151, and $100j+1$ for $j=1,\ldots,10$.

gyration radii of the cylindrical SAPs with radius r. In Refs. [18,19], 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_K^2/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_K^2/R^2 decreases to 1.0 as r increases.

C. The mean-squared gyration radius and the geometric complexity

Let us discuss the relation between the average crossing number and the average size of ring polymers. We shall show that it should be nontrivial. In Fig. 5 the mean-square radii of gyration R^2 and R_K^2's are plotted against the average crossing numbers A and A_K's in a double logarithmic scale for the cylindrical SAPs of $r=0.003$. Here K is given by the trivial or trefoil knots. We find in Fig. 5 that the estimates of R^2 and R_K^2's for the two knots are different for any given value of the average crossing numbers. It thus follows that the mean-squared gyration radius and the average crossing number are independent quantities describing some geometric properties of conformations of ring polymers, as far as finite-size behaviors are concerned. Here we note that in Fig. 5 R^2 is plotted against A, and R_K^2 is against A_K for each of the two knots.

With the same value of the average crossing numbers given, R_{triv}^2 and R_{tre}^2 are larger than R^2 when the value is large, as shown in Fig. 5. Thus, we may suggest that a topological constraint should make the average size of ring polymers larger with respect to the average crossing numbers when their value is large. We also observe that R_{triv}^2 is larger than R_{tre}^2 among the R_K^2's in Fig. 5. Thus, 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_K^2) can be approximated by some power of A (or A_K): $R^2 \sim A^\gamma$ for the case of the average over all knots; $R_K^2 \sim A_K^{\gamma_K}$ for the trivial and trefoil knots. Furthermore, we observe in Fig. 5 that the effective exponent γ_K should be independent of the knot type. The graphs of Fig. 5 for the trivial and trefoil knots become close to each other as A_K is getting large. Applying the power law approximation to the data of $N \geqslant 100$, we obtain the following estimates: $\gamma=0.860\pm0.001$, $\gamma_{triv}=0.952\pm0.004$, and $\gamma_{tre}=1.069\pm0.006$. Finally, we note that similar results are obtained also for the SAPs with the different values of cylinder radius r.

IV. CONCLUSIONS

Through numerical simulations we have discussed the average crossing number of self-avoiding polygons under some topological constraints. When N is large, the average crossing number of ring polymers under a topological constraint is smaller than that of no topological constraint. From the simulation result we may conclude that a topological constraint should make the conformation of ring polymers simpler with respect to the geometric complexity expressed in terms of the average crossing number. We may also 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_K^2.

ACKNOWLEDGMENTS

We would like to thank Professor K. Ito for helpful discussions.

[1] M. Doi and S.F. Edwards, *The Theory of Polymer Dynamics* (Clarendon Press, Oxford, 1986).
[2] E.J. Janse van Rensburg, D.A. Sumners, E. Wasserman, and S.G. Whittington, J. Phys. A **25**, 6557 (1992).
[3] E. Orlandini *et al.*, J. Phys. A **27**, L333 (1994).
[4] G.A. Arteca, Phys. Rev. E **49**, 2417 (1994).
[5] J.-Y. Huang and P.-Y. Lai, Phys. Rev. E **63**, 021506 (2001).
[6] A.L. Kholodenko and T.A. Vilgis, Phys. Rep. **298**, 251 (1998).
[7] P. Grassberger, J. Phys. A **34**, 9959 (2001).
[8] V. Katritch, J. Bednar, D. Michoud, R.G. Scharein, J. Dubochet, and A. Stasiak, Nature (London) **384**, 142 (1996).
[9] A. Stasiak, J. Dubochet, V. Katritch, and P. Pieranski, in *Ideal Knots*, edited by A. Stasiak, V. Katritch, and L.H. Kauffman (World Scientific, Singapore, 1998), pp. 1–19.
[10] A.Yu. Grosberg, A. Feigel, and Y. Rabin, Phys. Rev. E **54**, 6618 (1996).
[11] A. Yu. Grosberg, in *Ideal Knots*, edited by A. Stasiak, V. Katritch, and L.H. Kauffman (World Scientific, Singapore, 1998), pp. 129–142.
[12] M.K. Shimamura and T. Deguchi, Phys. Rev. E **66**, R040801 (2002).
[13] M.K. Shimamura and T. Deguchi, Phys. Lett. A **274**, 184 (2000).
[14] Y.D. Chen, J. Chem. Phys. **74**, 2034 (1981); **75**, 2447 (1981); **75**, 5160 (1981).

[15] K. Murasugi, *Knot Theory and Its Applications* (Birkhäuser, 1996, Boston).
[16] M. Polyak and O. Viro, Int. Math. Res. Notices **11**, 445 (1994).
[17] M.K. Shimamura and T. Deguchi, J. Phys. Soc. Jpn. **70**, 1523 (2001).
[18] M.K. Shimamura and T. Deguchi, Phys. Rev. E **64**, R020801 (2001).
[19] M.K. Shimamura and T. Deguchi, Phys. Rev. E **65**, 051802 (2002).