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Fluctuating filaments: Statistical mechanics of helices

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We examine the effects of thermal fluctuations on thin elastic filaments with noncircular cross section and arbitrary spontaneous curvature and torsion. Analytical expressions for orientational correlation functions and for the persistence length of helices are derived, and it is found that this length varies nonmonotonically with the strength of thermal fluctuations. In the weak fluctuation regime, the local helical structure is preserved and the statistical properties are dominated by long-wavelength bending and torsion modes. As the amplitude of fluctuations is increased, the helix ''melts'' and all memory of intrinsic helical structure is lost. Spontaneous twist of the cross section leads to resonant dependence of the persistence length on the twist rate.

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I. INTRODUCTION

Modern polymer physics is based on the notion that while real polymers can be arbitrarily complicated objects, their universal features are captured by a minimal model in which polymers are described as continuous random walks. While this approach has been enormously successful and led to numerous triumphs such as the understanding of rubber elasticity [1], the solution of the excluded volume problem and the theory of semidilute polymer solutions [2], it is ill suited for the description of nonuniversal features of polymers that may depend on their chemical structure in a way that cannot be captured by a simple redefinition of the effective monomer size or its second virial coefficient. For relatively simple synthetic polymers, such ''local details'' can be treated by polymer chemistry-type models (e.g., rotational isomer state model [3]). However, chemically detailed approaches become prohibitively difficult (at least as far as analytical modeling is concerned) in the case of complex biomolecules such as DNA, proteins, and their assemblies and a new type of minimal model is needed to model recent mechanical experiments on such systems [4–12]. Such an alternative approach is to model polymers in the way one usually thinks of them, i.e., as continuous elastic strings or filaments that can be arbitrarily deformed and twisted. However, while the theory of elasticity of such objects is well developed [13], little is known about the statistical mechanics of fluctuating filaments with arbitrary natural shapes. The main difficulty is mathematical in origin: the description of three-dimensional filaments with noncircular cross section and nonvanishing spontaneous curvature and twist [14], involves rather complicated differential geometry [15] and most DNA-related theoretical studies of such models assumed circular cross sections and focused on fluctuations around the straight rod configuration [16–20].

Recently, we reported a study of the effect of thermal fluctuations on the statistical properties of filaments with arbitrary spontaneous curvature and twist [21]. In this paper we present a detailed exposition of the theory and of its application to helical filaments. In Sec. II we introduce the description of the spatial configuration of the filament in terms of a triad of unit vectors oriented along the principal axes of the filament, and show that all the information about this configuration can be obtained from the knowledge of a set of generalized torsions. The elastic energy cost associated with any instantaneous configuration of the filament, is expressed in terms of the deviations of the generalized torsions that describe this configuration, from their spontaneous values in some given stress-free reference state. We use this energy to construct the statistical weights of the different configurations and show that the deviations of the generalized torsions behave as Gaussian random noises, whose amplitudes are inversely proportional to the bare persistence lengths that characterize the rigidity associated with the different deformation modes. We then derive the differential equations for the orientational correlation functions that can be expressed as averages of a rotation matrix that generates the rotation of the triad vectors as one moves along the contour of the filament. An expression for the persistence length in terms of one of the correlators is derived. In Sec. III we apply the general formalism to helical filaments and derive exact expressions for the correlators (see Appendix A) and for the effective persistence length of an untwisted helix. We show that the persistence length is, in general, a nonmonotonic function of the amplitudes of thermal fluctuations. We also show that in the weak fluctuation regime, our exact expressions for the correlators can be derived from a simplified long-wavelength description of the helix, which is equivalent to the incompressible rodlike chain model [18], and that the fluctuation spectrum is dominated by the Goldstone modes of this rodlike chain. Analytical expressions for the persistence length of a spontaneously twisted helix are derived (see Appendix B) and it is found that this length exhibits resonantlike dependence on the rate of twist. Finally, in Sec. IV we discuss our results and outline directions for future research.

II. GENERAL THEORY OF FLUCTUATING FILAMENTS

A filament of small but finite and, in general, noncircular cross section, is modeled as an inextensible but deformable

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physical curve parametrized by a contour length s $(0 \leqslant s \leqslant L$ where L is the length of the filament). To each point s one attaches a triad of unit vectors $\{\mathbf{t}(s)\}$ whose component $\mathbf{t}_3$ 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 two axes of symmetry of the cross section. The vectors $\{\mathbf{t}(s)\}$, together with the inextensibility condition $d\mathbf{x}/ds = \mathbf{t}_3$, give a complete description of the space curve $\mathbf{x}(s)$, as well as of the rotation of the cross section (i.e., twist) about this curve.

The rotation of all the vectors $\mathbf{t}_i$ of the triad as one moves from point s to point s' along the line, is generated by the rotation matrix $\mathbf{R}(s,s')$

$$\mathbf{t}_i(s) = \sum_j R_{ij}(s,s')\mathbf{t}_j(s'). \tag{1}$$

The rotation matrix has the property

$$\mathbf{R}(s,s') = \mathbf{R}(s,s'')\mathbf{R}(s'',s'), \tag{2}$$

where s'' is an arbitrary point on the contour of the filament. It satisfies the equation

$$\frac{\partial R_{ij}(s,s')}{\partial s} = -\sum_k \Omega_{ik}(s) R_{kj}(s,s'), \tag{3}$$

where

$$\Omega_{ij} = \sum_k \varepsilon_{ijk}\omega_k. \tag{4}$$

ε_{ijk} is the antisymmetric tensor and $\{\omega_k\}$ will be referred to as generalized torsions, for lack of a better term. The above equations are supplemented by the ''initial'' condition $R_{ij}(s,s) = \delta_{ij}$, where δ_{ij} is the Kronecker delta function. The formal solution of Eq. (3) is given by the ordered exponential

$$\begin{aligned}\mathbf{R}(s,s') &= T_s \exp\left(-\int_{s'}^{s} ds''\mathbf{\Omega}(s'')\right)\\ &= \lim_{\Delta s \to 0^+} e^{-\mathbf{\Omega}(s_n)\Delta s} \cdots e^{-\mathbf{\Omega}(s_2)\Delta s} e^{-\mathbf{\Omega}(s_1)\Delta s}.\end{aligned} \tag{5}$$

The ordering operator with respect to s, $\mathbf{T}_s$ is defined by the second equality in the above equation, where we broke the interval $s - s'$ into n parts of length Δs each, so that $s_1 = s'$ and $s_n = s$. The origin of the difficulty in calculating the above expression is that the matrices $\mathbf{\Omega}(s)$ and $\mathbf{\Omega}(s')$ do not commute for $s \neq s'$ [this is related to the non-Abelian character of the rotation group in three dimensions (3D)].

Equation (3) is equivalent to a set of generalized Frenet equations from which one can calculate the spatial configuration of the filament, given a set of generalized torsions $\{\omega_k\}$,

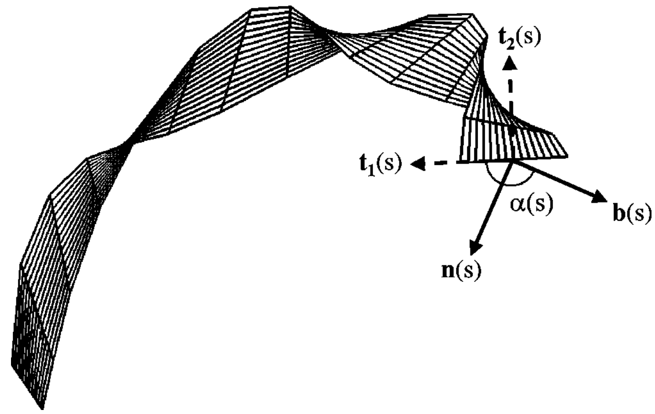

FIG. 1. Schematic drawing of a twisted ribbonlike filament. The vectors of the physical $(\mathbf{t}_1, \mathbf{t}_2)$ and the Frenet $(\mathbf{b}, \mathbf{n})$ triad can be brought into coincidence through rotation by angle α, about the common tangent $(\mathbf{t}_3)$.

$$\frac{d\mathbf{t}_1}{ds} = \omega_2\mathbf{t}_3 - \omega_3\mathbf{t}_2, \quad \frac{d\mathbf{t}_2}{ds} = -\omega_1\mathbf{t}_3 + \omega_3\mathbf{t}_1,$$

$$\frac{d\mathbf{t}_3}{ds} = \omega_1\mathbf{t}_2 - \omega_2\mathbf{t}_1. \tag{6}$$

Note that in the original Frenet description of space curves in terms of a unit tangent (which coincides with $\mathbf{t}_3$), normal $(\mathbf{n})$, and binormal $(\mathbf{b})$, one considers mathematical lines for which it would be meaningless to define twist about the centerline [22]. The Frenet equations contain only two parameters, the curvature κ and torsion τ:

$$\frac{d\mathbf{b}}{ds} = -\tau\mathbf{n}, \quad \frac{d\mathbf{n}}{ds} = -\kappa\mathbf{t}_3 + \tau\mathbf{b}, \quad \frac{d\mathbf{t}_3}{ds} = \kappa\mathbf{n}. \tag{7}$$

The two frames are related through rotation by an angle α about the common tangent direction (see Fig. 1),

$$\mathbf{t}_1 = \mathbf{b}\cos\alpha + \mathbf{n}\sin\alpha, \quad \mathbf{t}_2 = -\mathbf{b}\sin\alpha + \mathbf{n}\cos\alpha. \tag{8}$$

Substituting this relation into Eqs. (6) and using Eqs. (7), we relate the generalized torsions $\{\omega_k\}$ to the curvature κ, torsion τ, and twist angle α,

$$\omega_1 = \kappa\cos\alpha, \quad \omega_2 = \kappa\sin\alpha, \quad \omega_3 = \tau + d\alpha/ds. \tag{9}$$

The theory of elasticity of thin rods [13] is based on the notion that there exists a stress-free reference configuration defined by the set of spontaneous (intrinsic) torsions $\{\omega_{0k}\}$. The set $\{\omega_{0k}\}$ together with Eqs. (3) and (4) (with $\omega_k \to \omega_{0k}$) completely determines the equilibrium shape of the filament, in the absence of thermal fluctuations. Neglecting excluded-volume effects and other nonelastic interactions, it can be shown [23] that the elastic energy associated with some actual configuration $\{\omega_k\}$ of the filament is a quadratic form in the deviations $\delta\omega_k = \omega_k - \omega_{0k}$

$$U_{el}(\{\delta\omega_k\}) = \frac{kT}{2}\int_0^L ds \sum_k a_k \delta\omega_k^2, \tag{10}$$

where T is the temperature, k is the Boltzmann constant, and a_i are bare persistence lengths that depend on the elastic constants and on the principal moments of inertia with respect to the symmetry axes of the cross section, in a model-dependent way. Thus, assuming anisotropic elasticity (with elastic moduli E_i) and a particular form of the deformation, one obtains [23] $a_1=E_1I_1/kT$, $a_2=E_1I_2/kT$, and $a_3=E_2(I_1+I_2)/kT$, where I_i are the principal moments of inertia. In general, the theory of elasticity of incompressible isotropic rods with shear modulus μ yields [13] $a_1=3\mu I_1/kT$, $a_2=3\mu I_2/kT$, and $a_3=C/kT$, where the torsional rigidity C is also proportional to μ and depends on the geometry of the cross section [24] [for an elliptical cross section with semiaxes b_1 and b_2, $C=\pi\mu b_1^3b_2^3/(b_1^2+b_2^2)$].

The elastic energy $U_{el}(\{\delta\omega_k\})$ determines the statistical weight of the configuration $\{\omega_k\}$. The statistical average of any functional of the configuration $B(\{\omega_k\})$ is defined as the functional integral

$$\langle B(\{\omega_k\})\rangle=\frac{\int D\{\delta\omega_k\}B(\{\omega_k\})e^{-U_{el}\{\delta\omega_k\}/kT}}{\int D\{\delta\omega_k\}e^{-U_{el}\{\delta\omega_k\}/kT}}. \qquad (11)$$

Calculating the corresponding Gaussian path integrals we obtain

$$\langle\delta\omega_i(s)\rangle=0,\quad \langle\delta\omega_i(s)\delta\omega_j(s')\rangle=a_i^{-1}\delta_{ij}\delta(s-s'). \qquad (12)$$

We conclude that fluctuations of generalized torsions at two different points along the filament contour are uncorrelated, and that the amplitude of fluctuations is inversely proportional to the corresponding bare persistence length.

The statistical properties of fluctuating filaments are determined by the orientational correlation functions, which can be expressed as averages of the elements of the rotation matrix,

$$\langle\mathbf{t}_i(s)\mathbf{t}_j(s')\rangle=\langle R_{ij}(s,s')\rangle=\sum_k \langle R_{ik}(s,s'')R_{kj}(s'',s')\rangle \qquad (13)$$

The last equality was written using Eq. (2), with $s>s''>s'$. Inspection of Eqs. (5) and (4), shows that $\mathbf{R}(s,s'')$ depends only on the torsions $\omega_k(s_1)$ with $s>s_1>s''$, and that $\mathbf{R}(s'',s')$ depends only on $\omega_k(s_2)$ with $s''>s_2>s'$. Since fluctuations of the torsion in two nonoverlapping intervals are uncorrelated [see Eq. (12)], the average of the product of rotation matrices splits into the product of their averages:

$$\langle R_{ij}(s,s')\rangle=\sum_k \langle R_{ik}(s,s'')\rangle\langle R_{kj}(s'',s')\rangle. \qquad (14)$$

In order to derive a differential equation for the averaged rotation matrix, we consider the limit $\Delta s=s-s''\to 0$. Keeping terms to first order in Δs we find

$$\frac{\partial\langle R_{ij}(s,s')\rangle}{\partial s}=-\sum_k \Lambda_{ik}(s)\langle R_{kj}(s,s')\rangle, \qquad (15)$$

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

$$\Lambda_{ik}(s)=\lim_{\Delta s\to 0^+}\frac{\delta_{ik}-\langle R_{ik}(s,s-\Delta s)\rangle}{\Delta s}. \qquad (16)$$

Analogously to Eq. (5), the formal solution of Eq. (15) can be written as an ordered exponential,

$$\langle\mathbf{R}(s,s')\rangle=\mathbf{T}_s\exp\left(-\int_{s'}^{s}ds''\mathbf{\Lambda}(s'')\right). \qquad (17)$$

In order to calculate the matrix $\mathbf{\Lambda}$ we expand the exponential in Eq. (5) to second order in $\Delta s=s-s'$ and use the property of the ordering operator

$$\begin{aligned}\mathbf{T}_s\int_{s-\Delta s}^{s}ds_1\int_{s-\Delta s}^{s}ds_2\mathbf{\Omega}(s_1)\mathbf{\Omega}(s_2)\\=\int_{s-\Delta s}^{s}ds_1\left[\int_{s-\Delta s}^{s_1}ds_2\mathbf{\Omega}(s_1)\mathbf{\Omega}(s_2)\right.\\\left.+\int_{s_1}^{s}ds_2\mathbf{\Omega}(s_2)\mathbf{\Omega}(s_1)\right].\end{aligned} \qquad (18)$$

In order to average this equation, we first calculate the average of the product $\mathbf{\Omega}(s_1)\mathbf{\Omega}(s_2)$, using Eqs. (4) and (12)

$$\langle\mathbf{\Omega}(s_1)\mathbf{\Omega}(s_2)\rangle=\langle\mathbf{\Omega}(s_1)\rangle\langle\mathbf{\Omega}(s_2)\rangle+\boldsymbol{M}\delta(s_1-s_2), \qquad (19)$$

where $\boldsymbol{M}$ is a diagonal matrix with elements

$$\gamma_i=\sum_k\frac{1}{2a_k}-\frac{1}{2a_i}. \qquad (20)$$

Using Eqs. (18) and (19), and keeping terms up to first order in Δs [upon integration, the contribution of $\langle\mathbf{\Omega}(s_1)\rangle\langle\mathbf{\Omega}(s_2)\rangle$ is of order $(\Delta s)^2$], yields

$$\Lambda_{ik}=\gamma_i\delta_{ik}+\sum_l \varepsilon_{ikl}\omega_{0l}. \qquad (21)$$

The elements of the averaged rotation matrix are simply the correlators of the triad vectors [see Eq. (13)]. From the knowledge of the above correlators one can calculate other statistical properties of fluctuating filaments, the most familiar of which is the persistence length l_p, that can be interpreted as an effective statistical segment length of a coarse-grained model, in which one replaces the filament by a random walk with the same contour length L and rms end-to-end separation $\langle r^2\rangle$:

$$l_p=\lim_{L\to\infty}\frac{1}{2L}\langle r^2\rangle.$$

The end-to-end vector is defined as $\mathbf{r}=\int_0^L\mathbf{t}_3(s)ds$ and thus

$$l_p=\lim_{L\to\infty}\frac{1}{L}\int_0^L ds\int_0^s ds'\langle\mathbf{t}_3(s)\mathbf{t}_3(s')\rangle. \qquad (22)$$

The above equations describe the fluctuations of filaments of arbitrary shape and elastic properties, and in the following section this general formalism is applied to helical filaments.

III. FLUCTUATING HELICES

A. Untwisted helix: Correlation functions and persistence length

Consider a helical filament without spontaneous twist, such that the generalized spontaneous torsions $\{\omega_{0k}\}$ are independent of position s along the contour. In order to describe the stress-free configuration of such a filament, it is convenient to introduce the conventional Frenet triad, which consists of the tangent, normal and binormal to the space curve spanned by the centerline, supplemented by a constant angle of twist α_0, which describes the orientation of the cross section in the plane normal to the centerline. According to the general relation between the two frames, Eq. (9), $\omega_{01}=\kappa_0\cos\alpha_0$, $\omega_{02}=\kappa_0\sin\alpha_0$, and $\omega_{03}=\tau_0$, where κ_0 and τ_0 are the constant curvature and torsion of the space curve in terms of which the total spontaneous curvature that defines the rate of rotation of the helix about its long axis, is given by $\omega_0=(\kappa_0^2+\tau_0^2)^{1/2}$. The corresponding helical pitch is $2\pi\tau_0/\omega_0^2$ and the radius of the helical turn is κ_0/ω_0^2. We proceed to calculate the orientational correlation functions.

Since $\mathbf{\Lambda}$ is a constant matrix, Eq. (17) yields (for $s_1>s_2$)

$$\langle \mathbf{t}_i(s_1)\mathbf{t}_j(s_2)\rangle=[e^{-\mathbf{\Lambda}(s_1-s_2)}]_{ij}. \tag{23}$$

In order to calculate the matrix $e^{-\mathbf{\Lambda}(s_1-s_2)}$ we first find the eigenvalues λ_i of the matrix $\mathbf{\Lambda}$, which are determined by the characteristic polynomial

$$\lambda^3-\gamma\lambda^2+\mu\lambda-\nu=0, \tag{24}$$

where we introduced the notations

$$\gamma=\gamma_1+\gamma_2+\gamma_3=a_1^{-1}+a_2^{-1}+a_3^{-1}, \tag{25}$$

$$\mu=\omega_0^2+\gamma_1\gamma_2+\gamma_2\gamma_3+\gamma_1\gamma_3, \tag{26}$$

$$\nu=\kappa_0^2(\gamma_1\cos^2\alpha_0+\gamma_2\sin^2\alpha_0)+\tau_0^2\gamma_3+\gamma_1\gamma_2\gamma_3. \tag{27}$$

The solution of this cubic equation depends on the sign of the expression

$$\Delta=27(\nu-\nu_1)^2+4(\mu-\gamma^2/3)^3,\quad \nu_1=\frac{1}{3}\gamma\mu-\frac{2}{27}\gamma^3. \tag{28}$$

For $\Delta<0$ all the roots λ_i are real. In this parameter range, fluctuations are strong enough to destroy the helical structure on all length scales. In the limit of very strong fluctuations when the bare persistence lengths are much smaller than the radii of curvature $\gamma\gg\omega_0$, we have $\lambda_i\to\gamma_i$ and correlation functions become

$$\langle \mathbf{t}_i(s_1)\mathbf{t}_j(s_2)\rangle=e^{-\gamma_i(s_1-s_2)}\delta_{ij} \tag{29}$$

with $s_1-s_2>0$. Equation (29) shows that although angular correlations remain on length scales smaller than $1/\lambda_i$, they are identical to those of a persistent rod and do not carry any memory of the original helix.

In the case $\Delta>0$, there is one real eigenvalue, λ_1, and two complex ones, $\lambda_{2,3}=\lambda_R\pm i\omega$, where

$$\lambda_1=\frac{K}{6}-2\frac{\mu-\gamma^2/3}{K}+\frac{\gamma}{3},\quad \lambda_R=\frac{\gamma-\lambda_1}{2}, \tag{30}$$

$$\omega=\sqrt{3}\left(\frac{K}{12}+\frac{\mu-\gamma^2/3}{K}\right),\quad K=12^{1/3}[9(\nu-\nu_1)+\sqrt{3\Delta}]^{1/3}. \tag{31}$$

It is shown in Appendix A that the diagonal orientational correlation functions take the form

$$\langle \mathbf{t}_i(s_1)\mathbf{t}_i(s_2)\rangle=(1-c_i-c_i^*)e^{-\lambda_1 s}+(c_ie^{-i\omega s}+c_i^*e^{i\omega s})e^{-\lambda_R s}, \tag{32}$$

where $s=s_1-s_2>0$. The complex coefficients c_i are calculated in Appendix A.

In the limit of small fluctuations, $\gamma\ll\omega_0$, we have

$$\lambda_1=\sum_i(1-2c_i)\gamma_i,\quad \lambda_R=\sum_i c_i\gamma_i,$$

$$2c_i=1-\frac{\omega_{0i}^2}{\omega_0^2},\quad \omega^2=\omega_0^2. \tag{33}$$

In this limit, it is easy to generalize our results for the diagonal correlators and write down expressions for all the orientational correlation functions:

$$\langle \mathbf{t}_i(s_1)\mathbf{t}_j(s_2)\rangle=\frac{\omega_{0i}\omega_{0j}}{\omega_0^2}e^{-\lambda_1 s}+\left(\delta_{ij}-\frac{\omega_{0i}\omega_{0j}}{\omega_0^2}\right)\cos(\omega_0 s)e^{-\lambda_R s}-\sum_k\varepsilon_{ijk}\frac{\omega_{0k}}{\omega_0}\sin(\omega_0 s)e^{-\lambda_R s}, \tag{34}$$

where $s=s_1-s_2>0$. As expected, Eq. (34) satisfies the condition of orthonormality of triad vectors $\mathbf{t}_i(s_1)\mathbf{t}_j(s_1)=\delta_{ij}$ (this geometric condition must be satisfied for the instantaneous triad vectors, not only on the average). Note that in the limit of weak fluctuations the local helical structure is preserved on contour distances $s<\lambda_R^{-1}$ and the period of rotation of the helix about its axis is given by its spontaneous value, $2\pi\omega_0^{-1}$.

Using Eqs. (25)–(28) it can be shown that when $\Delta\to0$, the total curvature of the helix vanishes as $\omega\sim\Delta^{1/2}$. Since ω is positive for $\Delta>0$ and vanishes for $\Delta\leqslant0$, in a loose sense it plays the role of an order parameter associated with helical order, and the point $\Delta=0$ can be interpreted as the critical point at which a continuous helix to random coil transition takes place. However, although the dependence of ω on the various parameters exhibits surprisingly rich behavior, the investigation of the transition region is of limited physical significance. The change of the helical period from $2\pi\omega_0^{-1}$ to infinity takes place in the ‘‘overdamped’’ regime where this period is larger than the persistence length ($\omega\leqslant\gamma$), and local helical structure can no longer be defined in a statistically significant sense. An approximate but more physically meaningful criterion for the ‘‘melting’’ transition is that a helix of period $2\pi\omega^{-1}$ melts when the persistence length becomes of the order of this period.

We now return to Eq. (22) for the persistence length. Using the matrix equation $\int_0^\infty ds\,\exp(-\mathbf{\Lambda} s)=\mathbf{\Lambda}^{-1}$ and taking the appropriate matrix element we find

$$l_p=\frac{\tau_0^2+\gamma_1\gamma_2}{\kappa_0^2(\gamma_1\cos^2\alpha_0+\gamma_2\sin^2\alpha_0)+(\tau_0^2+\gamma_1\gamma_2)\gamma_3}. \quad (35)$$

The above expression diverges in the limit of a rigid helix $\gamma_i\to 0$ in which fluctuations have a negligible effect on the helix. Nonmonotonic behavior is observed for ''platelike'' helices, with large radius to pitch ratio, κ_0/τ_0. When no thermal fluctuations are present $(\gamma_i\to 0)$, the effective persistence length approaches zero. Weak thermal fluctuations ''inflate'' the helix by releasing stored length (by a mechanism similar to the stretching of the Slinky™ toy spring) and increase the persistence length. Eventually, in the limit of strong fluctuations, the persistence length vanishes again (as γ_3^{-1}) because of the complete randomization of the filament. Note that the sensitivity to the (constant) angle of twist increases with radius to pitch ratio.

In the opposite limit of ''rodlike'' helices $\kappa_0\to 0$, the effective persistence length approaches $1/\gamma_3$ and therefore depends on a_1 and a_2 only, and not on τ_0 and a_3, which describe the twist of the cross section about the centerline. This agrees with the expectation that since straight inextensible rods do not have stored length, their end-to-end distance and persistence length are determined by random bending and torsion (writhe) fluctuations only and are independent of twist.

B. Weak fluctuations: The rodlike chain model

From the discussion in the preceding section we expect that in the presence of weak thermal fluctuations, the filament will maintain its helical structure locally and that fluctuations will only affect its large scale conformation by introducing random bending and torsion of the helical axis, as well as random rotation of the filament about this axis. We now rederive the expressions for the correlators, Eq. (34), using a different approach that relates our paper to that of previous investigators [18] and, in the process, leads to important insights about the nature of the long-wavelength fluctuations that dominate the spectrum of fluctuations in this regime.

Note that in the absence of thermal fluctuations, $\gamma_i=0$, the triad vectors $\mathbf{t}_i$ attached to the helix can be expressed in terms of the space-fixed orthonormal triad $\{\mathbf{e}\}$ of vectors $\mathbf{e}_i$, where $\mathbf{e}_3$ is oriented along the long axis of the helix and $\mathbf{e}_1$ and $\mathbf{e}_2$ lie in the plane normal to it (Fig. 2). It is convenient to introduce the Euler angles $\phi_0(s)=\omega_0 s$, $\theta_0=\arctan(\kappa_0/\tau_0)$, and α_0 in terms of which the relation between the two frames is given by

$$\mathbf{t}^R(s)=\mathbf{R}_3(\alpha_0)\mathbf{R}_2(-\theta_0)\mathbf{R}_3[\phi_0(s)]\mathbf{e}, \quad (36)$$

where the rotation matrix

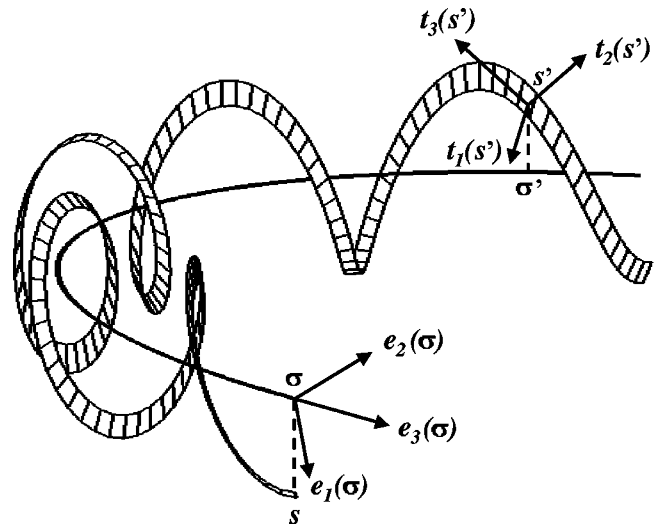

FIG. 2. Schematic plot of section of a ribbonlike helix. The helix-fixed coordinate system $\mathbf{t}$ at contour point s' is shown. The solid line describes the associated ''rodlike chain'' to which the coordinate system $\mathbf{e}$ is attached at point σ on its contour. The points σ and σ' on the rodlike chain are the projections of the points s and s', respectively.

$$\mathbf{R}_3(\phi_0)=\begin{pmatrix}\cos\phi_0 & \sin\phi_0 & 0\\ -\sin\phi_0 & \cos\phi_0 & 0\\ 0 & 0 & 1\end{pmatrix} \quad (37)$$

describes rotation by angle $\phi_0(s)$ with respect to the $\mathbf{e}_3$ axis. The matrix

$$\mathbf{R}_2(-\theta_0)=\begin{pmatrix}\cos\theta_0 & 0 & -\sin\theta_0\\ 0 & 1 & 0\\ \sin\theta_0 & 0 & \cos\theta_0\end{pmatrix} \quad (38)$$

gives the rotation by angle $-\theta_0$ with respect to the $\mathbf{e}_2'$ axis $(\mathbf{e}_2'=\mathbf{R}_3[\phi_0(s)]\mathbf{e}_2)$, and $\mathbf{R}_3(\alpha_0)$ is a rotation by angle α_0 about the $\mathbf{e}_3'$ axis $[\mathbf{e}_3'=\mathbf{R}_2(-\theta_0)\mathbf{e}_3]$. Note that while the space-fixed $\mathbf{e}$ was taken as a conventional right-handed triad, we chose the helix-fixed $\mathbf{t}$ as a left-handed triad. Although this choice does not affect our previous results, it does affect the geometric relation between the two coordinate systems and, for consistency, we replaced the left-handed $\mathbf{t}$ by the right-handed one, $\mathbf{t}^R=(-\mathbf{t}_1,\mathbf{t}_2,\mathbf{t}_3)$, in Eq. (36).

In the presence of weak thermal fluctuations, the axis of the helix slowly bends and rotates in space, resulting in rotation of the triad $\{\mathbf{e}\}$. Since with each point s on the helix we can associate its projection

$$\sigma=\tau_0 s/\omega_0 \quad (39)$$

on the long axis of the helix (see Fig. 2), the rotation of the triad $\{\mathbf{e}\}$ as one moves along this axis is given by the generalized Frenet equations,

$$\frac{d\mathbf{e}_1}{d\sigma}=\varpi_2\mathbf{e}_3-\varpi_3\mathbf{e}_2,\quad \frac{d\mathbf{e}_2}{d\sigma}=-\varpi_1\mathbf{e}_3+\varpi_3\mathbf{e}_1,$$
$$\frac{d\mathbf{e}_3}{d\sigma}=\varpi_1\mathbf{e}_2-\varpi_2\mathbf{e}_1. \tag{40}$$

The generalized torsions, $\varpi_i(s)$, are Gaussian random variables determined by the conditions

$$\langle\varpi_i(\sigma)\rangle=0,\quad \langle\varpi_i(\sigma)\varpi_j(\sigma')\rangle=\overline{a}_i^{-1}\delta_{ij}\delta(\sigma-\sigma'), \tag{41}$$

where the constants $\overline{a}_i$ should be determined by the requirement that the resulting expressions for the correlators (the averages of the elements of the rotation matrix) coincide with these in Eq. (34). A calculation similar to that in the previous section yields the correlators

$$\langle\mathbf{e}_i(\sigma)\mathbf{e}_j(\sigma')\rangle=\delta_{ij}\exp(-\overline{\gamma}_i|\sigma-\sigma'|), \tag{42}$$

where, analogously to Eq. (20), we have

$$\overline{\gamma}_i=\sum_k \frac{1}{2\overline{a}_k}-\frac{1}{2\overline{a}_i}. \tag{43}$$

Using Eqs. (36), the correlators of the original triad $\{\mathbf{t}\}$ can be expressed in terms of the correlators of the $\{\mathbf{e}\}$ triad. Comparing the results with Eq. (34), gives

$$\overline{a}_1^{-1}=\overline{a}_2^{-1}=\sum_i \gamma_i\frac{\omega_{0i}^2}{\omega_0\tau_0},\quad \overline{a}_3^{-1}=\sum_i\frac{1}{a_i}\frac{\omega_{0i}^2}{\omega_0\tau_0}, \tag{44}$$

where the equality $\overline{a}_1=\overline{a}_2$ is the consequence of symmetry under rotation in the $(\mathbf{e}_1,\mathbf{e}_2)$ plane.

The correlators (41) can be derived from an effective free energy that describes the long-wavelength fluctuations of the helical filament, on length scales larger than the period of the helix ω_0^{-1}.

$$U_{el}^{LW}=\frac{kT}{2}\int d\sigma[\overline{a}_1(\varpi_1^2+\varpi_2^2)+\overline{a}_3\varpi_3^2]. \tag{45}$$

This expression coincides with the elastic energy of a rodlike chain (RLC) introduced by Bouchiat and Mezard [18]. The persistence length $\overline{a}_1$ describes the elastic response to bending and torsion of the effective rodlike filament. The persistence length $\overline{a}_3$ controls the elastic response of the RLC to twist about its axis. As a consequence of the fluctuation-dissipation theorem, it also determines the amplitude of fluctuations $\Delta\phi$ of the angle $\phi(\sigma)=\omega_0^2\sigma/\tau_0+\Delta\phi(\sigma)$, where the correlator of the random angle of rotation about the axis of the RLC is given by

$$\langle[\Delta\phi(\sigma)-\Delta\phi(\sigma')]^2\rangle=\overline{a}_3^{-1}|\sigma-\sigma'|. \tag{46}$$

In Eq. (44) we calculated the effective persistence lengths of this model $(\overline{a}_i)$ in terms of the bare parameters of the underlying helical filament. In Ref. [18] where the analysis begins with the RLC model, these corresponding persistence lengths were introduced by hand. The difference between the two models becomes important if one considers the combined application of extension and twist: while such a coupling appears trivially in models of stretched helical filaments [23], twist has no effect on the extension in the RLC model [18], in contradiction with experimental observations [6]. Our analysis underscores the fact that the RLC model does not give a complete description of the fluctuating helix. Rather, it describes long-wavelength fluctuations of the ''phantom'' axes $\{\mathbf{e}_i\}$ which, by themselves, contain no information about the local helical structure of the filament. In order to recover this information and construct the correlators of the original helix $\langle\mathbf{t}_i(s_1)\mathbf{t}_i(s_2)\rangle$, one has to go beyond the RLC model and reconstruct the local helical geometry using the relation between $\mathbf{e}_i$ and the helix-fixed axes $\mathbf{t}_i$, Eqs. (36).

In deriving the expressions for the correlators $\langle\mathbf{t}_i(s)\mathbf{t}_j(0)\rangle$ in terms of the correlators of the RLC model, we did not take into account the possibility of fluctuations of the twist angle of the cross section of the helix about its centerline, $\alpha_0\to\alpha(s)=\alpha_0+\Delta\alpha(s)$. From the fact that the resulting correlators coincide with the exact expressions, Eq. (34), we conclude that such fluctuations do not contribute to the correlators. This surprising result follows from the fact that in the weak fluctuation regime, the statistical properties of the helix are completely determined by the low-energy part of the fluctuation spectrum. Such long-wavelength fluctuation modes (Goldstone modes) lead to the loss of helical correlations on length scales larger than all the natural length scales of the helix $(s\gg\gamma^{-1}\gg\omega_0^{-1})$. These Goldstone modes are associated with spontaneously broken continuous symmetries and correspond to bending (ϖ_1 and ϖ_2) and twist (ϖ_3) modes of the RLC. It is important to emphasize that these modes correspond to different deformations of the centerline of the helix and not to twist of its cross section about this centerline. Since the elastic energy, Eq. (10), depends on the spontaneous angle of twist of the helix about its centerline through the combinations $\delta\omega_1=\kappa\cos\alpha-\kappa_0\cos\alpha_0$ and $\delta\omega_2=\kappa\sin\alpha-\kappa_0\sin\alpha_0$, we conclude that the energy is not invariant under global rotation of the cross section about the centerline and that such a rotation is not a continuous symmetry of the helix. Therefore, twist fluctuations of the helical cross section are not Goldstone modes and do not contribute to the correlators in the weak fluctuation limit.

Another interesting observation is that there is no contribution from compressional modes to the long-wavelength energy, Eq. (10). This is surprising since the RLC is a coarse-grained representation of the helix and the latter may be expected to behave as a compressible object, with accordionlike compressional modes [19]. In order to check this point, we write down the spatial position of a point s on the helix as

$$\mathbf{x}(s)=\overline{\mathbf{x}}(\sigma)+\delta\mathbf{x}(s), \tag{47}$$

where $\overline{\mathbf{x}}(\sigma)$ describes the curve spanned by the long axis of the helix and, therefore, defines the spatial position of the point σ, Eq. (39), on the RLC contour. The deviation $\delta\mathbf{x}(s)$ describes the rotation of the locally helical filament about this axis. Since the original filament is incompressible, it satisfies $d\mathbf{x}/ds=\mathbf{t}_3$. From Eq. (36) we obtain an expression for $\mathbf{t}_3$ which, upon substitution into the incompressibility condition and averaging over length scales $\{|\varpi_i|^{-1}\} \gg s \gg \omega_0^{-1}$ (much larger than the inverse total curvature of the helix but much smaller than the radii of curvature of the RLC), yields

$$\frac{d\overline{\mathbf{x}}(\sigma)}{d\sigma} = \mathbf{e}_3(\sigma). \tag{48}$$

The fact that the long-wavelength fluctuations of the helix satisfy the above incompressibility conditions, implies that compressional fluctuations do not contribute to the long-wavelength correlators. The origin of this observation becomes clear if we recall that the energy of the helix depends on the spontaneous curvature κ_0 and torsion τ_0 and, since compressional modes change the local curvature and torsion, they have a gap in the energy spectrum and their energy does not vanish even in the long-wavelength limit. We conclude that similar to twist fluctuations of the helical cross section, compressional modes are not Goldstone modes.

The above deliberations have profound consequences for the elastic response of the filament to long-wavelength perturbations, such as tensile forces and moments applied to its ends. Using the fluctuation-dissipation theorem, we conclude that as long as the deformation of the filament remains small (on scale ω_0^{-1}), these forces and moments do not induce the twist of the cross section of the helix about its centerline, and that the deformation can be completely described by the incompressible RLC model.

C. Effect of spontaneous twist

We proceed to calculate the persistence length of a helix whose cross section is twisted by an angle $\alpha_0(s) = \dot{\alpha}_0 s$ about the centerline ($\dot{\alpha}_0$ is a constant rate of twist). It is convenient to rewrite Eq. (22) as

$$l_p = \lim_{L\to\infty} \frac{1}{L}\int_0^L ds' \int_0^{L-s'} ds \langle \mathbf{t}_3(s+s')\mathbf{t}_3(s')\rangle. \tag{49}$$

Recall that the correlator in the integrand of Eq. (49) is simply the (3,3) element of the averaged rotation matrix, and is therefore the solution of Eq. (15), the coefficients of which are the elements of the matrix $\mathbf{\Lambda}(s+s')$ defined in Eq. (21). The diagonal elements of this matrix are constants (γ_i), while the nondiagonal elements are given by the expressions

$$\Lambda_{12}(s+s') = -\Lambda_{21}(s+s') = \tau_0 + \dot{\alpha}_0,$$

$$\Lambda_{31}(s+s') = -\Lambda_{13}(s+s') = \kappa_0 \sin(\dot{\alpha}_0 s + \alpha_0),$$

$$\Lambda_{23}(s+s') = -\Lambda_{32}(s+s') = \kappa_0 \cos(\dot{\alpha}_0 s + \alpha_0), \tag{50}$$

where all the dependence on s' is contained in $\alpha_0 = \alpha_0(s')$.

The correlator in Eq. (49) decays exponentially fast with s, and thus the upper limit on the integral over s can be extended to infinity. Since the correlator is a periodic function of α_0, the integration over s' can be replaced by that over α_0 and we obtain

$$l_p = \int_0^{2\pi} \frac{d\alpha_0}{2\pi} \int_0^\infty ds \langle \mathbf{t}_3(s)\mathbf{t}_3(s-s_1)\rangle. \tag{51}$$

In deriving the above expression we assumed that the limit $L\to\infty$ is taken and that the total angle of twist is always large, $L\dot{\alpha}_0 \gg 2\pi$ (i.e., the product $L\dot{\alpha}_0$ remains finite for arbitrarily small $\dot{\alpha}_0$). This assumption will be used in the following analysis.

We first consider some limiting cases in which analytical results can be derived. In the limit of vanishing twist rates, $\dot{\alpha}_0 \to 0$, the persistence length is obtained by averaging Eq. (35) with respect to α_0. This yields

$$l_p = \frac{\tau_0^2 + \gamma_+^2 - \gamma_-^2}{\sqrt{[\kappa_0^2\gamma_+ + (\tau_0^2 + \gamma_+^2 - \gamma_-^2)\gamma_3]^2 - \kappa_0^4\gamma_-^2}}, \tag{52}$$

where

$$\gamma_\pm \equiv (\gamma_1 \pm \gamma_2)/2 \tag{53}$$

with γ_1 and γ_2 defined in Eq. (20).

In the limit of large twist rates, $\dot{\alpha}_0 \to \infty$, we can replace the denominator of Eq. (35) by its average with respect to α_0. This yields

$$l_p = \frac{\tau_0^2 + \gamma_+^2}{\kappa_0^2\gamma_+ + (\tau_0^2 + \gamma_+^2)\gamma_3}. \tag{54}$$

Finally, when $\gamma_1 = \gamma_2$ ($a_1 = a_2$), the persistence length becomes independent of twist and can be derived from either of Eqs. (52) and (54), by substituting $\gamma_- = 0$.

We now consider the case of arbitrary twist rates and fluctuation amplitudes. The calculation involves the solution of linear differential equations with periodic coefficients and details are given in Appendix B. We obtain

$$l_p = \frac{\gamma_3^{-1}}{1 + (\Xi - 1)^{-1} + (\Xi^* - 1)^{-1}}. \tag{55}$$

An analytical expression for the complex function $\Xi(\dot{\alpha}_0)$ is given in Appendix B.

In Fig. 3 we present a three-dimensional plot of the persistence length given in units of the helical pitch $l^* = l\omega_0^2/\pi\tau_0$, as a function of the dimensionless rate of twist $w = 2\omega_0^{-1}\dot{\alpha}_0$ and of the logarithm of the bare persistence length a_1 , for a ‘‘platelike’’ helix with large radius to pitch ratio κ_0/τ_0. Inspection of Fig. 3 shows that in the case of a circular cross section with $a_1 = a_2 = 1000$, the persistence length becomes independent of twist. With increasing asymmetry, $a_1 < a_2$, a maximum appears at vanishing twist rates, accompanied by two minima at $\dot{\alpha}_0 = \pm\omega_0/2$. The geometrical significance of the locations ($\dot{\alpha}_0 = 0, \pm\omega_0/2$) of these resonances is underscored by the observation that in the limit of vanishing pitch, a ribbonlike untwisted ($\dot{\alpha}_0 = 0$) helix degenerates into a ring. For $\dot{\alpha}_0 = \pm\omega_0/2$, the cross section of a twisted helix rotates by $\pm\pi$ with each period, and in the above limit the helix degenerates into a Möbius ring. As asymmetry increases ($a_1 \ll a_2$), each extremum splits into a

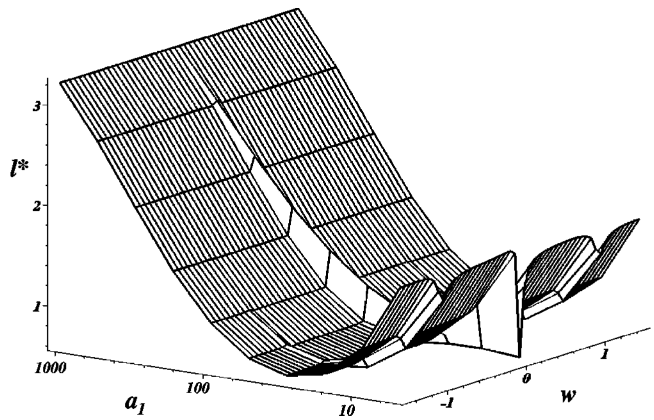

FIG. 3. Three-dimensional plot of the persistence length l^* as a function of the dimensionless rate of twist w and of the bare persistence length a_1 (logarithmic scale), for a helical filament with spontaneous curvature $\kappa_0=1$, and torsion $\tau_0=0.01$ (in arbitrary units). The bare persistence lengths are $a_2=1000$ and $a_3=5000$.

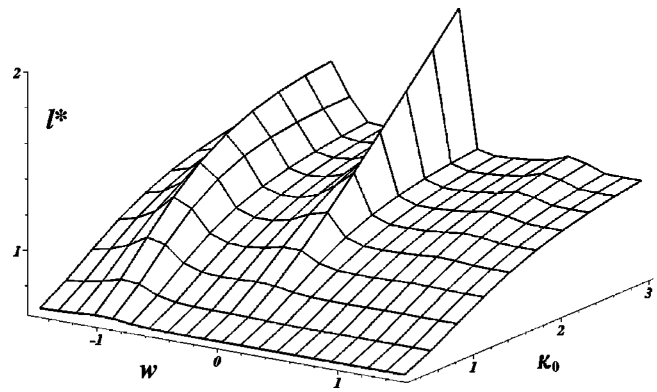

FIG. 5. Three-dimensional plot of the persistence length l^* as a function of the dimensionless rate of twist w and of the spontaneous curvature κ_0, for a helical filament with spontaneous torsion $\tau_0=1$ (in arbitrary units). The bare persistence lengths are $a_1=500$, $a_2=1$, and $a_3=500$.

minimum and a maximum and eventually one obtains a dip at $\dot{\alpha}_0=0$, accompanied by two symmetrical peaks at $\dot{\alpha}_0\simeq \pm\omega_0/2$. Note that the persistence length is a nonmonotonic function of the amplitude of thermal fluctuations (i.e., of $1/a_1$): it first slowly increases and eventually decreases rapidly with decreasing a_1. Several two-dimensional plots of the persistence length as a function of the rate of twist, for different combinations of the bare persistence lengths a_i, are shown in Fig. 4. The detailed behavior of the persistence length depends sensitively on the choice of the parameters: for example, in the limit of weak fluctuations three maxima are observed in Fig. 4, instead of a maximum accompanied by two minima in Fig. 3. In all cases, the locations of the extrema are determined by geometry only: $\dot{\alpha}_0=0$, $\pm\omega_0/2$.

In order to demonstrate how the initial choice of the handedness of the helix breaks the symmetry between the effects of under and over twist on the persistence length, in Fig. 5 we present a three-dimensional plot of the persistence length as a function of the dimensionless rate of twist w and of the inverse radius of curvature κ_0, for helices with radius to pitch ratios of order unity and large asymmetry of the cross section, $a_1\gg a_2$. Note that for $\kappa_0/\tau_0<1$ (rodlike helices), there is a single broad maximum at $\dot{\alpha}_0=-\omega_0/2$. Then, at $\kappa_0/\tau_0\simeq 1$, a central peak appears at $\dot{\alpha}_0=0$. This peak grows much faster than the $\dot{\alpha}_0=-\omega_0/2$ peak, with increasing κ_0/τ_0. At yet higher values of κ_0/τ_0 another peak appears at $\dot{\alpha}_0=\omega_0/2$ and eventually the amplitudes of the two Möbius side peaks become equal (and much smaller than the amplitude of the $\dot{\alpha}_0=0$ peak) in the limit of platelike helices, $\kappa_0/\tau_0\gg 1$ (see curve 1 in Fig. 4).

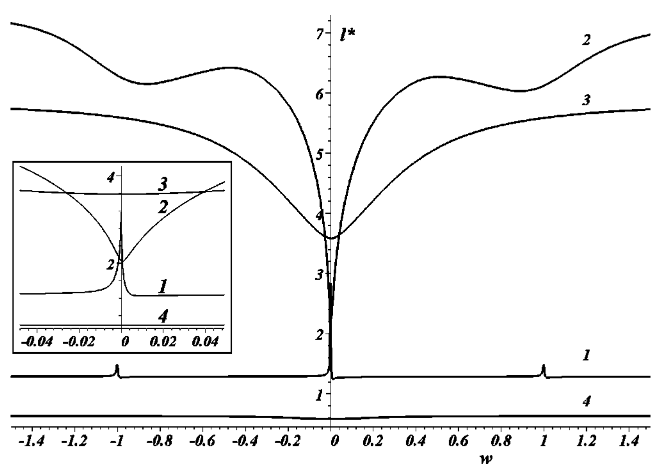

FIG. 4. Plot of the persistence length l^* as a function of the dimensionless rate of twist w for a helical filament with spontaneous curvature $\kappa_0=1$ and torsion $\tau_0=0.01$ (in arbitrary units). The different curves correspond to different bare persistence lengths: (1) $a_1=100$, $a_2=a_3=5000$, (2) $a_1=1$, $a_2=a_3=100$, (3) $a_1=0.1$, $a_2=a_3=10$, and (4) $a_1=0.01$, $a_2=a_3=10$. A magnified view of the region of small twist rates is shown in the inset.

What is the origin of the Möbius resonances observed in Figs. 3–5? Recall that the calculation of the persistence length of a twisted helix involves the solution of linear differential equations with periodic coefficients [Eqs. (B1) in Appendix B]. These equations were derived from linear differential equations with periodic coefficients and multiplicative random noise, Eqs. (3) and Eqs. (6), which are known to lead to stochastic resonances [25]. Some physical intuition can be derived from the following argument. While the persistence length is a property of the space curve described by the Frenet triad, the microscopic Brownian motion of the filament arises as the result of random forces that act on its cross section and therefore are given in the frame associated with the principal axes of the filament. Since the two frames are related by a rotation of the cross section by an angle $\alpha_0(s)$, the random force in the Frenet frame is modulated by linear combinations of $\sin\alpha_0(s)$ and $\cos\alpha_0(s)$. This gives a deterministic contribution to the persistence length which, to lowest order in the force, is proportional to the mean-square amplitude of the random force and therefore varies sinusoidally with $\pm 2\alpha_0(s)$. The Möbius resonances occur whenever the total curvature of the helix ω_0 coincides with the rate of variation of this deterministic contribution of the random force, $\pm 2\dot{\alpha}_0$.

IV. DISCUSSION

In this paper we studied the statistical mechanics of thermally fluctuating elastic filaments with arbitrary spontaneous curvature and twist. We constructed the equations for the orientational correlation functions and for the persistence length of such filaments. We would like to stress that our theory describes arbitrarily large deviations of a long filament from its equilibrium shape; the only limitation is that fluctuations are small on microscopic length scales, of the order of the thickness of the filament. Furthermore, since the equilibrium shape and the fluctuations of the filaments are completely described by the set of spontaneous torsions $\{\omega_{0k}\}$ and its fluctuations $\{\delta\omega_k\}$, respectively, our theory is set up in the language of intrinsic geometry of the space curves. All the interesting statistical information is contained in the correlators of the triad vectors $\{\mathbf{t}\}$ which can be expressed in terms of the known correlators of the fluctuations $\{\delta\omega_k\}$, using the Frenet equations. Since these equations describe pure rotation of the triad vectors, this has the advantage that fluctuations of the torsions introduce only random rotations of the vectors of the triad, and preserve their unit norm. The use of intrinsic geometry automatically ensures that the inextensibility constraint is not violated in the process of thermal fluctuations and therefore does not even have to be considered explicitly in our approach. We would like to remind the readers that the formidable mathematical difficulties associated with attempts to introduce this constraint, have hindered the development of persistent chain type models in the past and led to the introduction of the mean spherical approximation in which the constraint is enforced only on the average, and to perturbative expansions about the straight rod limit.

The general formalism was then applied to helical filaments both with and without twist of the cross section about the centerline. In the latter case we found that weak thermal fluctuations are dominated by long-wavelength Goldstone modes that correspond to bending and twist of the coarse-grained filament (the rodlike chain). Such fluctuations distort the helix on length scales much larger than its natural period but do not affect its local structure and, in particular, do not change the angle of twist of the cross section about the centerline. Strong thermal fluctuations lead to melting of the helix, accompanied by complete loss of local helical structure. Depending on the parameters of the helix, the persistence length is a nonmonotonic function of the strength of thermal fluctuations, and may first increase and then decrease as the amplitude of fluctuations is increased. Resonant peaks and dips in plots of the persistence length versus the spontaneous rate of twist are observed both for small twist rates and for rates equal to half the total curvature of the helix, phenomena which bear some formal similarity to stochastic resonances.

There are several possible directions in which the present paper can be extended. We did not consider here the effects of excluded volume and other nonelastic interactions, on the statistical properties of fluctuating filaments. Such an analysis requires the introduction of a field theoretical description of the filaments [26]. While this approach is interesting in its own right, we expect that the excluded volume exponent for the scaling of the end-to-end distance of a single filament will be identical to that of a Gaussian polymer chain (self-avoiding random walk). However, new effects related to liquid-crystalline ordering are expected in dense phases of such filaments. Another possible extension of the model relates to the elasticity of random heteropolymers, with quenched distribution of elastic constants and/or spontaneous torsions [27].

A natural application of our theory involves the modeling of mechanical properties and conformational statistics of chiral biomolecules such as DNA and RNA. The advantage of our theory is that it allows us to take into account, in an exact manner, the effects of thermal fluctuations on the persistence length and other elastic parameters of the filament. Thus, the generalization of the theory to include the effect of tensile forces and torques applied to the ends of the filament, is expected to lead to new predictions for mechanical stretching experiments in the intermediate deformation regime, for tensile forces that affect the global but not the local (on length scales $\leqslant l_p$) conformation of the filament. Measurements of the effect of elongation on thermal fluctuations of the molecule, can give information about its elastic constants, and help resolve long-standing questions regarding the natural curvature of DNA [28,29]. It is interesting to compare our expression for the persistence length to that of Trifonov *et al.* [28] who proposed that the apparent persistence length l_a of DNA depends not only on the rigidity (dynamic persistence length l_d), but also on the intrinsic curvature of the molecule (static persistence length l_s). The apparent persistence length is given in terms of the two others as

$$\frac{1}{l_a}=\frac{1}{l_d}+\frac{1}{l_s}. \tag{56}$$

Note that the philosophy of the above approach is very similar to ours — we begin with filaments which have some given intrinsic length (spontaneous radius of curvature/torsion), and find that the interplay between this length and thermal fluctuations gives rise to a persistence length l_p. In fact, taking for simplicity the case of a circular cross section, $a_1=a_2$, our expression Eq. (35), can be recast into the form of Eq. (56), with

$$l_a=l_p, \quad l_d=a_1, \quad l_s=\kappa_0^{-2}(\gamma_1+\tau_0^2/\gamma_1). \tag{57}$$

Indeed, in our model, a_1 is the bare persistence length that determines the length scale on which the filament is deformed by thermal bending and torsion fluctuations. Our analog of the static persistence length l_s depends on the spontaneous bending rate κ_0 and diverges in the case of a straight filament ($\kappa_0\rightarrow 0$), in which case $l_a\rightarrow l_d$. If we make the further assumption that twist rigidity is much smaller than the bending rigidity, $a_3\ll a_1$, the static persistence length becomes independent of the bending rigidity and depends on both the spontaneous curvature and the twist rigidity. Note, however, that the resulting κ_0^{-2} dependence of l_s differs from the originally proposed one (κ_0^{-1}) [28].

Another possible application of our theory involves a new way of looking into the protein folding problem. Usually, one assumes that the folded conformation of proteins is determined by the interactions between the constituent amino acids. A different approach, more closely related to the present paper, would be to reverse the common logic: instead of trying to understand what kind of spatial structure will result for a given primary sequence of amino acids, one can begin with a known equilibrium shape (native state) and attempt to identify the parameters of an effective filament (distributions of spontaneous torsions $\{\omega_{0i}(s)\}$) which will give rise to this three-dimensional structure [30]. Knowledge about the fluctuations and the melting of proteins can then be used to determine the distribution of the bare persistence lengths $\{a_i(s)\}$. Note that using $R_{ij}(s,s')=t_i(s)t_j(s')$, and Eqs. (16) and (21), yields

$$\gamma_i\delta_{ik}+\sum_l \varepsilon_{ikl}\omega_{0l}=\lim_{\Delta s\to 0^+}\frac{1}{\Delta s}[\delta_{ik}-\langle t_i(s)t_k(s-\Delta s)\rangle].$$

The diagonal elements of the correlator $\langle t_i(s)t_k(s-\Delta s)\rangle$ determine the $\{\gamma_i\}$ coefficients (and, consequently, the bare persistence lengths $\{a_i\}$), the nondiagonal elements determine the set $\{\omega_{0i}(s)\}$. We conclude that measurements of local correlations between the directions of the principal axes of symmetry of a fluctuating filament can, in principle, provide complete information about its equilibrium shape and elastic properties. While the question of whether such an approach can be successfully implemented in order to determine the relation between primary sequence and ternary structure remains open, our insights about the statistical properties of fluctuating filaments are clearly applicable to modeling of α helices and other elements (e.g., β sheets) of secondary structure of proteins.

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APPENDIX A: CALCULATION OF CORRELATION FUNCTIONS

We begin with the construction of the eigenvectors of the matrix $\mathbf{\Lambda}$, defined by Eq. (21), in the case $\Delta>0$ [see Eq. (28)], when there is one real eigenvalue λ_1 and two complex ones, $\lambda_R\pm i\omega$. Expanding this matrix over its eigenvectors, we get

$$\Lambda_{ij}=\lambda_1\overline{u}_iu_j+(\lambda_R+i\omega)\overline{v}_iv_j^*+(\lambda_R-i\omega)\overline{v}_i^*v_j, \quad \text{(A1)}$$

where the eigenvectors $\mathbf{u}$, $\overline{\mathbf{u}}$, $\mathbf{v}$, $\overline{\mathbf{v}}$ (and the complex conjugates of the latter two, $\mathbf{v}^*$ and $\overline{\mathbf{v}}^*$) obey the orthonormality conditions

$$\sum_{i=1}^3 \overline{u}_iu_i=\sum_{i=1}^3 \overline{v}_iv_i^*=1, \quad \sum_{i=1}^3 \overline{u}_iv_i=\sum_{i=1}^3 \overline{v}_iu_i=\sum_{i=1}^3 \overline{v}_iv_i=0. \quad \text{(A2)}$$

Using these conditions we can exponentiate the matrix $\mathbf{\Lambda}$

$$[e^{-\mathbf{\Lambda}s}]_{ij}=\overline{u}_iu_je^{-\lambda_1 s}+\overline{v}_iv_j^*e^{-(\lambda_R+i\omega)s}+\overline{v}_i^*v_je^{-(\lambda_R-i\omega)s}. \quad \text{(A3)}$$

Since we are interested only in the diagonal elements of this matrix, it is convenient to introduce the notations

$$c_i=\overline{v}_iv_i^*, \quad \sum_{i=1}^3 c_i=1. \quad \text{(A4)}$$

In addition, substituting $s=0$ in Eq. (A3) we get

$$\overline{u}_iu_i=1-c_i-c_i^*. \quad \text{(A5)}$$

In order to find the complex coefficients c_i we write down expressions for diagonal elements of the matrices $\mathbf{\Lambda}$ and $\mathbf{\Lambda}^2$

$$\gamma_i=(1-c_i-c_i^*)\lambda_1+c_i(\lambda_R+i\omega)+c_i^*(\lambda_R-i\omega),$$

$$(\gamma_i-\lambda_1)^2-\omega_0^2+\omega_{0i}^2=(1-c_i-c_i^*)\lambda_1^2+c_i(\lambda_R+i\omega)^2+c_i^*(\lambda_R-i\omega)^2. \quad \text{(A6)}$$

Looking for the solution of these equations in the form $c_i=\mathrm{Re}\,c_i+i\,\mathrm{Im}\,c_i$ we get expressions for real and imaginary parts of complex parameters c_i

$$2\,\mathrm{Re}\,c_i=\frac{-\gamma_i^2+2\varepsilon_i(\lambda_1+_R)+2\lambda_R\lambda_1+\omega_0^2-\omega_{0i}^2}{\omega^2+(\lambda_1-\lambda_R)^2},$$

$$2\omega\,\mathrm{Im}\,c_i=\lambda_1-\gamma_i+2(\lambda_R-\lambda_1)\mathrm{Re}\,c_i. \quad \text{(A7)}$$

APPENDIX B: PERSISTENCE LENGTH OF TWISTED HELIX

Since the persistence length is defined by the (3,3) element of the averaged rotation matrix, we will consider the $(i,3)$ component of Eq. (15) which, using Eq. (13), can be expressed as an equation for the corresponding correlator:

$$\frac{dg_i}{ds}=-\sum_l \Lambda_{il}(s+s')g_l, \quad g_i(s,s')\equiv\langle\mathbf{t}_i(s+s')\mathbf{t}_3(s')\rangle \quad \text{(B1)}$$

with initial conditions $g_1(0,s')=g_2(0,s')=0$ and $g_3(0,s')=1$. The matrix $\mathbf{\Lambda}(s+s')$ was defined in Eq. (50). Note that since the only s-dependent parameter of the helix is the angle of twist, the correlators $g_i(s,s')$ depend on s' only through the parameter $\alpha_0(s')=\alpha_0$ and, in order to simplify the notation, we will omit the second argument of these functions in the following.

It is convenient to introduce the complex function

$$f(s)=[g_1(s)+ig_2(s)]e^{-i(\dot{\alpha}_0s+\alpha_0)} \quad \text{(B2)}$$

such that f and g_3 obey the coupled equations

$$\frac{df}{ds}+\gamma_+f+\gamma_-f^*e^{-2i(\dot{\alpha}_0s+\alpha_0)}=-i\kappa_0g_3+i\tau_0f,$$

$$\frac{dg_3}{ds}+\gamma_3g_3=-i\kappa_0\frac{1}{2}(f-f^*). \quad \text{(B3)}$$

Taking a Laplace transform of these equations,

$$\tilde{f}(p) \equiv \int_0^\infty f(s) e^{-ps} ds, \quad \tilde{g}_3(p) \equiv \int_0^\infty g_3(s) e^{-ps} ds, \tag{B4}$$

where p is, in general, a complex parameter, we get

$$(p+\gamma_+ - i\tau_0)\tilde{f}(p) + i\kappa_0 \tilde{g}_3(p) = -\gamma_- e^{-2i\alpha_0} \tilde{f}^*(p+2i\dot{\alpha}_0), \tag{B5}$$

$$(p+\gamma_3)\tilde{g}_3(p) + i\kappa_0 \frac{1}{2}[\tilde{f}(p) - \tilde{f}^*(p)] = 1. \tag{B6}$$

In deriving these equations, we used the initial conditions, $f(0)=0$ and $g_3(0)=1$. Substituting $\tilde{g}_3$ from Eq. (B6) into Eq. (B5), we get a closed equation for the complex function $\tilde{f}$:

$$\left[(p+\gamma_+ - i\tau_0)(p+\gamma_3) + \frac{\kappa_0^2}{2}\right]\tilde{f}(p) + i\kappa_0 - \frac{\kappa_0^2}{2}\tilde{f}^*(p)$$
$$+ \gamma_-(p+\gamma_3) e^{-2i\alpha_0} \tilde{f}^*(p+2i\dot{\alpha}_0) = 0. \tag{B7}$$

Note that the persistence length is determined by $\tilde{g}_3(0)$, which can be expressed through $\tilde{f}(0) - \tilde{f}^*(0)$, Eq. (B6). The latter functions can be calculated from Eq. (B7), which upon substituting $p = -2in\dot{\alpha}_0$ (n integer), is recast in the standard form of difference equations,

$$a_n \kappa_0 \tilde{f}(-2in\dot{\alpha}_0) + 2i - \kappa_0 \tilde{f}^*(-2in\dot{\alpha}_0) + 2\gamma_- b_n$$
$$\times e^{-2i\alpha_0} \tilde{f}^*[-2i(n-1)\dot{\alpha}_0] = 0, \tag{B8}$$

where we defined

$$a_n = 1 + 2[\gamma_+ - i(\tau_0 + 2n\dot{\alpha}_0)](\gamma_3 - 2in\dot{\alpha}_0)/\kappa_0^2,$$
$$b_n = (\gamma_3 - 2in\dot{\alpha}_0)/\kappa_0. \tag{B9}$$

Since the persistence length is defined as the average of $\tilde{g}_3(0)$ with respect to α_0, it is convenient to introduce dimensionless functions h_n as

$$h_n = \kappa_0 \int_0^{2\pi} \frac{d\alpha_0}{2\pi} e^{2in\alpha_0} \tilde{f}(-2in\dot{\alpha}_0). \tag{B10}$$

We multiply Eq. (B8) by $\exp(2in\alpha_0)$ and average it with respect to α_0. Defining the parameter $\varepsilon = 2\gamma_-/\kappa_0$ we rewrite Eq. (B8) in the form

$$a_n h_n + 2i\delta_{n0} - h_{-n}^* + \varepsilon b_n h_{1-n}^* = 0 \tag{B11}$$

in which both h_n and h_m^* enter. In order to derive closed equations for the set of $\{h_n\}$ only, we apply complex conjugation to the above equation and change $n \to -n$. This yields

$$a_{-n}^* h_{-n}^* - 2i\delta_{n0} - h_n + \varepsilon b_n h_{n+1} = 0. \tag{B12}$$

Substituting the equations for h_{-n}^* and h_{1-n}^* into Eq. (B11) we find

$$(a_n - 1/a_{-n}^* - \varepsilon^2 b_n b_{n-1}/a_{1-n}^*) h_n + 2i(1 - 1/a_{-n}^*)\delta_{n0}$$
$$+ 2i\varepsilon \delta_{n1} b_n/a_{1-n}^* + \varepsilon h_{n+1} b_n/a_{-n}^*$$
$$+ \varepsilon h_{n-1} b_n/a_{1-n}^* = 0. \tag{B13}$$

Let us first consider the case $n \neq 0,1$. Introducing new variables y_n by the equality $h_{n+1} = \varepsilon y_n h_n$ we find

$$a_n - 1/a_{-n}^* - \varepsilon^2 b_n b_{n-1}/a_{1-n}^* + \varepsilon^2 y_n b_n/a_{-n}^*$$
$$+ y_{n-1}^{-1} b_n/a_{1-n}^* = 0. \tag{B14}$$

We now define

$$A_n = (a_n - 1/a_{-n}^*) a_{1-n}^*/b_n - \varepsilon^2 b_{n-1}, \quad B_n = a_{1-n}^*/a_{-n}^* \tag{B15}$$

and get the following recurrence relation, valid for $n = 2,3, \ldots$

$$A_n + 1/y_{n-1} + \varepsilon^2 B_n y_n = 0. \tag{B16}$$

We now take $n=2$ in the above equation, and solve for $y_1$in terms of y_2. Repeating this procedure (expressing y_2 in terms of y_3, etc.) we can write the solution as a continued fraction

$$y_1 = -1/\{A_2 - \varepsilon^2 B_2/[A_3 - \varepsilon^2 B_3/(A_4 - \cdots)]\}. \tag{B17}$$

Now consider the case $n=1$ in Eq. (B13). Using the definitions of A_1 and B_1, Eq. (B15), it can be recast into the form

$$(A_1 + \varepsilon^2 B_1 y_1) h_1 + 2i\varepsilon + \varepsilon h_0 = 0. \tag{B18}$$

In order to obtain a closed equation for h_0, we return to Eq. (B12) with $n=0$,

$$a_0^* h_0^* - 2i - h_0 + \varepsilon b_0 h_1 = 0. \tag{B19}$$

Eliminating h_1 from the above two equations we find

$$h_0 = -2i + \Xi h_0^*, \tag{B20}$$

where, using Eq. (B17), Ξ can be represented as a continued fraction:

$$\Xi = a_0^*/[1 + \varepsilon^2 b_0/(A_1 + \varepsilon^2 B_1 y_1)] \tag{B21}$$

$$= a_0^*/(1 + \varepsilon^2 b_0/\{A_1 - \varepsilon^2 B_1/[A_2 - \varepsilon^2 B_2/(A_3 - \cdots)]\}). \tag{B22}$$

The solution of Eq. (B20) is

$$h_0 = -2i \frac{1-\Xi}{1-|\Xi|^2}. \tag{B23}$$

Recall that h_0 was defined as the integral over α_0 of the function $\tilde{f}(0)$ [Eq. (B10)] which, in turn, determines the Laplace transform at $p=0$ of the correlator $\tilde{g}_3$ that appears in the definition of the persistence length, Eq. (51). Collecting the above expressions we find

$$l_p = \int_0^{2\pi} \frac{d\alpha_0}{2\pi} \tilde{g}_3(0) = \frac{1}{\gamma_3}\left[1 - i\frac{1}{2}(h_0 - h_0^*)\right] = \frac{\gamma_3^{-1}}{1 + (\Xi - 1)^{-1} + (\Xi^* - 1)^{-1}}. \tag{B24}$$

[1] P.J. Flory, *Principles of Polymer Chemistry* (Cornell University Press, Ithaca, NY, 1971).

[2] P.-G. deGennes, *Scaling Methods in Polymer Physics* (Cornell University Press, Ithaca, NY, 1979).

[3] P.J. Flory, *Statistical Mechanics of Chain Molecules* (Interscience, New York, 1969).

[4] S.B. Smith, L. Finzi, and C. Bustamante, Science **258**, 1122 (1992).

[5] T.T. Perkins, S.R. Quake, D.E. Smith, and S. Chu, Science **264**, 822 (1994).

[6] T.R. Strick, J.-F. Allemand, D. Bensimon, and V. Croquette, Science **271**, 1835 (1996).

[7] B. Houchmanzadeh, J.F. Marko, D. Chateney, and A. Libchaber, J. Cell Biol. **139**, 1 (1997).

[8] V. Katritch, C. Bustamante, and W.K. Olson, J. Mol. Biol. **295**, 29 (2000).

[9] M. Rief, M. Gautel, F. Oesterhelt, L.M. Fernandez, and H.E. Gaub, Science **276**, 1109 (1997).

[10] F.C. MacKintosh, J. Käs, and P.A. Janmey, Phys. Rev. Lett. **75**, 4425 (1995).

[11] D.K. Fygenson, M. Elbaum, B. Shraiman, and A. Libchaber, Phys. Rev. E **55**, 850 (1997).

[12] B. Hinner, M. Tempel, E. Sackmann, K. Kroy, and E. Frey, Phys. Rev. Lett. **81**, 2614 (1998).

[13] A.E.H. Love, *A Treatise on the Mathematical Theory of Elasticity* (Dover, New York, 1944).

[14] D. Garrivier and B. Fourcade, Europhys. Lett. **49**, 390 (2000).

[15] Y. Shi and J.E. Hearst, J. Chem. Phys. **101**, 5186 (1994).

[16] J.F. Marko and E.D. Siggia, Macromolecules **27**, 981 (1994).

[17] R.D. Kamien, T.C. Lubensky, P. Nelson, and C.S. O'Hern, Europhys. Lett. **38**, 237 (1997).

[18] C. Bouchiat and M. Mezard, Phys. Rev. Lett. **80**, 1556 (1998).

[19] J. Marko, Phys. Rev. E **57**, 2134 (1998).

[20] J.D. Moroz and P. Nelson, Macromolecules **31**, 6333 (1998).

[21] S. Panyukov and Y. Rabin, Phys. Rev. Lett. **85**, 2404 (2000).

[22] J.J. Koenderink, *Solid Shape* (MIT Press, Cambridge, MA, 1990).

[23] A.D. Drozdov and Y. Rabin, Phys. Rev. E (to be published).

[24] Strictly speaking, this derivation applies only to straight rods but the results are applicable to our case as long as the radii of curvature associated with the deformations are much larger than the thickness of the rod.

[25] V. Berdichevsky and M. Gitterman, Phys. Rev. E **60**, 1494 (1999).

[26] S. Panyukov and Y. Rabin (unpublished).

[27] P. Nelson, Phys. Rev. Lett. **80**, 5810 (1998).

[28] E.N. Trifonov, R.K.-Z. Tan, and S.C. Harvey, in *DNA Bending and Curvature*, edited by W.K. Olson, M.H. Sarma, and M. Sundaralingam (Adenine Press, Schenectady, NY, 1987).

[29] J. Bednar *et al.* J. Mol. Biol. **254**, 579 (1995).

[30] This approach was proposed by V.S. Pande, A.Yu. Grosberg, and T. Tanaka, Rev. Mod. Phys. **72**, 259 (2000). However, they assumed that primary structure is parametrized by binary interaction parameters between the amino acids, rather than by spontaneous torsion and elastic parameters of the protein molecule.