Transverse Fluctuations of Polyelectrolytes

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The ground state of an N-monomer charged polymer, in the absence of screening, is stretched, with nonextensive energy growing as $N \ln N$. If the allowed bond angles are discrete, only discrete changes in conformation are possible, and the elementary excitations have energy growing as $\ln N$. Using analytical arguments, and Monte Carlo simulations, we show that such a polymer is rigid (flat) at low temperature T, and flexible (rough) at high T. The roughness exponent, for the scaling of transverse fluctuations with N, varies continuously with T, reaching the value for models which permit continuous changes in geometry only at very high T.

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Polyelectrolytes (PEs), long chain molecules with charged monomers, are quite common in nature [1]; nucleic acids such as DNA are important examples. The Coulomb repulsion between monomers expands such polymers, to the extent that a uniformly charged PE is fully stretched in dimension $d = 3$. Usually, the presence of counterions in the solvent screens the Coulomb interaction, and the PE at long length scales can be described by short range forces. Nevertheless, the effective rigidity and persistence length ξ of the screened PE are strongly affected by the behavior of segments shorter than the screening length λ. There have been many analytical [2–4], numerical [5,6], and experimental [7] studies of the dependence of ξ upon λ. A key element is the extent of transverse fluctuations of unscreened segments, an issue reexamined in this Letter.

In d dimensions, the electrostatic energy of a PE scales with its number of monomers N, and size R, as N^2/R^{d-2}. When interactions are relevant, R can be estimated by equating this energy with temperature T [8], leading to $R \sim N^\nu$ with $\nu = 2/(d-2)$ for $4 < d < 6$. At $d = 4$, the exponent ν attains its maximal value of unity, and the polymer is asymptotically stretched. The stretched polymer can still be flexible, with transverse fluctuations, e.g., characterized by the second largest eigenvalue λ_2 of the shape or mass distribution tensor, that grow as $\sqrt{\lambda_2} \sim N^\zeta$. Simple dimensional analysis [9] suggests a *roughness exponent* of $\zeta = d/2 - 1$ for $2 < d < 4$. In particular, the value of $\zeta = 1/2$ (as in a directed random walk) in $d = 3$ is also confirmed in Ref. [4], which finds that the energy cost of the lowest transverse mode of the chain is proportional to its squared amplitude divided by N. These theoretical treatments model the PE as an inextensible string with *continuous deformations.*

However, $d = 3$ is a special space dimension in this problem: While for $d > 3$ the total energy of a PE is extensive, in $d \leq 3$ it is *overextensive,* i.e., grows faster than N. In particular, in $d = 3$ the energy of a stretched PE is proportional to $N \ln N$. A chain of harmonic springs is *unstable,* torn apart by the long-range interactions, and for a consistent treatment the chain must be regarded as unstretchable; i.e., its internal length should not change. Another consequence of the overextensivity of energy is that the elementary excitations have to be treated carefully. Unlike a continuous string, in real polymers the allowed directions of molecular bonds are discrete. Starting from the maximally stretched state, the simplest changes in configuration, obtained by changing the orientation of a few bonds, result in a reduction of the end to end length of the polymer by a finite amount a, of the order of an atomic spacing. This results in a large change in energy, proportional to $a \ln N$ [6]. The large energy cost renders such excitations unlikely, and as we shall demonstrate, a continuum description of the discrete chain is not possible at any finite temperature.

For simplicity, consider a model PE consisting of N atoms placed on a square or cubic lattice with lattice spacing a. (While discretizing the locations of atoms is convenient for simulations, our main results are equally valid for off-lattice polymers with discrete angles between adjacent bonds.) Each monomer has charge q, and the interaction energy of two charges at positions $\mathbf{r}_i$ and $\mathbf{r}_j$ is $q^2/|\mathbf{r}_i - \mathbf{r}_j|$. The lowest energy configuration is a straight line, and its energy, $E = (q^2/a)\sum_{1 \leq i \leq j \leq N} 1/|i-j| \approx (q^2/a)N \ln N$, is overextensive. The basic energy and temperature scale of the model is thus $\epsilon \equiv q^2/a$. The simplest excitations above the ground state have a single "kink" on an otherwise straight configuration: e.g., all the bonds remain in the $+\hat{\mathbf{x}}$ direction, except for a single ith bond which points along $\hat{\mathbf{y}}$, as in Fig. 1a. The misaligned bond shortens the separations of monomers on opposite sides of the kink approximately by a, thus increasing the Coulomb energy. Summing over all pairs, for $i \gg 1$ and $N - i \gg 1$, we obtain a kink energy

$$E_{\rm kink}(i) = \epsilon \ln[i(N-i)/N]. \qquad (1)$$

For kinks far away from the edges, the energy is $E_{\rm kink} = \epsilon \ln N$, and *diverges* with increasing PE size. Although the prefactor of ϵ is model specific, the logarithmic divergence

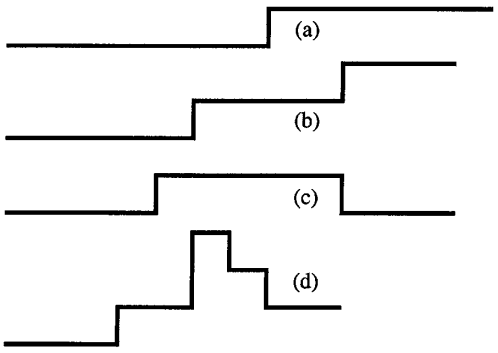

FIG. 1. (a) A single kink in an otherwise straight chain. A pair of kinks in the same (b) or opposite (c) directions. (d) A typical configuration of the directed self-avoiding walk.

of the kink energy is *universal*, and appears whenever discrete distortions in PE configurations occur.

The logarithmic behavior in Eq. (1) is a consequence of the $1/r$ decay of the electrostatic potential, and the discreteness of allowed configurations. As it is independent of the dimension of embedding space, for simplicity, we shall numerically study polymers on a two-dimensional square lattice with $1/r$ interactions between monomers. The spatial configurations of such a PE are $(N-1)$-step self-avoiding walks. Since strongly charged chains are asymptotically flat, we further restrict configurations to *directed* walks along the x direction: Each step of the walk is in the $+\hat{\mathbf{x}}$, $+\hat{\mathbf{y}}$, or $-\hat{\mathbf{y}}$ direction. (Figure 1d depicts a typical configuration.) (Undirected self-avoiding walk configurations appear only at temperatures $T \gg \epsilon N^{\nu}$. Our results do apply to weakly charged polymers which violate this condition.) The self-avoidance of the walk is now ensured by a *local* restriction that a step in the $+\hat{\mathbf{y}}$ direction is not followed by one in the $-\hat{\mathbf{y}}$ direction, and vice versa. An elementary move in our Monte Carlo (MC) simulation consists of rotating a randomly selected bond, without changing the directions of other bonds. The move is accepted according to its Boltzmann weight, as long as it does not violate the self-avoidance condition. Because of the long-range interactions, the number of operations in each MC time unit (of N elementary moves) increases as N^2. Because of the logarithmically large energies of elementary excitations, the acceptance rate is very low. Therefore, we used large times (10^7 MC time units for $N = 128$ at $T = 0.6\epsilon$), and limited our simulations to moderate lengths ($N \leq 256$).

The logarithmic divergence of the elementary excitation energies is reminiscent of the one-dimensional Ising model with ferromagnetic interactions decaying as $1/r^2$ with the separation between spins [10]. The energy cost of a wall between up and down spin domains also grows as $\ln N$. The latter model provided the inspiration for the Kosterlitz-Thouless analysis of vortices in the 2D XY model [11]. In these models there is an entropy of $\ln N$ from the possible locations of the defect, leading to $F_1 = \epsilon \ln N - T \ln N$, for the free energy of an isolated elementary excitation at temperature T. Ignoring interactions, this free energy predicts that the system is asymptotically free of defects at low temperatures, which are then liberated for $T > \epsilon$. For the 1D Ising model with $1/r^2$ interactions [10], and the 2D XY model [11], proliferation of defects signals the disordering transition. The 2D XY model is in turn dual [12] to a fluctuating surface in $d = 3$, where the heights are restricted to integer values [13]. There is a *roughening transition* to a low temperature flat phase where continuum descriptions of the surface are no longer valid. Similarly, continuum models fail to capture transverse fluctuations of discrete PEs.

However, there is a crucial difference between the discrete PE, and models undergoing a defect liberation transition. In the latter, defects of different sign (up and down vortices or domain walls) screen the long-range distortions, resulting in finite pair energies. Hence, these defects always appear at finite density. In the PE, subsequent kinks (independent of orientation) shorten the chain further, increasing its energy. The absence of screening prevents discrete PEs from having a finite kink density at *any finite temperature.*

Another consequence of the absence of screening is that the leading energy cost for a collection of n kinks is simply the sum of their individual energies, and interactions between kinks result only in subleading corrections (see later). Disregarding interactions greatly simplifies theoretical analysis of the model. The probability of a kink on the ith bond is given by $p_i = \{1 + \frac{1}{2}\exp[\beta E_{\rm kink}(i)]\}^{-1}$, with the kink energy taken from Eq. (1). The total number of kinks is obtained by adding these densities as $n = \sum_{i=1}^{N-1} p_i$. Figure 2 compares this prediction with the results of MC simulation for $N = 128$. There is surprisingly

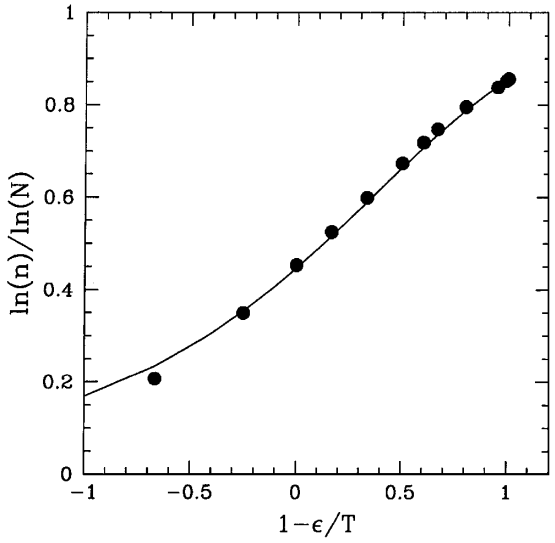

FIG. 2. The number of kinks n, as a function of temperature T, for $N = 128$. The continuous line is an analytic approximation which neglects interactions between kinks.

good agreement over the entire range of temperatures, justifying the neglect of interactions. For large N, the sum behaves as $n \sim N^{1-\epsilon/T}$. While the number of kinks grows for $T > \epsilon$, the asymptotic density is zero. (For $T < \epsilon$, n goes to a finite constant because of the ease of placing kinks at the edges.) The borderline temperature of $T = \epsilon$ is not a usual phase transition point, since there are no extensive thermodynamic quantities. Nonetheless, we observed a peak in the heat capacity, signaling strong energy fluctuations at this point.

Assuming that the orientations of the kinks are also independent, configurations of the PE at a fixed temperature should resemble a directed random walk. The squared transverse fluctuations would then grow as n, leading to $\lambda_2 \sim N^{2\zeta}$, with $\zeta = (1 - \epsilon/T)/2$. Figure 3 depicts the dependence of λ_2 on N at several temperatures. The simulated PEs are too short for quantitative comparison, but they clearly exhibit a decay of λ_2 with increasing N at low T, and sublinear increase at high T. In fact, orientations of the kinks are correlated, and the assumption of $\lambda_2 \propto n$ is not entirely correct. This is clearly manifested by the dependence of λ_2 on temperature for fixed N, as depicted in Fig. 4. While n increases monotonically with T (see Fig. 2), transverse fluctuations are actually nonmonotonic, reaching a maximum at a finite T. We confirmed this nonmonotonicity by numerically calculating the first term in the high temperature expansion of the squared transverse separation $\langle M^2 \rangle$, of the opposite ends of the PE. By examining the Coulomb energy of all random walk configurations, we find that in lattice constants $\langle M^2 \rangle = (N/2)[1 + A(N)\epsilon/T]$, where $A(N)$ is positive, and grows approximately as $\ln^2 N$ for $N \leq 256$.

To understand why assuming independent kinks provides a good description of the number of kinks in a PE (Fig. 2), but fails to capture the nonmonotonicity of its transverse fluctuations (Fig. 4), we need to examine the interactions between kinks. The energy of a pair is the sum of the energies of the two kinks, plus an interaction term *which depends on their relative orientations.* Figure 1b depicts two kinks with identical orientations, while the kinks in Fig. 1c are oppositely oriented. In the latter case, the end to end distance of the chain is slightly shorter, resulting in a higher energy. It is convenient to designate the orientation of each kink by a "spin" variable $\sigma = \pm 1$ (and $\sigma_i = 0$ if there is no kink at i). A detailed calculation shows that the interaction energy between kinks located on bonds i and j is described by

$$E_{\text{int}} = \frac{\epsilon}{|i - j|}\left(\sigma_i^2\sigma_j^2 - \frac{1}{2}\,\sigma_i\sigma_j\right), \qquad (2)$$

for $|i - j| \gg 1$, while at short distances E_{int} deviates from a power law. (For a PE embedded in three-dimensional space, $\sigma_i\sigma_j$ is replaced by the scalar product $\vec{\sigma}_i \cdot \vec{\sigma}_j$, where the vector $\vec{\sigma}_i$ denotes the direction of the kink.)

The first term in the parentheses in Eq. (2) is a repulsion between kinks, and we therefore expect the kinks to be approximately uniformly spaced. The interaction energy of n equidistant kinks is of order $\epsilon(n^2/N)\ln n$, which is much smaller than the leading energy of $\epsilon n \ln N$ required for the creation of these kinks. This is the *a posteriori* justification for the agreement between MC results for n, and the prediction based on noninteracting kinks.

The second term in Eq. (2) is a long-ranged "ferromagnetic" interaction that tends to align the kinks. To lowest order, the effect of this interaction is to introduce a correlation, such that $\langle \sigma_i\sigma_j \rangle = \epsilon p_i p_j/[2T|i - j|]$, where p_i

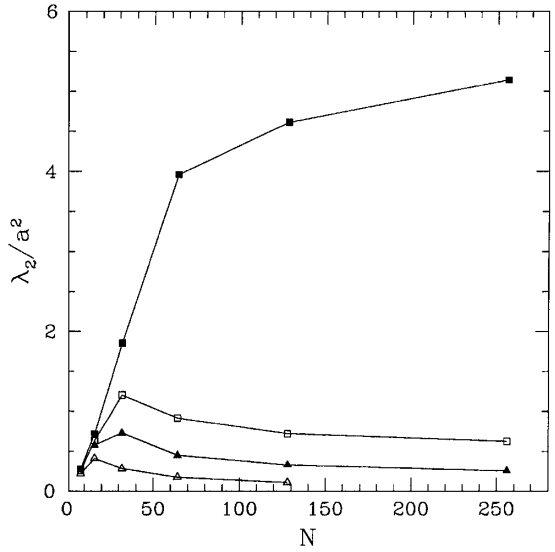

FIG. 3. Transverse fluctuations (the smaller eigenvalue of the shape tensor in lattice units) versus the number of atoms N, for (from bottom to top) $T/\epsilon = 0.6$, 0.8, 1, and 2.

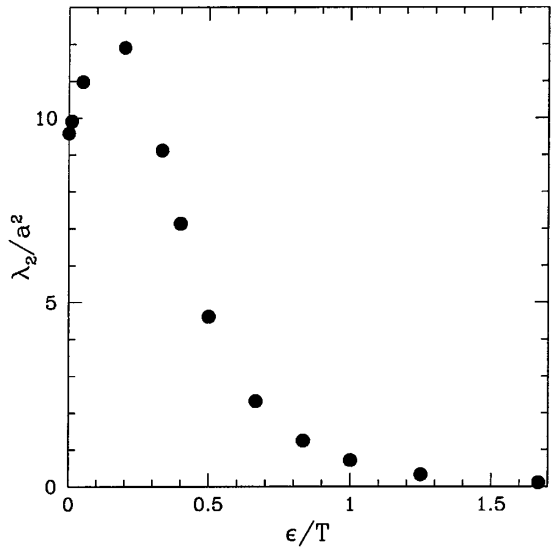

FIG. 4. Transverse fluctuations of the polymer (the smaller eigenvalue of the shape tensor in lattice units), versus inverse temperature, for $N = 128$.

is the local kink density introduced earlier. Despite its apparent long-range decay, this correlation is actually quite small because of the vanishing densities. Nonetheless, this term is responsible for the nonmonotonic behavior of transverse fluctuations. For the transverse separation (in lattice constants) $M = \sum_i \sigma_i$ of the end points of the PE, we have $\langle M^2 \rangle = \sum_i p_i + 2\sum_{i<j}\langle \sigma_i \sigma_j \rangle$. A plot of $\langle M^2 \rangle$, using the correlations calculated above, results in a curve that is qualitatively similar to Fig. 4. At high temperatures, the alignment of kinks increases the extent of transverse fluctuations, which then decay at lower T due to the rapid decrease in the total number of kinks. The form of the correction suggests that the peak in transverse fluctuations occurs at a temperature $T_m \sim \ln N$. Nonmonotonic fluctuations are thus a finite size effect; for a fixed T it is always possible to go to large enough N, such that the kinks are sufficiently far apart so that their correlations are negligible. Transverse fluctuations then grow as $\lambda_2 \sim \langle M^2 \rangle = n \sim N^{2\zeta}$, as concluded earlier.

What are the consequences of our results for real PEs? The flexibility of polymers arises mostly from changes in configurations of bonds at molecular level, e.g., between trans and gauche states. These discrete atomic changes must be accompanied by shortening of the length, and a logarithmically large energy cost for unscreened Coulomb interactions. Additionally, bond angles in polymers are not completely fixed, but have some flexibility. Therefore, continuous deformations may coexist with discrete changes. In terms of the Bjerrum length $\ell_B = q^2/k_B T$, our results indicate that the contribution of discrete deformations to transverse fluctuations scale as $(w_d/a)^2 \sim N^{1+\ell_B/a}$. On the other hand, dimensional analysis [9] suggests that continuous deformations lead to $(w_c/a)^2 \sim Na/\ell_B$. While the latter is asymptotically dominant, both effects are important for finite chains. A clearer signature of discrete behavior is the peak in heat capacity, which is present in the discrete model but absent for continuous deformations.

In solution, interactions are screened by counterions, but the persistence length of the polymer ξ, is strongly controlled by the stiffness of its shorter segments. Within Debye-Hückel theory interactions are screened at a distance λ. Following the work of Odijk, Skolnick, and Fixman (OSF) [2], there have been many studies of the dependence of ξ on λ. The OSF argument can be generalized and reformulated as follows: At distances shorter than λ, electrostatic interactions can be treated as unscreened, and therefore a typical change in orientation of the PE due to fluctuations on a segment of length λ is $\theta_\lambda \sim \lambda^{\zeta-1}$. At larger distances, angular fluctuations can be treated as a random walk, and at the persistence length ξ grow to the order of $\theta_\lambda\sqrt{\xi/\lambda}$. Setting the latter to unity gives $\xi \sim \lambda^{3-2\zeta} = \lambda^{2+\epsilon/T}$, where we substituted the value of ζ obtained here. The OSF result of $\xi \sim \lambda^2$ is recovered at infinite T, or by including finite deformations. (Again, these results apply only to strongly charged PEs which are stretched at scales less than λ.)

In conclusion, we have demonstrated important consequences of the nonextensivity of Coulomb interactions in PEs. The most important results are the breakdown of conventional continuum descriptions, and a roughness exponent that varies continuously with T. Unusual finite size effects include a peak in heat capacity, and nonmonotonicity of transverse fluctuations. Such effects may well appear in analysis of experimental data; we note at least one experimental study [14] which reports a nonmonotonic persistence length in a filamentous virus.

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