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Elasticity of semiflexible polymers in two dimensions

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We study theoretically the entropic elasticity of a semiflexible polymer, such as DNA, confined to two dimensions. Using the worm-like-chain model we obtain an exact analytical expression for the partition function of the polymer pulled at one end with a constant force. The force-extension relation for the polymer is computed in the long chain limit in terms of Mathieu characteristic functions. We also present applications to the interaction between a semiflexible polymer and a nematic field, and derive the nematic order parameter and average extension of the polymer in a strong field.

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I. INTRODUCTION

Mechanical properties of biomolecules, such as their response to an applied force, are important for understanding a variety of biological processes ranging from cell motility to gene regulation. Detailed mechanical studies of biopolymers using laser tweezers, magnetic tweezers, atomic force microscopy, and other single molecule techniques have provided the necessary experimental input for formulating precise mathematical models of their elasticity. In the case of double-stranded DNA (dsDNA) the favored theoretical model is the worm-like-chain (WLC) model, proposed by Kratky and Porod in 1949 [1]. Owing to the central role that DNA plays in biology, the last decade has seen a significant body of theoretical work on the WLC model, as well as its modifications and extensions [2–10]. Considerable experimental evidence has now accumulated that shows that the worm-like-chain model reproduces the mechanical behavior of dsDNA in the entropic regime quite well [2,3,11].

The effect of confinement on the statistical properties of polymers is of growing interest to scientists and engineers [12,13]. In the context of the cell, the important observation is that dsDNA is always found in a state of confinement. Namely, it occupies a volume which is considerably smaller than the volume it assumes free in solution. Here we examine dsDNA confined to two dimensions. While not immediately of relevance to cell biology, this type of confinement has been studied recently as an interesting polymer physics problem. Experiments have probed dynamics and thermodynamics of dsDNA confined to a mica surface [14] and the surface of a lipid bilayer [15]. More generally, two-dimensional confinement is emerging as an important experimental method, as it allows for the use of fluorescence microscopy and atomic force microscopy to obtain images of individual dsDNA molecules. For example, recent experiments have made use of dsDNA adsorbed on treated mica surfaces to study the effect of DNA-binding proteins on dsDNA conformations [16].

In this paper we study the effect of two-dimensional confinement on the entropic elasticity of a worm-like-chain polymer. In particular, we compute the partition function for the WLC model in the presence of an applied force when the chain is restricted to two dimensions. This allows us to derive an exact expression for the average end-to-end distance of the polymer as a function of applied force, which is the central result of this paper.

The paper is organized as follows. In Secs. II and III we introduce the WLC model and derive an exact closed-form expression for the tangent partition function and the force-extension relation of a WLC polymer pulled at one end by a constant force, in the limit of a large polymer length. In Sec. IV we discuss the asymptotic form of our result in the limit of strong and weak forces, and compare it to the approximate force-extension relation in three dimensions. We also give a simple algebraic approximation to the force-extension relation in two dimensions. In Sec. V we show that a minor transformation converts the partition function of Sec. II into the partition function of a semiflexible polymer in a nematic field. We use this to calculate the nematic order parameter for the polymer, as well as its relative extension in a strong nematic field.

The results reported here should be of practical use in stretching experiments where semiflexible polymers such as DNA are confined to a surface. On the purely theoretical side, they establish an interesting connection between the elastic properties of two-dimensional semiflexible polymers and Mathieu functions.

II. THE WORM-LIKE-CHAIN MODEL

The worm-like-chain model describes the polymer as an elastic filament characterized by a rigidity parameter κ, which has dimensions of length. For a three-dimensional polymer κ is the persistence length, i.e., the decay length associated with the tangent-tangent correlation function, which for DNA under physiological conditions is about 50 nm. The energy of bending a small arc of length s of the filament into a circular segment of radius R is given by $k_B T\kappa s/2R^2$, where $k_B T$ is the thermal energy (at room temperature $k_B T=4$ pNnm). If we describe polymer conformations by a smooth continuous curve, the Hamiltonian of the

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WLC can be expressed as the integral of this segmental bending energy over the entire polymer curve. Therefore, when a polymer is tethered at one end and pulled with a constant force $\boldsymbol{F}$ in the $\hat{\boldsymbol{x}}$ direction at the other, the Hamiltonian H can be written as:

$$H=\int_0^L ds\left\{\frac{\kappa k_B T}{2}\left(\frac{d\hat{\boldsymbol{t}}}{ds}\right)^2-\boldsymbol{F}\cdot\hat{\boldsymbol{t}}\right\}, \tag{1}$$

where $\hat{\boldsymbol{t}}$ is the unit tangent vector to the polymer curve, and L is the contour length of the polymer. In writing Eq. (1) we have made use of the standard relation between the radius of the curvature of a curve and the rate of change of its tangent vector, $|d\hat{\boldsymbol{t}}/ds|=1/R$.

Since this polymer is represented by a curve, its partition function is the sum of Boltzmann weights for all possible curves, subject to the constraint of fixed polymer length L. In terms of the tangent vector $\boldsymbol{t}(s)$ the partition function can be written as a path integral,

$$\mathcal{Z}(\hat{\boldsymbol{t}}_f,\hat{\boldsymbol{t}}_i;L)=\int\mathcal{D}[\hat{\boldsymbol{t}}(s)]\exp\left[-\int_0^L ds\left\{\frac{\kappa}{2}\left(\frac{d\hat{\boldsymbol{t}}}{ds}\right)^2-f\,\hat{\boldsymbol{t}}\cdot\hat{\boldsymbol{x}}\right\}\right], \tag{2}$$

where $f=\mathrm{F}/k_BT$ is the reduced force with units of inverse length. The dimensionless combination κf delineates regimes of high ($\kappa f\gg 1$) and low force ($\kappa f\ll 1$), which we take up in Sec. IV.

Experiments on stretching polymers that involve attaching the two ends of the polymer molecule to beads, constrain the first and final tangent vectors, usually making them lie along the direction of the force. This is indicated by specifying the initial and final tangent vectors, $\hat{\boldsymbol{t}}_i$ and $\hat{\boldsymbol{t}}_i$, explicitly in Eq. (2). In case the ends are free, we will need to integrate over these tangent vectors to obtain the appropriate partition function. This is the case, for example, when the polymer is dissolved in a nematic solvent, as we shall see in Sec. V.

From the partition function Eq. (2) we calculate the average end-to-end extension of the polymer in the direction of the force, $\langle X\rangle$. Namely, $\langle X\rangle$ is the conformational average of the end-to-end vector $\boldsymbol{R}=\int_0^L ds\,\hat{\boldsymbol{t}}$ projected in the direction of the applied force, i.e.,

$$\langle X\rangle=\left\langle\int_0^L ds\,\hat{\boldsymbol{t}}\cdot\hat{\boldsymbol{x}}\right\rangle. \tag{3}$$

From Eq. (2) we conclude that

$$\langle X\rangle=\frac{\partial\ln\mathcal{Z}}{\partial f}. \tag{4}$$

In two dimensions $\hat{\boldsymbol{t}}=(\cos\theta,\sin\theta)$, where $\theta(s)$ is the polar angle, and the partition function $\mathcal{Z}$ in Eq. (2) can be rewritten as

$$\mathcal{Z}(\theta_f,\theta_i;L)=\int\mathcal{D}[\theta(s)]\exp\left[-\int_0^L ds\left\{\frac{\kappa}{2}\left(\frac{d\theta}{ds}\right)^2-f\cos\theta\right\}\right], \tag{5}$$

where θ_f and θ_i are now the final and initial tangent angles. The calculation of $\mathcal{Z}(\theta_f,\theta_i;L)$ is made simple by the standard connection between the path integral and the Schrödinger differential equation [17]

$$\left(\frac{\partial}{\partial s}-\frac{1}{2\kappa}\frac{\partial^2}{\partial\theta^2}-f\cos\theta\right)\mathcal{Z}(\theta,\theta_i;s)=0\quad(s>0), \tag{6}$$

subject to the initial condition

$$\mathcal{Z}(\theta,\theta_i;0)=\delta(\theta-\theta_i). \tag{7}$$

Since Eq. (6) is separable in s and θ, we can express its solutions in terms of the eigenfunctions $Q(\theta)$ and eigenvalues E of the corresponding eigenvalue equation,

$$\left(\frac{1}{2\kappa}\frac{\partial^2}{\partial\theta^2}+f\cos\theta\right)Q=-EQ. \tag{8}$$

Note that the partition function, $\mathcal{Z}(\theta,\theta_i;s)$, is formally equivalent to the path integral for a quantum rotor with moment of inertia κ in an external field f, evolving in imaginary time s [2], or, equivalently, to a quantum pendulum in a gravitational field [18]. The correspondence is actually very intuitive, since thermal fluctuations of the tangent vector along the backbone of the polymer can be regarded as the time evolution of the quantum rotor in the external field. Each polymer conformation hence represents one particular time evolution of the quantum problem, in other words "the path is the polymer" [19]. The procedure for computing $\mathcal{Z}(\theta,\theta_i;s)$ we have outlined above is thus formally equivalent to obtaining the spectral representation of a quantum propagator in terms of the eigenstates of the associated Hamiltonian.

III. FORCE EXTENSION IN TWO DIMENSIONS

The eigenvalue equation, Eq. (8), can be transformed into the canonical Mathieu differential equation by the change of variables $\Theta=\pi/2-\theta/2$. As θ goes from π to $-\pi$ about the direction of the force, Θ varies between 0 and π. This transformation yields,

$$\frac{\partial^2 Q}{\partial\Theta^2}+(p-2q\cos 2\Theta)Q=0, \tag{9}$$

with $p=8E\kappa$ and $q=4f\kappa$. The solutions of this equation are the Mathieu functions [20,21]. The Mathieu differential equation always has a periodic solution and an aperiodic solution [20]. Since rotation of tangent vectors by 2π must leave Q unchanged, we desire a solution that is periodic in θ with a period of 2π, or, equivalently, periodic in Θ with period π.

Solutions of Eq. (9) with a period of either π or 2π are called "basically periodic" in the Mathieu function literature. A Mathieu function is basically periodic only for specific values of the parameters p and q [20–22]. The value of p that

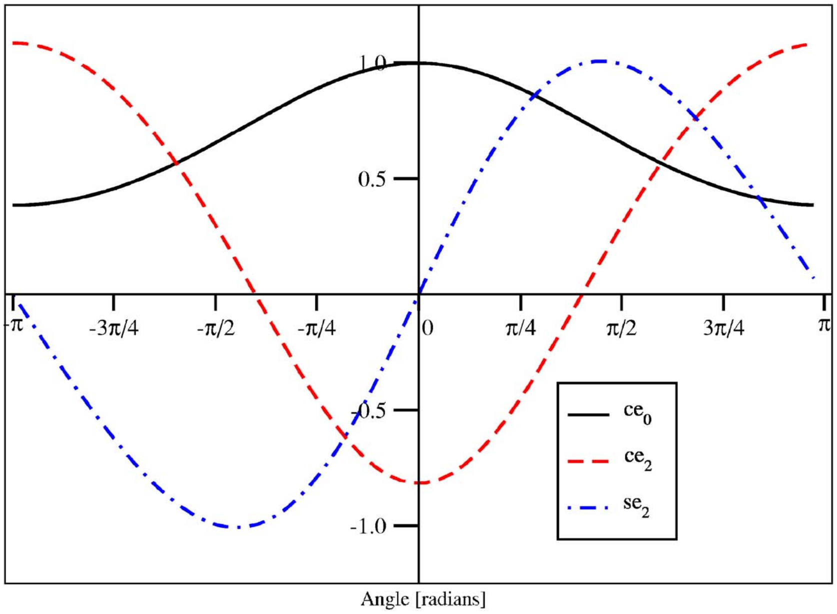

FIG. 1. (Color online) Eigenfunctions ce_0, se_2, and ce_2 plotted for $4f\kappa=1$ and for θ between $-\pi$ and π.

makes the function basically periodic is called the "characteristic value" of the Mathieu function, and is, in fact, a continuous function of q [20–22]. For a given q there is a countable set of such characteristic-value functions, usually denoted as $a_n(q)$ and $b_n(q)$, $n=0,1,2,\ldots$. The functions $a_n(q)$ are associated with the even Mathieu functions $ce_n(a_n,q,\Theta)$, while the functions $b_n(q)$ are associated with the odd Mathieu functions $se_n(b_n,q,\Theta)$; ce and se stand for *cosine elliptic* and *sine elliptic*, respectively [20–22]. Furthermore, for $q\neq 0$, the Mathieu characteristic functions satisfy [22]

$$a_0(q) < b_1(q) < a_1(q) < b_2(q) < a_2(q) < \cdots . \qquad (10)$$

We conclude that the periodicity of $Q(\Theta)$ imposes the quantization condition on the parameter $p=8E\kappa$, which must be from the countable set of Mathieu characteristic functions.

The periodicity of the Mathieu functions for different values of n can be deduced from their expansions in sine and cosine series. There are four types of basically periodic ce and se functions, and their expansions are

$$ce_{2n}(a_{2n},q,\Theta) = \sum_{r=0}^{\infty} A_{2r}^{(2n)} \cos 2r\Theta, \qquad (11)$$

$$ce_{2n+1}(a_{2n+1},q,\Theta) = \sum_{r=0}^{\infty} A_{2r+1}^{(2n+1)} \cos(2r+1)\Theta, \qquad (12)$$

$$se_{2n+1}(b_{2n+1},q,\Theta) = \sum_{r=0}^{\infty} B_{2r+1}^{(2n+1)} \sin(2r+1)\Theta, \qquad (13)$$

$$se_{2n+2}(b_{2n+2},q,\Theta) = \sum_{r=0}^{\infty} B_{2r+2}^{(2n+2)} \sin(2r+2)\Theta. \qquad (14)$$

Note that the coefficients A and B are functions of q. Perusal of the above equations shows that the class of functions that have period π in Θ, are the ce_{2n} and the se_{2n+2} functions. The normalization convention for the Mathieu functions is [20]

$$\int_0^{\pi} ce^2(a_n,q,\Theta)d\Theta = \int_0^{\pi} se^2(b_n,q,\Theta)d\Theta = \frac{\pi}{2}. \qquad (15)$$

The first few basically periodic Mathieu functions are plotted in Fig. 1, while the corresponding characteristic functions are plotted in Fig. 2.

With the eigenfunctions (ce_{2n} and se_{2n+2}) and the corresponding eigenvalues (a_{2n} and b_{2n+2}) of Eq. (8) in hand, the spectral representation of the partition function of the wormlike chain is

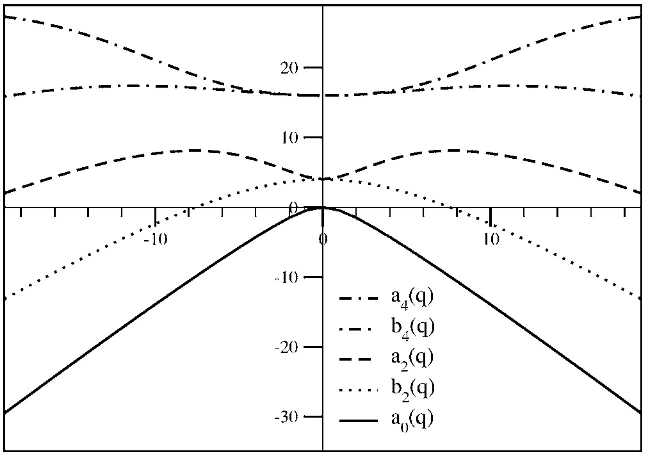

FIG. 2. Characteristic functions $a_0(q)$, $b_2(q)$, $a_2(q)$, $b_4(q)$, and $a_4(q)$ plotted against q.

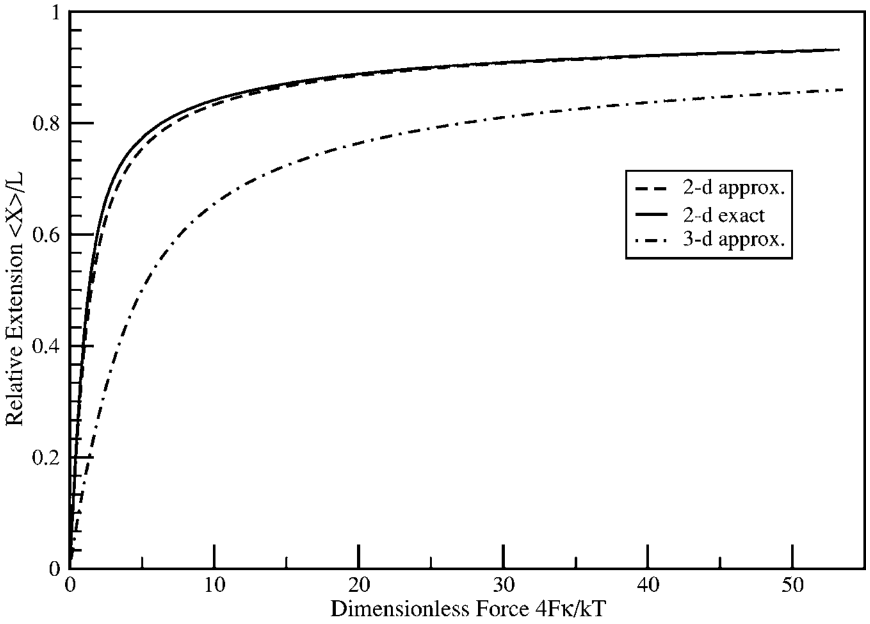

FIG. 3. Force extension curves for semiflexible polymers. The full line is the relative extension $\langle X\rangle/L$ plotted against the dimensionless force, $q=4F\kappa/k_BT$ using the exact formula, Eq. (19). The dashed line is the interpolation formula, Eq. (33). For comparison, the force-extension curve in three dimensions is plotted as a dot-dashed line, using the approximate interpolation formula described in Ref. [2].

$$\begin{aligned}\mathcal{Z}(\Theta_i,\Theta_f,L)=\sum_{n=0}^{\infty}\Bigg\{&\frac{2}{\pi}ce_{2n}(a_{2n},4f\kappa,\Theta_i)ce_{2n}(a_{2n},4f\kappa,\Theta_f)\\&\times\exp\left[-\frac{L}{8\kappa}a_{2n}(4f\kappa)\right]\\&+\frac{2}{\pi}se_{2n+2}(b_{2n+2},4f\kappa,\Theta_i)se_{2n+2}(b_{2n+2},4f\kappa,\Theta_f)\\&\times\exp\left[-\frac{L}{8\kappa}b_{2n+2}(4f\kappa)\right]\Bigg\},\end{aligned}\tag{16}$$

where Θ_i and Θ_f specify the tangent vectors at the two ends of the chain. To obtain the partition function with no constraints on the initial and final tangent vectors, we integrate over all possible values of the initial and final angles. Using the expansions, Eqs. (11), (14), and (15), we get

$$\mathcal{Z}(L)=\sum_{n=0}^{\infty}2\pi[A_0^{(2n)}]^2\exp\left[-\frac{L}{8\kappa}a_{2n}(4f\kappa)\right].\tag{17}$$

From the inequalities in Eq. (10) it follows that, for L large compared to κ, the above expansions for $\mathcal{Z}$ are dominated by the term containing $a_0(4f\kappa)$ in the exponential. Even for relatively short polymers, this term is a good approximation to the full partition function. Namely, as can be seen from Fig. 2, the difference between $b_2(4f\kappa)$ or $a_2(4f\kappa)$ and $a_0(4f\kappa)$ is 4 at $f=0$ and increases in absolute value with increasing f. Therefore, even for polymer length $L\approx 8\kappa$, the second exponential in the expansion in Eqs. (16) and (17) is at least $e^{-4}\approx 0.02$ times smaller than the first; the subsequent terms are exponentially smaller.

It remains to consider the coefficients. In the case of Eq. (16) the coefficients are products of Mathieu functions and when $\theta_f\approx\theta_i\approx 0$, which is a reasonable assumption for most experiments, the coefficient of the first term is larger than any of the subsequent ones. In the case of Eq. (17), the coefficients $(A_0^{(2n)})^2$ are complicated functions of the dimensionless force $q=4f\kappa$. However, all of them satisfy $(A_0^{(2n)})^2<1$ and they are all of the same order of magnitude when $q>1$. When $q=0$, $A_0^{(0)}=1/\sqrt{2}$, and all other coefficients are zero [20]. We conclude that the approximation,

$$\mathcal{Z}\approx c\exp\left(-\frac{L}{8\kappa}a_0(4f\kappa)\right),\tag{18}$$

where c is the appropriate coefficient from either Eq. (16) or Eq. (17), depending on the boundary conditions, is justified for polymer lengths $L>8\kappa$.

We can now calculate the relative extension from Eq. (4). The coefficient of the exponential yields a correction which is of order κ/L and hence can be safely ignored in the long chain limit. The resulting force extension relation is therefore given by

$$\frac{\langle X\rangle}{L}=-\frac{1}{8\kappa}\frac{da_0(4f\kappa)}{df}=-\frac{1}{2}\frac{da_0(q)}{dq},\tag{19}$$

where $q=4f\kappa$, as before.

The Mathieu characteristic functions are interesting in themselves. So far, no exact expression for them is known in terms of other functions, though good polynomial approximations are available for small and large q. They are usually expressed as roots of an equation involving infinite continued fractions [20–22]. They can also be shown to be the roots of an infinite tridiagonal determinant equation [21]. Both these representations allow numerical calculation as well as numerical differentiation by mathematical programs like Mathematica [23]. Mathematica executes the desired function as MATHIEUCHARACTERISTICA[R,Q], which we use to generate the plot of the relative extension as a function of the applied force, shown in Fig. 3.

It is worth noting that the higher order moments of the probability distribution of the end-to-end distance can be obtained by successive differentiation of the partition function,

$$\langle X^n \rangle = \frac{1}{\mathcal{Z}} \frac{\partial^n \mathcal{Z}}{\partial F^n}. \quad (20)$$

Having computed the exact expression for the force-extension relation for a two-dimensional worm-like chain in terms of Mathieu functions, in the next section we consider the small and large force limits of Eq. (19), which are readily obtained using more elementary methods.

IV. LIMITS OF SMALL AND LARGE FORCE

In order to gain a better understanding of the derived force-extension relation, Eq. (19), we analyze it in the small force ($q=4f\kappa \ll 1$) and the large force ($q \gg 1$) limits.

For small forces, we use the power series expansion [22] of $a_0(q)$,

$$a_0(q) = -\frac{q^2}{2} + \frac{7q^4}{128} + O(q^6). \quad (21)$$

Therefore, to first order in q, the extension becomes

$$\frac{\langle X \rangle}{L} = \frac{1}{2}q = 2f\kappa. \quad (22)$$

It is reassuring to find that a perturbation analysis of Eq. (8), in the limit of low force, yields the same result. If the potential $f \cos\theta$ is treated as a perturbation, the unperturbed equation describes a free particle on a ring,

$$\frac{1}{2\kappa} \frac{d^2 Q_n}{d\theta^2} = -E_n^{(0)} Q_n. \quad (23)$$

The solutions of this equation are sine and cosine functions, except for the $E_0^{(0)}=0$ solution which is $Q_0 = 1/\sqrt{2\pi}$. The eigenvalues are given by,

$$E_n^{(0)} = \frac{n^2}{2\kappa}, \quad n = 0,1,2,\ldots. \quad (24)$$

The first order correction to the zero eigenvalue is zero. Using orthogonality properties of sine and cosine functions, we obtain the second order correction

$$E_0^{(2)} = -\kappa f^2. \quad (25)$$

Using $\langle X \rangle / L = -dE_0/df$, which follows from Eq. (4), and the fact that in the long-chain limit $\mathcal{Z} \sim \exp(-E_0 L)$, we get Eq. (22).

Let us now consider the limit of large forces. We use the asymptotic expansions given in Ref. [22],

$$a_0(q) \sim -2q + 2q^{1/2} - \tfrac{1}{4} - \tfrac{1}{32}q^{-1/2} + O(q^{-1}). \quad (26)$$

This gives us, after ignoring terms of order $q^{-1/2}$ and smaller,

$$\frac{\langle X \rangle}{L} = 1 - \frac{1}{2\sqrt{q}} = 1 - \frac{1}{4\sqrt{f\kappa}}. \quad (27)$$

This formula can be derived independently by noting that at high forces the polymer is highly extended in the direction of the force, with only small transverse fluctuations, hence the angle θ that $\hat{\boldsymbol{t}}$ makes with $\hat{\boldsymbol{x}}$ is very small [2]. We can therefore use the approximation

$$\cos\theta \approx 1 - \tfrac{1}{2}\theta^2. \quad (28)$$

This transforms the differential equation to be solved, Eq. (8), into a form that is equivalent to the Schrödinger equation for a one-dimensional simple harmonic oscillator with $\hbar = 1$ and angular frequency $\omega = \sqrt{f/\kappa}$,

$$\frac{1}{2\kappa} \frac{\partial^2 Q_n}{\partial \theta^2} - \frac{1}{2} f \theta^2 Q_n = -(E_n + f) Q_n. \quad (29)$$

The eigenfunctions Q_n are Gaussian functions multiplied by Hermite polynomials, and the eigenvalues are given by the well-known expression,

$$E_n + f = (n + \tfrac{1}{2})\sqrt{f/\kappa}. \quad (30)$$

Therefore the partition function can be written as,

$$\mathcal{Z}(\theta_f, \theta_i; L) = \sum_{n=0}^{\infty} Q_n(\theta_i) Q_n(\theta_f) \exp[-E_n L]. \quad (31)$$

Taking only the first term, in the limit of large L, and integrating over all values of the initial and final angles, we get

$$\mathcal{Z} \sim \exp[-E_0 L] = \exp[(f - \tfrac{1}{2}\sqrt{f/\kappa})L]. \quad (32)$$

Using this result in Eq. (4) immediately gives Eq. (27), as expected.

In Fig. 3 we have plotted a comparison of the force-extension curves from Eq. (19) and the interpolating formula of Ref. [2]. The $2d$ curve is found to lie strictly above the $3d$ curve at a nonzero force. This is expected by entropic arguments since a three-dimensional polymer has larger entropy, hence a larger force is needed to extend it by the same amount. Note that in two dimensions DNA is highly stretched even at relatively low forces.

It is also possible to write down an approximate formula for the force extension of a two-dimensional polymer, which tends to the exact force-extension relation in the two limits, and is approximately true to within less than 10% in the remaining regime (see Fig. 3),

$$16f\kappa = 6\frac{\langle X \rangle}{L} - 1 + \frac{1}{\left(1 - \frac{\langle X \rangle}{L}\right)^2}. \quad (33)$$

V. SEMIFLEXIBLE POLYMER IN A NEMATIC FIELD

Another way to stretch a polymer is to put it in an aligning field, such as that produced by a nematic liquid crystal. In a recent experiment, semiflexible polymers were stretched by dissolving them in the nematic phase of rodlike *fd* viruses [24]. The nematic potential experienced by the polymer can be written as [7,25],

$$\frac{V}{k_B T} = -\Gamma \int_0^L ds \{(\hat{\boldsymbol{t}} \cdot \hat{\boldsymbol{n}})^2 - \tfrac{1}{2}\}, \quad (34)$$

where the square arises due to the reflection invariance of the unit nematic director $\hat{\boldsymbol{n}}$, which we assume again is in the $\hat{\boldsymbol{x}}$ direction. The coupling Γ, between the nematic field and the polymer depends upon the order parameter of the nematic liquid crystal in which the polymer is embedded. When the liquid crystal undergoes a phase transition from the isotropic to the nematic phase, Γ increases and the polymer stretches. This mean-field form of the interaction ignores the fluctuations in the nematic order parameter [26,27].

With the help of the trigonometric identity, $\cos^2\theta-\frac{1}{2}=(\cos 2\theta)/2$, the potential in Eq. (34) becomes similar to that of the constant pulling-force case, but with $\cos\theta$ replaced by $\cos 2\theta$. Following the treatment detailed in a previous section, the partition function can again be expressed in a spectral representation, using the eigen functions of the Mathieu differential equation, which for this case is

$$\frac{\partial^2 Q}{\partial\theta^2}+\Gamma\kappa Q\cos 2\theta=-2E\kappa Q. \tag{35}$$

As before the ce_{2n} and se_{2n+2} functions are the appropriate eigenfunctions. In the large-L limit, the smallest eigenvalue again dominates the spectral expansion and the partition function is well approximated by,

$$\mathcal{Z}=2\pi(A_0^{(0)})^2\exp\left[-\frac{L}{2\kappa}a_0\left(\frac{\Gamma\kappa}{2}\right)\right]. \tag{36}$$

The derivative of the free energy with respect to the coupling Γ is now

$$S\equiv\frac{\partial\ln\mathcal{Z}}{\partial\Gamma}=\left\langle\int_0^L ds\{\cos^2\theta-\tfrac{1}{2}\}\right\rangle, \tag{37}$$

which is a measure of the degree of alignment of the polymer with the external field. It can be seen that when the polymer lies perfectly along the $\hat{\boldsymbol{x}}$ direction, then $S=L/2$, but when the polymer conformation is completely random, $S=0$, since $\langle\cos^2\theta\rangle=\frac{1}{2}$. Therefore $2S/L$ is the nematic order parameter of the polymer. The partition function Eq. (36) enables us to calculate S/L as a function of the coupling strength Γ,

$$\frac{S}{L}=-\frac{1}{4}\frac{da_0(q)}{dq}, \tag{38}$$

where now $q=\Gamma\kappa/2$, and we have ignored terms of order κ/L. Using the above result we can also obtain the approximate relative extension of the polymer in the direction of the nematic director at high coupling Γ. Due to the reflection invariance of the nematic director, the extension along that direction is defined as,

$$\langle|X|\rangle=\left\langle\left|\int_0^L ds\cos\theta\right|\right\rangle. \tag{39}$$

When the coupling between the polymer and the field is large the polymer conformation would consist of roughly straight sections which have small fluctuations in the $\hat{\boldsymbol{y}}$ direction, interspersed by hairpin bends. A simple thermodynamic argument, based on comparison of the energy cost of a hairpin with the entropy of a hairpin, leads to the conclusion that the typical length of the straight segments grows as the exponential of the square root of the coupling strength,

$$L_{nem}\sim\pi\sqrt{\pi\kappa\Gamma^{-1}}\exp(2\sqrt{\pi\kappa\Gamma}). \tag{40}$$

This is similar to the relation discussed in Ref. [27]. For DNA, $\kappa\approx 50$ nm, therefore $L_{nem}\approx 50\ \mu$m when $\Gamma=0.05\ \text{nm}^{-1}$, and $L_{nem}\approx 3$ m when Γ is an order of magnitude larger. If the length of the polymer is smaller than L_{nem}, hairpin bends are ruled out, and $\cos\theta$ does not change sign along the polymer contour. Without loss of generality, we can take it to be positive and remove the absolute value in Eq. (39). This allows us to write the following approximate formula for the extension:

$$\langle X\rangle\approx\left\langle\int_0^L ds\sqrt{1-\sin^2\theta}\right\rangle\approx\left\langle\int_0^L ds(1-\tfrac{1}{2}\sin^2\theta)\right\rangle. \tag{41}$$

By arguments similar to those made earlier for the polymer under a constant force, we know that Eq. (36) is a good approximation for the partition function when $L/\kappa\gg 1$, and we may use it to calculate the right-hand side of Eq. (41). The relative extension of the polymer along $\hat{\boldsymbol{x}}$ when $L<L_{nem}$ and $L/\kappa\gg 1$ can therefore be expressed as,

$$\frac{\langle X\rangle}{L}\approx\frac{3}{4}-\frac{1}{8}\frac{da_0(q)}{dq}, \tag{42}$$

where $q=\Gamma\kappa/2$. In the limit $q\gg 1$, the relative extension has the simple form, $1-\frac{1}{8}\sqrt{q}$. These results can be used to estimate Γ from experiments that measure the relative extension.

It should be noted that the exponential dependence of L_{nem} on the square root of Γ implies that when $\Gamma\kappa>1$, L_{nem} could be quite large, hence it would be easy to satisfy both $L<L_{nem}$ and $L/\kappa\gg 1$. For example it was estimated above that L_{nem} was as much as 50 μm for DNA when $\Gamma\kappa\approx 2.5$. At this value of Γ, Eq. (42) predicts that the molecule would have extended to 87% of its contour length. While to our knowledge, experimental estimates of Γ for DNA embedded in a nematic liquid crystal do not exist at present, the experiment of Ref. [24] measured values up to $\Gamma\approx 800(\mu\text{m})^{-1}$ for wormlike micelles ($\kappa\approx 0.5\ \mu$m) in a solution of fd viruses. The regime of validity of Eq. (42) is therefore expected to be quite large. These arguments also imply that a dramatic straightening of the polymer should take place as the liquid crystal goes through an isotropic-nematic phase transition. This indicates that there is considerable scope for using liquid crystals for stretching DNA in the laboratory.

VI. CONCLUSION

At present several schemes exist to calculate the partition function of the worm-like-chain model in both two and three dimensions, to any degree of accuracy [2,5–7]. With the exception of Ref. [7], they all use eigenfunction expansions to obtain the partition function numerically. Reference [7] uses a method to express the partition function in terms of infinite continued fractions.

This multitude of approaches only underlines the rich physics of the worm-like-chain model, and also hints at interesting mathematical connections. In the present work, the use of Mathieu functions to derive an exact partition function yielded a simple closed-form expression for the free energy of the worm-like-chain in the long-chain limit. This allowed us to calculate the force-extension relation in two dimensions in terms of Mathieu characteristic functions. We also discussed the application of this result to the interaction between a semiflexible polymer and a nematic field, and derived the nematic order parameter and average extension of the polymer in a strong field. It should be noted that self-avoidance, which is more important in two dimensions than in three, has been ignored in our analysis. We address this question, as well as stretching by a force that does not remain constant along the contour, such as that produced by an electric field, in a future publication [28].

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