Mean-square radius of gyration and hydrodynamic radius for topological polymers evaluated through the quaternionic algorithm

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ABSTRACT

We evaluate numerically the mean-square (MS) radius of gyration and the diffusion coefficient for topological polymers such as ring, tadpole, double-ring, and caged polymers and catenanes. We consider caged polymers with any given number of subchains, and catenanes consisting of two linked ring polymers with a fixed linking number. Through Kirkwood's approximation we evaluate the hydrodynamic radius, which is proportional to the inverse of the diffusion coefficient, for various topological polymers. Here we take the statistical averages over configurations of topological polymers constructed through the quaternionic algorithm, which generates uniform random walks connecting given two points. It gives ideal chains with no excluded volume. We evaluate numerically the ratio of the square root of the MS radius of gyration to the hydrodynamic radius for several topological polymers, and show for them that the ratio decreases as the topology becomes more complex.

1. Introduction

Polymers with nontrivial topology such as cyclic polymers have attracted much interest in various fields of science [1]. Ring polymers are observed in nature such as circular DNA [2,3]. Topological structures have been discussed in association with protein folding [4]. Furthermore, naturally occurring proteins whose ends connected to give a circular topology has been recently discovered [5]. Due to novel developments in experimental techniques, ring polymers are now effectively synthesized in chemistry [6–12]. Moreover, various polymers of topologically complex structures, which are sometimes called topological polymers, have been synthesized through chemical reactions and separated with respect to their hydrodynamic radii through Gel Permeation Chromatography (GPC). Moreover, 8-shaped polymers, catenanes and caged polymers, have been synthesized [6,7,13–17]. Hereafter we shall call 8-shaped polymers and catenanes also as double-ring polymers and linked ring polymers, respectively. It is thus an interesting theoretical problem to calculate physical quantities such as the mean-square (MS) radius of gyration and the hydrodynamic radius for each topological type. Here we remark that the inverse of the hydrodynamic radius corresponds to the diffusion coefficient of the polymer.

In the paper we numerically evaluate the MS radius of gyration and the diffusion coefficient for various topological polymers in solution such as ring polymers, tadpole polymers, double-ring polymers, caged polymers and linked ring polymers with a given linking number. Furthermore, we calculate the diffusion coefficients of topological polymers through Kirkwood's approximation [18]. In order to construct an ensemble of configurations of a polymer having a nontrivial topological structure, we employ the quaternionic method for generating random walks [19]. By the method we can generate an ensemble of a given topological polymer with N segments in $O(N)$ time, i.e. the computation time grows linearly with respect to the number of vertices. Furthermore, the three-dimensional configurations in the ensemble are uniform along subchains of the topological polymer.

Statistical and dynamical properties of ring polymers in solution were first studied by Kramers [20]. The drift velocities of circular DNA in gel electrophoresis were measured in experiments for various knotted DNA [21]. In theoretical studies based on models it is found that the drift velocity of a circular DNA in gel electrophoresis should be proportional to the diffusion coefficient of the DNA in solution [22]. The diffusion coefficients of knotted ring polymers have been evaluated through Brownian dynamics [23]. For other topological polymers, the diffusion or sedimentation coefficients of double-ring polymers with excluded volume were theoretically studied by Fukatsu and Kurata [24]. For star polymers there have been theoretical and experimental studies

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rather extensively [1]. However, it seems that any topological polymer with loops or closed chains in its structure has not been extensively studied, yet, except for ring or double-ring polymer.

The theoretical estimates of the MS radius of gyration and the diffusion coefficient for topological polymers derived in the paper should be useful for further theoretical studies and experiments. The present simulation is based on the ideal model of topological polymers which has no excluded-volume effect. However, we expect that they should give good approximate values reflecting various topological structures, and hence they should be consistent with experimental values at least as first approximation.

The contents of the present paper consist of the following. In Section 2 we explain numerical methods for constructing random configurations of topological polymers such as tadpole polymers. In Section 3 we give the simulation results of some topological polymers such as ring, tadpole and double-ring polymers as shown in Fig. 1. In particular, we show that the ratio of the square root of the MS radius of gyration to the hydrodynamic radius of a given topological polymer decreases as the topology becomes more complex. In Section 4 we show the simulation results of caged polymers. In Section 5 we present the numerical results of catenanes (linked ring polymers) with a fixed linking number.

2. Numerical methods

2.1. Quaternionic method for generating random polygons and random walks

It is not straightforward to construct a large number of three-dimensional random configurations of topological polymers even for ring polymers. We construct ensembles of polymers of various nontrivial topological structures by the quaternionic method for generating random walks and random polygons [19].

Let us explain the quaternionic method for making closed random walks, i.e. random polygons [19]. It makes use of the Hopf map of quaternions. We express a quaternion h in terms of the basis I, j and k as follows.

$$h = \delta + \alpha i + \beta j + \gamma k. \tag{2.1}$$

Here α, β, γ, and δ are real numbers. The square of each basis i, j and k is given by -1:

$$i^2 = j^2 = k^2 = -1, \tag{2.2}$$

and anti-commutation relations are given by

$$ij = -ji = k, \ jk = -kj = i, \ ki = -ik = j. \tag{2.3}$$

We can express a given quaternion h in terms of two complex numbers u and v as follows.

$$h = u + vj. \tag{2.4}$$

Here, complex numbers u and v are expressed in terms of four real numbers u_{re}, u_{im}, v_{re} and v_{im} as

$$u = u_{re} + u_{im}i, \ v = v_{re} + v_{im}i. \tag{2.5}$$

We define the Hopf map by
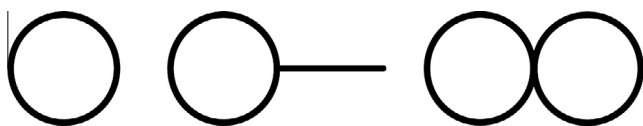
$$h \rightarrow h^*ih = (u + vj)^*i(u + vj). \tag{2.6}$$

It is straightforward to show that the real part of the Hopf map is given by zero so that it is given by a pure quaternion.

$$h^*ih = 0 + (|u|^2 - |v|^2)i - \text{Im}(2u^*v)j + \text{Re}(2u^*v)k. \tag{2.7}$$

Here we remark that if the real part of a quaternion is given by zero, we call it a pure quaternion. For a given pure quaternion $\alpha i + \beta j + \gamma k$ we identify the three coefficients α, β and γ, as the x, y and z coordinates of a position vector in the three-dimensional space.

Let us consider a sequence of pairs of complex numbers (u_n, v_n) for $n = 1, 2, \ldots N$. We introduce a sequence of quaternions $h_n = u_n + v_n j$ for $n = 1, 2, \ldots N$. Then we have

$$h_n^*ih_n = 0 + (|u_n|^2 - |v_n|^2)i - \text{Im}(2u_n^*v_n)j + \text{Re}(2u_n^*v_n)k$$
$$= 0 + \alpha_n i + \beta_n j + \gamma_n k. \tag{2.8}$$

We define bond vectors through the coefficient α_n, β_n and γ_n for $n = 1, 2, \ldots, N$, by

$$\vec{b}_n = (\alpha_n, \beta_n, \gamma_n) \text{ for } n = 1, 2, \ldots, N. \tag{2.9}$$

The position vector of the mth vertex of a random polygon is given by the sum of bond vectors from $n = 1$ to m. We can show that the sum of the j-th bond vectors from $j = 1$ to N vanishes if the N-dimensional complex vectors of unit length $\vec{u} = (u_1, u_2, \ldots, u_N)$ and $\vec{v} = (v_1, v_2, \ldots, v_N)$ are orthogonal with respect to the standard scalar product: $(\boldsymbol{u}, \boldsymbol{v}) = \boldsymbol{u}^\dagger \cdot \boldsymbol{v}$, where $\boldsymbol{u}^\dagger$ denotes the Hermitian conjugate of the N-dimensional complex vector $\boldsymbol{u}$. For instance, the x coordinate of the sum of the bond vectors is given by the following:

$$\sum_{j=1}^{N}(|u_j|^2 - |v_j|^2) = (\vec{u}, \vec{u}) - (\vec{v}, \vec{v}). \tag{2.10}$$

Therefore, it vanishes if the N-dimensional complex vectors $\boldsymbol{u}$ and $\boldsymbol{v}$ have the same length.

In the simulation, we generate two Gaussian N-dimensional complex vectors $\boldsymbol{u}$ and $\boldsymbol{v}$, randomly. Applying the Gram-Schmidt orthonormalization method to $\boldsymbol{u}$ and $\boldsymbol{v}$, we derive N-dimensional complex vector $\boldsymbol{v}'$ such that $\boldsymbol{v}'$ is perpendicular to $\boldsymbol{u}$ and of unit length. We then normalize them through multiplying by N as follows.

$$(\vec{u}, \vec{u}) = \boldsymbol{u}^\dagger \cdot \boldsymbol{u} = N^2,$$
$$(\vec{v}', \vec{v}') = \boldsymbol{v}'^\dagger \cdot \boldsymbol{v}' = N^2. \tag{2.11}$$

Under the normalization conditions (2.11), the MS length of bond vectors of generated random polygons is given by about 5.90 for $N = 100$–1000, as shown in Fig. 2. Here we remark that the expectation value of the MS length of bond vectors is rigorously given by $6/(1 + 1/N)$ (see Ref. [19]) and it is approximated for large N as

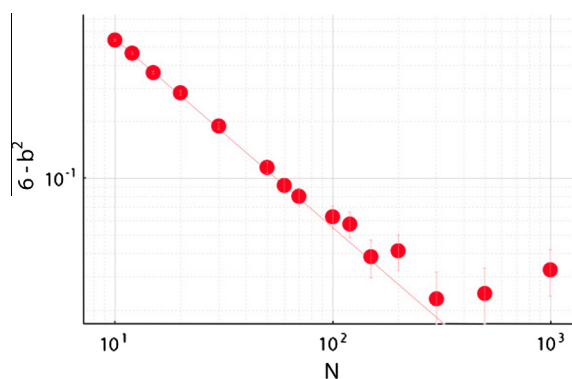$$6/(1 + 1/N) \cong 6 - 6/N. \tag{2.12}$$

Fig. 2. Double-logarithmic plot of the deviation $6 - b^2$ versus the number of segments N. The number of samples is given by 10^6. The fitting line is given by $5.5 N^{-1}$.

Fig. 1. Ring (left), tadpole (center) and double ring (right).