Biopolymer elasticity: Mechanics and thermal fluctuations

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We present an analytical study of the role of thermal fluctuations in shaping molecular elastic properties of semiflexible polymers. Our study interpolates between mechanics and statistical mechanics in a controlled way and shows how thermal fluctuations modify the elastic properties of biopolymers. We present a study of the minimum-energy configurations with explicit expressions for their energy and writhe and plots of the extension versus link for these configurations and a study of fluctuations around the local minima of energy and approximate analytical formulas for the free energy of stretched twisted polymers. The central result of our study is a closed-form expression for the leading thermal fluctuation correction to the free energy around the nonperturbative writhing family solution for the configuration of a biopolymer. From the derived formulas, the predictions of the wormlike chain model for molecular elasticity can be worked out for a comparison against numerical simulations and experiments.

I. INTRODUCTION

In recent years, the theoretical study of the elasticity of semiflexible polymers has emerged as an active area of research. These studies are motivated by micromanipulation experiments [1–3] on biopolymers in which single molecules are stretched and twisted to measure elastic properties. These experiments are designed to help in the understanding of the role of semiflexible polymer elasticity in the packaging of these polymers in a cell nucleus. Twist elasticity plays an important role in several biological functions. DNA, a long molecule (between micrometers and meters in length) that carries the genetic code, is neatly packed into the tiny cell nucleus, just a few micrometers across. The first step in packaging DNA in a cell nucleus involves the DNA-histone association, which makes use of supercoiling in an essential way. The process of DNA transcription can generate and be regulated by supercoiling [4].

The single-molecule experiments have been analyzed theoretically using the popular wormlike chain (WLC) model, which gives an excellent understanding of the bending elastic properties of DNA [5]. When the twist degree of freedom is explored by rotationally constraining the molecule the theoretical analysis gets complicated by subtle topological and differential geometric issues [6–9]. In a previous work [10] we treated these subtleties in the language of differential geometry and topology. Our present study builds on earlier mechanics-based research in this area [3,11–13] and goes on to incorporate the effects of thermal fluctuations in a quadratic approximation. We evaluate the partition function and present an explicit analytical form that can be compared against measured elastic properties or numerical simulations [14].

Two parallel streams of research have evolved in the study of semiflexible polymer elasticity. Some researchers use classical elasticity, which is conceptually simple but ignores thermal fluctuations that are important to the problem. Others use a statistical-mechanics approach that properly takes into account thermal fluctuations and entropic effects. This latter approach is beset by the geometrical and topological subtleties we alluded to earlier. In the real biological context of a cellular environment, these polymers are constantly jiggled around by thermal fluctuations and therefore a statistical-mechanics approach is necessary. Biological processes involve the entire range of flexibilities: Actin filaments, microtubules, and short DNA strands are energy dominated, while long DNA strands have appreciable entropy. The quantitative measure of flexibility is L/L_P, where L is the contour length of the polymer and L_P is its persistence length (16 μm for actin and 50 nm for DNA). In the energy-dominated short-polymer regime classical elasticity gives a fair understanding of the problem. In the absence of external forces and torques, long polymers require a statistical-mechanics treatment since the entropic contribution is not small. In this paper we consider polymers subject to a stretching force and torque and develop a theory of thermal fluctuations around the minimum-energy configurations. These minimum-energy configurations come in two families, the straight line family (SLF) and the writhing family (WF). The present paper relies on a key result proved in Ref. [15] that these minimum-energy configurations meet the conditions of Fuller's theorem [16,17]. This permits us to use a simplified local treatment of the writhe in our study of fluctuations about the minimum. We first present a treatment based on classical elasticity and then incorporate thermal fluctuations around the minimum-energy configurations. Members of the writhing family are far from straight and so our analysis goes far beyond perturbation theory about the straight line. While our general analysis applies to polymers of all lengths, some of our analytical formulas are derived in the long-polymer limit. Our treatment is analytical and complementary to numerical studies [14,18,19].

Two extreme situations are relatively well understood. If the polymer is nearly straight, one can use perturbation theory [20–22] about the straight line to calculate its elastic properties. In the opposite extreme when the polymer is wrung hard, it buckles and forms plectonemic structures [16,17,23] that are stabilized by the finite thickness of the DNA. The transitional regime where the polymer is neither straight nor plectonemic is not as easy. Perturbation theory about the straight line is not applicable and we do not benefit from simplifications that

arise from the energy-dominated plectonemic regime. More specifically, let the stretching force F be $2k_B T/L_P$ or higher. As we turn the bead to twist or wind up the molecule, it initially remains approximately straight. At high links the polymer buckles and winds around itself to form plectonemic structures. The intermediate-link regime, in which the polymer is neither straight nor plectonemic, is the subject of this paper. (These three regimes of low links, intermediate links, and high links, have also been referred to in Ref. [14] as straight-line, buckling, and supercoiled regimes.) We will study the straight-line and the writhing solutions and fluctuations around these solutions.

The central goal of this paper is to derive explicit analytic expressions for the free energy and the writhe of a twisted stretched polymer. Derivatives of the free-energy expressions computed here connect to measurable quantities that can be probed via single-molecule experiments or simulations. We arrive at the free energies by focusing on the stationary points of the energy functional dominating the partition function. While there is interest in the elastic properties of DNA at all length scales, the experiments [1,2,4] deal with long polymers, many times the persistence length of about 50 nm. Many theoretical treatments [14,24–26] also focus on this regime of long polymers, which leads to some simplification.

In order to formulate the problem we start from an idealized experiment. Let us imagine that a twist-storing semiflexible polymer (such as dsDNA or filamentary actin) is attached to a glass slide at one end and a bead at the other so that its tangent vector at both ends is constrained to point in the $\hat{z}$ direction. Supposing the glass slide end to be at the origin, we apply a force F and torque τ (both in the $\hat{z}$ direction) on the bead. The elastic response of the polymer can be described by its extension $z = \vec{r} \cdot \hat{F}$ (the position of the bead) and its link (the number of times the bead has turned about the $\hat{z}$ axis). Real experiments on DNA differ from the one described above mainly in that they deal with long polymers and it is usually the link rather than the torque that is held constant, though the experiments [2,27] could easily be adapted by using a feedback loop to maintain constant torque.

Actually, we will be interested in a wider class of thought experiments of which the above is a particular realization. We may, for instance, use more general boundary conditions, fixing the tangent vector at the ends to $\hat{t}(0) = \hat{t}_i$ and $\hat{t}(L) = \hat{t}_f$. (The force is still along $\hat{z}$ and the torque along $\hat{t}_f$.) As theorists, we may also explore the entire range of flexibilities and parameters, which are not practical in the currently accessible regime. Our study is not restricted to long polymers, though we will sometimes specialize to this case for simplicity. We will also regard all our parameters (contour length, persistence length, force, torque, temperature, elastic constants, and boundary conditions) as tunable without worrying about how this may be experimentally achieved. In the mechanical limit our analysis reduces to the classical theory of beams and cables. Our larger aim is a comprehensive understanding of the entire range of parameters covering the range from beams and cables to DNA. Thus we are not immediately concerned with any one experiment, but a class of them. Detailed treatments of actual experiments are contained in Refs. [3,23]. For example, these treatments take into account the chiral nature of the DNA molecule, which we ignore. We are more concerned here with mathematically working out the predictions of the simplest

wormlike chain model rather than a detailed modeling of specific experimental data. However, our focus is experimental relevance and we calculate from the model quantities such as link-extension relations, which are measured in laboratories.

The paper is organized as follows. Section II deals with the mechanics of semiflexible polymers. We start by noting that the problem of computing the partition function of a twist-storing polymer separates into two parts, a simple Gaussian over the twist and a harder problem involving the writhe. We derive the Euler-Lagrange (EL) equations describing the minimum-energy configurations. The solutions of the EL equations can be expressed using elliptic integrals. Section III deals with the role of thermal fluctuations. We perform the second variation of the energy and explain the methods we use to compute the thermal correction to the free energy due to fluctuations about the classical solutions. This gives the main result of our paper, an approximate expression for the free energy of a stretched twisted polymer that takes into account thermal fluctuations around nonperturbative solutions. We then suggest calculational schemes (Sec. IV) for a more ambitious treatment of thermal fluctuations. We end with some concluding remarks in Sec. V.

II. MECHANICS

We model the twist-storing polymer by a ribbon $[\vec{x}(s), \hat{e}^i(s)]$ ($i = 1, 2, 3$), which is a framed[1] space curve. Here $\vec{x}(s)$ describes the curve, $\hat{t}(s) = \frac{d\vec{x}}{ds}$ is its tangent vector, and $e^i(s)$ is the framing, with s the arclength parameter along the curve ranging from 0 to L, the contour length of the curve. Since one end is fixed at the origin, $\vec{x}(0) = 0$. The tangent vectors at both ends $\hat{t}_i = \hat{t}(0)$ and $\hat{t}_f = \hat{t}(L)$ are fixed. A force $\vec{F} = F\hat{z}$ along the $\hat{z}$ direction is applied at the free end at $\vec{x}(L)$ and also a torque τ is applied along the fixed end tangent vector $\hat{t}(L)$. We suppose $\hat{e}_3 = \hat{t}(s)$ and refer to $\hat{e}_1(s)$ as the ribbon vector that describes the twisting of the polymer about its backbone. Defining the angular velocity $\vec{\Omega}$ via

$$\frac{d\hat{e}_i}{ds} = \vec{\Omega} \times \hat{e}_i, \tag{1}$$

the body-fixed angular velocity components of $\vec{\Omega}$ are $\Omega_i = \hat{e}_i \cdot \vec{\Omega}$. The expression for the energy of a configuration is

$$\mathcal{E}_0(\mathcal{C}) = \int_0^L \frac{1}{2} \left[A \left(\Omega_1^2 + \Omega_2^2 \right) + C \Omega_3^2 \right] ds - \int_0^L \vec{F} \hat{t}\, ds - 2\pi \tau \mathcal{L}, \tag{2}$$

where $\mathcal{L}$ is the number of times the bead is turned around the $\hat{t}_f$ axis. The mathematical problem we face is to compute the partition function

$$Z_0(F, \tau) = \sum_{\mathcal{C}} \exp - \left(\frac{\mathcal{E}_0(\mathcal{C})}{k_B T} \right). \tag{3}$$

In Eq. (3) the sum is over all allowed configurations of the ribbons [10]. The ribbon can be closed with a fixed reference

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[1] Note that we *do not* use Serret-Frenet framing, which is popular in this field. Serret-Frenet framing becomes ill defined over locally straight pieces of the curve.

ribbon that goes a long way in the $\hat{t}_f$ direction, makes a wide circuit, and returns to the origin along the $\hat{t}_i$ direction.[2] In the calculations below we will set both A and $k_B T$ equal to unity and restore them when necessary.

We use the celebrated relation [28,29] decomposing the link into a twist and writhe

$$\mathcal{L} = \mathcal{T} + \mathcal{W}_{CW}, \quad (4)$$

where $\mathcal{T} = 2\pi \int \Omega_3(s)ds$ and $\mathcal{W}_{CW}$ is the writhe. The writhe is a nonlocal quantity defined on closed simple curves: Let the arclength parameter s range over the entire length L_0 of the closed ribbon (real ribbon plus reference ribbon) and let us consider the curve $\vec{x}(s)$ to be a periodic function of s with period L_0. Let $\vec{R}(s,\sigma) = \vec{x}(s+\sigma) - \vec{x}(s)$. The Călugăreanu-White writhe is given by [16,17,28–30]

$$\mathcal{W}_{CW} = \frac{1}{4\pi} \oint_0^{L_0} ds \int_{0+}^{L_0-} d\sigma \left(\frac{d\hat{R}(s,\sigma)}{ds} \times \frac{d\hat{R}(s,\sigma)}{d\sigma} \right) \cdot \hat{R}. \quad (5)$$

Because of White's theorem (4), we find that the problem neatly splits [10,16,20] into two parts

$$Z_0(F,\tau) = Z_1(F,\tau)Z_2(\tau), \quad (6)$$

where

$$Z_1(F,\tau) = \int \mathcal{D}[\vec{x}(s)]\exp - [\mathcal{E}_1[\vec{x}(s)] \quad (7)$$

and

$$\mathcal{E}_1[\vec{x}(s)] = \int_0^L ds \, \frac{1}{2} \frac{d\hat{t}}{ds} \cdot \frac{d\hat{t}}{ds} - \int_0^L \vec{F} \cdot \hat{t} ds - 2\pi\tau \mathcal{W}_{CW}. \quad (8)$$

The term $Z_2(\tau)$ is given by a Boltzmann sum over framings with $\mathcal{E}_2$ given by

$$\mathcal{E}_2(\tau) = \int ds \left(\frac{C}{2} \Omega_3^2 - \tau 2\pi \mathcal{T} \right). \quad (9)$$

Further, $Z_2(\tau)$ is easily evaluated as a Gaussian integral and gives

$$Z_2(\tau) = \exp\left(\frac{\tau^2 L}{2C} \right) = \exp[-\mathcal{G}_2(\tau)]. \quad (10)$$

Thus the problem that remains is to compute $Z_1(F,\tau)$ [Eq. (7)], which depends only on the curve $\vec{x}(s)$ and not its framing.

This problem is hard because of the appearance of the writhe $\mathcal{W}_{CW}[\vec{x}(s)]$, which is a nonlocal function of the curve. However, we will make progress by noting that variations of the writhe are local [10,15]. We will compute the partition function using the assumption that for high stretch forces, the sum over curves is dominated by configurations near minima of the energy. The approximation consists of using an expansion of the energy about the minimum-energy configuration and keeping fluctuation terms about the minimum to quadratic order. This section deals with the minimum of energy and

the following one with fluctuations. We thus derive explicit analytical expressions for the Gibbs free energy of the polymer $\mathcal{G}(F,\tau)$, which can be used to compute its elastic response.

Theoretically, it is easiest to deal with the constant torque ensemble. In the quadratic approximation, the conjugate ensembles are equivalent [31–34] even for polymers of finite length. This equivalence of ensembles holds exactly for long polymers since these are at the thermodynamic limit. (See, however, the remarks below concerning stability in different ensembles.)

In this section we ignore thermal fluctuations and consider a purely classical-mechanics analysis to study the configurations of a torsionally constrained stretched semiflexible biopolymer such as DNA. The classical problem of the torsional buckling of a bent and twisted closed wire was considered early on by Michell [6]. In the modern context of DNA, it was discussed by Benham [7,8] and Le Bret [9]. The problem also arises in the laying of oceanic cables and the writhing solutions we deal with in this paper were earlier discussed by Coyne [35]. A detailed treatment has also been given by Nizette and Goriely [36]. More recent treatments exist in the literature [11–13,16,37,38]. We will present a slightly different perspective, based on analogies with classical mechanics, which helps us incorporate thermal fluctuations.

The central quantity of interest is the bending, stretching, and writhing energy

$$\mathcal{E}(\mathcal{C}) = \frac{1}{2} \int_0^L \dot{\hat{t}} \cdot \dot{\hat{t}} \, ds - \int_0^L \vec{F} \cdot \hat{t} \, ds - 2\pi\tau \mathcal{W}_{CW} \quad (11)$$

of a space curve $\vec{x}(s)$ whose tangent vector is $\hat{t}(s) = \frac{d\vec{x}}{ds}$. The tangent vector is varied subject to the boundary conditions $\hat{t}(0) = \hat{t}_i$ and $\hat{t}(L) = \hat{t}_f$ fixing the tangent vector at both ends of the curve. Remembering that the variations of writhe are local [10,15], we arrive at the Euler-Lagrange equations [see Eq. (36) below] from Eq. (11):

$$-\ddot{\hat{t}} - \vec{F} = \tau(\hat{t} \times \dot{\hat{t}}) - \gamma\hat{t}, \quad (12)$$

where the term $\gamma\hat{t}$ arises since $\hat{t} \cdot \hat{t} = 1$. The problem is formally similar to a symmetric top, a fact that was well known to Kirchoff. The analogy is useful for integrating the Euler-Lagrange equations. We use quotes for the analogous top quantities. The "kinetic energy" is given by $T = \frac{1}{2}\dot{\hat{t}} \cdot \dot{\hat{t}}$ and the "potential energy" is $V = \vec{F} \cdot \hat{t}$. The total "energy"

$$\mathcal{H} = T + V = \frac{1}{2}\dot{\hat{t}} \cdot \dot{\hat{t}} + \vec{F} \cdot \hat{t} = \frac{1}{2}(\dot{\theta}^2 + \sin^2\theta\dot{\varphi}^2) + F\cos\theta \quad (13)$$

is a constant of the motion as is the z component of the "angular momentum"

$$J_z = (t \times \dot{\hat{t}})_z - \tau\hat{t}_z = \sin^2\theta\dot{\varphi} - \tau\cos\theta, \quad (14)$$

where we have introduced the usual polar coordinates on the sphere of tangent vectors. Using these "constants of the motion," we reduce the problem to quadratures as described in Ref. [39]. The basic equations are

$$\frac{\dot{\theta}^2}{2} = \mathcal{H} - F\cos\theta - \frac{(J_z + \tau\cos\theta)^2}{2\sin^2\theta}, \quad (15)$$

$$\dot{\varphi} = \frac{J_z + \tau\cos\theta}{\sin^2\theta}. \quad (16)$$

Setting $u = \cos\theta$, we find that

$$\dot{u} = \epsilon f(u), \qquad (17)$$

where $f(u) = \sqrt{\mathcal{P}(u)}$, $\quad \epsilon = \pm 1$, and

$$\mathcal{P}(u) \equiv 2(\mathcal{H} - Fu)(1 - u^2) - (J_z + \tau u)^2 \qquad (18)$$

is a cubic polynomial in u. Integration of Eq. (17) gives $u(s)$ in terms of elliptic integrals and Eq. (16) gives $\varphi(s)$. Further integration of the tangent vector gives us the polymer configuration $\vec{x}(s)$ in real space. Since our polymer is under stretch, we assume that F is positive. The term $\mathcal{P}(u)$ is positive for large positive u and negative (or zero) at $u = 1$ and -1. In order for there to be a physical solution there must be two real roots b and c (turning points) in the physical range of $u = \cos\theta$, $-1 \leqslant c \leqslant b \leqslant 1$, and a third real root $a \geqslant 1$. We have ordered the three roots so that $a \geqslant b \geqslant c$. The boundary data must lie between c and b, with $c \geqslant u_i, u_f \leqslant b$. The "motion" goes from u_i to u_f, possibly passing through turning points on its way.

The integration constants $\mathcal{H}$ and J_z are determined by the length of the polymer and the boundary conditions. From Hamilton-Jacobi theory we can write the energy of the solution of length L going from u_i, φ_i to u_f, φ_f as

$$\mathcal{E}(u_i, u_f, \varphi_i, \varphi_f, L) = \int_{u_i}^{u_f} du\, f(u) - \mathcal{H}L + J_z\Phi, \quad (19)$$

where L and $\Phi = \varphi_f - \varphi_i$, given by

$$L = \int_{u_i}^{u_f} \frac{du}{f(u)} \qquad (20)$$

and

$$\Phi = \int_{u_i}^{u_f} \frac{du}{f(u)} h(u), \qquad (21)$$

determine $\mathcal{H}$ and J_z and $h(u) = (J_z + \tau u)/(1 - u^2)$. These integrations must include turning points if there are any. For instance, if u goes from u_i to u_f via c, $\int_{u_i}^{u_f} = \int_c^{u_i} + \int_c^{u_f}$, allowing for sign changes in the integrand (17). We will use these relations below in computing the fluctuation determinant in the following section.

A. Symmetric boundary conditions

As an illustrative example, we specialize to boundary conditions $\hat{t}_i = \hat{t}_f = \hat{z}$. These boundary conditions imply that $\theta = 0$ is a point on the solution. Since $\dot{\theta}^2$ has to be finite and non-negative at $\theta = 0$, we have $J_z = -\tau$ and $\mathcal{H} \geqslant F$. The form of $\mathcal{P}(u)$ simplifies to

$$\mathcal{P}(u) = (1 - u)[2(\mathcal{H} - Fu)(1 + u) - \tau^2(1 - u)]$$

and Eq. (16) reduces to

$$\dot{\varphi} = -\frac{\tau}{1 + u}. \qquad (22)$$

We want to find the minimum-energy configurations subject to the writhe constraint. These configurations satisfy the Euler-Lagrange equations. The simplest solution is the straight line $\hat{t}(s) = \hat{z}$ or $\theta(s) = 0$ for all s. This configuration globally minimizes $\mathcal{E}(\mathcal{C})$,

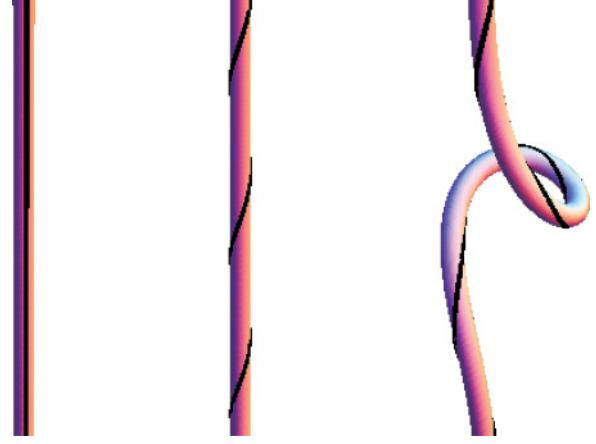$$\mathcal{E}_{ST} = -FL, \qquad (23)$$

FIG. 1. (Color online) Typical polymer configurations solving the Euler-Lagrange equations. From left to right the parameters link, twist, and writhe $(\mathcal{L}, \mathcal{T}, \mathcal{W})$ are the untwisted straight line $(0,0,0)$, the twisted straight line $(3.4, 3.4, 0)$, and the writhing solution $(3.6, 3.4, 0.2)$. The tube represents the polymer backbone and the black line represents the twisting of the ribbon vector about the backbone.

but since $\mathcal{W}_{CW} = 0$, it cannot accommodate writhe. For this we need the writhing solution, in which the tangent vector $\hat{t}$ starts from $\hat{z}$ at $s = 0$ and θ increases to a maximum of θ_0 at $s = s_0$, the turning point, and then returns to $\hat{z}$ at $s = 2s_0$. The period of the orbit is $P = 2s_0$. As shown in Ref. [15], the configuration is a local minimum of the energy only if the length L of the polymer is equal to P (and not a multiple of it). We illustrate polymer configurations for the untwisted straight line, the twisted straight line, and the writhing family (Fig. 1).

It has been shown earlier [15] that the local minima of the energy are "good curves" [24], i.e., they satisfy the conditions of Fuller's [16,17] theorem, and so the writhe can be computed from a simple local formula[3]

$$\mathcal{W}_{CW} = \int_{u_i}^{u_f} \frac{du(1 - u)h(u)}{f(u)}. \qquad (24)$$

Below we will sometimes drop the subscript on $\mathcal{W}_{CW}$; it is understood that we deal only with good curves.

B. Long polymers

One gets further simplification by confining to the limit of long polymers. In this limit the "period" $P = L \to \infty$. As a result, the doubly periodic functions that appear for finite L become simple trigonometric functions (since one of the periods tends to infinity). We will briefly restrict our attention to infinitely long polymers in this section to arrive at an explicit analytical form for the writhing family of solitons. To reach this limit, the length (20) must diverge. For $\mathcal{H} > F$, the function $\mathcal{P}(u) = f^2(u)$ vanishes linearly as $u \to 1$. The corresponding integral converges and does not lead to $L \to \infty$. Thus we must require that $\mathcal{P}(u)$ vanishes quadratically as $u \to 1$ so that $\int_{u_0}^1 \frac{du}{f(u)}$ diverges logarithmically at the upper limit. This situation obtains if $\mathcal{P}(u)$ has coincident roots at the upper

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[3]As a side remark we mention that our approach is guided by geometric phase ideas [40–43].

limit. Now, demanding that $\frac{\mathcal{P}(u)}{(1-u)}$ vanishes as we take $u \to 1$ in Eq. (17) gives us the condition $\mathcal{H} = F$. Thus the form of $\mathcal{P}(u)$ simplifies to

$$\mathcal{P}(u) = (1-u)^2 [2F(1+u) - \tau^2].$$

The turning points of u are at $u_{\max} = 1$ and $u_{\min} = u_0$, where

$$u_0 = \frac{\tau^2}{2F} - 1.$$

The solutions are found by elementary integration [11,44]

$$u(s) = (1 - u_0)\tanh^2 \mu(s - s_0) + u_0, \tag{25}$$

$$\varphi(s) = -\frac{\tau(s - s_0)}{2} - \arctan\left(\frac{2\mu}{\tau}\tanh\mu(s - s_0)\right), \tag{26}$$

where $\mu^2 = F - \tau^2/4$. The energy of the writhing family parametrized by F, τ, and L is given by

$$\mathcal{E}_W = -FL + 8\mu \tanh\frac{\mu L}{2} - 2\pi\tau \mathcal{W}_{CW}(\tau). \tag{27}$$

Since we have already established [15] that the writhing family consists of good curves [24] we may compute the writhe using the simpler Fuller formula $\mathcal{W}_F$, which (apart from normalization) measures the solid angle swept out by the unique shorter geodesic connecting the tangent vector to the north pole. We find by a straightforward calculation that the writhe of the writhing family is

$$\mathcal{W}_{CW} = \mathcal{W}_F = \frac{2 \,\mathrm{sgn}[\tau]}{\pi}\arctan\left(\frac{2\mu}{|\tau|}\tanh\frac{\mu L}{2}\right), \tag{28}$$

in agreement with Ref. [3]. Including the twist energy (10) $-\tau^2 L/2C$, the Gibbs free energy $\mathcal{G}_W(F,\tau)$ of the writhing family in the mechanics approximation is

$$\mathcal{G}_{\mathcal{W}}^{cl}(F,\tau) = -FL + 8\mu \tanh\left(\frac{\mu L}{2}\right) - 2\pi\tau \mathcal{W}_{CW}(F,\tau)$$
$$- L\tau^2/2C, \tag{29}$$

where $\mathcal{W}_{CW}$ is given by Eq. (28). Correspondingly, the Gibbs free energy $\mathcal{G}(F,\tau)$ of the straight-line family in the mechanics approximation is

$$\mathcal{G}_{SL}^{cl}(F,\tau) = -FL - \frac{L\tau^2}{2C}. \tag{30}$$

These two Gibbs free energies are plotted in Fig. 2 as functions of τ for a fixed force. In our expressions (28) and (29) for the energy and writhe of the writhing family, we have retained expressions like $\tanh(\mu L/2)$, which become 1 in the long-polymer limit provided μ is not small [11]. If one drops these expressions our energy difference coincides with that in Refs. [11,13] after correcting for an overall factor ($\sqrt{F/2}$). [Reference [13] also contains misprints in Eqs. (13) and (16).]

The writhing family always has a higher energy [11] than the straight-line family for fixed force and torque. However, this difference is not extensive in the length L and remains finite as $L \to \infty$. The energy difference at zero torque is $8\sqrt{FA}$. At higher torques (see Fig. 1) this energy difference narrows and disappears at the buckling torque ($\sqrt{4FA}$, for long polymers). At the buckling torque, the writhing solution
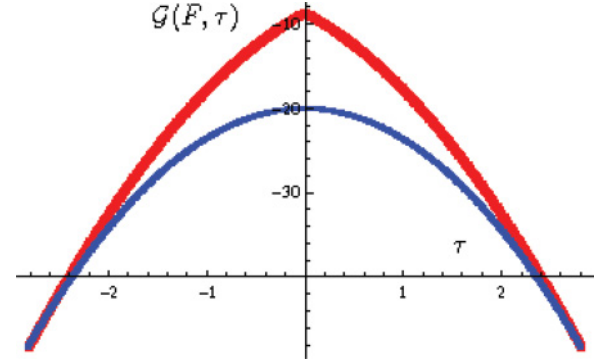

FIG. 2. (Color online) Gibbs free energies $\mathcal{G}(F,\tau)$ (from a purely mechanical approach) of the writhing family (thick red curve) and the straight-line family (thin blue line) plotted against torque τ for $L = 10$, $F = 2$, and twist elastic constant $C = 1.4$. The parameters A, $k_B T$, and L_P are set equal to 1. Note that the writhing family has higher energy and that this difference narrows as one nears buckling.

merges with the straight line and there are no classical solutions beyond this torque.

The writhing family becomes relevant when there is a need to accommodate writhe. As one can see by toying with a tube, applying a link to the ends of the tube results in deformations that cause the tube to deviate considerably from the straight line. If one applies a fixed link to the tube, the elastic response of the tube depends on C, the twist elastic constant. In Fig. 3 we plot the relative extension $\xi = z/L$ versus a link for a fixed force for large and small values of C. If C is large (Fig. 3), there is a critical link above which the SLF ceases to exist. The WF is then the only solution to the mechanics problem. Further increasing the link causes the writhing family to buckle into plectonemes. Thus the writhing family represents the transition from the straight line to plectonemes. The figures were generated by parametrically varying τ in equal steps and using LISTPLOT in MATHEMATICA. The dotted regions in Figs. 3–5 reveal discontinuous behavior.

For smaller values of C, the behavior is as shown in Fig. 4, which plots the relative extension of the polymer versus link. If one takes a straight ribbon and twists it, it remains straight
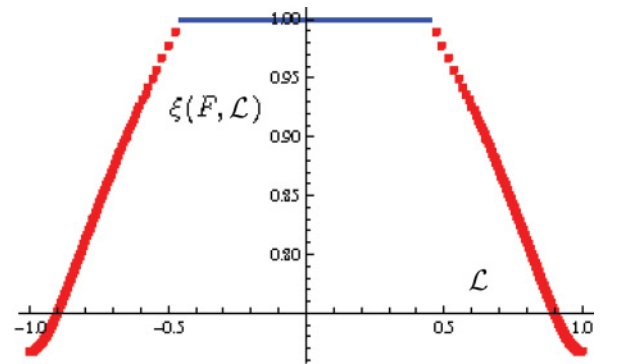

FIG. 3. (Color online) Relative extension ξ of the polymer versus the applied link for the straight-line family (thin blue line) and the writhing family (thick red line) for a stretching force of $F = 2$ (in dimensionless units of $k_B T/L_P$) and $L = 10$. This plot has a twist elasticity $C = 10$ in dimensionless units. At high links the straight-line family ceases to exist; only the writhing family can store writhe.
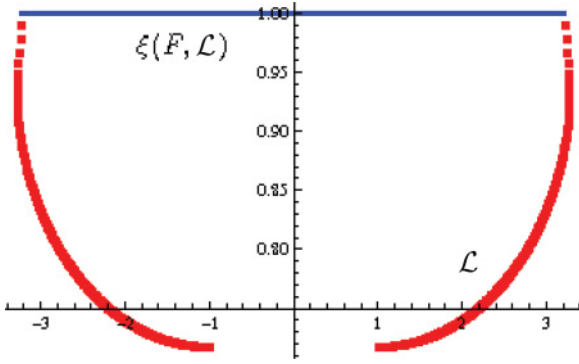
FIG. 4. (Color online) Relative extension ξ of the polymer versus applied link for the straight-line family (thin blue line) and the writhing family (thick red line). This plot uses $C = 1.4$ and a stretching force $F = 2$ and $L = 10$. Similar curves are seen in simulations [14].

and acquires link, following the thin blue line in the figure. At a critical torque, the straight line meets the writhing family (thick red line in the figure) and becomes unstable; it then follows the red line of the writhing family and buckles. This is exactly the behavior seen in the simulations of Ref. [14]. See the section of the curve from b_0 to b_1 in Fig. 2 of Ref. [14]. The rest of the curve in this figure of Ref. [14] is not relevant to our analysis since it involves self-contact of the polymer and goes beyond our analytic approach. A drop in extension at buckling has also been seen in the experiments of Ref. [2].

III. FLUCTUATIONS

In a thermal environment, the polymer fluctuates around its minimum-energy configuration. This contributes a fluctuation term [45] to the partition function and gives a thermal correction to the classical energy computed in the preceding section. Interpretation of the experiments on DNA elasticity [4] requires an inclusion of thermal effects. By taking appropriate derivatives of the free energy computed here one can find the theoretical predictions of the wormlike chain model for the experimentally accessible extension versus link or torque twist relations. (See Ref. [2] for experimental graphs of these.)
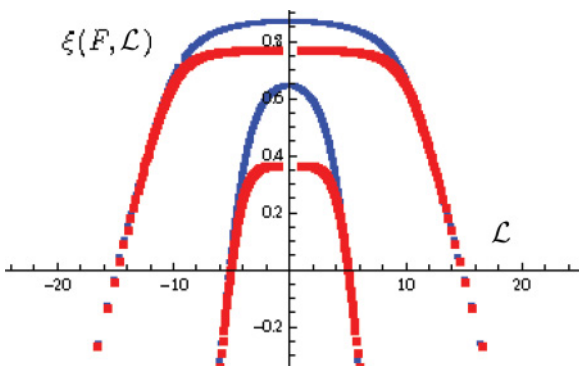

FIG. 5. (Color online) Relative extension ξ versus a link for a fluctuating polymer for the straight-line family (thin blue line) and the writhing family (thick red line). The inner curves correspond to $F = 2$ and the outer ones to $F = 15$ for $C = 2$.

For a system with a finite number of degrees of freedom q^i (for $i = 1, \ldots, N$) with a potential $V(q)$, the mechanical energy in equilibrium is given by the value of the potential $V(q^*)$ at its minimum q^* where

$$\partial V|_{q^*} = 0, \tag{31}$$

$$\partial \partial V|_{q^*} > 0, \tag{32}$$

where we formally write the gradient of V as ∂V and the Hessian matrix as $\partial \partial V$. (The Hessian is positive at local minima.) By performing a Gaussian integration, we find that the free energy in the presence of thermal fluctuations is

$$\mathcal{F} = V(q^*) + \frac{1}{2} k_B T \ln \det \partial \partial V|_{q^*}. \tag{33}$$

Our objective here is to present a calculation of the free energy of twisted semiflexible polymers by considering fluctuations about the mechanical solutions of the preceding section. At fixed force and torque we have the minimum-energy classical solution, which satisfies $\delta \mathcal{E}_{BS} = 2\pi \tau \delta \mathcal{W}_{CW}$, where $\mathcal{W}_{CW}$ is the writhe and $\mathcal{E}_{BS}$ is the bending and stretching energy. Formally, what we wish to do is to expand the energy and writhe around the classical configuration, retaining terms to quadratic order. The quadratic integration is a functional Gaussian integration that can then be performed and gives an answer in terms of the determinant of the fluctuation operator. The problem reduces to computing the determinant of the fluctuation operator.

Computing the functional determinant of the WLC polymer involves some subtleties. If one evaluates the determinant as an infinite product of eigenvalues, one finds that the product does not converge and needs regularization. This is an artifact of the fact that we have modeled the polymer as a space curve (or ribbon), which has an infinite number of degrees of freedom. Physically, we know that the polymer consists of a finite number of atoms and has finite free energy. There is a well-developed mathematical theory to deal with such situations. Multiplicative (additive) constants can be dropped in evaluating the partition function (free energy) and the infinities do not affect physical predictions. Another subtlety arises from zero modes of the classical solution. If the energy functional (as well as boundary conditions) has continuous symmetries that are broken by the classical solution, there are Goldstone modes that cost no energy and have zero eigenvalue. Such zero modes need separate handling. We will face both these problems below.

Let us now consider a family of polymer configurations parametrized by σ. The first variation of the energy is (where a prime denotes the σ derivative)

$$\mathcal{E}'[\hat{t}(s)] = \int_0^L (-\ddot{\hat{t}} \cdot \hat{t}' - \vec{F} \cdot \hat{t}') ds \tag{34}$$

and the first variation of the writhe is

$$\mathcal{W}'[\hat{t}(s)] = \frac{1}{2\pi} \int_0^L [\hat{t}(s) \times \dot{\hat{t}}(s)] \cdot \hat{t}'(s) ds. \tag{35}$$

The Euler-Lagrange equations read $\mathcal{E}' - 2\pi \tau \mathcal{W}' = 0$ or

$$\int_0^L \{-\ddot{\hat{t}} - \vec{F} - \tau[\hat{t}(s) \times \dot{\hat{t}}(s)]\} \cdot \hat{t}' ds = 0 \tag{36}$$

for arbitrary $\hat{t}'$ satisfying $\hat{t}' \cdot \hat{t} = 0$.

Now consider the second variation of the energy

$$\mathcal{E}''[\hat{t}(s)] = \int_0^L \dot{\hat{t}} \cdot \dot{\hat{t}}'' - \int_0^L \vec{F} \cdot \hat{t}'' + \int_0^L \dot{\hat{t}}' \cdot \dot{\hat{t}}' \, ds \quad (37)$$

and the writhe

$$\mathcal{W}''[\hat{t}(s)] = \frac{1}{2\pi} \int_0^L (\hat{t} \times \dot{\hat{t}}) \cdot \hat{t}'' \, ds + \frac{1}{2\pi} \int_0^L [\hat{t}(s) \times \dot{\hat{t}}'] \cdot \hat{t}' ds. \quad (38)$$

By computing $\mathcal{E}'' - 2\pi\tau\mathcal{W}''$ we find that the $\hat{t}''$ terms combine, due to the Euler-Lagrange equations (12), to give $\gamma \int_0^L \hat{t}' \cdot \hat{t}' ds$. (We use the identity $\hat{t} \cdot \hat{t}'' + \hat{t}' \cdot \hat{t}' = 0$.)

The form of the second variation functional is

$$\mathcal{E}'' - 2\pi\tau\mathcal{W}'' = \int_0^L \{\dot{\hat{t}}' \cdot \dot{\hat{t}}' - \tau[\hat{t}_{cl}(s) \times \dot{\hat{t}}'] \cdot \hat{t}' + \gamma_{cl}(s)\hat{t}' \cdot \hat{t}'\}ds. \quad (39)$$

This is a quadratic form in $\hat{t}'$, which we assume is non-negative [since we suppose that $\hat{t}_{cl}(s)$ is a minimum of the energy, either local or global]. The subscript on $\hat{t}_{cl}(s)$ and $\gamma_{cl}(s)$ indicates that it is the classical solution about which we wish to compute the determinant of this quadratic form. Varying $\hat{t}'$ to find the fluctuation operator (analogous to $\partial\partial V$ above), we find the eigenvalue equation [for $\hat{t}'$ satisfying $\hat{t}_{cl} \cdot \hat{t}'(s) = 0$]

$$\hat{O}\hat{t}' = -\ddot{\hat{t}}' - \tau\hat{t}_{cl} \times \dot{\hat{t}}' + \gamma_{cl}\hat{t}' = \lambda\hat{t}', \quad (40)$$

which gives us the spectrum of the fluctuation operator. If we could find all the eigenvalues of $\hat{O}$, we could compute its determinant. While this works in special cases (such as for the SLF) it not usually possible in general.

To compute the determinant of the fluctuation operator $\hat{O}$, we use a technique due to Gelfand and Yaglom (GY) [46,47]. This technique has been applied to the bend elasticity of polymers under stretch by Kulić *et al.* [48,49] and under compression by Emanuel*et al.* [50]. We consider the energy (11) as a function of the boundary conditions at the end of the polymer. (This is similar to considering the action in classical mechanics as a function of the end points in Hamilton-Jacobi theory.) We consider classical solutions that go from $\hat{t}_i$ at $s = 0$ to $\hat{t}_f$ at $s = L$. Although our physical problem fixes $\hat{t}_i$ and $\hat{t}_f$, the calculational technique (from GY) requires that we consider variations of the energy under such changes. The result of GY is that the computation of an infinite-dimensional functional determinant (the determinant of the operator $\hat{O}$) reduces to the computation of a finite-dimensional one, the van Vleck determinant of semiclassical physics. The final answer is expressed in terms of the variation of the classical energy with respect to variations of the boundary conditions. Let $\mathcal{E}(\hat{t}_i, \hat{t}_f, L)$ be the energy of the configuration of length L that goes from $\hat{t}_i$ to $\hat{t}_f$ (where $\hat{t}_i$ and $\hat{t}_f$ are the small variations of the boundary conditions about the actual boundary conditions in our problem). The infinite-dimensional functional determinant after regularization is reduced to the computation of a simple finite-dimensional determinant

$$\det\hat{O} = \left[\det \frac{\partial^2 \mathcal{E}}{\partial\hat{t}_i\partial\hat{t}_f}\right]^{-1} \quad (41)$$

evaluated at the physical boundary data. From Hamilton-Jacobi theory we can write the quantity in square brackets

in Eq. (41) as

$$\det \frac{\partial p_f^\alpha}{\partial t_i^\beta}, \quad (42)$$

where p_f^α is the "final momentum" $\vec{p}(L)$ of the classical configuration of length L that reaches $\hat{t}_f$ from $\hat{t}_i$.

The method of GY is used in many fields of physics (see, for example, Ref. [51]) for computing van Vleck determinants (fluctuation determinants). Reference [50] contains an application of the technique to polymer physics in which it is used to compute the thermal corrections to Euler buckling of polymers under compression. Our present application is to stretched and twisted polymers. The great advantage of GY's technique is that one does not have to diagonalize the fluctuation operator $\hat{O}$ to compute its determinant. All one has to do is study the linearized Euler-Lagrange equations.

We saw in the preceding section that the minima of the energy come in two families, the straight-line family and the writhing family. Since GY's technique may not be familiar to many readers, we illustrate its use by applying it to a case where the answer is known, the straight-line family. We calculate the fluctuation determinant by two methods, first explicitly diagonalizing the fluctuation operator and then by GY's technique. We then apply GY's idea to the writhing family to obtain our results.

A. Straight-line family

For the straightline family, $\hat{t}_{cl}(s) = \hat{z}$ (for any F, τ). As is well known [11,20], there is a range of (F, τ) [$\tau < \tau_c = \sqrt{4F + (\frac{\pi}{L})^2}$] for which the straight-line family is stable against perturbations. The eigenvalue equation (40) reads

$$-\ddot{\hat{t}}' - \tau(\hat{z} \times \dot{\hat{t}}') + F\hat{t}' = \lambda\hat{t}', \quad (43)$$

where $\hat{t}' \cdot \hat{z} = 0$ The eigenvalues are easily worked out and the thermal correction to the free energy is computed. This involves regularizing a divergent sum $2k_BT \sum_{n=1}^{\infty} \ln(\mu^2 + \frac{n^2\pi^2}{L^2})$, which can be done by standard methods. The final answer turns out to be $\det\hat{O} = (\sinh\mu L/\mu)^2$, which leads to the thermal correction to the free energy

$$k_BT \ln\left(\frac{\sinh L\mu}{\mu}\right), \quad (44)$$

in agreement with Ref. [22].

This computation can also be performed by linearizing the Euler-Lagrange equations about the straight line. After some simple transformations, it reduces to the inverted oscillator (in a magnetic field) and the solutions can be written in terms of hyperbolic functions (unlike the trigonometric functions of the usual oscillator). Varying the relations between final and initial data, we easily find

$$\delta Z(L) = \exp(-i\tau L/2)[(\cosh\mu L)\delta Z(0) \\ + \mu^{-1}(\sinh\mu L)\delta P(0)], \quad (45)$$

$$\delta P(L) = \exp(-i\tau L/2)[\mu(\sinh\mu L)\delta Z(0) \\ + (\cosh\mu L)\delta P(0)], \quad (46)$$

where $Z = \hat{t}_x + i\hat{t}_y$ are complex coordinates in the tangent plane at the north pole and P are the conjugate momenta. Setting $\delta Z(L) = 0$ and solving for $\delta P(L)$, performing the differentiation (42) yields the determinant

$$\det\hat{\mathcal{O}} = \left(\det \frac{\partial P(L)}{\partial Z(0)}\right)^{-1} = (\sinh \mu L/\mu)^2$$

as before. Computing $k_B T/2 \ln \det|\frac{\partial P(L)}{\partial Z(0)}|^2$ gives us the same answer as Eq. (44). This illustrates the efficacy of GY's technique in a familiar context.

B. Writhing family

For the writhing family, the eigenvalue equation (40) is considerably more complicated [note the presence of the functions $\hat{t}_{cl}(s)$ and $\gamma_{cl}(s)$] and the eigenvalues and eigenvectors are not available in closed form, but we can still use GY's method. The writhing family breaks the azimuthal symmetry (rotation about the $\hat{z}$ axis) that is present in the energy and the boundary conditions. As a result, the solution has zero modes that need careful handling. There are two routes open to us and we briefly describe both of them. We can alter the boundary conditions so that they break the azimuthal invariance. For instance, we could make one of $\hat{t}_i$ and $\hat{t}_f$ not point along the $\hat{z}$ direction. The other route is to exploit the symmetry of the rotational invariance and treat the azimuthal degrees of freedom exactly. This leaves a one-dimensional problem (θ or u), which we can treat either approximately or exactly, depending on the desired degree of accuracy. We present the main results of our analysis below.

C. Asymmetric boundary conditions

We suppose that one of u_i, φ_i and u_f, φ_f, the initial and final tangent vectors, is not in the $\hat{z}$ direction. We make a variation in the initial positions while holding the final positions fixed. We are interested in the resultant variation in the final momenta. To compute this, we proceed as follows, exploiting the integrability of the system. We will keep the final configuration (u_f, φ_f) fixed and perform variations in (u_i, φ_i), the initial configuration, and look at the variations in Φ, L, and $\mathcal{E}$. These are

$$\delta L = \frac{\epsilon_i \delta u_i}{f(u_i)} + \frac{\partial L}{\partial \mathcal{H}}\delta \mathcal{H} + \frac{\partial L}{\partial J_z}\delta J_z,$$

$$\delta \Phi = \frac{\epsilon_i \delta u_i}{f(u_i)}h(u_i) + \frac{\partial \Phi}{\partial \mathcal{H}}\delta \mathcal{H} + \frac{\partial \Phi}{\partial J_z}\delta J_z, \quad (47)$$

$$\delta \mathcal{E} = \epsilon_i f(u_i)\delta u_i + \delta J_z \Phi + J_z \delta \Phi - \delta \mathcal{H}L - \mathcal{H}\delta L.$$

The Jacobian of interest is Eq. (42), which can be expressed as (writing p_f for p_{u_f} and J_z for p_{φ_f})

$$\frac{\partial(p_f, J_z)}{\partial(u_i, \varphi_i)} = \frac{\partial(p_f, J_z)}{\partial(\mathcal{H}, J_z)}\frac{\partial(\mathcal{H}, J_z)}{\partial(u_i, \varphi_i)}.$$

From

$$\epsilon_f \delta p_f = \delta f(u_f)/\left(1 - u_f^2\right) = \frac{\delta \mathcal{H}}{f(u_f)} - \frac{h(u_f)}{f(u_f)}\delta J_z$$

we find

$$\begin{pmatrix} \delta p_f \\ \delta J_z \end{pmatrix} = \begin{pmatrix} \frac{\epsilon_f}{f(u_f)} & \frac{-h(u_f)\epsilon_f}{f(u_f)} \\ 0 & 1 \end{pmatrix}\begin{pmatrix} \delta \mathcal{H} \\ \delta J_z \end{pmatrix} = \mathcal{A}\begin{pmatrix} \delta \mathcal{H} \\ \delta J_z \end{pmatrix}, \quad (48)$$

where $\mathcal{A}$ is a 2×2 matrix defined by Eq. (48). Setting $\delta L = 0$ and $\delta \Phi = \delta(\varphi_2 - \varphi_i) = -\delta\varphi_i$ in Eq. (47) we find

$$\mathcal{D}\begin{pmatrix} \delta \mathcal{H} \\ \delta J_z \end{pmatrix} = \begin{pmatrix} \frac{\partial L}{\partial \mathcal{H}} & \frac{\partial L}{\partial J_z} \\ \frac{\partial \Phi}{\partial \mathcal{H}} & \frac{\partial \Phi}{\partial J_z} \end{pmatrix}\begin{pmatrix} \delta \mathcal{H} \\ \delta J_z \end{pmatrix} \quad (49)$$

$$= \begin{pmatrix} \frac{-\epsilon_i}{f(u_i)} & 0 \\ \frac{-h(u_i)\epsilon_i}{f(u_i)} & -1 \end{pmatrix}\begin{pmatrix} \delta u_i \\ \delta \varphi_i \end{pmatrix} = \mathcal{C}\begin{pmatrix} \delta u_i \\ \delta \varphi_i \end{pmatrix}, \quad (50)$$

where the 2×2 matrices $\mathcal{D}$ and $\mathcal{C}$ are defined in Eq. (50). From

$$(\det\hat{\mathcal{O}})^{-1} = \det\left(\frac{\partial p_f}{\partial q_i}\right), \quad (51)$$

we finally arrive at

$$\det\hat{\mathcal{O}} = (\det \mathcal{A})^{-1}(\det \mathcal{D})(\det \mathcal{C})^{-1}$$
$$= f(u_i)f(u_f)\det\mathcal{D} \quad (52)$$

$$= f(u_i)f(u_f)\left(\frac{\partial L}{\partial \mathcal{H}}\frac{\partial \Phi}{\partial J_z} - \frac{\partial \Phi}{\partial \mathcal{H}}\frac{\partial L}{\partial J_z}\right)\epsilon_i\epsilon_f, \quad (53)$$

where $\mathcal{D}$ is the 2×2 matrix defined in Eq. (50). The final answer for the total free energy including thermal corrections is

$$\mathcal{G}_{\mathcal{W}}(F, \tau, k_B T) = \mathcal{E}_{cl} + \frac{k_B T}{2}\ln\left[\epsilon_i\epsilon_f f(u_i)f(u_f)\left(\frac{\partial L}{\partial \mathcal{H}}\frac{\partial \Phi}{\partial J_z}\right.\right.$$
$$\left.\left. - \frac{\partial \Phi}{\partial \mathcal{H}}\frac{\partial L}{\partial J_z}\right)\right]. \quad (54)$$

These derivatives are evaluated at constant u_i, u_f. While this final answer may appear to be abstract, it is in fact quite amenable to numerical methods. All the functions appearing here [Eqs. (19)–(21)] can be expressed in terms of elliptic integrals and numerically evaluated.

Although Eq. (54) is written for asymmetric boundary conditions, the thermal correction to the free energy for long polymers with symmetric boundary conditions can be teased out of it since the free energy for long polymers is expected to be independent of the boundary conditions. We take the limit of $u_i \to 1$, which leads to $f(u_i)$ vanishing. In Eq. (54), of the terms that multiply $f(u_i)$, we need to keep only those terms that diverge as $u_i \to 1$. This results in a simple expression for the leading correction to the free energy:

$$\Delta\mathcal{G}_W = k_B T L \mu = k_B T L \sqrt{F - \tau^2/4}. \quad (55)$$

In Eq. (55) we have dropped lower-order terms that are not extensive in L. Notice that the numerical value of the thermal correction to the free energy is the same as for the straight line family. This can be understood physically since for any finite μ, most of the polymer is straight. We would not in general expect the fluctuation energies of the SLF and WF to be equal in short polymers. The expressions (53)–(55) contain the main results of this study: an analytic calculation of the thermal corrections to the free energy for the writhing family.

Our main result expressing the fluctuation determinant in simple terms sheds considerable light on the stability of polymer configurations. Note that the determinant vanishes as either u_i or u_f approaches a turning point. This signals the appearance of null eigenvalues for the Hessian or fluctuation operator (40). Such effects have been well studied in optics and mechanics [52], where they reveal the appearance of caustics, focusing, and conjugate points. If the polymer configuration goes from u_i to u_f passing through turning points, it is not stable against small perturbations. The Gibbs free energy $\mathcal{G}_\mathcal{W}(\tau, F)$ can be lowered at constant torque by such perturbations. At constant torque, such configurations will decay to lower-energy configurations.

However, if one works in the corresponding Helmholtz ensemble, at a constant link, which is how most experiments are done, the allowed perturbations are also required to maintain constant writhe (supposing for simplicity, C to be infinite) and this instability disappears. However, if u_i and u_f are separated by two turning points, there are two independent perturbations, which lower the energy. Working to second order in the perturbation, one of these lowers the writhe and the other increases it. One can take a linear combination of these two perturbations to maintain constant writhe. Such configurations are unstable at both constant torque and a constant link. Note that polymer configurations that extend for more than a period P are therefore unstable to perturbations, in accord with the findings of Ref. [15]. They are not local minima of either the Helmholtz or Gibbs energy.

IV. TOWARDS STATISTICAL MECHANICS

Up to this point we have relied on the mechanical approach, dealing with individual polymer configurations and considering small fluctuations around them. This has the advantage that we know which individual configuration we are dealing with and can show [15] that the dominant configurations admit a local writhe formula. We now move toward a more statistical-mechanics approach and integrate over configurations. In the process we lose touch with individual configurations, but we gain by getting a fuller treatment. From the mechanical approach, we have gained confidence that the sum over configurations is dominated by good curves that admit a local writhe formula. Using this idea, we will now extrapolate to more general situations where the thermal fluctuations are appreciable and continue to use a local writhe formula. The justification for this is given in Refs. [10,15].

Let us assume that the boundary conditions are azimuthally symmetric and exploit the symmetry to treat the φ degrees of freedom exactly by integrating them out. We reduce the problem to a single variable θ (or u). In the process of reduction the effective potential picks up an extra contribution from the thermal fluctuations of the φ degrees of freedom. As a result, the effective potential explicitly depends on the temperature. The origin of this effect is that path integration in general coordinates has subtleties coming from the measure,[4] as pointed out by Edwards and Gulyaev [53]. These techniques

have been applied [54] to compute the quantum corrections to soliton energies. Our calculation is mathematically similar but physically different since we deal with thermal corrections rather than quantum ones. Our treatment below closely follows these earlier studies, with appropriate modifications. After integrating out the φ degrees of freedom, the θ motion is governed by an effective potential

$$V_{\text{eff}}(\theta) = F \cos\theta - \frac{k_B T}{8 L_P} + \tau^2 \frac{(1 - \cos\theta)}{1 + \cos\theta} - \frac{k_B T}{8 L_P \sin^2\theta} \tag{56}$$

and the earlier equation (17) is replaced by

$$\dot{u}^2 = \mathcal{P}_T(u) = [f_T(u)]^2 = 2 \left[\left(\mathcal{H} + \frac{k_B T}{8 L_P} \right) - F u \right] (1 - u^2)$$
$$- \tau^2 (1 - u)^2 + \frac{k_B T}{4 L_P}. \tag{57}$$

Note the appearance of temperature-dependent terms in Eqs. (56) and (57) emerging from thermal fluctuation corrections. Note that $u = 1$ is no longer an allowed solution. The straight line is destabilized by entropic effects. Indeed it would be hard to distinguish between the SLF and the WF here because we are no longer dealing with single configurations but ensembles of them. However, we can continue to use a local writhe formula for torques large enough that the turning point c is positive. Such curves have tangent vectors entirely in the northern hemisphere and are good curves.

We now treat the θ (or u) motion approximately by considering the configurations $u(s)$ that satisfy the Euler-Lagrange equations. One finds the classical contribution by evaluating the energy on the "classical" solution. ("Classical" is in quotes because it is a bit of a misnomer since the effective potential includes contributions from thermal fluctuations.) The thermal correction to the free energy can now be computed:

$$\mathcal{F}(T, F, \tau) = \mathcal{E}_{\text{``cl''}}(T, F, \tau) + k_B T / 2 \ln \left[-4(\mathcal{H} - F) \left(\frac{\partial L}{\partial \mathcal{H}} \right) \right]. \tag{58}$$

In the first term in Eq. (58) $\mathcal{E}_{\text{``cl''}}$ is computed using the thermally corrected $\mathcal{P}_T(u)$. In the second term, which is already of order $k_B T$, we have used the previous $\mathcal{P}(u)$ since the difference is higher order in $k_B T$. The term L is given in terms of $\mathcal{H}$ by formula (20). These formulas involving elliptic integrals are numerically tractable and can be used to work out the predictions of the model.

V. CONCLUSION

We have analyzed the mechanics and fluctuations of semiflexible polymers. Our central goal in this paper has been to bridge the gap between mechanics and statistical mechanics by taking into consideration thermal fluctuation effects to quadratic order around mechanically stable configurations. To summarize, our main results are an explicit characterization of the mechanics of the writhing family, its energy, and writhe and a study of fluctuations about these equilibrium configurations and formulas that can be used to calculate the thermal correction to the free energy. There have been earlier studies of quadratic fluctuation effects in the context

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[4]This can also be seen by operator methods, where it emerges from the need to make the reduced differential operator self-adjoint.

of stretched semiflexible polymers [48,49]. However, these have been analyzed in the absence of a torsional constraint. In contrast, we present a detailed analysis of quadratic fluctuation effects on torsionally constrained biopolymers. In particular we have presented explicit approximate analytic expressions for the free energy [Eqs. (54) and (58)] of a semiflexible polymer ribbon. A curious feature of the energy (and free energy) of the writhing family is the cusp at $\tau = 0$. On differentiation this results in a discontinuity in the link between positive and negative values of τ. The discontinuity is visible in Fig. 3 (the gap in the thick red curve) and is also present in simulations (see Fig. 2 of Ref. [14]).

We find that thermal fluctuations have a considerable effect on the elastic properties of semiflexible polymers, as is clear from a comparison of Figs. 3–5. Notice that in Figs. 3 and 4 the extension of the polymer (shown by the thin blue line) is maximal, independent of the applied link. This situation changes drastically when thermal fluctuations are incorporated (see Fig. 5). The straight-line family no longer has maximal extension (the thin blue line curves down). Thus the applied link is stored entirely in the thermal fluctuations of the molecule. The molecule has helical fluctuations and stores writhe by preferentially writhing with one helicity. This is in sharp contrast to the writhing solutions, which can store writhe even without thermal fluctuations.

A mechanical treatment is expected to work well for short polymers. For long polymers without applied force, the system is entropy dominated and therefore our treatment does not apply. For long polymers under a very high stretching force (for example, the regime $F \approx 10$ in Ref. [2] corresponding to 1 pN), the entropic fluctuations are tamed and a mechanical approach is again possible. As the force is lowered, entropic effects begin to gain importance. Our treatment considers fluctuations about nonperturbative solutions of the writhing family and therefore goes beyond perturbation theory about the straight line. We expect this paper to generate interest in the experimental and simulation community in testing our predictions.

ACKNOWLEDGMENTS

[1] C. Bustamante, S. B. Smith, J. Liphardt, and D. Smith, Curr. Opin. Struct. Biol. **10**, 279 (2000).

[2] S. Forth, C. Deufel, M. Y. Sheinin, B. Daniels, J. P. Sethna, and M. D. Wang, Phys. Rev. Lett. **100**, 148301 (2008).

[3] B. C. Daniels, S. Forth, M. Y. Sheinin, M. D. Wang, and J. P. Sethna, Phys. Rev. E **80**, 040901 (2009).

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

[5] J. Marko and E. D. Siggia, Macromolecules **28**, 8759 (1995).

[6] J. H. Michell, Messenger Math. **11**, 181 (1889).

[7] C. J. Benham, Proc. Natl. Acad. Sci. USA **74**, 2397 (1977).

[8] C. J. Benham, Biopolymers **18**, 609 (1979).

[9] M. LeBret, Biopolymers **18**, 1709 (1979).

[10] J. Samuel, S. Sinha, and A. Ghosh, J. Phys.: Condens. Matter **18**, S253 (2006).

[11] B. Fain and J. Rudnick, Phys. Rev. E **60**, 7239 (1999).

[12] N. Chouaieb, A. Goriely, and J. H. Maddocks, Proc. Natl. Acad. Sci. USA **103**, 9398 (2006).

[13] B. Fain, J. Rudnick, and S. Östlund, Phys. Rev. E **55**, 7364 (1997).

[14] S. Neukirch, Phys. Rev. Lett. **93**, 198107 (2004).

[15] J. Samuel and S. Sinha, J. Stat. Phys. **143**, 399 (2011).

[16] F. B. Fuller, Proc. Natl. Acad. Sci. USA **75**, 3557 (1978).

[17] F. B. Fuller, Proc. Natl. Acad. Sci. USA **68**, 815 (1971).

[18] M. Monastrysky, *Computational Studies of DNA and RNA* (Springer, Berlin, 2007).

[19] A. V. Vologodskii and J. F. Marko, Biophys. J. **73**, 123 (1997).

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

[21] S. Sinha, Phys. Rev. E **70**, 011801 (2004).

[22] A. Ghosh, J. Samuel, and S. Sinha, Phys. Rev. E **76**, 061801 (2007).

[23] J. F. Marko, Phys. Rev. E **76**, 021926 (2007).

[24] S. Neukirch and E. L. Starostin, Phys. Rev. E **78**, 041912 (2008).

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

[26] V. Rossetto and A. C. Maggs, Phys. Rev. Lett. **88**, 089801 (2002).

[27] A. La Porta and M. D. Wang, Phys. Rev. Lett. **92**, 190801 (2004).

[28] J. White, Am. J. Math **91**, 693 (1969).

[29] G. Călugăreanu, Czech. Math. J **11**, 588 (1961).

[30] M. R. Dennis and J. H. Hannay, Proc. R. Soc. London Ser. A **461**, 3245 (2005).

[31] D. Keller, D. Swigon, and C. Bustamante, Biophys. J. **84**, 733 (2003).

[32] S. Sinha and J. Samuel, Phys. Rev. E **71**, 021104 (2005).

[33] Y. Seol, J. Li, P. Nelson, T. T. Perkins, and M. D. Betterton, Biophys. J. **93**, 4360 (2007).

[34] S. Sinha, Phys. Rev. E **77**, 061903 (2008).

[35] J. Coyne, IEEE J. Oceanic Eng. **15**, 72 (1990).

[36] M. Nizette and A. Goriely, J. Math. Phys. **40**, 2830 (1999).

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

[38] A. E. H. Love, *A Treatise On the Mathematical Theory Of Elasticity* (Dover, New York, 1944).

[39] H. Goldstein, *Classical Mechanics* (Addison-Wesley, Reading, MA, 1978).

[40] A. Shapere and F. Wilczek, *Geometric Phases in Physics* (World Scientific, Singapore, 1989).

[41] A. C. Maggs and V. Rossetto, Phys. Rev. Lett. **87**, 253901 (2001).

[42] J. Samuel and R. Bhandari, Phys. Rev. Lett. **60**, 2339 (1988).

[43] J. Samuel and S. Sinha, Phys. Rev. Lett. **90**, 098305 (2003).

[44] D. M. Stump and W. B. Fraser, Proc. R. Soc. London **456**, 455 (2000).

[45] H. Kleinert, *Path Integrals in Quantum Mechanics, Statistics, Polymer Physics and Financial Markets* (World Scientific, Singapore, 2006).

[46] I. M. Gelfand and A. M. Yaglom, J. Math. Phys. **1**, 48 (1960).

[47] P. Muratore-Ginanneschi, Phys. Rep. **383**, 299 (2003).

[48] I. M. Kulić, H. Mohrbach, V. Lobaskin, R. Thaokar, and H. Schiessel, Phys. Rev. E **72**, 041905 (2005).

[49] I. M. Kulić, H. Mohrbach, R. Thaokar, and H. Schiessel, Phys. Rev. E **75**, 011913 (2007).

[50] M. Emanuel, H. Mohrbach, M. Sayar, H. Schiessel, and I. M. Kulić, Phys. Rev. E **76**, 061907 (2007).

[51] G. V. Dunne, J. Phys. A **41**, 164041 (2008).

[52] V. I. Arnold, *Mathematical Methods of Classical Mechanics* (Springer, Berlin, 1978).

[53] S. F. Edwards and Y. V. Gulyaev, Proc. R. Soc. London Ser. A **279**, 229 (1964).

[54] R. Rajaraman and E. J. Weinberg, Phys. Rev. D **11**, 2950 (1975).