Semiflexible Polymer Confined to a Spherical Surface

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We develop a formalism for describing the kinematics of a wormlike chain confined to the surface of a sphere that simultaneously satisfies the spherical confinement and the inextensibility of the chain contour. We use this formalism to study the statistical behavior of the wormlike chain on a spherical surface. In particular, we provide an exact, closed-form expression for the mean square end-to-end distance that is valid for any value of chain length L, persistence length l_p, and sphere radius R. We predict two qualitatively different behaviors for a long polymer depending on the ratio R/l_p. For $R/l_p > 4$, the mean square end-to-end distance increases monotonically with the chain length, whereas for $R/l_p < 4$, a damped oscillatory behavior is predicted.

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A polymer in a confined geometry is a fundamental problem in polymer physics that underlies some important biological processes and technological applications. For example, polymer confinement is relevant to DNA or RNA packaging in viruses [1] and DNA packaging in eukaryotic cells [2], where, in both cases, the genome is confined within a cavity that is many orders of magnitude smaller than its unconfined radius of gyration.

While the effect of confinement for a flexible polymer is primarily entropic [3], confining a semiflexible polymer involves both energetic and entropic effects, with the balance controlled by the stiffness of the chain and the length scale of confinement [4–6]. Consider a long, ideal polymer chain confined to a spherical cavity. In the case of a flexible polymer, the chain has the entropic tendency to fill the available space, with the highest concentration of chain segments in the center of the cavity [7]. In the limit of high stiffness, on the other hand, the chain is forced to circle near the surface of the cavity due to its tendency to minimize the bending energy cost. The interplay among the three length scales, namely, the length of the chain, the persistence length, and the characteristic size of the confinement, is thus a fundamental feature in the study of a semiflexible polymer in a confined geometry. Unfortunately, few problems involving semiflexible chains admit exact, closed-form solutions, and we are not aware of such solutions for a semiflexible chain in a confined geometry.

In this Letter, we present an exact, closed-form solution for the conformation of a semiflexible chain confined to the surface of a sphere using the wormlike chain model [8]. This problem is relevant to systems involving strongly adsorbed polymers on spherical surfaces which are often used as simple models for studying DNA/protein complexes and adsorption of a polymer on colloidal particles [5,9,10]. By exploiting a novel representation of the differential geometry of an inextensible curve on a spherical surface, we arrive at a simple and concise description of the chain kinematics, which in turn permits the evaluation of the mean square end-to-end distance in a simple, closed-form expression valid for arbitrary chain length, stiffness, and sphere radius.

We consider a wormlike chain of contour length L that is confined to the surface of a sphere of radius R. The chain trajectory defines a space curve $\vec{r}(s)$ where the path-length parameter s has units of length and runs from zero at one end of the polymer chain to L at the other end. The chain contour is assumed inextensible, which requires that the tangent vector $\vec{u} \equiv \partial_s \vec{r}(s)$ satisfies $|\vec{u}(s)| = 1$. The energetics of the wormlike chain model is given by a bending Hamiltonian of the form [11]

$$\beta\mathcal{H} = \frac{l_p}{2}\int_0^L ds\left(\frac{\partial^2 \vec{r}}{\partial s^2}\right)^2, \tag{1}$$

where $\beta = 1/(k_B T)$ and l_p is the persistence length of the free polymer chain. Since we are interested in the equilibrium statistical behavior of an open chain with free ends, the twist degrees of freedom are irrelevant. In problems where the polymer is either closed or torsionally constrained, twist plays a crucial role in the equilibrium and dynamic properties of the polymer; these problems are beyond the scope of this Letter, however.

The constraint that the chain must lie on the surface of the sphere requires that the position vector $\vec{r}(s)$ be a fixed distance R away from the center of the sphere. We now seek a convenient description of the chain kinematics that automatically satisfies this constraint as well as the local inextensibility of the chain contour. Setting the origin of the coordinate system to be the center of the sphere, we define a local orthogonal unit triad $\vec{t}_i$ $(i = 1, 2, 3)$ and choose the position vector to lie in the third direction $[\vec{r}(s) = R\vec{t}_3(s)]$; this guarantees that the chain is confined to the spherical surface. The rotation of the triad system as we progress along the chain contour is given by a rotation vector $\vec{\omega}$ that acts as $\partial_s \vec{t}_i = \vec{\omega} \times \vec{t}_i$; thus the chain position is determined by the rotation of $\vec{t}_3$ over s. The tangent vector is easily shown to be $\vec{u} = R(\omega_2 \vec{t}_1 - \omega_1 \vec{t}_2)$, and the chain inextensibility constraint is satisfied by requiring $\omega_1^2 + \omega_2^2 = R^{-2}$. By choosing this coordinate frame, we have effectively altered the complicated constraints on

the chain conformation to a simple relationship between ω_1 and ω_2 that can be trivially satisfied.

We now relate the rotation vector $\vec{\omega}$ to the three Euler angles of rotation ϕ, θ, and ψ. Performing an infinitesimal rotation of the triad system, we can express the components of $\vec{\omega}$ in terms of $\partial_s\phi$, $\partial_s\theta$, $\partial_s\psi$ [8]. We complete our description of the spherical chain kinematics by setting $\partial_s\phi$ equal to zero and $\partial_s\theta$ equal to R^{-1}, leaving only the angle ψ to describe the chain conformation that satisfies the constraints. Our mathematical description of the chain kinematics is more clearly understood by considering the chain curvature vector

$$\frac{\partial \vec{u}}{\partial s} = 2\cos\psi \frac{\partial \psi}{\partial s}\vec{t}_1 + 2\sin\psi \frac{\partial \psi}{\partial s}\vec{t}_2 - \frac{1}{R}\vec{t}_3, \qquad (2)$$

which shows that the choice of ψ as the chain coordinate effectively decouples the curvature due to the spherical confinement from the curvature due to deflection of the chain on the spherical surface.

A physically intuitive description of the conformation is to consider the triad system as a spinning top. For stretches of the chain where the angle ψ is constant, the top rotates about a fixed axis, and the chain lies along an equator of the spherical body. When the angle ψ is altered, the spinning top wobbles and resets its axis of rotation such that the pathlength of the chain is maintained during the deflection. We can consider a reference frame of the spinning top that removes the wobbling motion associated with deflection of the angle ψ [12]. This frame is constructed by removing the accumulated wobble by rotating $\vec{t}_1$ and $\vec{t}_2$ about the vector $\vec{t}_3$ by the total wobble angle $\psi(s) - \psi(0)$. We set $\psi(0)$ to zero without loss of generality and define the complex tangent $\vec{\epsilon} \equiv (\vec{t}_1 + i\vec{t}_2)\exp(i\psi)$ and the complex curvature $\eta \equiv iR^{-1}\exp(i2\psi)$ to give the rate of rotation of this reference frame. Using these definitions, the kinematic equations describing the polymer conformations lying on a spherical surface are given by

$$\frac{\partial \vec{\epsilon}}{\partial s} = \frac{i}{R}e^{i2\psi}\vec{t}_3, \qquad (3)$$

$$\frac{\partial \vec{t}_3}{\partial s} = -\mathrm{Real}\left(\frac{i}{R}e^{i2\psi}\vec{\epsilon}^{\,*}\right), \qquad (4)$$

where the asterisk indicates complex conjugation.

We now give two examples of the solution to Eqs. (3) and (4) to clarify the use of this coordinate frame. The simplest example is the function $\psi = \nu s$ which describes a circle with radius $R(1 + 4R^2\nu^2)^{-1/2}$ and period $2\pi/\omega$ where $\omega^2 = R^{-2} + 4\nu^2$. As the second example, we consider a function ψ that is a sawtooth function of s with a slope ν and period $2\pi/\omega$. This function results in a conformation with a constant curvature similar to wrapping yarn in a spool. Figure 1 shows such a conformation that comes to a closed orbit after ten periods around a sphere. Chain conformations like this are of particular importance when dealing with chain self-interaction, and are very difficult to describe in terms of Cartesian coordinates.

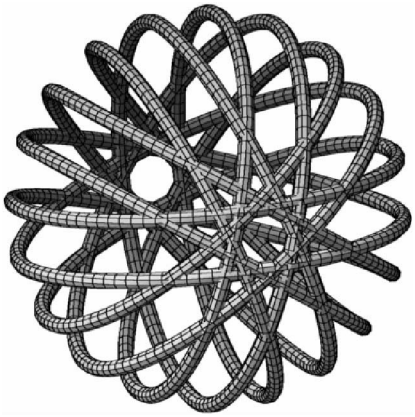

FIG. 1. The conformation of a polymer chain wrapping around a unit sphere with a constant curvature that orbits after ten revolutions around the sphere.

With our description of the chain kinematics, the bending Hamiltonian becomes

$$\beta\mathcal{H} = 2l_p\int_0^L ds\left(\frac{\partial \psi}{\partial s}\right)^2 + \frac{Ll_p}{2R^2}, \qquad (5)$$

where the first term is due to chain curvature deformation in the spherical surface and the second term is due to the curvature of the confining surface. The chain statistics are given by the probability that a chain with initial angle $\psi(0) = \psi_0$ will have a final angle $\psi(L) = \psi$ defined as the Green's function $G(\psi|\psi_0, L)$. The Green's function is found by summing all of the statistical contributions of the paths between ψ_0 and ψ of the fluctuating field $\psi(s)$, weighted by the Boltzmann factor $\exp(-\beta\mathcal{H}[\psi(s)])$ [8]. The result can be written as an eigenfunction expansion

$$G(\psi|\psi_0, L) = \sum_{m=-\infty}^{\infty}\frac{1}{2\pi}e^{im(\psi-\psi_0)}\exp\left(-\frac{m^2L}{8l_p}\right). \qquad (6)$$

Equation (6) is equivalent to the quantum mechanical propagator for a particle confined to a circle, with the bending energy in Eq. (5) playing the role of the kinetic energy and the contour length acting as an imaginary time. Use of Eq. (6) in finding chain averages requires expressing the quantity of interest in terms of the function ψ, thus making our compact expressions for the chain kinematics [Eqs. (3) and (4)] extremely useful.

We note that the bending deformation due to the confinement of the sphere is uncoupled from undulations within the surface of the sphere; thus conformation fluctuations within the spherical surface are unaffected by the overall spherical confinement. This is consistent with previous work which demonstrates that, in a tightly bent semiflexible polymer, those fluctuations that do not affect the constraint are not suppressed [6].

We now evaluate the mean square end-to-end distance for the polymer. Using the definition of the end-to-end vector $\vec{R} = \vec{r}(L) - \vec{r}(0)$, we can write $\vec{R}^2$ as

$$\begin{aligned}\vec{R}^2 &= 2R^2[1 - \vec{t}_3(0)\cdot\vec{t}_3(L)] \\ &= 2R^2 \sum_{n=1}^{\infty} \frac{(-1)^{n+1}}{2^n R^{2n}} \left(\prod_{j=1}^{2n} \int_0^{s_{j-1}} ds_j \right) \\ &\quad \times \left\{ \prod_{k=1}^{n} \mathrm{Real}[e^{i2(\psi_{2k-1} - \psi_{2k})}] \right\}, \end{aligned} \tag{7}$$

where $s_0 = L$ and $\psi_k = \psi(s_k)$. The second line of Eq. (7) is obtained by eliminating the complex tangent $\vec{\epsilon}$ from Eqs. (3) and (4) iteratively starting from the initial position. The average of Eq. (7) is performed by inserting a propagator [Eq. (6)] between each successive function of ψ in the expansion. The resulting expression is

$$\langle \vec{R}^2 \rangle = -\sum_{n=1}^{\infty} 2R^2(-1)^n \left(\frac{2l_p}{R} \right)^{2n} A_n(N), \tag{8}$$

where we define $N = L/(2l_p)$. The coefficients of the expansion $A_n(N)$ are compactly defined through the recursive relation

$$A_n(N) = \int_0^N d\tau_1 \int_0^{\tau_1} d\tau_2 \exp(-\tau_1 + \tau_2) A_{n-1}(\tau_2), \tag{9}$$

with $A_0(N) = 1$. The recursive relation is more conveniently written in the differential form $(\partial_N^2 + \partial_N)A_n(N) = A_{n-1}(N)$, with the initial conditions $A_n(0) = 0$ and $\partial_N A_n(0) = 0$. This differential recursive equation can be readily solved by a Laplace transform from the variable N to p to give $A_n(p) = p^{-n-1}(p+1)^{-n}$. Inserting this result into Eq. (8), performing the straightforward summation, and inverse Laplace transforming the resulting expression lead to our final result for the mean square end-to-end distance of a chain confined to a spherical surface

$$\begin{aligned}\langle \vec{R}^2 \rangle &= 2R^2 - 2R^2 \exp\left(-\frac{L}{4l_p} \right) \\ &\quad \times \left\{ \cosh\left[\frac{L}{4l_p} \left(1 - \frac{16l_p^2}{R^2} \right)^{1/2} \right] \right. \\ &\quad \left. + \left(1 - \frac{16l_p^2}{R^2} \right)^{-1/2} \sinh\left[\frac{L}{4l_p} \left(1 - \frac{16l_p^2}{R^2} \right)^{1/2} \right] \right\}. \end{aligned} \tag{10}$$

It can be easily verified that Eq. (10) recovers several important limiting results. If the chain length is much less than the radius, we expect that the chain will not feel the effect of the spherical confinement. As the radius goes to infinity, the leading order term in the l_p/R expansion of Eq. (10) yields the two-dimensional solution for a free wormlike chain $4l_pL + 8l_p^2\{\exp[-L/(2l_p)] - 1\}$ [13]. Similarly, as the chain length goes to zero, Eq. (10) approaches L^2 for any finite sphere radius. Finally, for a fixed radius R, we expect that for a sufficiently long chain the end position becomes uncorrelated from the initial position, thus leading to a uniform coverage of the sphere by the chain segments. This results in a mean square end-to-end distance of $2R^2$ as can be seen from Eq. (10) in the limit of L approaching infinity for fixed l_p and R.

In Fig. 2, we present a plot of Eq. (10) as a function of the chain length for a fixed value of R/l_p of 40. The mean square end-to-end distance in Fig. 2 exhibits three distinct scaling regimes due to the three relevant length scales. With $R/l_p = 40$, the radius is large enough that short stretches of the chain behave as a chain in two dimensions. Figure 2 scales as L^2 for short chains ($L < 2l_p$), which is the rigid-rod behavior. In the intermediate regime [$2l_p < L < R^2/(2l_p)$], the chain behaves with the random walk scaling of L. Essentially, the chain is sufficiently long such that the end orientations are uncorrelated; however, the chain is not long enough to feel the finite area of the confining spherical surface. For a sufficiently long chain [$L > R^2/(2l_p)$], the polymer has diffused over a distance where the curvature of the confining surface restricts the magnitude of the end-to-end vector; thus the final regime approaches a value of $2R^2$. Our results for these latter two regimes agree with those predicted using the flexible Gaussian chain model [14].

A qualitatively different behavior emerges when the radius of the sphere is smaller than the persistence length. Specifically, for $R < 4l_p$, the arguments of the hyperbolic functions in Eq. (10) are imaginary, resulting in an oscillatory mean square end-to-end distance. Physically, the chain revolves around the sphere due to the orientation correlation. In the limit of infinite chain stiffness, the mean square end-to-end distance becomes $2R^2 - 2R^2\cos(L/R)$, which corresponds to a polymer chain confined to the equator of a sphere. For finite chain stiffness, the L dependence of Eq. (10) contains an exponentially decaying oscillation with a periodicity in L of

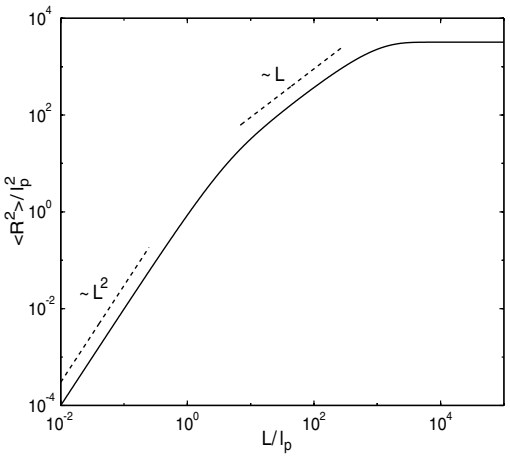

FIG. 2. The mean square end-to-end distance of a polymer chain confined to a sphere with $R/l_p = 40$.

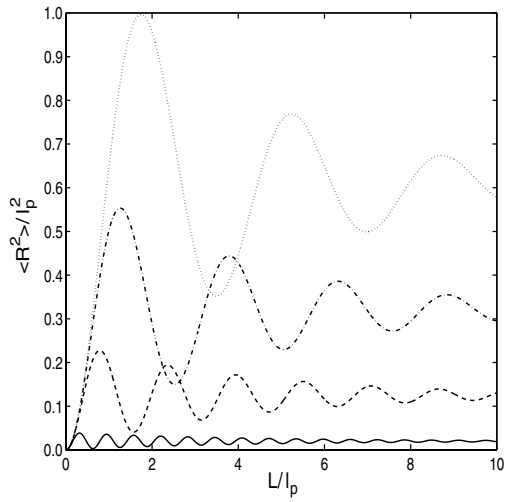

FIG. 3. The mean square end-to-end distance versus the polymer chain length for $R/l_p = 1/10$ (solid curve), $R/l_p = 1/4$ (dashed curve), $R/l_p = 2/5$ (dash-dotted curve), and $R/l_p = 11/20$ (dotted curve).

$8\pi l_p R(16l_p^2 - R^2)^{-1/2}$. The exponential decay of the oscillations reflects the eventual loss of correlation due to the thermal fluctuations of the semiflexible chain. The periodicity in L is larger than that at infinite chain stiffness ($2\pi R$) because of the wrinkling of the chain due to fluctuation. For $R > 4l_p$, the chain orientation becomes uncorrelated before the polymer completes a single pass over the sphere, manifested in the lack of oscillation in Fig. 2. The crossover at $R = 4l_p$ is analogous to a damped harmonic oscillator where critical damping occurs when the damping coefficient [$1/(4l_p)$ in our case] is equal to the natural frequency of the oscillation ($1/R$) [15].

The oscillatory behavior of Eq. (10) for $R < 4l_p$ is shown in Fig. 3. As expected, the short chain ($L \ll l_p$) behavior is independent of the radius. The damping of the oscillations occurs exponentially in L with a correlation length of $4l_p$ (independent of R); however, since the period of the oscillations is shorter for smaller radius, the number of correlated spherical wraps decreases with increasing sphere radius. As the chain length goes to infinity, all of the curves in Fig. 3 approach $2R^2$.

The behavior of the mean square end-to-end distance suggests the nature of the surface coverage by the polymer as the length of the polymer increases. In the regime corresponding to Fig. 2, the polymer covers the sphere in a diffusive manner from the starting point. The scenario is that of the polymer chain creeping over the sphere starting at one pole towards the opposite pole as the length of the chain increases. For the high chain stiffness shown in Fig. 3, the orientation correlation causes the chain to lie on the equator of the sphere, and conformation fluctuations cause the segment density to spread from the equator toward the poles.

Our treatment ignores the interactions between chain segments, which will modify the predicted behavior. However, some salient features predicted by our work will remain. For example, our predicted change in the manner in which the chain wraps the sphere as the stiffness increases is consistent with the Monte Carlo results in Ref. [10], which included both excluded volume and electrostatic interactions. Thus our results both provide a concise and unified expression for elucidating the dominant effects due to the interplay among the three length scales in the problem and serve as a useful reference for examining new effects due to additional interactions.

The main advantage of the chain kinematics we have developed is that it provides a convenient way to satisfy the constraints associated with the wormlike chain model and the chain confinement. Physically, strict confinement of the chain to a sphere surface corresponds to infinitely strong adsorption. However, our formalism can be extended to allow radial fluctuations away from the sphere surface while still conserving the contour length. This will enable us to treat a wormlike chain near an attractive spherical particle or within a spherical cavity.

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