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Gyration radius of a circular polymer under a topological constraint with excluded volume

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It is nontrivial whether the average size of a ring polymer should become smaller or larger under a topological constraint. Making use of some knot invariants, we numerically evaluate the mean-square radius of gyration for ring polymers having a fixed knot type, where the ring polymers are given by self-avoiding polygons consisting of freely jointed hard cylinders. We obtain plots of the gyration radius versus the number of polygonal nodes for the trivial, trefoil, and figure-eight knots. We discuss possible asymptotic behaviors of the gyration radius under the topological constraint. In the asymptotic limit, the size of a ring polymer with a given knot is larger than that of no topological constraint when the polymer is thin, and the effective expansion becomes weak when the polymer is thick enough.

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I. INTRODUCTION

The effect of a topological constraint should be nontrivial on physical quantities of a ring polymer such as the size of the ring polymer. Once a ring polymer is formed, its topological state, which is given by a knot, is fixed. However, it has not been established how to formulate the topological constraint on the ring polymer in terms of analytic methods. On the other hand, several numerical simulations have been performed, investigating some statistical properties of ring polymers under topological constraints [1–13]. Through the simulations, it has been found that a topological constraint may severely restrict the available degrees of freedom in the configuration space of a ring polymer, and can be significant in its physical properties.

Recently, DNA knots are synthesized in experiments, and then separated into various knot types by the agarose-gel-electrophoresis technique [14–17]. Under the electric field, the charged macromolecules move through the network of the gel, and the migration rates should depend on their sizes, shapes, and charges. It is remarkable that the electrophoretic mobility of a circular DNA depends also on its knot type. It is observed that the more complicated the DNA knot is, the higher its mobility. The fact could be related to a common belief that the gyration radius of a knotted DNA should depend on its knot type.

In this paper, we discuss the mean-square radius of gyration of circular polymers having a fixed knot type. We consider the question how the size of a ring polymer should depend on the length N under the topological constraint. Here the length N corresponds to the number of polygonal nodes, when we model the ring polymers by some self-avoiding polygons. We find that the effect of the topological constraint is not trivial. In fact, the mean-square radius of gyration for ring polymers under the topological constraint can be smaller or larger than that of the ring polymers under no topological constraint.

II. CYLINDRICAL SELF-AVOIDING POLYGONS

Let us explain the model of ring polymers consisting of freely jointed hard cylinders [6,18]. The segments are given by hard cylinders with radius r. They are ''hard'' in the sense that there is no overlap allowed between any pair of nonadjacent cylindrical segments, while adjacent segments can overlap: there is no constraint on any pair of adjacent cylinders. The model was first introduced in Ref. [6] with the Monte Carlo algorithm using the ''hedgehog'' configurations of polygons. Recently, another method was introduced for constructing the cylindrical self-avoiding polygons [18]. It is based on the algorithm of ring dimerization [5,19] for the rod-bead model of self-avoiding polygons. We call it the cylindrical ring-dimerization method. All the cylindrical self-avoiding polygons in this paper are constructed by the alternative method.

The cylinder radius r and the number N of segments of the model are important in the theoretical explanation of DNA knots [15]: radius r corresponds to the effective radius of negatively charged DNA's surrounded by the clouds of counter ions. Thus, the model is closely related to the worm-like chain model for polyelectrolytes in electrolyte solutions.

The mean-square radius of gyration R^2 for the cylindrical self-avoiding polygons is defined by $R^2 = \Sigma_{n,m=1}^{N} \langle (\vec{R}_n - \vec{R}_m)^2 \rangle / 2N^2$, where $\vec{R}_n$ is the position vector of the n-th monomer and N is the number of nodes. The symbol $\langle \cdot \rangle$ denotes the average over M samples of polygons. In this paper, we have constructed 18×15 sets of $M = 10^4$ self-avoiding polygons of N cylindrical segments with radius r, where N is given by 18 numbers from 20 to 1000 and r by 15 different values from 0.0 to 0.07.

III. METHOD FOR SELECTING POLYGONS WITH THE SAME GIVEN KNOT

For a given knot K, we enumerate the number M_K of such polygons out of the M polygons that have the same set of values of some knot invariants for the knot type K. We employ two knot invariants, the determinant $\Delta_K(-1)$ of knot and the Vassiliev-type invariant $v_2(K)$ of the second degree, as the tool for detecting the knot type of a given polygon [20,21].

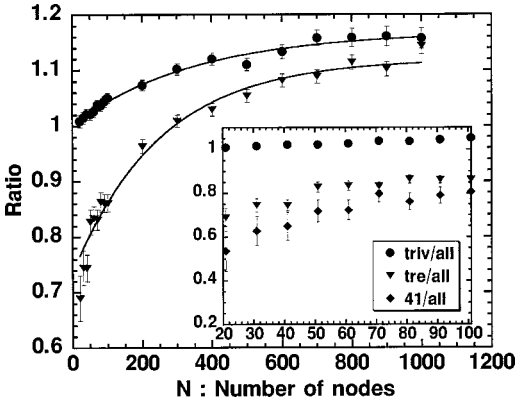

FIG. 1. The ratio R_K^2/R^2 versus the number N of polygonal nodes of the cylindrical self-avoiding polygons. Numerical estimates of R_{triv}^2/R^2 for $r=0.005$ are shown by black circles and those of R_{tre}^2/R^2 for $r=0.005$ by black triangles. In the inset, the enlarged figure shows the numerical estimates of R_K^2/R^2 from $N=20$ to 100 for the cases of trivial, trefoil, and figure-eight (41) knots.

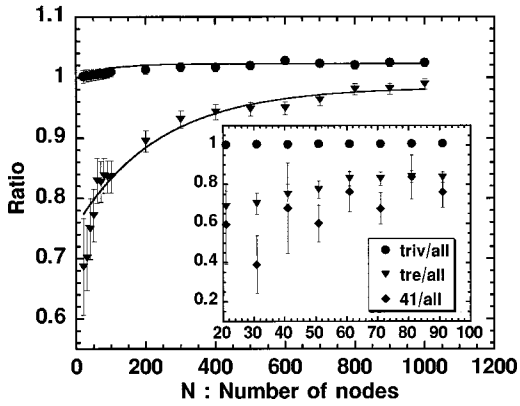

FIG. 2. The ratio R_K^2/R^2 versus the number N of polygonal nodes of the cylindrical self-avoiding polygons. Numerical estimates of R_{triv}^2/R^2 for $r=0.04$ are shown by black circles and those of R_{tre}^2/R^2 for $r=0.04$ by black triangles. The fitting parameters are given by the follwing: for trivial knot, $\nu_K-\nu=-0.0004\pm0.068$, $A_K/A=1.04\pm0.59$, $B_K-B=-0.3\pm3.1$, and $\chi^2=1.1$; for trefoil knot, $\nu_K-\nu=0.006\pm0.101$, $A_K/A=1.01\pm0.84$, $B_K-B=-2.0\pm4.0$, and $\chi^2=3.2$. In the inset, the enlarged figure shows the numerical estimates of R_K^2/R^2 from $N=20$ to 100 for the cases of trivial, trefoil, and figure-eight (41) knots.

The number M_K depends not only on the knot type, but also on the step number N and cylinder radius r. Let us consider the probability $P_{triv}(N,r)$ of a cylindrical self-avoiding polygon of N nodes with the cylinder radius r being a trivial knot [18]. Then, it is given by

$$P_{triv}(N,r)=\exp(-N/N_c(r)) \tag{1}$$

Here $N_c(r)$ is called the characteristic length of random knotting and can be approximated by an exponential function of r: $N_c(r)=N_c(0)\exp(\gamma r)$, where γ is a constant [18].

IV. GYRATION RADIUS OF RING POLYMERS UNDER A TOPOLOGICAL CONSTRAINT

The mean-square radius of gyration R_K^2 for knot type K is given by

$$R_K^2=\frac{1}{M_K}\sum_{i=1}^{M_K} R_{K,i}^2, \tag{2}$$

where $R_{K,i}^2$ denotes the gyration radius of the ith cylindrical self-avoiding polygon that has the knot type K, in the set of M polygons. For the rod-bead model of self-avoiding polygons, R_K^2 has been evaluated for some different knots [22].

Let us discuss our data of numerical estimates of R_K^2. For trivial, trefoil, and figure-eight knots, we find that the mean-square radius of gyration increases monotonically with respect to the number N of polygonal nodes. However, the ratio R_K^2/R^2 is not constant with respect to N. The graphs of the ratio R_K^2/R^2 against the step number N are plotted in Fig. 1 for trivial and trefoil knots. Here the cylinder radius is given by 0.005, i.e., the diameter is given by 0.01. Here we recall that R^2 denotes the mean-square radius of gyration for the self-avoiding polygons with all possible knot types. In terms of R_K^2, R^2 is given by the following: $R^2=\Sigma_K M_K R_K^2/M$. We recall that the number M_K gives different values for different step numbers N or different knots K. When the knot K is complicated, M_K can be very small and it may give a poor statistics to R_K^2.

Let us discuss the plots of the trivial knot shown in Fig. 1. The ratio R_{triv}^2/R^2 at $N=21$ is almost given by 1.0. This is consistent with the fact that trivial knots are dominant when N is small. Here we recall that the probability of being a trivial knot is given by Eq. (1). On the other hand, the ratio R_{triv}^2/R^2 increases with respect to the step number N. Thus, the size of the ring polymer enlarges under the topological constraint of being a trivial knot. The topological constraint gives an effective swelling effect in this case.

Let us consider the case of trefoil knot. The ratio R_{tre}^2/R^2 is not always larger than 1.0. In fact, it is smaller than 1.0 when $N<200$. The ratio R_{tre}^2/R^2 is given by about 0.7 when $N=21$. Thus, the topological constraint gives an effective shrinking effect on the ring polymer. When $N>300$ or 400, the ratio R_{tre}^2/R^2 becomes larger than 1.0 for $r=0.005$. Thus, the topological constraint makes the ring polymer enlarge for large N. However, when $r>0.03$, the ratio R_{tre}^2/R^2 becomes smaller than 1.0 even for $N=1000$, as shown in Fig. 2.

In Figs. 1 and 2, we see that the difference among the ratios of the gyration radii for trivial, trefoil, and figure-eight knots is much more clear in the small-N region than in the large-N region. The dependence of the gyration radius of the ring polymer on its knot type could be more significant for small N than for large N. The effective shrinking of a thick and finite ring polymer with a nontrivial knot might be associated with the concept of ideal knots or tight knots [23,24].

The fitting curves in Figs. 1 and 2 are given by

$$\frac{R_K^2}{R^2}=\gamma_K(1-\delta_K\exp(-\eta_K N)). \tag{3}$$

Here, the constants γ_K, δ_K, and η_K are fitting parameters. We see that the fitting curves in Figs. 1 and 2 are consistent with all the numerical estimates of R_K^2 in the range from $N=21$ to 1000. Thus, the formula (3) effectively describes the finite-size behavior of R_K^2, although there is no *a priori* reason for assuming it. For instance, the formula (3) can be not appropriate as an asymptotic expansion. In Sec. 5, we shall introduce another formula to discuss the possible asymptotic behaviors of R_K^2.

V. ASYMPTOTIC BEHAVIORS OF R_K^2

Let us discuss possible asymptotic behaviors of the gyration radius of the ring polymer under a topological constraint. We may assume that when N is very large, R_K^2 can be approximated by

$$R_K^2 = A_K N^{2\nu_K}[1 + B_K N^{-\Delta_K} + O(1/N)]. \tag{4}$$

The expansion is consistent with renormalization group arguments, and hence it should be valid for the case of asymptotically large N. The exponent ν_K and the amplitude A_K can be evaluated by applying the formula (4) to the numerical data of R_K^2 for large values of N. Here we note that the expansion (4) is not effective for small N. In fact, when $N \leqslant 200$, it does not give any good fitting curves to the data in Figs. 1 or 2.

Let us now discuss the exponent ν_K. We have analyzed the plots of R_K^2/R^2 given in Fig. 1 for trivial and trefoil knots by the least-square method with respect to the following formula: $R_K^2/R^2 = (A_K/A)N^{\nu_K-\nu}(1+(B_K-B)N^{-\Delta}+O(1/N))$. Here we have assumed $\Delta_K=\Delta=0.5$, which is consistent with the scaling expansion. Then, we obtain the following estimates: for trivial knot, $\nu_K-\nu=0.005\pm0.103$, $A_K/A=1.18\pm0.99$, $B_K-B=-1.7\pm4.0$; for trefoil knot, $\nu_K-\nu=0.009\pm0.090$, $A_K/A=1.18\pm0.85$, $B_K-B=-3.5\pm3.0$. To each of the knots, we have applied the formula (4) to the eight points with $N\geqslant300$ in Fig. 1. The χ^2 values are given by 4.3 and 6.2 for trivial and trefoil knots, respectively. For other values of radius r, we have similar results. Thus, for trivial and trefoil knots, the exponent ν_K should agree with the exponent ν of the mean-square radius of gyration R^2, within the error bars.

There are also other evidences supporting $\nu_K=\nu$, i.e., $\nu_K=0.588$, for trivial and trefoil knots. In fact, the plots of the ratio R_K^2/R^2 versus the number N in Figs. 1 and 2 are likely to approach some horizontal lines at some large N. It is also the case with some other values of cylinder radius r. It is clear particularly for trivial knot. Thus, at least for trivial knot, we can easily conclude that the exponent ν_K should coincide with the exponent ν. We note that even the fitting formula (3) is consistent with the coincidence of the exponents: $\nu_K=\nu$. Thus, all the numerical results obtained in the paper suggest $\nu_K=\nu$ for trivial and trefoil knots. It is also consistent with the observation for the self-avoiding polygon on a lattice in Refs. [12,13] that the exponent ν_K should be independent of the knot type.

Let us now consider the amplitude A_K of the asymptotic expansion (4). In Fig. 3, the numerical plots of the ratio A_K/A versus the radius r are shown for trivial and trefoil knots. The ratio is evaluated by the following formula: $R_K^2/R^2=(A_K/A)(1+(B_K-B)N^{-\Delta}+O(1/N))$. Here, we have assumed $\nu_K=\nu$ and $\Delta_K=\Delta=0.5$. Furthermore, we have applied it only to the data with $N\geqslant300$.

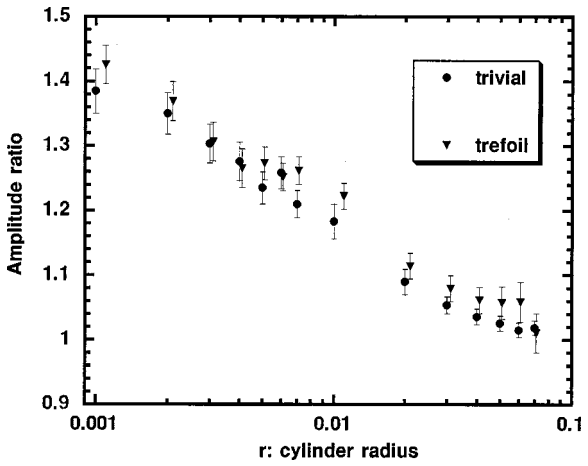

FIG. 3. The ratio A_K/A versus the cylinder radius r for the cylindrical self-avoiding polygons. The values of A_K/A for the trivial knot and the trefoil knot are shown by black circles and black triangles, respectively. Each of the black triangles are slightly shifted rightward by one tenth of the value of radius r, for graphical convenience.

When r is small, the ratio A_K/A in Fig. 3 is larger than 1.0 for both trivial and trefoil knots. It is remarkable that the asymptotic ratio A_K/A can be larger than 1.0 when the ring polymer is thin enough. We can easily confirm it also in Fig. 1, observing the increasing behavior of the plots of R_{triv}^2/R^2 versus N. Thus, the topological constraint gives an effective expansion to the ring polymer with small radius r.

Interestingly, we see in Fig. 3 that the ratio A_K/A decreases monotonically with respect to the cylinder radius r. One might expect that the ring polymer with larger excluded volume should become much larger. In reality, however, for the ring polymer under the topological constraint, the ratio A_K/A decreases if the excluded volume parameter becomes large. It is as if the excluded volume effect could weaken the effective expansion derived from the topological constraint. We notice in Fig. 3 that A_K/A might become close to the value 1.0 when r is thick enough. Due to the poor statistics, we cannot determine whether it really does or not. However, if it does, then it is consistent with the interpretation on the lattice model of Refs. [12,13]—that A_K should be independent of knot type.

It is quite nontrivial that A_K/A that is valid in the asymptotic expansion can be larger than 1.0, and the ratio decreases with respect to the radius r. Let us give one possible explanation for it. First, we note that R^2 is given by the average of R_K^2 over all possible knots: $R^2=\Sigma_K R_K^2 P_K(N)$. The fact: $A_K/A>1.0$ suggests that there are large number of knots smaller than the knot K. Second, we recall the finite-N behavior of R_{tre}^2: In Figs. 1 and 2 we see that the ratio R_{tre}^2/R^2 is much smaller than 1.0 when N is small, while it increases with respect to N and finally becomes constant. We

consider that when N is small, the size of trefoil knot is small due to a finite-size effect, while when N is asymptotically large then R^2_{tre}/R^2 becomes almost constant. For a given knot K_1, if we take N large enough, then the ratio $R^2_{K_1}/R^2$ becomes constant with respect to N, while the majority of knots possible in N-noded polygons should be much more complex than the knot K_1 and their sizes should be much smaller than that of the knot K_1. Thus, R^2 can be smaller than $R^2_{K_1}$ and the ratio A_{K_1}/A can be larger than the value 1.0.

We remark that R^2_{triv}/R^2 is always larger than 1.0 both for finite N and asymptotically large N. For the finite-N case, it is clear from Figs. 1 and 2 that $R^2_{triv}/R^2>1$. For the asymptotic case, it is suggested from Fig. 3 that A_{triv}/A should be larger than 1.0 for some small values of radius r. Thus, the property: $R^2_{triv}/R^2>1$ should persist in the asymptotic limit, as far as the data analysis is concerned.

Summarizing the numerical results on the asymptotic behaviors, we conclude that the topological constraint on a ring polymer gives an effective expansion when the radius r is small, and also that the expanding effect becomes weaker when the radius r becomes larger and it may vanish when the radius r is large enough. The results suggest that there should be a ''phase transition,'' where it is controlled by the excluded-volume parameter whether the topological constraint gives an effective expansion to the ring polymer or not.

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