

Force-Extension Curve of a Polymer in a High-Frequency Electric Field

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We study theoretically the conformation and force-extension curve of a semiflexible polymer in a spatially uniform ac electric field. The polymer backbone minimizes its energy by aligning along one of two orientations parallel to the field. In a strong ac field, hairpin kinks develop between regions of opposite alignment. These kinks are mathematically described as sine-Gordon solitons. We calculate the equation of state of the one-dimensional kink gas, which yields the force-extension curve of the polymer. A sufficiently strong ac field causes the polymer to extend spontaneously to almost its full contour length. The theory is applied to recent experiments on dielectrophoretic stretching of DNA.

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There is increasing interest in using high-frequency electric fields to manipulate polymer molecules, especially DNA, in solution [1–7]. A field interacts with the molecular polarizability to generate forces, torques, and internal stresses, a phenomenon known as dielectrophoresis (DEP) [8]. DEP-induced stresses may lead to functionally significant conformational changes in biomolecules. For instance, 16- μm -long λ -DNA, tethered by one end to an electrode, extends to its full contour length away from the electrode when an ac voltage is applied [6]. This stretching is counterintuitive because the electrode generates a field gradient which seeks to pull the DNA towards the electrode. In this Letter we develop a model for the conformation of a polymer strand in an ac field. The model explains the stretching phenomenon and suggests other experiments related to DEP manipulation of macromolecules. A recent study by Netz [9] examined short polymer strands in dc fields. We find qualitatively different behavior for long strands in ac fields.

The model consists of a polyelectrolyte strand of length L , subject to a spatially uniform ac field of rms amplitude E , and a tension F , applied to the ends of the strand and parallel to the field. The tension could occur in a single-molecule pulling experiment or serve as a proxy for more complex body forces induced by fluid flow or inhomogeneities in the field.

When dielectrophoresis is performed in water, ac fields are used rather than dc fields, to avoid ionic screening, electrochemistry, and electrophoresis. Typical ac fields in DEP have frequencies of 100 KHz–5 MHz. Polarization of polyelectrolytes such as DNA is largely due to motion of counterions, some condensed on the molecule, and some surrounding it in a diffuse cloud. This polarizability is highly anisotropic, being greatest parallel to the molecular backbone. The theory of polarization of polyelectrolytes is reviewed in [10,11].

For long molecules in high-frequency fields, the local polarization depends only on the local field. This is not the case for short molecules or for low-frequency fields, where the field can induce a global reorganization of the

counterions. If the frequency of the field is ν , in a half-period an ion diffuses a distance $\delta_D = \sqrt{D/\nu}$, where D is the diffusion constant. The ion also oscillates with an amplitude $\delta_\mu = \mu E/2\pi\nu$, where μ is the mobility (with the ionic charge included in its definition). For a Na^+ ion in water ($D = 1.3 \times 10^{-9} \text{ m}^2/\text{s}$, $\mu = 5 \times 10^{-8} \text{ m}^2/\text{Vs}$), under typical conditions for stretching DNA ($E = 1 \text{ MV/m}$, $\nu = 1 \text{ MHz}$), we find $\delta_D = 36 \text{ nm}$ and $\delta_\mu = 8 \text{ nm}$. The induced polarization in any bit of the polymer can depend only on the field averaged over a ball whose radius is of order δ_D . DEP stretching is typically studied in DNA strands many microns long, so it is justified to assign the molecule a polarizability *per unit length*, α .

Assuming negligible transverse polarizability, the induced linear polarization density at position s is $d\mathbf{p}(s) = \alpha(\mathbf{E} \cdot \mathbf{u})d\mathbf{u}$, where $\mathbf{u}(s)$ is the unit-vector locally tangent to the polymer. The polarization interacts with the field to give a time-averaged electrostatic free energy per unit length,

$$U_n(s) = -V\cos^2\theta(s), \quad (1)$$

where $V \equiv \frac{1}{2}E^2\alpha$ and $\theta(s)$ is the angle between the polymer backbone and the field. This energy seeks to align the polymer backbone with the closer of two orientations along the field axis.

Nematic polymer liquid crystals have a similar $\cos^2\theta$ term in their Hamiltonian, arising from a Maier-Saupe mean field interaction between the polymer and its neighbors [12]. In analogy to the case of polymer liquid crystals, we call U_n the *nematic energy*. Below we examine the conformation of a polymer in an ac field, first in the limit of weak field and weak tension, then in the limit of strong field and weak tension, and finally in the limit of either very strong field or very strong tension. The meanings of these limits will be explained.

For weak tension and weak ac field, it is acceptable to model the polymer as a freely jointed chain (FJC) of N rigid sticks, each of length b , and each assuming an orientation independent of its neighbors. For consistency

with the more realistic wormlike chain (WLC) model, the stick length should be $b = 2l_p$, where l_p is the persistence length of the WLC.

The orientation-dependent energy of each stick due to tension, F , and a parallel ac field, is $U_{\text{FJC}} = -Fb \cos\theta - Vb \cos^2\theta$. The ac field biases the sticks to point towards either pole, and tension favors one pole over the other. The partition function of a single stick is

$$Z_{\text{FJC}} = \int_0^\pi \sin\theta \exp\left(\frac{Fb \cos\theta + Vb \cos^2\theta}{k_B T}\right) d\theta. \quad (2)$$

The integral in Eq. (2) may be evaluated explicitly in terms of error functions, and from the resulting expression any thermodynamic property of the FJC determined. For example, each stick has a mean end-to-end extension of $\langle x_1 \rangle = k_B T \partial_F (\ln Z_{\text{FJC}})$. Since the sticks are independent, the total extension is $\langle x \rangle = N \langle x_1 \rangle$. The zero-extension spring constant of the FJC is then given by $k = (\partial_F \langle x \rangle|_{F=0})^{-1}$.

A weak ac field softens the zero-extension spring constant by favoring steps with a larger displacement along the field axis. In the absence of a field, the spring constant of a FJC is $k_0 = 3k_B T / Lb$. Expanding the expression for k in the ac field strength yields

$$k \approx \frac{3k_B T}{Lb} - \frac{4V}{5L}. \quad (3)$$

The softer spring constant also implies a larger radius of gyration, $R_G^2 = (kk_B T)^{-1}$, along the field axis. We find

$$R_G^2 \approx \frac{Nb^2}{3} + \frac{4NVb^3}{45k_B T}. \quad (4)$$

Thus a weak ac field turns a roughly spherical random coil into a prolate spheroid aligned along the field. However, no field strength will lead to spontaneous extension of the FJC; rather in the strong-field limit the FJC undergoes a one-dimensional random walk parallel to the field.

The FJC model breaks down in an intense ac field because it ignores the large bending energy that arises when a stick and its neighbor point towards opposite poles. An ac field is strong when its dimensionless magnitude is $Vb/k_B T > 1/2$. As this quantity surpasses $1/2$, the distribution of stick orientations switches from unimodal to bimodal. The curvature in the vicinity of an orientation reversal becomes comparable to the thermally induced curvature, and thus the bending energy is no longer negligible.

To include the bending energy it is necessary to adopt a continuum description. The effective energy in the absence of tension is

$$U = \int_0^L \left(\frac{1}{2} K \left| \frac{d\mathbf{u}}{ds} \right|^2 - V \cos^2\theta \right) ds. \quad (5)$$

In this coarse-grained description, the first term arises from the bending energy, where K [J m] is the bending

constant, and the second term is the nematic energy where V [J/m] is the effect of the ac field.

DeGennes studied contours, $\mathbf{u}(s)$, that minimize Eq. (5), in application to nematic polymer liquid crystals [12]. He showed that hairpin kinks are described by the sine-Gordon soliton:

$$\theta_{\text{hp}}(s) = 2 \cot^{-1} \exp(-s/s_0), \quad (6)$$

where $s_0 \equiv \sqrt{K/2V}$ is the characteristic size of bends in the polymer. Figure 1 shows the shape of a hairpin and a typical conformation of a polymer with ten hairpins. The lateral displacement (see Fig. 1) across a kink is $l = \pi s_0$. The total energy stored in a kink is given by substituting $\theta_{\text{hp}}(s)$ from Eq. (6) into Eq. (5) to yield

$$U_k = 2\sqrt{2KV} = 2k_B T \frac{l_p}{s_0}, \quad (7)$$

where $l_p = K/k_B T$.

Kinks have well-defined size and energy, so we think of them as particles. In addition to the kink of Fig. 1(a), there exists an antikink formed by reflecting Fig. 1(a) about the vertical. Clearly kinks and antikinks must alternate along the polymer. At finite temperature, thermal fluctuations nucleate kink-antikink pairs. Each kink diffuses along the polymer until it encounters an antikink, whereupon the two annihilate.

Now we study the thermodynamics of the kink gas. On a chain with free ends, the equilibrium number of kinks should have the form $n_{\text{eq}}^0 = (L/l^*) e^{-U_k/k_B T}$. The as-yet-unknown quantity l^* represents the length separating independent attempts by the polymer to reorient. Warner and co-workers calculated l^* by drawing an analogy between direction-reversals of the polymer and quantum mechanical tunneling of a rigid rotator in a quadrupolar field [13–15]. They found $l^* = k_B T / 16V$. This result can also be derived more intuitively from soliton theory [16]. It is noteworthy that the attempt-length, l^* , is independent of the polymer stiffness, K , although by assumption

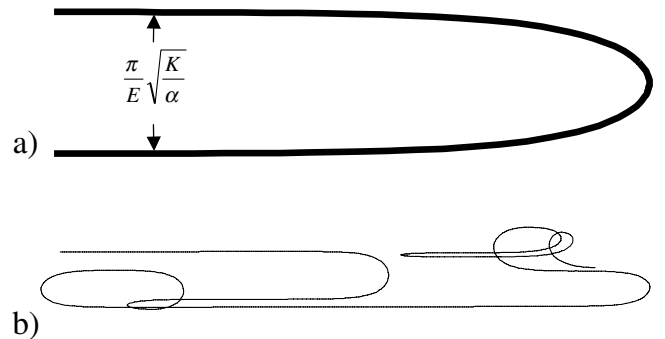


FIG. 1. (a) Shape of a hairpin kink in a polymer strand subject to a strong ac field. (b) Conformation of a polymer containing ten kinks of random position and orientation. All kinks are the same size: those that appear thinner are viewed edge on.

of a strong nematic field we have $l^* \ll l_p$. The equilibrium number of kinks is

$$n_{\text{eq}}^0 = 16 \frac{LV}{k_B T} \exp\left(-\frac{U_k}{k_B T}\right). \quad (8)$$

To calculate the force-extension curve in the kink-gas regime we map the problem onto the 1D Ising model. Approximating the polymer as perfectly straight between kinks, the unit-tangent vector takes on only two values, mapped to “spin up” and “spin down.” The number of independent “spins” on the polymer is $N = L/l^*$. The coupling to the tension, l^*F , corresponds to the coupling to the magnetic field, μB . The energy of a kink, U_k , corresponds to the energy of an orientation reversal, $2J$, where J is the nearest-neighbor coupling in the Ising model.

Making the above substitutions into the well-known solution of the 1D Ising model [17] and taking the limit $U_k \gg k_B T$, we find that the equilibrium number of kinks is related to the end-to-end extension, x_0 , by

$$n_{\text{eq}} = n_{\text{eq}}^0 \sqrt{1 - \frac{x_0^2}{L^2}}, \quad (9)$$

the free energy, A , is directly proportional to the equilibrium number of kinks,

$$A = -k_B T n_{\text{eq}}, \quad (10)$$

and the force-extension relation is

$$x_0 = L \left[1 + \left(\frac{k_B T n_{\text{eq}}^0}{FL} \right)^2 \right]^{-1/2}. \quad (11)$$

The zero-extension spring constant derived from Eq. (11), $k = k_B T n_{\text{eq}}^0 / L^2$, is much smaller than that of the FJC [Eq. (3)], because the field *exponentially* suppresses n_{eq}^0 [Eq. (8)]. The suppression arises from the energetic cost of orientation reversals, which was neglected in the FJC model. Equation (11) implies that in the kink-gas regime the polymer is very easily extended to almost its full contour length.

The Ising model does not take into account small fluctuations along the sections of the polymer between kinks. To calculate the effect of these fluctuations we introduce the tension, F , explicitly into the effective energy of Eq. (5):

$$U = \int_0^L \left(\frac{1}{2} K \left| \frac{d\mathbf{u}}{ds} \right|^2 - F \cos\theta - V \cos^2\theta \right) ds. \quad (12)$$

Far from a kink, θ is close to 0 or π , depending on whether the polymer is aligned or antialigned with the tension. The contour lengths of the aligned sections, L^+ , and the antialigned sections, L^- , are obtained from Eq. (11) via $L^\pm = (L \pm x_0)/2$. Expanding Eq. (12) about $\theta = 0$ on L^+ and about $\theta = \pi$ on L^- , the energies of these two segments become:

$$U^\pm \approx \frac{1}{2} \int_{L^\pm} \left(K \left| \frac{d\mathbf{u}}{ds} \right|^2 + F_{\text{eff}}^\pm \theta^2 \right) ds, \quad (13)$$

where the effective tension, $F_{\text{eff}}^\pm = 2V \pm F$, arises because the energies due to the tension and the ac field are both quadratic in θ . On L^+ , the ac field and tension both act to extend the polymer, while on L^- , the ac field acts to extend the polymer and the tension acts to compress the polymer.

The energy of Eq. (13) is identical to that of a WLC under tension in the absence of a field, with the replacement of F_{eff} for F . Thus we can quote the well-known force-extension relation of a WLC under large extension [18] to get

$$x^\pm = L^\pm \left(1 - \sqrt{\frac{k_B T}{4l_p F_{\text{eff}}^\pm}} \right), \quad (14)$$

where x^+ and x^- are the actual end-to-end lengths of the sections of the polymer aligned, and antialigned with the tension, respectively. The net end-to-end extension is given by $x = x^+ - x^-$, which is less than the extension predicted by the pure Ising model. Even when the tension is sufficient to completely eliminate kinks, so that $L^+ = L$ and $L^- = 0$, Eq. (14) shows that small thermal fluctuations prevent complete extension of the polymer. Figure 2 illustrates the force-extension curve of a WLC in the presence and absence of a nematic field. The initial steep rise in the extension is due to the kink gas. After the kinks have been suppressed, the extension grows much more gradually as the tension suppresses small thermal ripples.

For a polymer of finite length, a sufficiently strong field may send $n_{\text{eq}}^0 \ll 1$. A polymer with no kinks will show spontaneous extension to a length given by Eq. (14). The

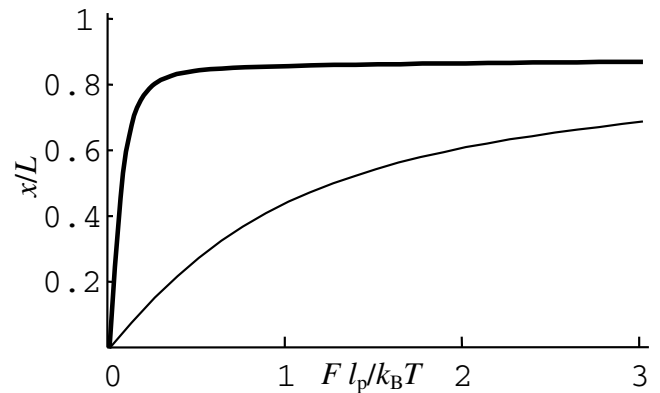


FIG. 2. Force-extension curve of a polymer in a strong ac field (bold). The Marko-Siggia interpolation formula for extension of a wormlike chain (without an ac field) is plotted for comparison. Under sufficiently strong tension, both curves reach $x/L = 1$. The dimensionless nematic field strength is $Vl_p/k_B T = 6$.

effective tension, F_{eff} , is positive even if $F = 0$. Tension ($F > 0$) further penalizes fluctuations in orientation and leads to additional extension. Under compression ($F < 0$), the polymer may lower its energy by an amount $2FL$ if it reverses direction. This reversal can occur through nucleation of a kink and antikink which are driven apart by the compressive force. For weak compression, the time scale for spontaneous formation of a critical kink-antikink nucleus is $\tau \propto \exp(-U_k/k_B T)$ [19].

We expect qualitatively similar features (i.e., drastic reduction of the restoring force, followed by spontaneous extension) to arise in polymers confined to a capillary of width comparable to the persistence length. In a polymer in a capillary, adjacent sections of the polymer may point in opposite directions, joined by an energetically costly hairpin kink. These are the conditions for description by the Ising model. The microscopic structure of a kink enters only in its free energy, which determines n_{eq}^0 . Under sufficiently strong confinement, thermally activated kinks become suppressed and we expect the polymer to show spontaneous extension. Such situations may arise with the advent of nanofluidic devices for processing DNA.

In experiments on dielectrophoretic manipulation of DNA, the electrode geometry typically creates an inhomogeneous field which attracts the DNA to regions of high intensity near the electrode corners. As the DNA moves towards the electrode, it also straightens and extends to its full contour length into the solution. If the DNA experienced simple attraction, it would ball up on the surface. In the model presented here, the molecule straightens because the field is strong enough to suppress the formation of kinks. Without the inclusion of the bending energy (i.e., in the FJC model), the polymer does not spontaneously extend in any ac field strength. Experiments are underway to provide a quantitative test of this theory. Single-molecule force-extension curves measured in an ac field should provide a quantitative test of the predictions in the various regimes, given by Eqs. (3), (11), and (14).

In conclusion, we have studied the restoring force and conformation of a polymer across the entire range of tensions and ac field strengths. In zero ac field the polymer is well-approximated by a freely jointed chain (FJC). A weak field biases the steps of the FJC to lie along the field axis. This bias decreases the entropic spring constant and increases the radius of gyration parallel to the field. A stronger ac field aligns almost all of the polymer backbone with the field. Freely diffusing hairpin kinks connect regions of opposite alignment, and the restoring force is *exponentially* suppressed by the ac field. A sufficiently strong field drives the density of kinks to less than one per polymer length, so the polymer approximately maintains its initial orientation along its entire length.

The activity of many DNA-active enzymes depends on the conformation of the underlying strand. Through its effect on conformation, an intense ac field may provide a way to rapidly and reversibly modulate both the kinetics and thermodynamics of biochemical processes, supplementing the traditional tools of temperature and chemical environment. Furthermore, it may be possible to design nanoscale polymeric actuators in which an ac field drives a conformational change.

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- [1] M. Washizu and O. Kurosawa, *IEEE Trans. Ind. Appl.* **26**, 1165 (1990).
- [2] M. Washizu, O. Kurosawa, I. Arai, S. Suzuki, and N. Shimamoto, *IEEE Trans. Ind. Appl.* **31**, 447 (1995).
- [3] S. Suzuki, T. Yamanashi, S. Tazawa, O. Kurosawa, and M. Washizu, *IEEE Trans. Ind. Appl.* **34**, 75 (1998).
- [4] C. L. Asbury and G. van den Engh, *Biophys. J.* **74**, 1024 (1998).
- [5] M. Ueda, K. Yoshikawa, and M. Doi, *Polym. J.* **31**, 637 (1999).
- [6] W. A. Germishuizen, C. Wälti, R. Wirtz, P. Tosch, M. Pepper, A. G. Davies, and A. P. J. Middelberg, in *Proceedings of 11th Conference on Electrostatics* (IOP, Bristol, 2003).
- [7] F. Dewarrat, M. Calame, and C. Schonenberger, *Single Mol.* **3**, 189 (2002).
- [8] T. B. Jones, *Electromechanics of Particles* (Cambridge University Press, Cambridge, United Kingdom, 1995).
- [9] R. R. Netz, *Phys. Rev. Lett.* **90**, 128104 (2003).
- [10] U. Mohanty and Y. Zhao, *Biopolymers* **38**, 377 (1996).
- [11] H. Washizu and K. Kikuchi, *J. Phys. Chem. B* **106**, 11 329 (2002).
- [12] P. G. de Gennes, in *Polymer Liquid Crystals*, edited by A. Ciferri, W. R. Krigbaum, and R. B. Meyer (Academic Press, New York, 1982), Chap. 5.
- [13] M. Warner, J. M. F. Gunn, and A. B. Baumgärtner, *J. Phys. A* **18**, 3007 (1985).
- [14] D. R. M. Williams and M. Warner, *J. Phys. (France)* **51**, 317 (1990).
- [15] J. M. F. Gunn and M. Warner, *Phys. Rev. Lett.* **58**, 393 (1987).
- [16] A. E. Cohen (to be published).
- [17] R. K. Pathria, *Statistical Mechanics* (Butterworth Heinemann, Stoneham, Massachusetts, 1996), 2nd ed.
- [18] J. F. Marko and E. D. Siggia, *Macromolecules* **28**, 8759 (1995).
- [19] M. Büttiker and R. Landauer, *Phys. Rev. A* **23**, 1397 (1981).