Universality in the diffusion of knots

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(Received 30 May 2008; revised manuscript received 5 January 2009; published 27 February 2009)

We have evaluated a universal ratio between diffusion constants of the ring polymer with a given knot K and a linear polymer with the same molecular weight in solution through the Brownian dynamics under hydrodynamic interaction. The ratio is found to be constant with respect to the number of monomers, N, and hence the estimate at some N should be valid practically over a wide range of N for various polymer models. Interestingly, the ratio is determined by the average crossing number (N_{AC}) of an ideal conformation of knotted curve K, i.e., that of the ideal knot. The N_{AC} of ideal knots should therefore be fundamental in the dynamics of knots.

I. INTRODUCTION

Novel knotted structures of polymers have recently been found in various research fields such as DNA, proteins, and synthetic polymers [1–4]. The topology of a ring polymer is conserved under thermal fluctuations in solution and represented by a knot [5–9]. Topological constraints may lead to nontrivial statistical mechanical and dynamical properties of ring polymers [6,10–19].

Recent progress in experiments of ring polymers should be quite remarkable. Diffusion constants of linear, relaxed circular, and supercoiled DNAs have been measured quite accurately [20]. Here the DNA double helices are unknotted. Furthermore, hydrodynamic radius of circular DNA has also been measured [21]. Ring polymers of large molecular weights are synthesized not only quite effectively [22] but also with small dispersions and of high purity [23,24]. Circular DNAs with various knot types are derived, and they are separated into knotted species by gel electrophoresis [25]. We should remark that synthetic ring polymers with nontrivial knots have not been synthesized and separated experimentally, yet. However, it is highly expected that ring polymers of nontrivial knot types should be synthesized and their topological effects will be confirmed experimentally in near future.

In the paper we discuss diffusion constant D_K of a ring polymer with fixed topology K in good solution for various knot types. We evaluate it numerically via the Brownian dynamics with hydrodynamic interaction in which bond crossing is effectively prohibited through the finite extensible nonlinear elongational (FENE) potential [26]. We evaluate diffusion constant D_L of a linear polymer with the same molecular weight and derive ratio D_K/D_L. The ratio should correspond to a universal amplitude ratio of critical phenomena and play a significant role in the dynamics of knotted ring polymers. According to the renormalization-group (RG) arguments, ratio D_K/D_L should be universal if the number of monomers, N, is large enough [27–29].

The ratio D_K/D_L may have some experimental applications. Ring polymers of different knot types can be separated experimentally with respect to their topologies by making use of the difference among the sedimentation coefficients, which can be calculated from the diffusion constants [30]. Here we remark that the diffusion constant of a ring polymer under no topological constraint, D_R, and that of the corresponding linear polymer has been numerically evaluated, and the ratio $C = D_R/D_L$ has been studied [26,31,32].

Through simulation we find that ratio D_K/D_L is approximately constant with respect to N for various knots. Thus, if we evaluate ratio D_K/D_L at some value of N, it is practically valid for other values of N. We can therefore predict the diffusion constant D_K of a polymer model at some value of N, multiplying the ratio D_K/D_L by the estimate of D_L. Here we remark that the value of D_L may depend on the number N and on some details of the model [33,34].

Furthermore, we show numerically that ratio D_K/D_L is a linear function of the average crossing number (N_{AC}) of the ideal knot of K, an ideal configuration of knotted curve K, which will be defined shortly. Since the ratio D_K/D_L is almost independent of N, it follows that the linear fitting formula should be valid practically in a wide range of finite values of N. Thus, the ideal knot of a knotted curve K should play a fundamental role in the dynamics of finite-size knotted ring polymers in solution.

Let us introduce the ideal knot, briefly. For a given knot K it is given by the trajectory that allows maximal radial expansion of a virtual tube of uniform diameter centered around the axial trajectory of the knot K [35,36]. We define the N_{AC} of a knotted curve as follows: we take its projection onto a plane and enumerate the number of crossings in the knot diagram on the plane. Then, we consider a large number of projections onto planes whose normal vectors are uniformly distributed on the sphere of unit radius and take the average of the crossing number (N_{AC}) over all the normal directions.

The paper consists of the following: in Sec. II, the simulation method is explained. In Sec. III, we present the estimates of the diffusion constant of a ring polymer in solution of knot type K for various knot types. Then, we show numerically that the graph of D_K/D_0 is almost independent of N and also that ratio D_K/D_L is fitted by a linear function of N_{AC} of the ideal knot of K. We also discuss the simulation result in terms of the ratio of equivalent radii [37], a_G/a_T, which corresponds to the universal ratio of the radius of gy-

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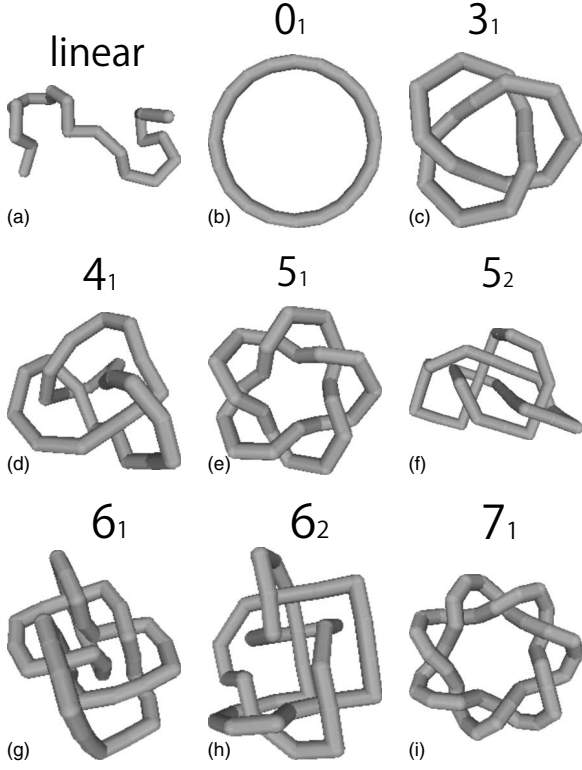
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FIG. 1. Figures of a linear polymer and knotted ring polymers with the symbols of knots given in Rolfsen's textbook [38]. They are drawn by using OCTA (http://octa.jp).

ration to the hydrodynamic radius [33]. We shall define the equivalent radii explicitly in Sec. III. Finally, we give conclusion in Sec. IV.

Throughout the paper, we employ the symbols of knots following Rolfsen's textbook [38], as shown in Fig. 1.

II. SIMULATION METHOD

The ring polymer is modeled as a cyclic bead-and-spring chain with N beads connected by N FENE springs with force given by

$$\boldsymbol{F}(\boldsymbol{r}) = -H\boldsymbol{r}/(1 - r^2/r_{\max}^2), \tag{1}$$

where $r = |\boldsymbol{r}|$. We denote by b the unit of distance, which gives the average distance between neighboring monomers approximately. We set constants H and $r_{\max}$ by $H = 30k_BT/b^2$ and $r_{\max} = 1.3b$. We assume the Lennard-Jones (LJ) potential by

$$V(r_{ij}) = 4\epsilon_{\mathrm{LJ}}\{(\sigma_{\mathrm{LJ}}/r_{ij})^{12} - (\sigma_{\mathrm{LJ}}/r_{ij})^6\}. \tag{2}$$

Here r_{ij} is the distance of beads i and j, and ϵ_{LJ} and σ_{LJ} denote the minimum energy and the zero energy distance, respectively [39]. We set the Lennard-Jones parameters as $\sigma_{\mathrm{LJ}} = 0.8b$ and $\epsilon_{\mathrm{LJ}} = 0.1k_BT$ so that they give good solvent conditions [40]. Here k_B denotes the Boltzmann constant.

We employ the predictor-corrector version [41] of the Ermak-McCammon algorithm for generating time evolution of a ring polymer in solution. The hydrodynamic interaction is taken into account through the Rotne-Prager-Yamakawa

TABLE I. Estimates of diffusion constants D_L and D_K and the mean-square radius of gyration $\langle R_G^2 \rangle$ and for a linear polymer of $N = 45$ and ring polymers of $N = 45$ with various knot types.

Knot type	D	$\langle R_G^2 \rangle$
Linear	0.12038 ± 0.00085	9.33029 ± 0.03219
0	0.13059 ± 0.00089	5.26539 ± 0.00913
3_1	0.14530 ± 0.00079	3.21052 ± 0.00505
4_1	0.14876 ± 0.00074	2.78817 ± 0.00160
5_1	0.15277 ± 0.00085	2.72300 ± 0.00261
5_2	0.15640 ± 0.00078	2.61427 ± 0.00132
6_1	0.15927 ± 0.00078	2.47449 ± 0.00137
6_2	0.15902 ± 0.00095	2.37272 ± 0.00126
7_1	0.16416 ± 0.00083	2.47162 ± 0.00109

tensor [39,42,43] where the bead friction is given by $\zeta = 6\pi\eta_s a$ with the bead radius $a = 0.257b$ and a dimensionless hydrodynamic interaction parameter $h^* = (\zeta/6\pi\eta_s)\sqrt{H/\pi k_BT} = 0.25$.

In the present simulation, physical quantities are given in dimensionless units such as in Ref. [39]. We divide length by b, energy by k_BT, and time by $\zeta b^2/k_BT$. Let us indicate dimensionless quantities by an asterisk as superscript. We have $H^* = 30$ and $r_{\max}^* = 1.3$. We take the simulation time step $\Delta t^* = 10^{-4}$.

We have set the FENE potential so that the topology of the ring polymer should be effectively conserved [26]. However, bond crossing may occur with very small probability. Calculating knot invariants, we have confirmed that the fraction of nontrivial knots is very small. If the initial knot type is the trivial knot it is given by $10^{-8} - 10^{-7}$, and if the initial knot type is a nontrivial knot, it is given by approximately 10^{-7}.

III. SIMULATION RESULTS

We define the diffusion constant of a polymer by

$$D = \lim_{t \to \infty} \frac{1}{6t}\langle [\vec{r}_G(t) - \vec{r}_G(0)]^2 \rangle. \tag{3}$$

Here $\vec{r}_G(t)$ denotes the position vector of the center of mass of the polymer at time t. Making use of Eq. (3) we have evaluated diffusion constants D_L and D_K.

The estimates of diffusion constants D_L and D_K at $N = 45$ are listed in Table I together with those of the mean-square radius of gyration $\langle R_G^2 \rangle$. The data of D_L and D_K are plotted against N in Fig. 2. The fitting curves to them are given by $D = aN^{-\nu}(1 + bN^{-\Delta})$. Here the errors of the diffusion constants are as small as 10^{-4}.

Ratios D_K/D_L should correspond to universal amplitude ratios in critical phenomena. Numerically we find that ratio D_{K_1}/D_{K_2} of two different knots K_1 and K_2 is almost constant with respect to N, at least in the range investigated. For instance, the graph of ratio D_{3_1}/D_0 versus N and that of ratio D_{4_1}/D_0 versus N for the data are almost flat, as shown in Figs. 3 and 4, respectively. Here 0, 3_1, and 4_1 denote the
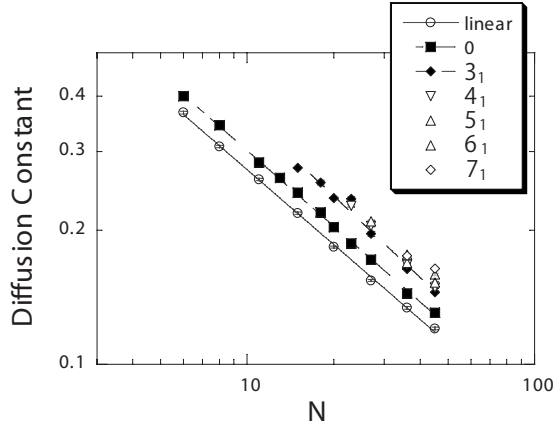
FIG. 2. Diffusion constants of linear and knotted ring chains with knots 0, 3_1, 4_1, 5_1, 6_1, and 7_1 versus N. Fitted by $D=aN^{-\nu}(1+bN^{-\Delta})$ with the following best estimates: For a linear chain, $a=0.90\pm0.23$, $\nu=0.53\pm0.06$, $b=0.51\pm0.93$, $\Delta=1.14\pm2.39$, and $\chi^2=17$; for the trivial knot (0), $a=1.03\pm1.11$, $\nu=0.55\pm0.18$, $b=0.14\pm0.78$, $\Delta=0.60\pm6.09$, and $\chi^2=28$; for the trefoil knot (3_1), $a=1.00\pm3.87$, $\nu=0.52\pm0.67$, $b=1.18\pm1.12$, $\Delta=0.77\pm6.09$, and $\chi^2=27$.

trivial, the trefoil, and the figure-eight knot, respectively, as shown in Fig. 1. The numerical values of D_{3_1}/D_0 are given from 1.14 to 1.17 in Fig. 3, and those of D_{4_1}/D_0 are given from 1.14 to 1.21 in Fig. 4. Thus, the estimate of D_K/D_0 evaluated at a value of N, say $N=45$, for some knot K should also be valid at other finite values of N since it is almost independent of N.

For the diffusion constant of a ring polymer, D_R, the ratio D_R/D_L should correspond to a universal amplitude ratio and should be universal if N is large enough [27–29]. For the diffusion constant D_R, there is no topological constraint in the ring polymer model and D_R does not mean D_K of a knot K [26,31,32]. In the previous simulation [26] it has been found that ratio D_0/D_L is given by about 1.1 for the present polymer model and almost independent of N within the range investigated.

From the numerical observations and the RG arguments, we have two conjectures: (a) D_0/D_L should be given by 1.1
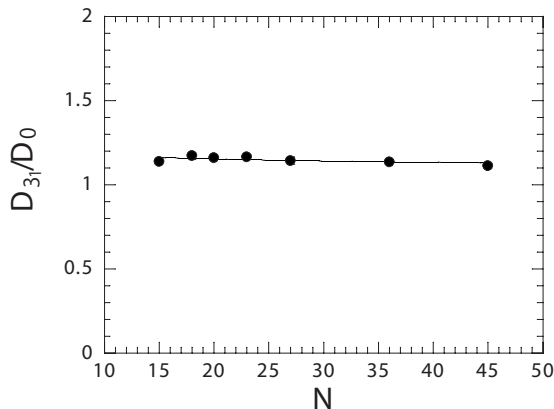

FIG. 3. Ratio D_{3_1}/D_0 of diffusion constants for the trefoil knot (3_1) and the trivial knot (0) versus the number of segments N. Fitting curve is given by $D_{3_1}/D_0=a(1+bN^{-c})$, where $a=1.07\pm0.64$, $b=0.25\pm0.39$, and $c=0.39\pm3.29$ with $\chi^2=6$.
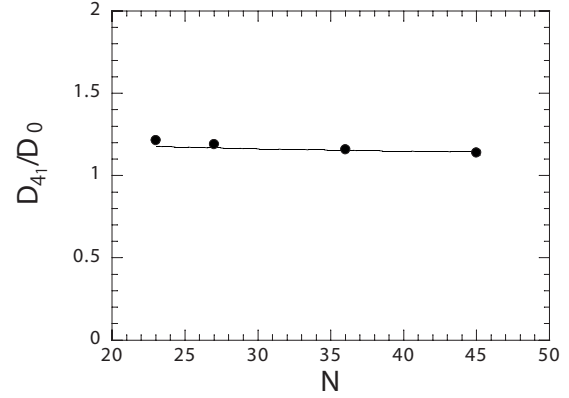

FIG. 4. Ratio D_{4_1}/D_0 of diffusion constants for the figure-eight knot (4_1) and the trivial knot (0) versus the number of segments N. Fitting curve is given by $D_{4_1}/D_0=a(1+bN^{-c})$, where $a=1.02\pm0.56$, $b=1.76\pm8.26$, and $c=0.70\pm2.58$ with $\chi^2=0.03$.

for some wide range of finite values of N and also in the large N limit; (b) ratio D_K/D_0 for a nontrivial knot K should remain almost the same value in a wide range of finite values of N, i.e., the N dependence should be very small.

Quite interestingly we find that ratio D_K/D_L can be approximated by a linear function of the average crossing number (N_{AC}) of ideal knots, i.e., the ideal representations of the corresponding knots. In Fig. 5 simulation data of D_K/D_L are plotted against N_{AC} of ideal knots. We find that the data points are fitted well by the following empirical formula:

$$D_K/D_L = a + bN_{AC}. \qquad (4)$$

Here, the estimates of a and b are given in the caption of Fig. 5. Thus, the diffusion constant D_K of a knot K can be estimated in terms of the N_{AC} of the ideal knot of K.

Let us discuss the χ^2 values. We have $\chi^2=2$ for the fitting line of Fig. 5, which is for the data of $N=45$. For the data of $N=36$ we have a good fitting line with $\chi^2=3$. The estimates of a and b for $N=36$ are similar to those for $N=45$. Thus, we may conclude that the graph of D_K/D_L versus N_{AC} is fitted by a linear line.
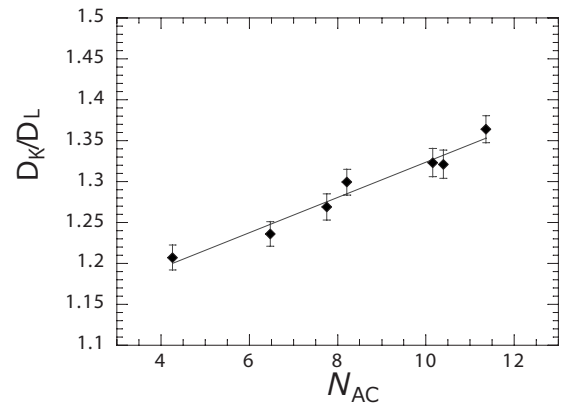

FIG. 5. D_K/D_L versus the average crossing number (N_{AC}) of ideal knot K for $N=45$: The data are approximated by $D_K/D_L=a+bN_{AC}$, where $a=1.11\pm0.02$ and $b=0.0215\pm0.0003$ with $\chi^2=2$.

For a finite value of N, we can estimate the diffusion constant D_K of a knot K through formula (4) by the N_{AC} of the ideal knot of K. Here we have assumed that coefficients a and b of Eq. (4) are independent of N since the graphs of D_K/D_0 and D_0/D_L are almost flat with respect to N. In fact, there is almost no numerical support for suggesting a possible N dependence of a and b, directly.

We thus summarize the simulation results so far as follows: ratio D_K/D_0 for a knot K should be almost constant with respect to N in a wide range of N and can be expressed by the linear function of N_{AC} of ideal knots. Equation (4) should be useful in separating synthetic ring polymers into various knotted species by making use of the difference among sedimentation coefficients.

Ideal knots should play a fundamental role in the dynamics of knotted ring polymers in solution. In fact, we have shown it for the diffusion constants. In experiments of gel electrophoresis drift velocities of different knots formed on the same DNA molecules were shown to be simply related to the N_{AC} of ideal knots [25]. The two independent results suggest the importance of the N_{AC} of ideal knots in the dynamics of knotted ring polymers although the physical situations are different.

Let us now discuss the simulation results from the viewpoint of equivalent radii [37]. The equivalent radius for any solution property is the radius of a spherical particle having the same value of solution property as that of the macromolecule under consideration. The ratio of equivalent radii should be universal, and it should play a similar role as the universal amplitude ratio such as the ratio of diffusion constants [33]. We define equivalent radii a_G and a_T explicitly by

$$a_G = \sqrt{\frac{5}{3}\langle R_G^2 \rangle}, \tag{5}$$

$$a_T = \frac{k_B T}{6\pi\eta_s D}. \tag{6}$$

Here a_G and a_T correspond to the radius of gyration $R_G = \sqrt{\langle R_G^2 \rangle}$ and the translational friction coefficient D, respectively. The ratio a_G/a_T corresponds to the ratio of the radius
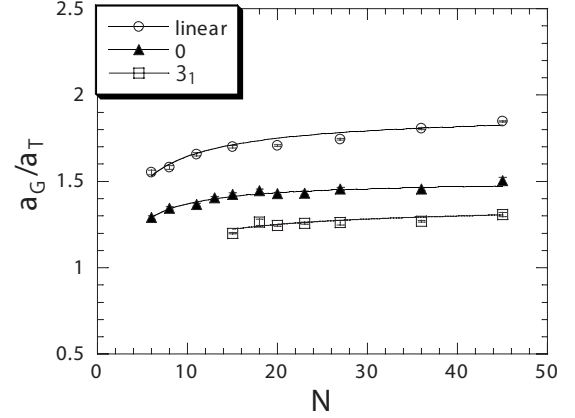

FIG. 6. a_G/a_T of linear and knotted ring chains with knots 0, 3_1, 4_1, 5_1, 6_1, and 7_1 versus N. Fitted by $a_G/a_T = a(1 - bN^{-c})$ with the following best estimates: For a linear chain, $a = 2.37 \pm 0.29$, $b = 0.52 \pm 0.03$, $c = 0.22 \pm 0.10$, and $\chi^2 = 55$; for the trivial knot (0), $a = 1.51 \pm 0.03$, $b = 0.72 \pm 0.23$, $c = 0.89 \pm 0.22$, and $\chi^2 = 14$; for the trefoil knot (3_1), $a = 1.30 \pm 0.03$, $b = 2.10 \pm 3.71$, $c = 1.27 \pm 0.76$, and $\chi^2 = 20$.

of gyration to the hydrodynamic radius and should be universal.

The numerical estimates of a_G/a_T for $N=45$ for the present simulation are listed in Table II for linear and ring polymers with various knot types. In Fig. 6, the ratio a_G/a_T is plotted against the number of segments, N, for linear and ring polymers with various knot types. Interestingly, the graphs show a weak N dependence. They are fitted by a function $a_G/a_T = a(1 - bN^{-c})$, with parameters a, b, and c being positive. It suggests that the graphs become constant with respect to N if N is large enough. We thus expect that the ratio a_G/a_T in the large N limit should be universal.

It is interesting to note in Fig. 6 that the estimate of ratio a_G/a_T in the large N limit is distinct for the different topologies such as linear polymers and ring polymers of the trivial and trefoil knots. The ratio could thus be useful for detecting the knot type of a ring polymer in solution.

IV. CONCLUSION

We have evaluated universal ratios among the diffusion constants of knotted ring polymers in good solution for several knots, where bond crossing is effectively prohibited in the Brownian dynamics under hydrodynamic interaction. The universal ratio of diffusion constants D_K/D_L is almost constant with respect to the number of polymer segments, N. Moreover, it is found that the ratio D_K/D_L is determined by the N_{AC} of the ideal knot of K. Through the linear relation, we can estimate the diffusion constant of a given knot.

TABLE II. Estimates of ratio $a_G/a_T = \sqrt{5\langle R_G^{2*}\rangle/3}D^*/a^*$ for a linear polymer of $N=45$ and ring polymers of $N=45$ with various knot types. Here, $\langle R_G^{2*}\rangle = \langle R_G^2 \rangle / b^2$, $D^* = 6\pi\eta_s aD/k_BT$, and $a^* = a/b$.

Knot type	a_G/a_T
Linear	1.8471 ± 0.00475
0	1.5053 ± 0.01869
3_1	1.3079 ± 0.01151
4_1	1.20824 ± 0.00055
5_1	1.26636 ± 0.00077
5_2	1.27029 ± 0.00052
6_1	1.25865 ± 0.00084
6_2	1.23046 ± 0.00058
7_1	1.29643 ± 0.00050

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