Fluctuating elastic rings: Statics and dynamics

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We study the effects of thermal fluctuations on elastic rings. Analytical expressions are derived for correlation functions of Euler angles, mean-square distance between points on the ring contour, radius of gyration, and probability distribution of writhe fluctuations. Since fluctuation amplitudes diverge in the limit of vanishing twist rigidity, twist elasticity is essential for the description of fluctuating rings. We discover a crossover from a small scale regime in which the filament behaves as a straight rod, to a large scale regime in which spontaneous curvature is important and twist rigidity affects the spatial configurations of the ring. The fluctuation-dissipation relation between correlation functions of Euler angles and response functions, is used to study the deformation of the ring by external forces. The effects of inertia and dissipation on the relaxation of temporal correlations of writhe fluctuations, are analyzed using Langevin dynamics.

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I. INTRODUCTION

Small circular loops of DNA (plasmids) play an important role in biological processes such as gene transfer between bacteria and in biotechnological applications where they are used as vectors for DNA cloning [1]. The simplest minimal model that captures both the topology and the physical properties of such an object is that of an elastic ring that has both bending and twist moduli. This model was used in a recent study of writhe instability of a twisted ring [2,3]. However, since this work focused on the mechanical aspects of the problem and did not consider the effects of thermal fluctuations, it cannot be directly applied to plasmids and other microscopic rings. The consideration of fluctuations is important since they dominate the physics of macromolecules and determine their statistical properties, such as characteristic dimensions, dynamics in solution [4], kinetics of loop formation, and dissociation of short DNA segments [5] and molecular beacons [6]. Recently, we developed a theory of fluctuating elastic filaments, with arbitrary spontaneous curvature, torsion, and twist in their stress free state [7]. Since topological constraints were not taken into account in this paper, our analysis was limited to open filaments and could not be directly applied to the study of closed objects that have the topology of a ring.

The present paper is an expanded version of a letter in which we presented the solution of this problem for weakly fluctuating rings [8]. The analysis of Ref. [8] is generalized to the case of ribbonlike filaments, with two principal axes of inertia in the cross-sectional plane. We calculate the correlation functions of Euler angles, and use them to obtain other statistical properties of fluctuating rings, such as mean-square spatial distance between points on the ring contour, and the radius of gyration. Analytical expressions for the complete probability distribution function of writhe fluctuations and for all its moments, are derived. A crossover length scale is found, below which straight rod behavior dominates and the twist of the cross section with respect to the center line is uncorrelated with the conformation of the center line. Above this length scale the nonvanishing spontaneous curvature of the ring begins to play a role and twist rigidity affects the three-dimensional conformation of the center line of the ring. The correlation functions of Euler angles are used to predict the mechanical response to external torques and forces, and to examine the effect of spontaneous orientation of the cross section, on the deformation of ribbonlike rings. The dynamic correlation function of writhe fluctuations is calculated in both the inertial and the dissipative regimes. In the former case, oscillatory decay of the correlations with time is observed. When inertia is negligible, the relaxation is monotonic and there is a transition from a short-time regime in which the relaxation rate depends only on the bending rigidity, to a long-time regime where the decay is affected by both bending and twist modes.

In Sec. II we present the generalized Frenet equations that describe the conformation of a filament, and introduce the elastic energy that governs its fluctuations about the stress-free state. We express the curvature and torsion parameters that characterize this conformation, in terms of the Euler angles, and write down the elastic energy as a quadratic form in the deviations of these angles from their values in the undeformed ring. The topological constraints corresponding to a ring are introduced as integral conditions on the fluctuations of the Euler angles, and result in the vanishing contribution of some of the lowest Fourier modes to the fluctuation spectrum. In Sec. III we diagonalize the elastic energy, obtain the spectrum of normal modes, and discuss their physical meaning. In Sec. IV we use this eigenmode expansion to calculate the correlation functions of Euler angles. We study the dependence of the correlators on physical parameters such as bending and twist rigidities, and on the spontaneous orientation of the principal axes of inertia of the cross section with respect to the plane of the ring, and discuss the geometry of typical configurations of the ring. In Sec. V we derive explicit expressions for the orientational correlation function of the tangents to the ring, root-mean-square (rms) distance

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between points on the ring contour, and the radius of gyration, in terms of correlation functions of Euler angles computed in the preceding sections. In Sec. VI we express the writhe and twist numbers that characterize an instantaneous configuration of the ring, in terms of Euler angles. We then use the correlation functions of Euler angles to calculate the probability distribution function of writhe fluctuations and study its dependence on the bending and twist rigidities. We find that the amplitude of writhe fluctuations exhibits a crossover from a small-scale, straight-rodlike regime in which a twist of the cross section has no effect on the spatial conformations of the center line, to a large-scale regime in which the two types of fluctuations become strongly coupled due to the spontaneous curvature of the ring. In Sec. VII we use the fluctuation-dissipation theorem that relates the previously calculated equilibrium correlation functions of Euler angles to the response functions, in order to study the linear response of a ring to small externally applied forces and moments. We show that the deformation of a ribbonlike ring depends in an essential way on the orientation of its cross section in the undeformed reference state. In Sec. VIII, we derive the Langevin equations that describe both the inertial and the dissipative dynamics of Euler angles, and use them to study the effects of bending and twist rigidities and of the orientation of the cross section of the ribbon, on the frequency spectrum and temporal relaxation of its writhe modes. Details of the derivation of the Langevin equations and the calculation of the dynamic correlation functions, are given in Appendixes A and B, respectively. In Sec. IX we summarize our main results and discuss the domain of validity of our theory.

II. GENERAL APPROACH

The general theory of fluctuating noninteracting elastic filaments was presented in Ref. [7]. To each point s one attaches a triad of unit vectors $\{\mathbf{t}_i(s)\}$ where $\mathbf{t}_3(s)$ is the tangent vector to the curve at s, and the vectors $\mathbf{t}_1(s)$ and $\mathbf{t}_2(s)$ are directed along the axes of symmetry of the (in general, noncircular) cross section. The spatial conformation $\mathbf{x}(s)$ of the filament is given by the generalized Frenet equations

$$\frac{d\mathbf{t}_i}{ds}=-\sum_{jk} e_{ijk}\omega_j\mathbf{t}_k, \tag{1}$$

together with the inextensibility condition,

$$d\mathbf{x}/ds=\mathbf{t}_3, \tag{2}$$

where e_{ijk} is the antisymmetric unit tensor and the parameters $\{\omega_j(s)\}$ characterize the curvature, torsion, and twist of the filament. The components of these vectors can be expressed in terms of the Euler angles θ, φ, and ψ:

$$\mathbf{t}_1=\begin{pmatrix}\cos\theta\cos\varphi\cos\psi-\sin\varphi\sin\psi\\ \cos\theta\sin\varphi\cos\psi+\cos\varphi\sin\psi\\ -\sin\theta\cos\psi\end{pmatrix}, \tag{3}$$

$$\mathbf{t}_2=\begin{pmatrix}-\cos\theta\cos\varphi\sin\psi-\sin\varphi\cos\psi\\ -\cos\theta\sin\varphi\sin\psi+\cos\varphi\cos\psi\\ \sin\theta\sin\psi\end{pmatrix}, \tag{4}$$

$$\mathbf{t}_3=\begin{pmatrix}\sin\theta\cos\varphi\\ \sin\theta\sin\varphi\\ \cos\theta\end{pmatrix}. \tag{5}$$

Substituting Eqs. (3) – (5) into Eq. (1), the Frenet equations can be rewritten in the form:

$$\begin{gathered}\frac{d\,\theta}{ds}=\omega_1\sin\psi+\omega_2\cos\psi,\\ \frac{d\varphi}{ds}\sin\theta=-\omega_1\cos\psi+\omega_2\sin\psi,\\ \frac{d\psi}{ds}\sin\theta=(\omega_1\cos\psi-\omega_2\sin\psi)\cos\theta+\omega_3\sin\theta.\end{gathered} \tag{6}$$

Solving these equations with respect to $\{\omega_i\}$ yields

$$\omega_1=-\frac{d\varphi}{ds}\sin\theta\cos\psi+\frac{d\theta}{ds}\sin\psi, \tag{7}$$

$$\omega_2=\frac{d\varphi}{ds}\sin\theta\sin\psi+\frac{d\theta}{ds}\cos\psi, \tag{8}$$

$$\omega_3=\frac{d\psi}{ds}+\cos\theta\frac{d\varphi}{ds}. \tag{9}$$

We assume that the center line of the undeformed ring forms a circle of radius r in the xy plane, and that its cross section is rotated by angle $\psi_0(s)$ around this center line. The Euler angles that describe this configuration are

$$\theta_0=\pi/2,\quad \varphi_0=s/r,\quad \psi_0=ks/2r+\psi_{00}, \tag{10}$$

where k is an integer and ψ_{00} is a constant, independent of s. Eqs. (7) – (9) can be rewritten in the form

$$\omega_{01}=-(1/r)\cos\psi_0,\quad \omega_{02}=(1/r)\sin\psi_0,$$
$$\text{and}\quad \omega_{03}=d\psi_0/ds. \tag{11}$$

Although, in general, the stress-free state of the ring can be arbitrarily twisted (e.g., because of the intrinsic tendency of the filament to twist), in this paper we will not consider the spontaneous twist ($\omega_{03}=0$), and taking $k=0$, we set $\psi_0=\psi_{00}$ (for brevity, we will denote this constant by ψ_0 in the following). This angle characterizes the orientation of the principal axes of the cross section with respect to the plane of the undeformed ring. In the case of a circular cross section, all physical observables are independent of ψ_0 and it is convenient to set $\psi_0=0$.

The corresponding Euler parametrization of the triad vectors is

$$\mathbf{t}_{01} = \begin{pmatrix} -\sin(s/r)\sin\psi_0 \\ \cos(s/r)\sin\psi_0 \\ -\cos\psi_0 \end{pmatrix}, \quad \mathbf{t}_{02} = \begin{pmatrix} -\sin(s/r)\cos\psi_0 \\ \cos(s/r)\cos\psi_0 \\ \sin\psi_0 \end{pmatrix},$$

$$\mathbf{t}_{03} = \begin{pmatrix} \cos(s/r) \\ \sin(s/r) \\ 0 \end{pmatrix}. \tag{12}$$

In the absence of excluded volume and other nonelastic interactions, the energy of a filament is of a purely elastic origin and can be represented as a quadratic form in the deviations $\delta\omega_k = \omega_k - \omega_{0k}$ [2,7],

$$U = \frac{k_B T}{2}\int_0^{2\pi r} ds \sum_{k=1}^{3} a_k \delta\omega_k^2, \tag{13}$$

where k_B is the Boltzmann constant, T is the temperature, and the bare persistence lengths a_k represent the rigidity with respect to the corresponding deformation modes. The above expression for the energy is based on the linear theory of elasticity and applies to deformations whose characteristic length scale (e.g., radius of curvature) is much larger than the diameter of the filament [9]. Since the persistence lengths are determined by material properties on length scales of the order of this diameter, they are the same as those of a straight rod. We conclude that a_1 and a_2 are associated with the bending rigidities of the filament with respect to the two principal axes of inertia I_1 and I_2 (they differ if the cross section is not circular), and that a_3 is associated with twist rigidity. In the special case of incompressible isotropic rods with shear modulus μ, the theory of elasticity yields [9]

$$a_1 = 3\mu I_1/k_B T, \quad a_2 = 3\mu I_2/k_B T, \quad \text{and} \quad a_3 = C/k_B T, \tag{14}$$

where the torsional rigidity C is also proportional to μ and depends on the geometry of the cross section [for an elliptical cross section with semi-axes d_1 and d_2, $C = \pi\mu d_1^3 d_2^3/(d_1^2 + d_2^2)$]. In this paper, we will treat a_i as given material parameters of the ring.

In the following, we consider only small fluctuations of the Euler angles about their values in the undeformed state, Eq. (10). This approximation remains valid as long as the bare persistence lengths are much larger than the radius of the ring, i.e., $a_k \gg r$. Expanding Eqs. (7) – (9) in small deviations from the stress-free state, we find

$$\delta\omega_1 = \left(\frac{\delta\psi}{r} + \frac{d\,\delta\theta}{ds}\right)\sin\psi_0 - \frac{d\,\delta\varphi}{ds}\cos\psi_0,$$

$$\delta\omega_2 = \left(\frac{\delta\psi}{r} + \frac{d\,\delta\theta}{ds}\right)\cos\psi_0 + \frac{d\,\delta\varphi}{ds}\sin\psi_0, \tag{15}$$

$$\delta\omega_3 = \frac{d\,\delta\psi}{ds} - \frac{\delta\theta}{r}.$$

It is instructive to relate the above parameters to the curvature κ and torsion τ familiar from differential geometry of space curves [10]. A circular planar ring has $\kappa_0 = 1/r$ and $\tau_0 = 0$. Expanding in small deviations about these values yields

$$\delta\kappa = \frac{d\,\delta\varphi}{ds} \quad \text{and} \quad \delta\tau = \tau = -\frac{\delta\theta}{r} - r\frac{d^2\delta\theta}{ds^2}. \tag{16}$$

As expected, fluctuations of the curvature represent bending deformations in the plane of the ring, and depend only on the angle φ that describes the rotation of the tangent to the ring, in the xy plane [see Eq. (5)]. Torsion describes deviations of the filament from this plane, and its fluctuations depend only on the deviations of the angle θ from $\pi/2$. The specification of the local curvature and torsion completely determines the configuration of the center line of any curved filament, and the Euler angle ψ complements the description by specifying the rotation of the cross section about this center line. However, the elastic energy cannot be factorized into a sum of contributions due to deformation of the center line and rotation about it. As will be shown in Sec. VI, $\omega_3(s)$ defines the rate of twist and therefore the persistence length a_3 is associated with twist. Twist represents not only the rotation about the center line [the $d\psi/ds$ term in Eq. (9)], but also contains a contribution due to the curvature of the center line (the $\cos\theta d\varphi/ds$ term in the above equation). Similarly, although inspection of Eq. (1) suggests that $\omega_1(s)$ and $\omega_2(s)$ completely determine the variation of the tangent $\mathbf{t}_3(s)$ as one moves along the contour, this variation depends on the main axes of the cross section at s [the vectors $\mathbf{t}_1(s)$ and $\mathbf{t}_2(s)$], that themselves rotate with the cross section. This explains the ψ dependence of ω_1 and ω_2 in Eqs. (7) and (8). The relation between the two descriptions ($\{\theta,\varphi,\psi\}$ and $\{\omega_i\}$) is a special case of the more general relation between Eulerian and Lagrangian descriptions in the theory of elasticity [11]. While the Euler angles describe the orientation of the triad $\{\mathbf{t}_i(s)\}$ in the laboratory frame, the parameters $\omega_i(s)$ describe the local variation of this orientation as one moves along the curve, in the frame associated with the triad itself. The simple form of the energy, Eq. (13), is a direct consequence of this Lagrangian description.

Substituting Eqs. (15) into the elastic energy, Eq. (13), yields

$$U = k_B T\int_0^{2\pi r} ds\left[\frac{A_1}{2}\left(\frac{d\,\delta\theta}{ds} + \frac{\delta\psi}{r}\right)^2 + \frac{A_2}{2}\left(\frac{d\,\delta\varphi}{ds}\right)^2 + A_3\left(\frac{d\,\delta\theta}{ds} + \frac{\delta\psi}{r}\right)\frac{d\,\delta\varphi}{ds} + \frac{a_3}{2}\left(\frac{d\,\delta\psi}{ds} - \frac{\delta\theta}{r}\right)^2\right], \tag{17}$$

where the coefficients A_i are defined as,

$$A_1 = a_1\cos^2\psi_0 + a_2\sin^2\psi_0, \quad A_2 = a_1\sin^2\psi_0 + a_2\cos^2\psi_0,$$

$$A_3 = (a_2 - a_1)\cos\psi_0\sin\psi_0. \tag{18}$$

For $a_2 > a_1$, the constant Euler angle ψ_0 measures the angle between the major axis of inertia and the xy plane. The case

$\psi_0=0$ ($\psi_0=\pi/2$) corresponds to major axis that lies in the xy plane (normal to the xy plane). The coefficients A_i obey the relations

$$A_1A_2-A_3^2=a_1a_2, \quad A_1+A_2=a_1+a_2. \tag{19}$$

The periodic boundary conditions on the Euler angles

$$\delta\,\theta(2\pi r)=\delta\,\theta(0), \quad \delta\,\psi(2\pi r)=\delta\,\psi(0),$$
$$\delta\,\varphi(2\pi r)=\delta\,\varphi(0), \tag{20}$$

are supplemented by the condition that the ring is closed in three-dimensional space, $\mathbf{x}(2\pi r)=\mathbf{x}(0)$. Using Eq. (2), this condition can be recast into an integral form,

$$\int_0^{2\pi r} ds\,\delta\mathbf{t}_3(s)=0. \tag{21}$$

For small deviations from equilibrium we get from Eq. (5),

$$\delta\mathbf{t}_3(s)=\begin{pmatrix} -\delta\,\varphi(s)\sin(s/r)\\ \delta\,\varphi(s)\cos(s/r)\\ -\delta\,\theta(s)\end{pmatrix}, \tag{22}$$

and the boundary conditions can be written as

$$\int_0^{2\pi r} ds\,\delta\,\theta(s)=\int_0^{2\pi r} ds\,\delta\,\varphi(s)\cos(s/r)$$
$$=\int_0^{2\pi r} ds\,\delta\,\varphi(s)\sin(s/r)=0. \tag{23}$$

Since the deviations of the Euler angles are periodic functions of s, they can be expanded in Fourier series

$$\delta\eta(s)=\sum_n \tilde{\eta}(n)e^{ins/r}, \quad \tilde{\eta}(-n)=\tilde{\eta}^*(n), \tag{24}$$

for each $\eta=\theta,\varphi,\psi$, where the sum goes over all positive and negative integers n. The boundary conditions Eqs. (23) can be expressed as conditions on the Fourier coefficients,

$$\tilde{\theta}(0)=\tilde{\varphi}(1)=0. \tag{25}$$

Substituting Eqs. (24) into Eq. (17) we find,

$$\frac{U}{2\pi r k_BT}=\frac{1}{r^2}\left[\frac{A_1}{2}|\tilde{\psi}(0)|^2+(A_1+a_3)|i\tilde{\theta}(1)+\tilde{\psi}(1)|^2\right]$$
$$+\frac{1}{r^2}\sum_{n=2}^{\infty}\{A_1|in\tilde{\theta}(n)+\tilde{\psi}(n)|^2$$
$$+A_2n^2|\tilde{\varphi}(n)|^2-2A_3[in\tilde{\theta}(n)+$$
$$\tilde{\psi}(n)]in\tilde{\varphi}(-n)+a_3|in\tilde{\psi}(n)-\tilde{\theta}(n)|^2\}. \tag{26}$$

The energy does not depend on modes $\tilde{\psi}(1)=-i\tilde{\theta}(1)$ and $\tilde{\varphi}(0)$ that correspond to a rigid body rotation of the entire ring, with respect to axes lying in the plane of the ring and normal to it, respectively.

The quadratic form inside the sum over$n$ in Eq. (26) can be represented as a matrix in the space spanned by the Fourier components $\tilde{\theta}(n),\tilde{\varphi}(n)$, and $\tilde{\psi}(n)$ (this applies to $n>1$; the cases $n=0,\pm1$ will be considered separately),

$$\mathbf{Q}(n)=\begin{pmatrix} A_1n^2+a_3 & A_3n^2 & -i(A_1+a_3)n\\ A_3n^2 & A_2n^2 & -iA_3n\\ i(A_1+a_3)n & iA_3n & a_3n^2+A_1\end{pmatrix}. \tag{27}$$

III. SPECTRUM OF FLUCTUATIONS

In order to obtain the spectrum of fluctuations of the ring, we diagonalize the free energy Eq. (26) by expanding the Fourier components $\tilde{\eta}(n)$ in the eigenvectors $\eta_k(n)$ of the matrix $\mathbf{Q}(n)$,

$$\tilde{\eta}(n)=\sum_k c_k(n)\,\eta_k(n), \tag{28}$$

where $\eta=\theta,\varphi,\psi$ and $\eta_k(n)$ is the ηth component of the eigenvector$\boldsymbol{\eta}_k(n)=\{\theta_k(n),\varphi_k(n),\psi_k(n)\}$ of the quadratic form Eq. (26) corresponding to the eigenvalue $\lambda_k(n)$. They are normalized by the conditions,

$$\sum_\eta \eta_k(n)\,\eta_l(-n)=\delta_{kl}, \quad \sum_k \eta_k(n)\,\eta'_k(-n)=\delta_{\eta\eta'}. \tag{29}$$

Expanding the elastic energy in the eigenmodes gives

$$U=\frac{\pi k_BT}{r}\sum_{n=0}^{\infty}\sum_k \lambda_k(n)|c_k(n)|^2. \tag{30}$$

The three eigenvalues $\lambda_k(n)$ corresponding to the Fourier mode n, are the roots of the characteristic cubic polynomial,

$$\lambda^3-b_2\lambda^2+b_1\lambda-b_0=0, \tag{31}$$

with coefficients

$$b_0=a_1a_2a_3n^2(n^2-1)^2,$$
$$b_1=(a_1a_2+a_2a_3+a_1a_3)n^2(n^2+1)-A_1a_3(3n^2-1), \tag{32}$$
$$b_2=(a_1+a_2+a_3)n^2+A_1+a_3,$$

where we used Eqs. (18) and (19) to simplify cumbersome mathematical expressions. Since the matrix $\mathbf{Q}(n)$ is Hermitian, its eigenvalues are real.

Inspection of Eqs. (31) and (32) shows that $\lambda_k(-n)=\lambda_k(n)$ and that all eigenvalues with $n>1$ are positive. Because of the boundary conditions, Eqs. (25), there are only two independent normal modes corresponding to each of the cases, $n=0$ and $n=1$. In order to understand the physical meaning of these modes, we introduce the components of the Fourier transforms of the curvature and torsion, Eq. (16),

$$\tilde{\kappa}(n)=\frac{in}{r}\tilde{\varphi}(n) \quad \text{and} \quad \tilde{\tau}(n)=\frac{n^2-1}{r}\tilde{\theta}(n). \qquad (33)$$

Substituting the boundary conditions $\tilde{\theta}(0)=\tilde{\varphi}(1)=0$ into the above expressions we conclude that for modes with $n=0$ and 1, both $\delta\kappa$ and $\delta\tau$ vanish and, therefore, these modes do not affect the planar circular configuration of the center line of the ring. There are two zero energy modes that correspond to symmetry operations on the undeformed ring. One $n=0$ mode, with eigenfunction $\varphi_1(0)=1;\ \psi_1(0)=0$, describes the rotation of the ring about the z axis. One $n=1$ mode, with eigenfunction $\theta_1(1)=1;\ \psi_1(1)=-i$, corresponds to the rotation of the ring about an axis in the xy plane. The two remaining modes have an energy gap and are twist modes that leave the center line undisturbed. The $n=0$ mode with eigenfunction $\varphi_2(0)=0;\ \psi_2(0)=1$ has an eigenvalue $\lambda_2(0)=A_1$, and describes the uniform twist of the ring about its center line. Since this eigenvalue does not vanish for arbitrary a_1 and a_2, we conclude that the uniform twist of a ring costs energy even if the ring has a circular cross section. This conclusion agrees with Ref. [12], where the dynamics of the uniform twist mode was studied. The $n=1$ mode with eigenfunction $\theta_2(1)=1;\ \psi_2(1)=i$ has the eigenvalue $\lambda_2(1)=2(A_1+a_3)$ and corresponds to the rotation of the ring with respect to an axis that passes through the center line and lies in the xy plane, accompanied by the twist of the cross section by the angle ψ that varies periodically [as $\cos(s/r)$] along the contour of the ring. The dynamics of this mode was studied in Ref. [13].

In the limit $n\gg 1$, fluctuations of the three Euler angles are decoupled and $\lambda_k(n)\simeq a_k n^2$. In general, each normal mode of the ring corresponds to fluctuations of all three Euler angles, $\delta\theta(s)$, $\delta\varphi(s)$ and $\delta\psi(s)$, and describes a complex three-dimensional configuration.

The eigenvalue problem is simplified for a circular cross section ($a_2=a_1$), or when the cross section is asymmetric but $\psi_0=0$ (the case $\psi_0=\pi/2$ is reduced to $\psi_0=0$ by the substitution $a_1\leftrightarrow a_2$). In these cases, the mode $\delta\varphi(s)$ decouples from the other two modes and has the spectrum $\lambda_1(n)=a_1 n^2 (n\neq\pm 1)$. This mode corresponds to bending fluctuations that lie entirely in the plane of the ring. The other two modes are linear combinations of $\delta\theta(s)$ and $\delta\psi(s)$, with eigenvalues

$$\lambda_{2,3}(n)=\frac{a_2+a_3}{2}(n^2+1) \pm\sqrt{\left(\frac{a_2-a_3}{2}\right)^2(n^2+1)^2+4n^2a_2a_3}. \qquad (34)$$

Equation (34) can be further simplified in the limit of large rigidity with respect to twist $a_3\gg a_2$ in which case

$$\lambda_2(n)=a_2\frac{(n^2-1)^2}{n^2+1} \quad \text{for} \quad n\geqslant 1,$$

$$\lambda_3(n)=a_3(n^2+1) \quad \text{for} \quad n\geqslant 2. \qquad (35)$$

In the opposite limit $a_3\ll a_2$, the eigenvalues can be found by substituting $a_2\leftrightarrow a_3$ in Eq. (35).

Inspection of Eq. (34) shows that $\lambda_3(n)$ vanishes identically for all n when $a_3=0$ [this statement applies even to rings with noncircular cross section—see Eqs. (31) and (32)], indicating that the amplitudes of the corresponding fluctuation modes grow without limit in the absence of twist rigidity. Examining the expression for the elastic energy, Eq. (17), we conclude that these zero energy modes correspond to fluctuations for which

$$d\delta\theta/ds=-\delta\psi/r. \qquad (36)$$

In the absence of twist rigidity, twist fluctuations carry no energy penalty and the angle of the twist of the cross section ($\delta\psi$) can always adjust itself to an arbitrary deviation of the center line from the plane of the unperturbed ring ($\delta\theta$), so that this condition Eq. (36) is satisfied. The presence of an infinite number of zero energy modes means that the twist rigidity ($a_3\neq 0$) is absolutely essential for stabilizing the ring against out-of-plane fluctuations, and that bending elasticity alone cannot suppress this instability.

IV. CORRELATIONS OF EULER ANGLES

Applying the equipartition theorem to Eq. (30), we get

$$\langle c_k(n)c_{k'}(-n')\rangle=\frac{r}{\pi\lambda_k(n)}\delta_{nn'}\delta_{kk'}. \qquad (37)$$

Using expansion (28) and averaging with the help of Eq. (37), the correlation functions of Euler angles can be expressed in terms of the eigenvalues $\lambda_k(n)$ and the eigenfunctions $\eta_k(n)$ of the $\mathbf{Q}(n)$ matrix:

$$\langle\delta\eta(s)\delta\eta'(s')\rangle=\sum_n e^{in(s-s')/r}\langle\tilde{\eta}(n)\tilde{\eta}'(-n)\rangle =\frac{r}{\pi}\sum_n e^{in(s-s')/r}\sum_k\frac{\eta_k(n)\eta_k'(-n)}{\lambda_k(n)}, \qquad (38)$$

where $\delta\eta,\delta\eta'=\delta\theta,\ \delta\varphi,\ \delta\psi$. Care should be exercised in evaluating the above expression, when considering the contribution of the modes with $n=0,\pm 1$, since modes with vanishing eigenvalues should be excluded. A straightforward calculation gives

$$\sum_{n=0,\pm 1} e^{in(s-s')/r}\sum_k \frac{\eta_k(n)\,\eta_k(-n)}{\lambda_k(n)}=\frac{1}{A_1}\begin{pmatrix}0&0&0\\0&0&0\\0&0&1\end{pmatrix}+\frac{1}{A_1+a_3}\begin{pmatrix}\cos\left(\frac{s-s'}{r}\right)&0&-\sin\left(\frac{s-s'}{r}\right)\\0&0&0\\\sin\left(\frac{s-s'}{r}\right)&0&\cos\left(\frac{s-s'}{r}\right)\end{pmatrix}, \tag{39}$$

where $\eta_k\eta_k$ denotes the direct product of two vectors $\boldsymbol{\eta}_k$, the $\eta\eta'$ component of which is $\eta_k\eta_k'$.

For $n\neq 0,\pm 1$ we find

$$\sum_k \frac{\eta_k(n)\,\eta_k'(-n)}{\lambda_k(n)}=Q^{-1}_{\eta\eta'}(n), \tag{40}$$

where $\mathbf{Q}^{-1}(n)$ is the inverse of the matrix $\mathbf{Q}$ defined in Eq. (27),

$$\mathbf{Q}^{-1}(n)=\begin{pmatrix}\frac{1}{a_3(n^2-1)^2}+\frac{n^2}{a_\perp(n^2-1)^2} & \frac{-A_3}{a_1a_2(n^2-1)} & \left(\frac{1}{a_3}+\frac{1}{a_\perp}\right)\frac{in}{(n^2-1)^2}\\ \frac{-A_3}{a_1a_2(n^2-1)} & \frac{1}{a_\parallel n^2} & \frac{-iA_3}{a_1a_2(n^2-1)}\\ -\left(\frac{1}{a_3}+\frac{1}{a_\perp}\right)\frac{in}{(n^2-1)^2} & \frac{iA_3}{a_1a_2n(n^2-1)} & \frac{n^2}{a_3(n^2-1)^2}+\frac{1}{a_\perp(n^2-1)^2}\end{pmatrix}, \tag{41}$$

and where

$$\frac{1}{a_\perp}=\frac{\cos^2\psi_0}{a_1}+\frac{\sin^2\psi_0}{a_2},\quad \frac{1}{a_\parallel}=\frac{\sin^2\psi_0}{a_1}+\frac{\cos^2\psi_0}{a_2}. \tag{42}$$

Effective persistence lengths a_3 and $a_\perp$ control both fluctuations perpendicular to the plane of the ring and fluctuations of the twist angle ψ, and $a_\parallel$ controls fluctuations in the plane of the ring. Using Eqs. (38) and (41), we obtain the correlation functions of Euler angles (here $s=|s_2-s_1|$, $0<s<2\pi r$)

$$\langle\delta\theta(s_1)\,\delta\theta(s_2)\rangle=\frac{r}{\pi}\frac{\cos(s/r)}{A_1+a_3}+\frac{r}{\pi a_3}f_3\left(\frac{s}{r}\right)+\frac{r}{\pi a_\perp}f_1\left(\frac{s}{r}\right),$$

$$\langle\delta\varphi(s_1)\,\delta\varphi(s_2)\rangle=\frac{r}{\pi a_\parallel}f_2\left(\frac{s}{r}\right),$$

$$\langle\delta\psi(s_1)\,\delta\psi(s_2)\rangle=\frac{r}{\pi A_1}+\frac{r}{\pi}\frac{\cos(s/r)}{A_1+a_3}+\frac{r}{\pi a_3}f_1\left(\frac{s}{r}\right)+\frac{r}{\pi a_\perp}f_3\left(\frac{s}{r}\right), \tag{43}$$

$$\langle\delta\theta(s_1)\,\delta\varphi(s_2)\rangle=-\frac{r\sin(2\psi_0)}{2\pi}\left(\frac{1}{a_2}-\frac{1}{a_1}\right)\times\left[f_1\left(\frac{s}{r}\right)-f_3\left(\frac{s}{r}\right)\right],$$

$$\langle\delta\theta(s_1)\,\delta\psi(s_2)\rangle=-\frac{r}{\pi}\frac{\sin(s/r)}{A_1+a_3}+\frac{r}{\pi}\left(\frac{1}{a_3}+\frac{1}{a_\perp}\right)f_4\left(\frac{s}{r}\right),$$

$$\langle\delta\varphi(s_1)\,\delta\psi(s_2)\rangle=-\frac{r\sin(2\psi_0)}{2\pi}\left(\frac{1}{a_2}-\frac{1}{a_1}\right)f_5\left(\frac{s}{r}\right),$$

where we defined, for $0<x<2\pi$,

$$f_1(x)=\sum_{n=2}^{\infty}\frac{n^2\cos nx}{(n^2-1)^2}=\left[\frac{(\pi-x)^2}{8}-\frac{\pi^2}{24}+\frac{1}{16}\right]\cos x-\frac{\pi-x}{4}\sin x,$$

$$f_2(x)=\sum_{n=2}^{\infty}\frac{\cos nx}{n^2}=\frac{(\pi-x)^2}{4}-\frac{\pi^2}{12}-\cos x,$$

$$f_3(x)=\sum_{n=2}^{\infty}\frac{\cos nx}{(n^2-1)^2}=\left[\frac{(\pi-x)^2}{8}-\frac{\pi^2}{24}-\frac{3}{16}\right]\cos x+\frac{\pi-x}{4}\sin x-\frac{1}{2}, \tag{44}$$

$$f_4(x)=\sum_{n=2}^{\infty}\frac{n\sin nx}{(n^2-1)^2}=\left[\frac{(\pi-x)^2}{8}-\frac{\pi^2}{24}+\frac{1}{16}\right]\sin x,$$

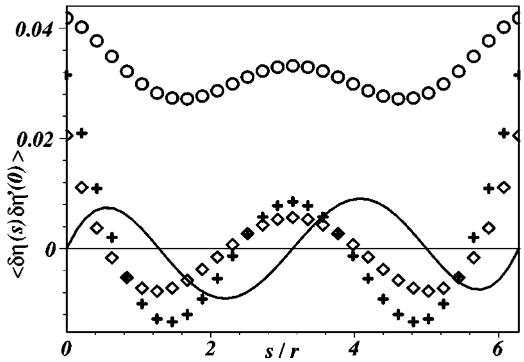

FIG. 1. Plots of two-point correlation functions of Euler angles $\langle \delta\eta(s)\delta\eta'(0)\rangle$ vs the contour distance between the points s in the interval $0 \leqslant s \leqslant 2\pi r$: $\langle \delta\theta(s)\delta\theta(0)\rangle$ (cross), $\langle \delta\varphi(s)\delta\varphi(0)\rangle$ (diamond), $\langle \delta\psi(s)\delta\psi(0)\rangle$ (circle), and $\langle \delta\theta(s)\delta\psi(0)\rangle$ (solid line). The parameters are $\psi_0=0$ and $a_1=a_2=10r$, $a_3=100r$.

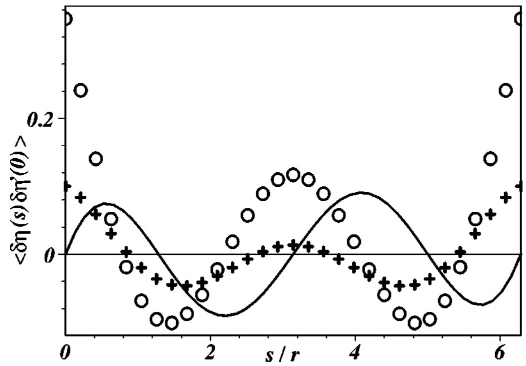

FIG. 2. Plots of two-point correlation functions of Euler angles $\langle \delta\eta(s)\delta\eta'(0)\rangle$ vs the contour distance between the points s in the interval $0 \leqslant s \leqslant 2\pi r$: $\langle \delta\theta(s)\delta\theta(0)\rangle$ (cross), $\langle \delta\psi(s)\delta\psi(0)\rangle$ (circle), and $\langle \delta\theta(s)\delta\psi(0)\rangle$ (solid line). The parameters are $\psi_0=0$ and $a_1=a_2=10r$, $a_3=r$.

$$f_5(x)=\sum_{n=2}^{\infty}\frac{\sin nx}{n(n^2-1)}$$

$$=\frac{3}{4}\sin x+\frac{\pi-x}{2}(\cos x-1).$$

Inspection of Eqs. (43) shows that the bare persistence length associated with the twist rigidity a_3 plays a fundamentally important role: fluctuations of the angles ψ and θ and the correlation between these angles, diverge in the limit $a_3 \rightarrow 0$! Therefore, simplified models of elastic filaments with nonvanishing spontaneous curvature that do not take into account twist rigidity, cannot describe fluctuations and elastic response of the ring. This is not the case for a straight rod, whose spatial fluctuations can be successfully described by the wormlike chain model [14] (with $a_3=0$). The reason for the difference stems from the fact that the elastic energy of straight rods contains no coupling between the angles that describe the spatial conformation of the center line (θ and φ) and the angle that describes the twist of the cross section about this center line (ψ). When twist rigidity vanishes ($a_3=0$) there is no energy penalty for twisting the cross section about the center line and the amplitude of twist fluctuations of the cross section about the center line diverges, but the presence of bending rigidity ($a_1, a_2 \neq 0$) suffices to suppress spatial fluctuations of the center line about its straight stress-free configuration. For rings, the elastic energy in Eq. (17) contains cross terms in the angles $\delta\psi$ and $\delta\theta$ that couple both types of fluctuations. Inspection of Eq. (17) shows that when $a_3=0$, fluctuations with $d\delta\theta/ds+\delta\psi/r=0$ have zero energy cost [see Eq. (36)] and, since in the absence of twist rigidity the angle $\delta\psi$ can always adjust itself to satisfy the condition $\delta\psi=-r d\delta\theta/ds$, for $a_3=0$ there is no elastic energy penalty for out-of-plane fluctuations of the ring and the amplitude of such fluctuations diverges. We conclude that standard wormlike chain theories in which only bending rigidity is taken into account, can not model fluctuating rings.

In Figs. 1–2 we plot correlation functions of Euler angles, for a ring with circularly symmetric cross section. Substituting $a_1=a_2$ in the expressions for the angular correlators in Eqs. (43) we find $\langle \delta\theta(s_1)\delta\varphi(s_2)\rangle=\langle \delta\varphi(s_1)\delta\psi(s_2)\rangle=0$. The physical reason for this behavior becomes clear when one recalls the discussion of the eigenvalue problem for a ring with circularly symmetric cross section [see Eq. (34)]. In this case, fluctuations of $\varphi(s)$ decouple from those of the other two angles and therefore, cross correlation functions involving $\delta\varphi$ vanish identically. In Fig. 1, we consider the case $a_1=a_2 \ll a_3$, i.e., twist rigidity is much larger than the that of the bending modes. The diagonal angular correlation functions are oscillatory functions of the contour distance, with maxima at $|s_2-s_1|=0$, πr and $2\pi r$ (they are symmetric with respect to reflection about the point $|s_2-s_1|=\pi r$). These behaviors result from interference of two wave packets propagating along two opposite directions along the ring. As a consequence of the large twist rigidity, the correlator of the twist angle is always positive, while $\langle \delta\theta(s_1)\delta\theta(s_2)\rangle$ and $\langle \delta\varphi(s_1)\delta\varphi(s_2)\rangle$ fluctuate around zero. The cross correlation function, $\langle \delta\theta(s_1)\delta\psi(s_2)\rangle$, vanishes as $|s_2-s_1|\rightarrow 0$. The physical reason for this surprising behavior is that a short segment of the ring confined between these points can be considered as a nearly straight incompressible rod. Since the twist of such a rod does not produce any deformation, local fluctuations of twist, and of the other two modes are not correlated with each other. For larger contour separations, spontaneous curvature begins to play a role and fluctuations of θ and ψ become coupled. This is a manifestation of the crossover from small scale (twist and spatial conformation fluctuate independently) to large scale (coupled twist and center line fluctuations) behavior, that will be discussed in greater detail in Sec. VI.

In Fig. 2 we present the case of small twist rigidity, $a_1=a_2 \gg a_3$. The twist correlation function develops four nodes (i.e., points at which it vanishes) and, at the same time, its amplitude is strongly enhanced. In Fig. 2 we did not plot the correlation function $\langle \delta\varphi(s_1)\delta\varphi(s_2)\rangle$, since it depends only on the bending rigidities [see the second of Eqs. (43)] and is therefore the same as in Fig. 1. Figure 3 deals with the case of an asymmetric cross section (or asymmetric rigidity in the cross sectional plane), $a_1 \neq a_2$. The cross correlations $\langle \delta\theta(s_1)\delta\varphi(s_2)\rangle$ and $\langle \delta\varphi(s_1)\delta\psi(s_2)\rangle$ no longer vanish (for $\psi_0 \neq 0,\pi/2$), even though their amplitude is much

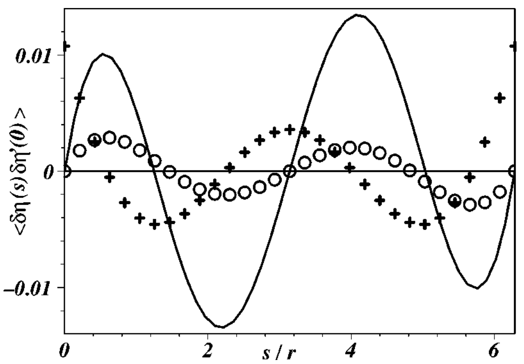

FIG. 3. Plots of nondiagonal two-point correlation functions of Euler angles $\langle \delta\eta(s)\delta\eta'(0)\rangle$ vs the contour distance between the points s in the interval $0 \leqslant s \leqslant 2\pi r$: $\langle \delta\theta(s)\delta\varphi(0)\rangle$ (cross), $\langle \delta\varphi(s)\delta\psi(0)\rangle$ (circle), and $\langle \delta\theta(s)\delta\psi(0)\rangle$ (solid line). The parameters are $\psi_0=\pi/4$ and $a_1=10r, a_2=100r,\ a_3=10r$.

smaller than that of $\langle \delta\theta(s)\delta\psi(0)\rangle$. Since the arguments presented in the preceding paragraph apply here as well, the two cross correlation functions involving $\delta\psi$ vanish as $s_2 \to s_1$. The cross correlation function $\langle \delta\theta(s_1)\delta\varphi(s_2)\rangle$ behaves in a way similar to that of the diagonal correlation functions and is symmetric about $|s_2-s_1|=\pi r$.

We would like to comment on the physical meaning of fluctuations of the angle $\varphi(s)$. We find from Eq. (43)

$$\langle[\delta\varphi(s_2)-\delta\varphi(s_1)]^2\rangle=\frac{s_\parallel}{a_\parallel}-\frac{2r}{\pi}\frac{1}{a_\parallel}\left[1-2\cos\left(\frac{s}{r}\right)\right], \tag{45}$$

where the ''parallel'' persistence length $a_\parallel$ is defined in Eq. (42), and where $s_\parallel=s(1-s/2\pi r)$ is the effective contour length for the parallel connection of two segments, one of length $s=|s_2-s_1|$ and the second of length $2\pi r-s$ (analogously to parallel connection of resistors in an electrical circuit). The effective elastic modulus between points s_1 and s_2 is proportional to

$$\frac{1}{s_\parallel}=\frac{1}{s}+\frac{1}{2\pi r-s}, \quad \text{or} \quad s_\parallel=s\left(1-\frac{s}{2\pi r}\right). \tag{46}$$

The second term on the right-hand side of Eq. (45) arises due to subtraction of the contribution of the mode $\tilde{\varphi}(1)$ because of the closure of the ring. Eq. (45) describes the Brownian fluctuations of phase $\varphi(s)$ on a circle, with effective ''diffusion'' coefficient $a_\parallel^{-1}$. This means that the angle φ can jump discontinuously from point to point and therefore, the amplitude of its derivative $d\varphi/ds$ diverges. Since $d\varphi/ds$ is the local curvature of the filament [see Eq. (16)], we conclude that $\langle[\delta\kappa(s)]^2\rangle\to\infty$. A similar calculation for the second derivative of the angle θ shows that its amplitude diverges and therefore $\langle[\delta\tau(s)]^2\rangle\to\infty$ as well. The above divergences are eliminated by a cutoff on length scales of the order of the thickness of the filament and, on length scales larger than this diameter, the contour of the ring remains a smooth and continuous curve in the process of thermal fluctuations.

V. SPATIAL CORRELATIONS AND RADIUS OF GYRATION

We proceed to calculate the correlation function $\langle[\mathbf{x}(s_1)-\mathbf{x}(s_2)]^2\rangle$ that measures the mean-square spatial separation between points s_1 and s_2 on the contour of the filament. Integrating Eq. (2), yields $\mathbf{x}(s_1)-\mathbf{x}(s_2)=\int_{s_2}^{s_1}\mathbf{t}_3(s')ds'$ and we can express this correlation function in terms of the correlator of tangents to the ring, at two arbitrary points on the contour, $\langle \mathbf{t}_3(s')\cdot\mathbf{t}_3(s'')\rangle$. We show below that this orientational correlation function of the tangent vectors can be expressed in terms of correlation functions of Euler angles. Expanding the vector $\mathbf{t}_3$ to second order in deviations of Euler angles $\delta\eta$ from their unperturbed values gives,

$$\mathbf{t}_3\equiv\mathbf{t}_{03}+\delta\mathbf{t}_3=\delta\theta\mathbf{t}'_{01}+\delta\varphi\mathbf{t}'_{02}+\left[1-\frac{1}{2}(\delta\theta^2+\delta\varphi^2)\right]\mathbf{t}_{03}, \tag{47}$$

where the vectors $\mathbf{t}'_{0i}(s)$ are defined by

$$\mathbf{t}'_{01}(s)=\begin{pmatrix}0\\0\\-1\end{pmatrix}, \quad \mathbf{t}'_{02}(s)=\begin{pmatrix}-\sin(s/r)\\\cos(s/r)\\0\end{pmatrix},$$

$$\mathbf{t}_{03}(s)=\begin{pmatrix}\cos(s/r)\\\sin(s/r)\\0\end{pmatrix}. \tag{48}$$

When $\psi_0=0$, these vectors coincide with the vectors of unperturbed triad, Eq. (12). Using Eq. (47) we find (in matrix notation)

$$\begin{aligned}\langle \mathbf{t}_3(s_1)\mathbf{t}_3(s_2)\rangle=&(1-\langle\delta\theta^2\rangle-\langle\delta\varphi^2\rangle)\mathbf{t}_{03}(s_1)\mathbf{t}_{03}(s_2)\\&+\langle\delta\theta(s_1)\delta\theta(s_2)\rangle\mathbf{t}'_{01}(s_1)\mathbf{t}'_{01}(s_2)\\&+\langle\delta\varphi(s_1)\delta\varphi(s_2)\rangle\mathbf{t}'_{02}(s_1)\mathbf{t}'_{02}(s_2)\\&+\langle\delta\theta(s_1)\delta\varphi(s_2)\rangle\mathbf{t}'_{01}(s_1)\mathbf{t}'_{02}(s_2)\\&+\langle\delta\varphi(s_1)\delta\theta(s_2)\rangle\mathbf{t}'_{02}(s_1)\mathbf{t}'_{01}(s_2),\end{aligned} \tag{49}$$

where $\mathbf{t}_{0i}\mathbf{t}_{0j}$ denotes the direct product of two vectors $\mathbf{t}_{0i}$ and $\mathbf{t}_{0j}$. The correlation functions of the Euler angles that appear in the above expressions are given in Eq. (43). As expected, the normalization condition for unit vectors, $\langle \mathbf{t}_3(s)\cdot\mathbf{t}_3(s)\rangle=1$, is satisfied up to terms of second order in $\delta\eta$.

Using the equality

$$\int_0^s ds_1\int_0^s ds_2 f\left(\frac{s_2-s_1}{r}\right)=2r^2\int_0^{s/r}du\left(\frac{s}{r}-u\right)f(u), \tag{50}$$

valid for any even function $f(x)$, we obtain

$$\langle[\mathbf{x}(s_1)-\mathbf{x}(s_2)]^2\rangle=\int_{s_1}^{s_2}ds'\int_{s_1}^{s_2}ds''\langle\mathbf{t}_3(s')\cdot\mathbf{t}_3(s'')\rangle$$
$$=2r^2\left[1-\cos\left(\frac{s}{r}\right)\right]-\frac{r^3}{\pi}\left[\frac{1}{a_\parallel}g_\parallel\left(\frac{s}{r}\right)+\frac{1}{a_\perp}g_\perp\left(\frac{s}{r}\right)+\frac{1}{a_3}g_3\left(\frac{s}{r}\right)\right], \qquad (51)$$

where $s=|s_2-s_1|$, $0<s<2\pi r$. and where $a_\perp^{-1}$ is defined in Eq. (42). The functions $g_\parallel, g_\perp$ and g_3 are given by

$$g_\parallel(x)=2\int_0^x(x-u)[f_2(0)-f_2(u)]\cos u\,du$$
$$=-(1+\cos x)\left(\pi x-\frac{x^2}{2}\right)-\frac{1}{2}(1+\cos x)^2+2(\pi-x)\sin x+2,$$

$$g_\perp(x)=2\int_0^x(x-u)[f_1(0)\cos u-f_1(u)]du$$
$$=-\frac{1}{2}\left(x\pi-\frac{x^2}{2}+1\right)\cos x+\frac{1}{2}(\pi-x)\sin x+\frac{1}{2}, \qquad (52)$$

$$g_3(x)=2\int_0^x(x-u)[f_3(0)\cos u-f_3(u)]du$$
$$=-\frac{1}{2}\left(x\pi-\frac{x^2}{2}+3\right)\cos x+\frac{3}{2}(\pi-x)\sin x-x\pi+\frac{x^2}{2}+\frac{3}{2}.$$

For small $x\ll1$ we have $g_\parallel(x)\simeq g_\perp(x)\simeq\pi x^3/12$ and $g_3(x)\simeq x^4/32\ll g_\parallel(x)$. Combining these expressions into Eq. (51), we conclude that the lowest-order corrections to the straight line result, $\langle[\mathbf{x}(s)-\mathbf{x}(0)]^2\rangle_{s/r\to0}=s^2$, depend only on the effective bending persistence length $2/(a_1^{-1}+a_2^{-1})$, in agreement with the wormlike chain model. For general s this correlator depends on all the bare persistence lengths, a_1, a_2, and a_3.

In Fig. 4 we plot the mean-square distance between two points on the ring contour, $\langle[\mathbf{x}(s)-\mathbf{x}(0)]^2\rangle$, as a function of s, in the interval $0\le s\le 2\pi r$. As expected, it increases parabolically with s (straight rod behavior for small s) and exhibits a maximum at $s=\pi r$ (the maximum is determined by the geometry of the undeformed ring). Fluctuations suppress this maximum in a way that depends on the various rigidity parameters. Thus, decreasing the twist rigidity a_3 has a much smaller effect on the amplitude of the maximum, than decreasing the bending rigidities a_1 or a_2. The origin of this effect is that twist rigidity does not affect the spatial conformations of a short segment of the ring that can be considered as a nearly straight incompressible rod. Therefore, twist fluctuations affect only the conformations of long segments, for which deviations from a straight rod become significant (compare solid line and boxes in Fig. 4).

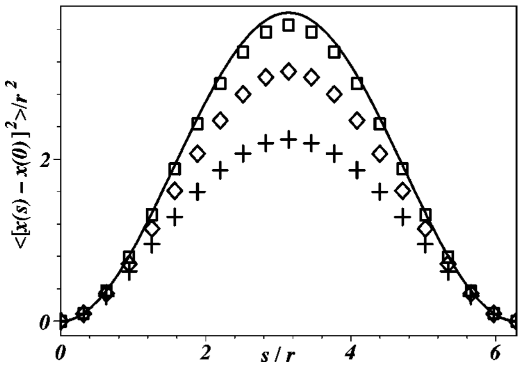

FIG. 4. Plot of dimensionless rms distance between points on the ring contour $\langle[\mathbf{x}(s)-\mathbf{x}(0)]^2\rangle/r^2$ vs the contour distance between the points s in the interval $0\le s\le 2\pi r$. The parameters are $\psi_0=0$ and $a_1=a_2=a_3=10r$ (solid line), $a_1=a_2=10r$, $a_3=r$ (box), $a_1=a_2=r$, $a_3=10r$ (cross), and $a_1=10r$, $a_2=a_3=r$ (diamond).

The radius of gyration is defined as

$$R_g^2=\frac{1}{2\pi r}\oint ds\left[\mathbf{x}(s)-\frac{1}{2\pi r}\oint ds'\,\mathbf{x}(s')\right]^2. \qquad (53)$$

Averaging this expression over fluctuations, we can express $\langle R_g^2\rangle$ in terms of the two-point correlation function

$$\langle R_g^2\rangle=\frac{1}{8\pi^2r^2}\oint ds_1\oint ds_2\langle[\mathbf{x}(s_1)-\mathbf{x}(s_2)]^2\rangle. \qquad (54)$$

Using Eqs. (51) and (52) we find

$$\langle R_g^2\rangle=r^2\left[1-\left(\frac{17}{8\pi}-\frac{\pi}{6}\right)\frac{r}{a_\parallel}-\frac{3}{4\pi}\frac{r}{a_\perp}-\left(\frac{7}{4\pi}-\frac{\pi}{6}\right)\frac{r}{a_3}\right]. \qquad (55)$$

All the corrections to the unperturbed result (r^2) are negative, and we conclude that fluctuations make the ring more compact. Since our weak fluctuation approximation is only valid in the range $a_i\gg r$, these fluctuation corrections are rather small. Because of the small coefficient in front of the r/a_3 term, the effect of twist fluctuations on the radius of gyration is relatively weak, but fluctuations diverge and the expression for the radius of gyration becomes unphysical in the limit of vanishing twist rigidity, $a_3\to0$.

VI. WRITHE FLUCTUATIONS

The twist number Tw associated with a configuration of the ring can be expressed through the Euler angles,

$$Tw=\frac{1}{2\pi}\oint\omega_3(s)ds=\frac{1}{2\pi}\int_0^{2\pi r}\left(\frac{d\psi}{ds}+\cos\theta\frac{d\varphi}{ds}\right)ds, \qquad (56)$$

where we used the definition of the rate of twist $\omega_3(s)$ about the tangent vector, in terms of the Euler angles, Eq. (9). In order to understand the physical meaning of ω_3, consider the variation of the triad vector $\mathbf{t}_1$ (or $\mathbf{t}_2$) as one moves an infinitesimal contour distance ds along the center line of the curved filament. The projection of the vector $\mathbf{t}_1(s+ds)$ on the cross section at s [the plane normal to the tangent $\mathbf{t}_3(s)$], rotates by an angle $\omega_3(s)ds$ compared to its original direction, $\mathbf{t}_1(s)$. Inspection of Eq. (56) shows that this rotation consists of two contributions. The first term corresponds to the contribution of a straight filament of length ds (the normal planes at points s and $s+ds$ remain parallel to each other), whose cross section is twisted around the center line, by an angle $d\psi$. The second term $\cos\theta d\varphi/ds$ arises due to the curvature of the center line; since the cross sections at points s and $s+ds$ are, in general, tilted with respect to each other, the projection of $\mathbf{t}_1(s+ds)$ on the cross section at s will rotate by $\cos\theta d\varphi$. Notice that because of the interplay of the two effects, a curved filament can have zero twist even if $d\psi/ds\neq 0$. This effect will be demonstrated in Sec. VII (see Fig. 6).

In addition to the twist of the filament that is closely associated with the rotation of the cross section about a curved center line, and can be defined both locally [the twist ''density'' $\omega_3(s)$] and globally (Tw), one can introduce an integral characteristic of the spatial configuration of the center line that reflects its tortuosity, known as writhe number. In order to express the writhe number Wr of a given configuration of the ring in terms of Euler angles, one usually begins with the Fuller equation for the writhe of a closed curve [15]:

$$Wr=\frac{1}{2\pi}\oint\frac{(\mathbf{t}_{03}\times\mathbf{t}_3)\cdot\dfrac{d}{ds}(\mathbf{t}_{03}+\mathbf{t}_3)}{1+\mathbf{t}_{03}\cdot\mathbf{t}_3}ds, \tag{57}$$

where $\times$ and $\cdot$ denote, respectively, vector and scalar products. In the above expression, we made use of the fact that the writhe number of a planar circular ring vanishes [16]. The above expression is valid as long as $|\mathbf{t}_{03}\cdot\mathbf{t}_3(s)|<1$ in the denominator, for all points s on the contour of the ring. This condition is satisfied in our work, since we only consider small fluctuations about a planar undeformed ring that lies in the xy plane.

A more physically transparent definition of writhe is based on the existence of a topological invariant of a ring, called the linking number [17] Lk. The total rotation of the cross section as one moves around the contour of the ring is given by $2\pi Lk$ where the linking number

$$Lk=Tw+Wr, \tag{58}$$

does not depend on the conformation of the ring and is therefore a conserved quantity. In the absence of spontaneous twist, both the twist and the writhe numbers of a planar circular ring vanish, and $Lk=Lk_{eq}=0$. In general, since Lk is a constant for a given topology, $\delta Lk=\delta Wr+\delta Tw=0$, and expanding the integrand in Eq. (56) in small deviations of the Euler angles from their spontaneous values in the unperturbed ring, the deviations of writhe and twist can be expressed as

$$\delta Wr=-\delta Tw=\frac{1}{2\pi}\int_0^{2\pi r}\frac{d\,\delta\varphi}{ds}\delta\,\theta ds=\sum_n\, in\tilde{\varphi}(n)\tilde{\theta}(-n), \tag{59}$$

where we used $\oint d\,\delta\varphi=0$ and $\oint\delta\,\theta ds=0$ [see Eq. (23)]. The last equality in Eq. (59) was derived using Eq. (24). Notice that the integrand in Eq. (59) depends on the product of $\delta\varphi$ and $\delta\theta$, and we conclude that writhe deviations vanish both when fluctuations of the angles are confined to the plane of the ring ($\delta\theta=0$), and when they are normal to this plane ($\delta\varphi=0$).

Since $\langle\tilde{\varphi}(n)\tilde{\theta}(-n)\rangle$ is an even function of n, multiplying by n and summing over all positive and negative integer values of n yields

$$\langle\delta Wr\rangle=\sum_n\, in\langle\tilde{\varphi}(n)\tilde{\theta}(-n)\rangle=0. \tag{60}$$

The dispersion of the writhe number is given by

$$\langle\delta Wr^2\rangle=\sum_{n\neq 0,\pm 1} Wr^2(n),$$

$$\begin{aligned}Wr^2(n)=n^2[&\langle\tilde{\theta}(n)\tilde{\theta}(-n)\rangle\langle\tilde{\varphi}(n)\tilde{\varphi}(-n)\rangle\\&-\langle\tilde{\varphi}(n)\tilde{\theta}(-n)\rangle^2],\end{aligned} \tag{61}$$

where we excluded modes with $n=0$ and $n=\pm 1$, because of the boundary conditions $\tilde{\theta}(0)=\tilde{\varphi}(1)=0$. Using Eqs. (43) for the correlation functions of Euler angles, we obtain the mean-square amplitude of writhe fluctuations at wavelength r/n,

$$Wr^2(n)=\frac{r^2}{\pi^2 a_1a_2a_3}\frac{A_1+a_3n^2}{(n^2-1)^2}. \tag{62}$$

Notice that the amplitude of writhe fluctuations diverges at $a_3=0$ and we conclude that twist rigidity plays an essential role in stabilizing the contour of the ring against writhe fluctuations. The origin of this divergence is the same as that of the correlator $\langle\delta\theta(s)\,\delta\,\theta(0)\rangle$ in Eq. (43) and has been discussed following Eq. (44).

For large wave vectors $|n|\gg 1$ the mean-square amplitude of the nth mode of writhe fluctuations depends only on the bending persistent lengths, a_1 and a_2. The physical reason is that on sufficiently small scales, the filament behaves as a straight incompressible rod whose properties do not depend on the twist persistence length a_3 (see Ref. [14]). In the limit $A_1\ll a_3n^2$, the writhe-writhe correlation function for a straight rod takes the form,

$$Wr^2(q)=\frac{4}{a_1a_2q^2}, \tag{63}$$

where we defined the wave vector $q=2\pi n/r$. Eq. (63) is valid for straight rods when $2\pi/q\ll a_b$, where the persistence length a_b of the rod is defined by

$$\frac{1}{a_b}=\frac{1}{2}\left(\frac{1}{a_1}+\frac{1}{a_2}\right). \tag{64}$$

The crossover to a long wave-length regime in which writhe modes become affected by twist rigidity, takes place at a length scale $\xi_t=r\sqrt{a_3/a_b}$ and, therefore, such a regime exists for a ring of radius r only if $a_3/a_b\ll 1$. As a consistency check, notice that the straight rod case follows from the above expression for ξ_t by substituting $r=\infty$, and since ξ_t diverges in this limit, Eq. (63) applies throughout the entire range of parameters.

Substituting Eq. (62) back in to Eq. (61) yields

$$\langle\delta Wr^2\rangle=\left(\frac{1}{6}+\frac{1}{8\pi^2}\right)\frac{r^2}{a_1a_2}+\left(\frac{1}{6}-\frac{11}{8\pi^2}\right)\frac{r^2}{a_\parallel a_3}. \tag{65}$$

Notice that $\langle\delta Wr^2\rangle\sim r^2$, in agreement with the scaling estimates in Ref. [18]. Indeed, since writhe is a quadratic form of $\delta\varphi$ and $\delta\theta$ [see Eq. (59)], each of which has typical fluctuations of $\sqrt{r/a}$ (a is a characteristic persistence length), the characteristic amplitude of writhe fluctuations is $\delta Wr\approx r/a$.

The entire probability distribution of writhe can also be computed. Beginning with the formal definition of this distribution

$$P(\delta Wr)=\left\langle\delta\left[\delta Wr-\sum_{n\neq 0,\pm 1} in\tilde{\varphi}(n)\tilde{\theta}(-n)\right]\right\rangle, \tag{66}$$

and using the exponential representation of the δ function, yields

$$P(\delta Wr)=\int_{-\infty}^{\infty}\frac{dk}{2\pi}e^{ik\delta Wr}\left\langle\exp\left[k\sum_n n\tilde{\varphi}(n)\tilde{\theta}(-n)\right]\right\rangle$$
$$=\int_{-\infty}^{\infty}\frac{dk}{2\pi}e^{ik\delta Wr}\prod_{n\neq 0,\pm 1}\sqrt{\frac{\det\mathbf{Q}(n)}{\det[\mathbf{Q}(n)+kn\mathbf{Y}]}}, \tag{67}$$

where the matrix $\mathbf{Y}$ is defined as

$$\mathbf{Y}=\frac{r}{\pi}\begin{pmatrix}0&-1&0\\1&0&0\\0&0&0\end{pmatrix}. \tag{68}$$

Calculating the corresponding determinants gives,

$$P(\delta Wr)=\int_{-\infty}^{\infty}\frac{dk}{2\pi}\frac{e^{ik\delta Wr}}{\prod_{n=2}^{\infty}[1+Wr^2(n)k^2]}. \tag{69}$$

This integral can be calculated by expanding the integrand into partial fractions and we get

$$P(\delta Wr)=\sum_{n=2}^{\infty}\pi(n)\frac{1}{2Wr(n)}\exp\left[-\frac{|\delta Wr|}{Wr(n)}\right], \tag{70}$$

$$\pi(n)=\prod_{\substack{k>1\\k\neq n}}\left[1-\frac{Wr^2(k)}{Wr^2(n)}\right]^{-1}. \tag{71}$$

Evaluating the product in Eq. (71) yields,

$$\pi(n)=(-1)^n\frac{\pi n^2(n^2+\alpha)(1+\alpha)\sqrt{\alpha}}{2(n^2-1)\sinh(\pi\sqrt{\alpha})}, \tag{72}$$

$$\alpha(n)\equiv\frac{(n^2-2)A_1-a_3}{A_1+n^2a_3}.$$

The above expression for $\pi(n)$ can be used to calculate all the even moments of writhe fluctuations (odd moments vanish due to the radial symmetry of the undeformed ring),

$$\langle\delta Wr^k\rangle=k!\sum_{n=2}^{\infty}\pi(n)Wr^k(n),$$

$$\sum_{n=2}^{\infty}\pi(n)=1,\quad k=2,4,\ldots,. \tag{73}$$

Since moments with $k>2$ do not vanish, it is obvious that the writhe distribution is not Gaussian. Furthermore, inspection of Eq. (70) shows that the distribution has an exponential tail at large δWr. For strongly writhing rings, $\langle\delta Wr^2\rangle^{1/2}\ll|\delta Wr|$, the $n=2$ term dominates the sum in Eq. (70) and the free energy $F=-k_BT\ln P(\delta Wr)$ is given by (up to logarithmic corrections),

$$\frac{F}{k_BT}=\frac{\delta Wr}{Wr(2)}\quad\text{for}\quad\langle\delta Wr^2\rangle^{1/2}\ll|\delta Wr|\ll 1. \tag{74}$$

The second inequality, $|\delta Wr|\ll 1$, follows from the assumption that the deviations of Euler angles from their equilibrium values, are small.

The writhe distribution function can be written in the form

$$P(\delta Wr)=\frac{\pi\sqrt{a_1a_2}}{r}p\left(\frac{\pi\sqrt{a_1a_2}}{r}\delta Wr,\frac{A_1}{a_3}\right). \tag{75}$$

Plots of the dimensionless function $p(x,A_1/a_3)$ for $A_1/a_3=0.1$, 5, and 20 are shown in Fig. 5. As intuitively expected, the probability of large writhe fluctuations (large $\pi\sqrt{a_1a_2}\delta Wr/r$) decreases with increasing twist rigidity (decreasing A_1/a_3), but the effect saturates for $A_1/a_3<0.1$. The shape of the curves bears close resemblance to the results of recent computer simulations [19].

VII. ELASTIC RESPONSE OF THE RING

According to the fluctuation-dissipation theorem, the correlation functions of the Euler angles determine the elastic response of the ring to external distributed torque $\mathbf{M}(s)$, applied along its contour. In the following, we use this information in order to study the deformation of the ring by external torques and forces. Since we are not interested in rigid

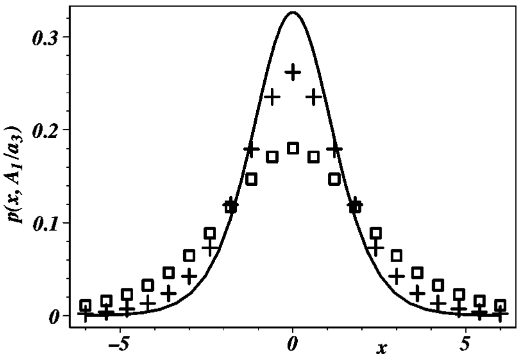

FIG. 5. Plot of probability distribution function of writhe $p(x,A_1/a_3)$ vs $x=(\pi\sqrt{a_1a_2}/r)\delta Wr$ for $A_1/a_3=0.1$ (solid line), 5 (cross), and 20 (box).

body rotation, we assume that the total torque on the ring vanishes, i.e.,

$$\oint ds\mathbf{M}(s)=0. \tag{76}$$

The deviations of the Euler angles from their unperturbed values are given by

$$\delta\eta(s)=\frac{1}{k_BT}\sum_{\eta'}\oint ds'\langle\delta\eta(s)\delta\eta'(s')\rangle M_{\eta'}(s'), \tag{77}$$

where $\eta,\eta'=\theta,\varphi,\psi$, and $M_{\eta'}$ are the corresponding components of the torque. In order to calculate the elastic response to external force, $\mathbf{F}(s)$, applied to the center line of the ring, we rewrite the work done by this force, $W=\oint ds\mathbf{F}(s)\cdot\delta\mathbf{x}(s)$, in the form

$$W=\oint ds\mathbf{m}(s)\cdot\delta\mathbf{t}_3(s),\quad \text{where}\quad \mathbf{m}(s)=\int_s^{2\pi r}ds'\mathbf{F}(s'). \tag{78}$$

Since we are not interested in translation of the ring as a whole, we assume that the total force acting on the ring vanishes, $\oint ds\mathbf{F}(s)=0$, which means that the function $\mathbf{m}(s)$ is continuous at $s=0$, i.e., $\mathbf{m}(2\pi r)=\mathbf{m}(0)=0$. Using Eq. (22) we can recast the expression for the work done by the force, Eq. (78), in the form

$$W=\oint ds\{[-m_1(s)\sin(s/r)+m_2(s)\cos(s/r)]\times\delta\varphi(s)-m_3(s)\delta\theta(s)\}. \tag{79}$$

Inspection of this equation shows that in the presence of external force we have to modify the expressions for the moments

$$M_\varphi(s)\to M_\varphi(s)-m_1(s)\sin(s/r)+m_2(s)\cos(s/r),$$
$$M_\theta(s)\to M_\theta(s)-m_3(s), \tag{80}$$

in Eq. (77). The condition that the total torque due to the external force vanishes [Eq. (76)] imposes additional conditions on the force $\mathbf{F}(s)$. Upon some algebra, these conditions can be written in the form,

$$\int_0^{2\pi r}F_t(s)ds=\int_0^{2\pi r}sF_3(s)ds=0, \tag{81}$$

where $F_t(s)=\mathbf{F}(s)\cdot\mathbf{t}_{03}(s)$ is the tangential component of the force $\mathbf{F}$. Inspection of Eq. (80) shows that a small force with $m_1(s)=-F_r(s)r\cos(s/r)$, $m_2(s)=-F_r(s)r\sin(s/r)$ and $m_3(s)=0$ does not deform the ring. From Eq. (78) we find that $F_r(s)$ is the radial component of the force $\mathbf{F}(s)$, while its tangential component is $F_t(s)=rd[F_r(s)]/ds$. This tensile force balances the contribution of variation of the radial force $F_r(s)$ along the contour of the ring and prevents buckling until a critical value of the radial force is reached.

Equations (47) and (48), together with Eqs. (77) and (80) and inextensibility condition Eq. (2), determine the conformation of the deformed ring, under the action of small external torque and force. As an illustration, consider the deformation of the ring under external forces F applied to two opposite points $s=\pi/2$ and $s=3\pi/2$ on the ring contour,

$$F_1(s)=F[\delta(s-\pi/2)-\delta(s-3\pi/2)]. \tag{82}$$

Using Eqs. (77), (78), and (80), we obtain the following expressions for the resulting variations of Euler angles,

$$\delta\theta(s)=-F\frac{r^2\sin2\psi_0}{2\pi}\left(\frac{1}{a_2k_BT}-\frac{1}{a_1k_BT}\right)h_\theta\left(\frac{s}{r}\right),$$
$$\delta\varphi(s)=F\frac{r^2}{\pi a_\parallel k_BT}h_\varphi\left(\frac{s}{r}\right), \tag{83}$$
$$\delta\psi(s)=-F\frac{r^2\sin2\psi_0}{2\pi}\left(\frac{1}{a_2k_BT}-\frac{1}{a_1k_BT}\right)h_\psi\left(\frac{s}{r}\right),$$

where

$$h_\theta(x)=\frac{dh_\psi(x)}{dx}=\sum_{k=1}^{\infty}\frac{4k(-1)^k}{(4k^2-1)^2}\sin(2kx)=-\frac{\pi}{4}x\cos x,$$
$$h_\varphi(x)=\sum_{k=1}^{\infty}\frac{(-1)^k}{k(4k^2-1)}\sin(2kx)=x-\frac{\pi}{2}\sin x, \tag{84}$$
$$h_\psi(x)=-2\sum_{k=1}^{\infty}\frac{(-1)^k}{(4k^2-1)^2}\cos(2kx)=1-\frac{\pi}{4}\cos x-\frac{\pi}{4}x\sin x.$$

The above series are calculated in the interval $|x|<\pi/2$. Using the periodicity condition, $h_i(x+\pi)=h_i(x)$, the functions $h_i(x)$ can be extended outside this interval. Inspection of Eq. (14) shows that the persistence lengths a_i are inversely proportional to temperature. Since temperature enters Eq. (83) only in combinations a_ik_BT, it cancels from the above ex-

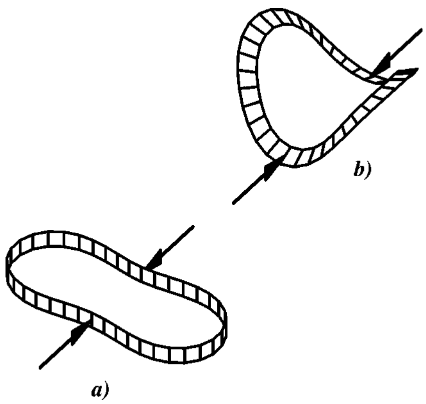

FIG. 6. Plots of deformation of ribbonlike rings (with $a_2/a_1=10^4$) by compressional forces (see arrows). (a) $\psi_0=\pi/2$ and (b) $\psi_0=10^{-3}$.

pressions and can affect the results only through temperature dependence of elastic moduli and moments of inertia.

Equation (83) shows that the deformation of the ring under the action of the force given in Eq. (82), does not depend on twist rigidity a_3. Therefore, such external forces do not produce any twist and can only lead to a bending of the ring. This result remains valid for more general distributed forces on the center line, provided they act only in the plane of the undeformed ring. Inserting the expressions for the deviations of the Euler angles Eqs. (83) and (84) into Eq. (15), we find that $\delta\omega_3=0$, and consequently, the variation of angle ψ can be expressed in terms of the conformation of the center line (angle θ), as $rd[\delta\psi(s)]/ds=\delta\theta(s)$. Since the sum of twist and writhe numbers is a topologically conserved number, writhe is invariant under such deformations.

Figure 6 shows the effect of spontaneous (constant) angle of twist, ψ_0, on the response of a ribbonlike ($a_2\gg a_1$) ring to compressional forces applied at opposite points of the center line. The forces, shown by arrows, lie in the plane of the undeformed ring. In the case of a ribbon with a short axis lying in the plane of the undeformed ring $\psi_0=\pi/2$, the ring remains planar in the course of deformation [Fig. 6(a)]. A ribbon with a short axis lying normal to the plane of the ring, $\psi_0\to 0$, undergoes three dimensional deformation [Fig. 6(b)]. At first sight, Fig. 6(b) appears to suggest that the ring is twisted, in contradiction with the previously made statement that its configuration is twist free. However, as is evident from Eq. (15), for the density of twist, $\delta\omega_3=d\delta\psi/ds-\delta\theta/r$, and from the discussion in Sec. VI, the mathematical definition of the twist of a filament with nonvanishing spontaneous curvature ($r\neq\infty$) involves both the rotation of the cross section about the center line and the curvature of the center line itself. The fact that the two effects cancel exactly in Figs. 6(a) and 6(b) is a consequence of the fact that the forces act entirely in the xy plane and do not produce a component of torque along the contour of the ring, which could give rise to twist.

VIII. DYNAMICS

Consider small instantaneous deviations $\delta\mathbf{x}(s,t)=\mathbf{x}(s,t)-\mathbf{x}_0(s)$ of the center line of the ring from its stress-free position, $\mathbf{x}_0(s)$. We express $\delta\mathbf{x}(s,t)$ in terms of its projections on the triad vectors of the undeformed ring, $\mathbf{t}_{0k}(s)$,

$$\delta\mathbf{x}(s,t)=\sum_k \delta x_k(s,t)\mathbf{t}_{0k}(s). \tag{85}$$

We proceed to write the Langevin equations that govern the dynamics of fluctuations of the center line, $\delta\mathbf{x}$, and the dynamics of angular fluctuations of the cross section about the center line, $\delta\psi$. Some care should be exercised in deriving the Langevin force from the expression for the elastic energy Eq. (13) since up to this point, we have used the inextensibility constraint Eq. (2). In order to avoid complications associated with the introduction of rigid constraints [20], we replace the strict inextensibility condition, $d\delta x_3/ds=\omega_{02}\delta x_1-\omega_{01}\delta x_2$ (see Appendix A), by an energy penalty

$$U_{ext}=\frac{k_BT}{2r^2}a_{ext}\int_0^{2\pi r}ds\left(\frac{d\delta x_3}{ds}-\omega_{02}\delta x_1+\omega_{01}\delta x_2\right)^2. \tag{86}$$

The persistence length a_{ext} describes the rigidity of the filament with respect to local compression and extension. The total elastic energy $U_{tot}=U+U_{ext}$ is the sum of contributions of bending and twist modes Eq. (17) and extensional modes Eq. (86). We will use the above expression for the total energy of an extensible filament in the Langevin equations, and take the limit of an inextensible filament ($a_{ext}/r\to\infty$) only in the end of the calculation.

The Langevin equations are

$$m\frac{d^2\delta\mathbf{x}(s,t)}{dt^2}+\varsigma\frac{d\delta\mathbf{x}(s,t)}{dt}+\frac{\delta U_{tot}}{\delta[\delta\mathbf{x}(s,t)]}=\mathbf{f}(s,t), \tag{87}$$

$$I\frac{d^2\delta\psi(s,t)}{dt^2}+\varsigma_\psi\frac{d\delta\psi(s,t)}{dt}+\frac{\delta U_{tot}}{\delta[\delta\psi(s,t)]}=\xi_\psi(s,t). \tag{88}$$

Here, m and I are mass and moment of inertia (with respect to the center line) per unit length and ς and ς_ψ are translational and angular friction coefficients. The fluctuation-dissipation theorem relates the amplitudes of the random forces $\mathbf{f}$ and ξ_ψ to these friction coefficients,

$$\langle f_i(s,t)\rangle=0,$$

$$\langle f_i(s,t)f_j(s',t')\rangle=2k_BT\varsigma\delta_{ij}\delta(s-s')\delta(t-t'), \tag{89}$$

$$\langle\xi_\psi(s,t)\rangle=0,$$

$$\langle\xi_\psi(s,t)\xi_\psi(s',t')\rangle=2k_BT\varsigma_\psi\delta(s-s')\delta(t-t'). \tag{90}$$

In writing the above equations we neglected hydrodynamic interactions and therefore the treatment is analogous to the Rouse model of polymer solution dynamics [20].

Using the relation between the deviations of the coordinates $\delta\mathbf{x}$ and those of Euler angles $\delta\theta$, $\delta\varphi$, and $\delta\psi$ (see Appendix A) and neglecting rigid body translation and rotation of the ring, we rewrite the above Langevin equations in terms of the Fourier components of the deviations of Euler angles from their equilibrium values [see Eq. (24)],

$$\hat{\alpha}_\eta \tilde{\eta}(n,t) = -L_\eta(n)\frac{\delta U}{\delta\tilde{\eta}(-n,t)} + \tilde{\xi}_\eta(n,t), \tag{91}$$

$$\langle \tilde{\xi}_\eta(n,t)\rangle = 0,$$
$$\langle \tilde{\xi}_\eta(n,t)\tilde{\xi}_{\eta'}(-n,t')\rangle = 2k_BT\delta_{\eta\eta'}\varsigma_\eta L_\eta(n)\delta(t-t'). \tag{92}$$

The time derivative operators $\hat{\alpha}_\eta$ associated with the three Euler angles are,

$$\hat{\alpha}_\theta = \hat{\alpha}_\varphi = \hat{\alpha} = m\frac{d^2}{dt^2} + \varsigma\frac{d}{dt} \quad \text{and} \quad \hat{\alpha}_\psi = I\frac{d^2}{dt^2} + \varsigma_\psi\frac{d}{dt}, \tag{93}$$

where the corresponding friction coefficients are $\varsigma_\theta = \varsigma_\varphi = \varsigma$ and ς_ψ. The elastic energy that appears in the Langevin Eqs. (91), is given in terms of the amplitudes of the Fourier modes in Eq. (26). Conveniently, the matrix of kinetic coefficients $\mathbf{L}$ is diagonal in the Euler angle representation,

$$L_\theta(n) = n^2/r^2, \quad L_\varphi(n) = (n^2-1)^2/(n^2+1)r^2$$
$$\text{and} \quad L_\psi(n) = 1/r^2. \tag{94}$$

In the following, we proceed to solve the Langevin equations and obtain explicit expressions for the dynamic correlation function of writhe fluctuations. We focus on this correlator since it is an integral characteristic of the ring and is therefore simpler than the two-point correlation functions of Euler angles, which depend on the separation between the points. Although the general solution of the linear equations can be obtained, we will assume (as it is often done in the literature [18,21,22]) that the relaxation of the twist angle ψ is much faster than that of the angles θ and φ. Consequently, we can minimize the energy with respect to $\tilde{\psi}(n,t)$ and express it in terms of $\tilde{\theta}(n,t)$ and $\tilde{\varphi}(n,t)$. With this substitution, the (3×3) matrix $\mathbf{Q}(n)$ in $\tilde{\theta}(n,t)$, $\tilde{\varphi}(n,t)$, $\tilde{\psi}(n,t)$ space Eq. (27) is reduced to a (2×2) matrix $\mathbf{Q}'(n)$ in $\tilde{\theta}(n,t)$, $\tilde{\varphi}(n,t)$ space,

$$\mathbf{Q}'(n) = \frac{1}{a_3n^2 + A_1}\begin{pmatrix} a_3A_1(n^2-1)^2 & A_3a_3n^2(n^2-1) \\ A_3a_3n^2(n^2-1) & (a_3A_2n^2 + a_1a_2)n^2 \end{pmatrix}. \tag{95}$$

As shown in Appendix B, the solutions of the Langevin equations can be expressed in terms of the eigenvalues $\Lambda_{1,2}(n)$ of the matrix $\mathbf{P}(n)$ of the linear form

$$L_\eta(n)\frac{\delta U}{\delta\tilde{\eta}(-n,t)} = \sum_{\eta'} P_{\eta\eta'}(n)\tilde{\eta}'(n,t), \qquad \eta,\eta' = \theta,\varphi \tag{96}$$

that appears in the Langevin Eq. (91). Explicit expressions for these eigenvalues are given in Appendix B, Eq. (B2).

Taking the Fourier transform of Eq. (B9) (Appendix B) with respect to the frequency ω, we find the two-time correlation function of the Fourier components of Euler angles,

$$\begin{aligned}\langle \tilde{\eta}(n,t)\tilde{\eta}'(-n,0)\rangle &= \frac{1}{\Lambda_2(n)-\Lambda_1(n)}\{[\Lambda_2(n)g_1(n,t) - \Lambda_1(n)g_2(n,t)] \\ &\quad \times\langle\tilde{\eta}(n)\tilde{\eta}'(-n)\rangle - k_BTL_\eta(n) \\ &\quad \times[g_1(n,t)-g_2(n,t)]\delta_{\eta\eta'}\},\end{aligned} \tag{97}$$

where $g_k(n,t)$ describes temporal decay of correlations of normal modes with wave vector $2\pi n/r$ $[g_k(n,0)=1]$, and where $\langle\tilde{\eta}(n)\tilde{\eta}'(-n)\rangle$ is the previously calculated equal-time equilibrium correlation function (see Sec. IV).

In the inertial limit (i.e., for modes with inertial time scale shorter than viscous relaxation time), $4m\Lambda_k(n) > \varsigma^2$, the function $g_k(n,t)$ describes damped oscillations with characteristic frequency $\omega_k(n)$,

$$g_k(n,t) = \left[\cos\omega_k(n)t + \frac{\varsigma}{2m\omega_k(n)}\sin\omega_k(n)t\right]\exp\left(-\frac{t\varsigma}{2m}\right), \tag{98}$$

$$\omega_k^2(n) = \frac{\Lambda_k(n)}{m} - \frac{\varsigma^2}{4m^2}. \tag{99}$$

The characteristic relaxation time is $2m/\varsigma$, independent of the wavelength of the mode. At short times, $t \ll m/\varsigma$,

$$g_k(n,t) \simeq \cos[\sqrt{\Lambda_k(n)/m}t]. \tag{100}$$

In the dissipative limit $4m\Lambda_k(n) < \varsigma^2$ the function $g_k(n,t)$ describes pure decay of correlations, with characteristic times $\tau_1(n)$ and $\tau_2(n)$,

$$g_k(n,t) = \frac{\tau_1}{\tau_1-\tau_2}\exp\left(-\frac{t}{\tau_1}\right) + \frac{\tau_2}{\tau_2-\tau_1}\exp\left(-\frac{t}{\tau_2}\right), \tag{101}$$

$$\tau_{1,2}(n) = \frac{\varsigma}{2\Lambda_k(n)} \pm \sqrt{\frac{\varsigma^2}{4\Lambda_k^2(n)} - \frac{m}{\Lambda_k(n)}}. \tag{102}$$

In the limit of negligible inertia $m\to 0$ we get $\tau_2(n)\to 0$ and the relaxation can be described by simple exponential decay,

$$g_k(n,t) \simeq \exp[-t\Lambda_k(n)/\varsigma]. \tag{103}$$

The dynamic writhe correlation function is derived in Appendix B:

$$\begin{aligned}\langle\delta Wr(t)\delta Wr(0)\rangle &= \sum_{n\neq 0,\pm 1} Wr^2(n,t) \\ &= \sum_{n\neq 0,\pm 1} Wr^2(n)g_1(n,t)g_2(n,t),\end{aligned} \tag{104}$$

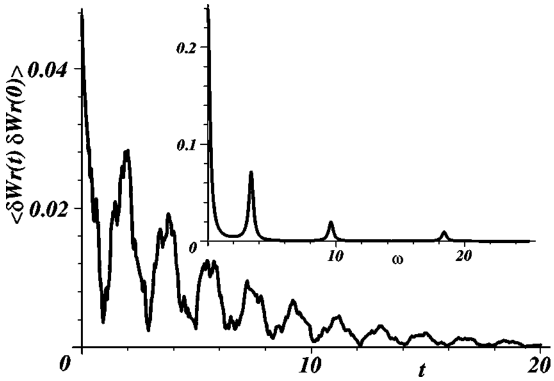

FIG. 7. Plot of dynamic correlation function of writhe fluctuations $\langle \delta Wr(t)\delta Wr(0)\rangle$ vs time t (in units of $\varsigma r^2/\pi k_B T$), for a ring with a circular cross section and persistence lengths $a_1 = a_2 = a_3 = 2r$, in the inertial range $2\pi m k_B T/\varsigma^2 r^2 = 10$. Plot of the Fourier transform of the correlation functions vs frequency ω (in units of $\pi k_B T/\varsigma r^2$) is shown as an inset in the upper-right-hand side of the figure.

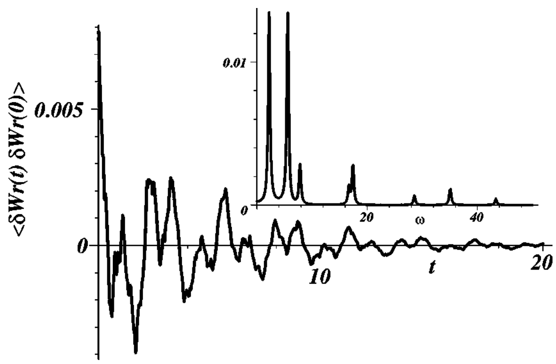

FIG. 8. Plot of dynamic correlation function of writhe fluctuations $\langle \delta Wr(t)\delta Wr(0)\rangle$ vs time t (in units of $\varsigma r^2/\pi k_B T$), for a ribbonlike ring with persistence lengths $a_1 = a_3 = 2r$ and $a_2 = 20r$ ($\psi_0 = \pi/4$), in the inertial range $2\pi m k_B T/\varsigma^2 r^2 = 10$. Plot of the Fourier transform of the correlation functions vs frequency ω (in units of $\pi k_B T/\varsigma r^2$) is shown as an inset in the upper-right-hand side of the figure.

where the equilibrium mean-squared amplitude of fluctuations of writhe $Wr^2(n)$ is given in Eq. (62). In the limit of negligible inertia $m \to 0$ we substitute Eq. (103) for $g_k(n,t)$ into Eq. (104), and find that the writhe correlation function for mode n decays exponentially with time

$$Wr^2(n,t) = Wr^2(n) e^{-t/\tau(n)}. \tag{105}$$

The characteristic decay time $\tau(n)$ is given by

$$\tau(n) = \frac{\varsigma r^3}{\pi k_B T} \frac{n^2+1}{n^2(n^2-1)^2} \frac{a_3 n^2 + A_1}{(a_1+a_2)a_3 n^2 + A_1 a_3 + a_1 a_2}. \tag{106}$$

In the short wavelength limit $n \gg 1$ only the sum of bending persistence lengths $a_1 + a_2$ appears in $\tau(n)$. Indeed, on small scales, the filament behaves as a straight inextensible rod whose properties do not depend on the twist persistence length a_3, or on the spontaneous twist angle ψ_0.

In Figs. 7 and 8, we plot the writhe correlation function as a function of time measured in units of $\varsigma r^2/\pi k_B T$, in the inertial regime, for $2\pi m k_B T/\varsigma^2 r^2 = 10$. Its Fourier transform plotted as a function of the frequency ω measured in units of $\pi k_B T/\varsigma r^2$, is shown in the inset, on the upper-right side of the figure. In Fig. 7, the parameters correspond to a circular cross section and identical persistence lengths, $a_1 = a_2 = a_3 = 2r$. Oscillatory decay of writhe correlations as a function of time is observed, but the correlation remains always positive. A small number of fundamental frequencies can be detected in the oscillatory pattern, and identified with peaks observed in the frequency spectrum. The amplitudes of these peaks decrease monotonically with the frequency, and the largest peak is at $\omega = 0$. The case of an asymmetric cross section and dominant bending rigidity, $a_1 = a_3 = 2r$ and $a_2 = 20r$ ($\psi_0 = \pi/4$) is shown in Fig. 8. The correlation function decays rapidly to zero and, at later times, oscillates between positive and negative values. Since for $t \ll m/\varsigma$, dissipation is negligible, the fast initial decay of correlations is the result of dephasing of the oscillatory contributions of a large number of modes. In the frequency domain, there is no peak at $\omega = 0$ and the peak amplitudes have a nonmonotonic dependence on the frequency.

In Fig. 9, we plot the writhe correlation function in the dissipative regime where inertia is negligible $2\pi m k_B T/\varsigma^2 r^2 = 10^{-3}$ for ribbonlike rings with different bending and twist rigidities. The amplitude of writhe fluctuations is smallest for a ribbon whose shorter axis of inertia is normal to the plane of the ring [see Fig. 6(b)]. The amplitude increases by more than a factor of two when the shorter axis of inertia lies in the plane of the ring [see Fig. 6(a)]. Twist rigidity decreases the fluctuation amplitude but the effect is rather weak. Since inertial oscillations are completely suppressed in this overdamped regime, the correlations decay monotonically with time. The curves exhibit fast short-time relaxation, followed by an exponential decay, in qualitative agreement with numerical simulations reported in Ref. [19]. An analytic expression for the time dependence of the correlator at short times can be derived [see Eq. (B18) in Ap-

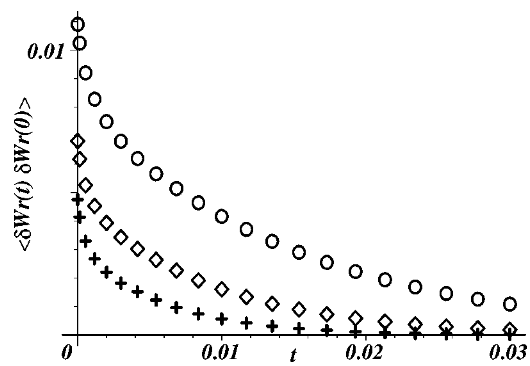

FIG. 9. Plot of dynamic correlations function of writhe fluctuations $\langle \delta Wr(t)\delta Wr(0)\rangle$ vs time t (in units of $\varsigma r^2/\pi k_B T$), for ribbonlike rings in the dissipative range $2\pi m k_B T/\varsigma^2 r^2 = 10^{-3}$: The parameters are $\psi_0 = 0$ and $a_1 = 2r$, $a_2 = 20r$, $a_3 = 2r$ (cross), $a_1 = 20r$, $a_2 = 2r$, $a_3 = 2r$ (circle), and $a_1 = 20r$, $a_2 = 2r$, $a_3 = 10r$ (diamond).

pendix B]. The predicted $\langle[\delta Wr(t)-\delta Wr(0)]^2\rangle \propto t^{1/4}$ dependence of the writhe correlation function and the fact that it depends only on the bending rigidity (a_1 and a_2), are direct consequences of the observation that at short times, the relaxation is dominated by straight rod contributions to the spectrum [$\tau(q)\propto 1/q^4$].

The above results can be directly applied to the study of deformation of macroscopic rings by external forces and torques. Unlike the case of microscopic filaments, where dissipation dominates inertia and only overdamped behavior is expected, inertial effects play an important role in the dynamic response of macroscopic objects (for this reason, they were included in the preceding analysis). According to the fluctuation-dissipation theorem, dynamic correlation functions of Euler angles can be treated as generalized susceptibilities that determine the response of the ring to externally applied torques and forces. The time-dependent generalization of the static relation between deformation (in terms of the deviation of the Euler angles from their equilibrium values) and applied force Eq. (77) is

$$\delta\eta(s,t)=\frac{1}{k_BT}\int_{-\infty}^{t}dt'\sum_{\eta'}\oint ds'\frac{d}{dt'}\langle\delta\eta(s,t)\delta\eta'(s',t')\rangle \times M_{\eta'}(s',t'), \tag{107}$$

where the moments $\mathbf{M}$ due to external forces, are given by Eq. (80). The relaxation of the deformation following the release of external moments at time $t=0$, $\mathbf{M}(s,t)=\mathbf{M}(s)\theta(-t)$, for $t>0$ is given by

$$\delta\eta(s,t)=\frac{1}{k_BT}\sum_{\eta'}\oint ds'\langle\delta\eta(s,t)\delta\eta'(s',0)\rangle M_{\eta'}(s'). \tag{108}$$

IX. DISCUSSION

In this paper, we presented the statistical mechanics of fluctuating rings. We derived analytical expressions for various static properties of such rings, including two-point correlation functions of Euler angles, the correlation function of tangents to the ring, rms distance between points on the ring contour, radius of gyration, and probability distribution function of writhe, as a function of persistence lengths associated with bending and twist deformations of the ring. We found that the amplitudes of fluctuations of the Euler angles ψ and θ diverge in the limit of vanishing twist rigidity. We would like to emphasize that the situation differs from the case of straight filaments for which the twist density $\delta\omega_3^{rod}=d\delta\psi/ds$ depends only on the fluctuations of the Euler angle ψ. For such filaments, vanishing twist rigidity ($a_3=0$) implies that there is no energy penalty for twisting the cross section about the center line, but the presence of bending rigidity ($a_1,a_2\neq 0$) suffices to suppress spatial fluctuations of the center line about its straight stress free configuration. Thus, if we are only interested in the statistical mechanics of the spatial conformations of the center line, accounting for bending rigidity suffices to provide an accurate description of straight fluctuating filaments. For rings, inspection of the elastic energy, Eq. (17), shows that when $a_3=0$, fluctuations with $d\delta\theta/ds+\delta\psi/r=0$ have zero energy cost and, since in the absence of twist rigidity the angle $\delta\psi$ can always adjust itself to satisfy the condition $\delta\psi=-rd\delta\theta/ds$, there is no elastic energy penalty for out-of-plane fluctuations of the ring and the amplitude of such fluctuations diverges even if the bending rigidity remains finite. Therefore, wormlike chain theories in which only bending rigidity is taken into account, cannot model the spatial conformation of fluctuating rings.

We found that a crossover length scale $\xi_t=r\sqrt{a_3/a_b}$ exists, below which straight rod behavior dominates and writhe of the center line and twist of the cross section about it are decoupled, and above which spontaneous curvature becomes important and twist affects the three-dimensional configurations of the center line of the ring. In this context, we would like to propose the as yet unproven but plausible conjecture, that the existence of this crossover does not depend on the topology of the ring and is characteristic of filaments with spontaneous curvature in their stress-free state.

Although the main focus of this work is on the statistical mechanics of fluctuating rings, we used the fluctuation-dissipation theorem in order to predict mechanical response to external torques and forces, and showed that the deformation of ribbonlike rings depends, in an essential way, on the orientation of the cross section in the stress-free state. Finally, we derived the Langevin equations that govern the dynamics of fluctuating rings, and calculated the two-time correlation function of writhe fluctuations. Depending on the values of the parameters, one can move from an inertial regime where relaxation is accompanied by temporal oscillations, to a non-oscillatory, purely dissipative regime. In the dissipation dominated range, the relaxation at short times is determined by bending rigidity only. This agrees with the expectation that short-time relaxation is dominated by small scale, straight rod behavior. At longer times, the decay of writhe correlations depends on both bending and twist rigidities. While inertial effects are not expected to be important for microscopic objects such as small plasmids, our dynamic response functions can describe the relaxation of rings of arbitrary mass and size, following the cessation of externally applied forces and torques.

We would like to comment on the limitations of the approach presented in this paper. The domain of applicability of our theory is limited to the weak fluctuation regime, in the sense that the deviations of the Euler angles from their values in the undeformed ring, must be sufficiently small. Although, in principle, our general formalism is applicable to rings with arbitrary spontaneous twist in their stress-free reference state, the analysis of this problem meets with considerable mathematical difficulties and is the subject of ongoing work. Finally, we would like to emphasize that since our theory is based on the linear theory of elasticity of thin rods, all persistence lengths and radii of curvature are assumed to be much larger than the diameter of the filament that serves as a small scale cutoff. Consideration of microscopic physics on length scales smaller than this diameter requires the introduction of additional model assumptions (see Refs. [23–25]) and is beyond the scope of this paper.

After this paper was submitted for publication, we learned about a related study of thermal fluctuations in DNA plasmids in which the writhe distribution function was also calculated [26]. This work is complementary to ours: while we assume that the equilibrium stress-free state of our filament is that of a planar untwisted circular ring, Ref. [26] deals with filaments with straight untwisted stress-free state. Conceptually, the ring is then formed by bringing the ends together and sealing them, with or without the addition of twist. Since such rings have locked-in internal stresses, the two procedures are nonequivalent in general.

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APPENDIX A: DERIVATION OF LANGEVIN EQUATIONS

For small deviations from the stress-free state, the variation of a triad of vectors can be written as

$$\delta\mathbf{t}_1 = -(\delta\theta\cos\psi_0 + \delta\varphi\sin\psi_0)\mathbf{t}_{03} + \delta\psi\mathbf{t}_{02},$$

$$\delta\mathbf{t}_2 = (\delta\theta\sin\psi_0 - \delta\varphi\cos\psi_0)\mathbf{t}_{03} - \delta\psi\mathbf{t}_{02}, \tag{A1}$$

$$\delta\mathbf{t}_3 = -(\delta\theta\sin\psi_0 - \delta\varphi\cos\psi_0)\mathbf{t}_{02} + (\delta\theta\cos\psi_0 + \delta\varphi\sin\psi_0)\mathbf{t}_{01},$$

where the vectors $\mathbf{t}_{0i}$ are defined in Eq. (12). Substituting Eqs. (A1) into the inextensibility condition Eq. (2) we obtain the following equations for the deviation $\delta\mathbf{x}(s)$ of the position vector of a point s on the ring contour, from its value in the undeformed state,

$$\frac{d\,\delta x_3}{ds} - \omega_{02}\delta x_1 + \omega_{01}\delta x_2 = 0, \tag{A2}$$

$$-\frac{d\,\delta x_2}{ds} + \omega_{01}\delta x_3 - \omega_{03}\delta x_1 = \delta\theta\sin\psi_0 - \delta\varphi\cos\psi_0, \tag{A3}$$

$$\frac{d\,\delta x_1}{ds} + \omega_{02}\delta x_3 - \omega_{03}\delta x_2 = \delta\theta\cos\psi_0 + \delta\varphi\sin\psi_0. \tag{A4}$$

Equation (A2) is the linearized form of the inextensibility condition, and Eqs. (A3) and (A4) relate the deviations of Euler angles to those of spatial positions.

Fourier transforming Eqs. (87) and (88), yields the Langevin equations for the Fourier components $\tilde{\mathbf{x}}(n)$ and $\tilde{\psi}(n)$,

$$\hat{\alpha}\tilde{\mathbf{x}}(n,t) + \frac{\delta U}{\delta\tilde{\mathbf{x}}(-n,t)} + \mu(n,t)\mathbf{c}^*(n) = \tilde{\mathbf{f}}(n,t), \tag{A5}$$

$$\hat{\alpha}_\psi\tilde{\psi}(n,t) + \frac{\delta U}{\delta\tilde{\psi}(-n,t)} = \tilde{\xi}_\psi(n,t), \tag{A6}$$

where $\hat{\alpha}$ and $\hat{\alpha}_\psi$ are defined in Eq. (93) and

$$\mu(n,t) = \frac{a_{ext}k_BT}{r^2}\tilde{\mathbf{x}}(n,t)\cdot\mathbf{c}(n),$$

$$\mathbf{c}(n) = -(\sin\psi_0, -\cos\psi_0, in). \tag{A7}$$

In the limit $a_{ext}\to\infty$, $\mu(n,t)$ can be considered as a Lagrange multiplier that accounts for the inextensibility condition, Eq. (A2) or, equivalently, for its Fourier transform, $\tilde{\mathbf{x}}(n,t)\cdot\mathbf{c}(n) = 0$. The correlators of random forces in Eqs. (A5) and (A6), take the form,

$$\langle\tilde{f}_i(n,t)\rangle = 0, \quad \langle\tilde{f}_i(n,t)\tilde{f}_j(-n,t')\rangle = 2\varsigma k_BT\delta_{ij}\delta(t-t'), \tag{A8}$$

$$\langle\tilde{\xi}_\psi(n,t)\rangle = 0, \quad \langle\tilde{\xi}_\psi(n,t)\tilde{\xi}_\psi(-n,t')\rangle = 2\varsigma_\psi k_BT\delta(t-t'). \tag{A9}$$

Using Fourier transforms of Eqs. (A2)–(A4) we rewrite the Langevin Eqs. (A5)–(A9) in terms of Euler angles Eqs. (91) and (92).

APPENDIX B: SOLUTION OF LANGEVIN EQUATIONS

In order to find the solution of the Langevin equations, we first calculate the eigenvalues and eigenfunctions of the matrix (see Eq. (96) for its definition),

$$\mathbf{P}(n) = \frac{\pi k_BT}{r^3}\frac{n^2(n^2-1)}{a_3n^2+A_1} \times \begin{pmatrix} A_1a_3(n^2-1) & A_3a_3n^2 \\ A_3a_3\dfrac{(n^2-1)^2}{n^2+1} & (A_2a_3n^2+a_1a_2)\dfrac{n^2-1}{n^2+1} \end{pmatrix}. \tag{B1}$$

Eigenvalues of this matrix have the form

$$\Lambda_{1,2}(n) = \frac{\pi k_BT}{2r^3}\frac{n^2(n^2-1)^2}{n^2+1} \times \frac{(a_1+a_2)a_3n^2 + A_1a_3 + a_1a_2 \pm \Delta}{a_3n^2+A_1}, \tag{B2}$$

$$\Delta^2 = [(a_1-a_2)a_3n^2 + A_1a_3 - a_1a_2]^2 + 4n^2a_2a_3(a_1-a_2)(a_1-a_3)\sin^2\psi_0.$$

The eigenvalues $\Lambda_k(n)$ vanish when $n=0,1$. These modes are associated with rigid body rotations of the ring and are not considered further below. In the limit $|n|\gg 1$ both eigenvalues increase with the fourth power of n, $\Lambda_k(n) \simeq \pi k_BTa_kn^4/r^3$. This q^4 dependence of the eigenvalues (q

$=2\pi n/r$ is the wave vector corresponding to the nth mode) is characteristic of bending fluctuations of straight rods, in accord with the expectation that small-scale fluctuations of a ring are indistinguishable from those of a straight rod.

The matrix $\mathbf{P}(n)$ becomes diagonal (and the angles θ and φ become decoupled), in the case of a circularly symmetric cross section ($A_3=0$), when $\psi_0=0$ or $\pi/2$, and in the limit $a_3\to 0$. In all of these cases, the mode $\Lambda_1(n)$ describes both fluctuations perpendicular to the plane of the ring and twist fluctuations, and the mode $\Lambda_2(n)$ describes fluctuations in the plane of the ring. Since $\Lambda_1(n)\to 0$ when $a_3\to 0$, twist fluctuations destroy the circular shape of the ring in the wormlike chain model, where twist rigidity is not taken into account.

The eigenvalues take a particularly simple form for $\psi_0=0$,

$$\Lambda_1(n)=\frac{\pi k_B T}{r^3}\frac{n^2(n^2-1)^2a_1a_3}{a_3n^2+a_1},$$

$$\Lambda_2(n)=\frac{\pi k_B T}{r^3}\frac{n^2(n^2-1)^2a_2}{n^2+1}. \tag{B3}$$

Since the matrix $\mathbf{P}(n)$ Eq. (B1) is not symmetric, it has different right and left eigenfunctions. We denote the right eigenfunctions, corresponding to eigenvalues $\Lambda_k(n)$, by $\overline{\eta_k}(n)=\{\overline{\theta_k}(n),\overline{\varphi_k}(n)\}$, (where $k=1,2$). Left eigenfunctions can be written as $\overline{\eta_k}(-n)L_\eta^{-1}(n)$. Since the matrix $\mathbf{P}(n)$ is real, we have $\overline{\eta_k}(-n)=\overline{\eta_k^*}(n)$. For each $n\neq 0,\pm 1$, the above eigenfunctions are normalized by conditions:

$$\sum_\eta L_\eta^{-1}(n)\,\overline{\eta_k}(n)\,\overline{\eta_l}(-n)=\delta_{kl},$$

$$\sum_k \overline{\eta_k}(n)\,\overline{\eta'_k}(-n)=L_\eta(n)\,\delta_{\eta\eta'}. \tag{B4}$$

Expanding the matrix $\mathbf{P}(n)$ over its eigenfunctions we find:

$$P_{\eta\eta'}(n)=\sum_k \Lambda_k(n)\,\overline{\eta_k}(n)\,\overline{\eta'_k}(-n)L_{\eta'}^{-1}(n). \tag{B5}$$

The solution of Eq. (91) can be found by Fourier transforming it with respect to the time t, and substituting Eqs. (96) and (B5). This yields

$$\tilde{\eta}_\omega(n)=\sum_k\frac{\overline{\eta_k}(n)}{\tilde{\alpha}_\omega+\Lambda_k(n)}\sum_{\eta'}\overline{\eta'_k}(n)\tilde{\xi}_{\eta'\omega}(n), \tag{B6}$$

$$\tilde{\alpha}_\omega=-m\omega^2+i\varsigma\omega, \tag{B7}$$

where the correlators of the Gaussian random force are

$$\langle\tilde{\xi}_{\eta\omega}(n)\rangle=0,\quad \langle\tilde{\xi}_{\eta\omega}(n)\tilde{\xi}_{\eta'-\omega}(-n)\rangle=2k_BT\varsigma L_\eta\delta_{\eta\eta'}. \tag{B8}$$

Calculating the correlation functions of Euler angles, we get

$$\langle\tilde{\eta}_\omega(n)\tilde{\eta}'_{-\omega}(-n)\rangle=2k_BT\varsigma\sum_k\frac{\overline{\eta_k}(n)\,\overline{\eta'_k}(-n)}{|\tilde{\alpha}_\omega+\Lambda_k(n)|^2}, \tag{B9}$$

where $\eta,\eta'=\theta,\varphi$. In the time domain this gives the following expression for the dynamic correlation functions of the Fourier transforms of Euler angles,

$$\langle\tilde{\eta}(n,t)\tilde{\eta}'(-n,0)\rangle=k_BT\sum_k\frac{\overline{\eta_k}(n)\,\overline{\eta'_k}(-n)}{\Lambda_k(n)}g_k(n,t), \tag{B10}$$

where

$$g_k(n,t)=\frac{2\varsigma\Lambda_k(n)}{\pi}\int_0^\infty\frac{d\omega\cos\omega t}{[\Lambda_k(n)-m\omega^2]^2+\varsigma^2\omega^2}. \tag{B11}$$

The function $g_k(n,t)$ describes temporal decay of correlations of normal modes, with wave vector $2\pi n/r$. One can verify that for $t=0$, integration gives $g_k(n,0)=1$, independent of m and ς. Instead of calculating the eigenfunctions $\overline{\eta_k}(n)$, we notice that the combinations $\overline{\eta_k}(n)\overline{\eta'_k}(-n)/\Lambda_k(n)$ in the above expression, can be evaluated using the previously derived expressions for the equilibrium (equal time) correlators $\langle\tilde{\eta}(n)\tilde{\eta}'(-n)\rangle$, and the normalization conditions, Eq. (B4). Substituting these expressions into Eq. (B10), we arrive at Eq. (97).

We now turn to writhe fluctuations [see Eq. (59)],

$$\delta Wr(t)=-\sum_n in\int\frac{d\omega}{2\pi}\tilde{\varphi}_\omega(n)e^{i\omega t}\int\frac{d\omega'}{2\pi}\tilde{\theta}_{\omega'}(-n)e^{i\omega' t}, \tag{B12}$$

and proceed to calculate the dynamic correlation function of these fluctuations,

$$\langle\delta Wr(t)\delta Wr(0)\rangle=\sum_{n\neq 0,\pm 1}Wr^2(n,t), \tag{B13}$$

where the contribution of mode n is

$$\begin{aligned}Wr^2(n,t)=k_B^2T^2n^2\int\frac{d\omega}{2\pi}\int\frac{d\omega'}{2\pi}\cos[(\omega+\omega')t]\\ \times[\langle\tilde{\theta}_\omega(-n)\tilde{\theta}_{-\omega}(n)\rangle\langle\tilde{\varphi}_{\omega'}(n)\tilde{\varphi}_{-\omega'}(-n)\rangle\\ -\langle\tilde{\theta}_\omega(-n)\tilde{\varphi}_{-\omega}(n)\rangle\langle\tilde{\theta}_{-\omega'}(n)\tilde{\varphi}_{\omega'}(-n)\rangle].\end{aligned} \tag{B14}$$

Substituting Eq. (43) for the correlation functions of Euler angles yields,

$$Wr^2(n,t)=k_B^2T^2n^2\sum_{kk'}\frac{g_k(n,t)g_{k'}(n,t)}{\Lambda_k(n)\Lambda_{k'}(n)}\times[\overline{\theta}_k(n)\overline{\theta}_k(-n)\overline{\varphi}_{k'}(n)\overline{\varphi}_{k'}(-n)-\overline{\theta}_k(n)\overline{\varphi}_k(-n)\overline{\varphi}_{k'}(n)\overline{\theta}_{k'}(-n)]. \quad \text{(B15)}$$

The only nonvanishing contributions to the sum in Eq. (B15) are $k=1,k'=2$, and $k=2,k'=1$, and both have the same value. As a result, we find that the contribution of the nth mode to the dynamic correlation function can be recast in the form

$$Wr^2(n,t)=Wr^2(n)g_1(n,t)g_2(n,t), \quad \text{(B16)}$$

where $Wr^2(n)$ is the mean-squared amplitude of the nth mode of writhe fluctuations in equilibrium, calculated earlier in Eq. (62).

Finally, we would like to comment on the short-time behavior of the correlation function in the dissipative regime. Using Eq. (105) we find

$$\langle[\delta Wr(t)-\delta Wr(0)]^2\rangle=\frac{4r^2}{\pi^2a_1a_2a_3}\times\sum_{n=2}^{\infty}\frac{A_1+a_3n^2}{(n^2-1)^2}[1-e^{-t/\tau(n)}]. \quad \text{(B17)}$$

At small times $t\ll\tau(2)$ this sum is dominated by terms with $n\gg1$. Replacing the sum by an integral we find

$$\langle[\delta Wr(t)-\delta Wr(0)]^2\rangle=\frac{4r^2}{\pi^2a_1a_2}\Gamma\left(\frac{3}{4}\right)\times\left[\frac{\pi k_BT}{\varsigma r^3}(a_1+a_2)t\right]^{1/4}, \quad \text{(B18)}$$

where Γ is the gamma function. The characteristic relaxation rate $\pi k_BT(a_1+a_2)/\varsigma r^3$ depends only on the bending rigidity of the ring.

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