Fluctuations and Persistence Length of Charged Flexible Polymers

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ABSTRACT: We analyze the effect of conformational fluctuations of charged flexible polymers in the presence of screening. We find that the fluctuations do not invalidate the classical theory of electrostatic persistence length due to Odijk and to Skolnick and Fixman. We show that there are strong local fluctuations with wavelength smaller than the screening length κ^{-1}. These fluctuations significantly decrease the direct distance between two monomers separated by a contour length smaller than κ^{-1}, although they do not affect the persistence length on much larger length scales. Our theory accounts for the apparent short persistence length recently reported by Barrat and Boyer.

I. Introduction

Charged polymers are quite common in nature. Most water-soluble polymers (e.g., biopolymers) consist of monomers with ionizable groups. When dissolved in water, the ionic groups dissociate, leaving charges on the chain. The interactions among the charges then tend to elongate the polymer. In the absence of screening, the conformation of the chain is known to be linearly stretched.[1,2] When screening is introduced, either by increased polymer concentration or by addition of salt, the situation is much more complicated. A crucial concept in describing such a system is the charge-induced bending stiffness, or electrostatic persistence length, independently introduced by Odijk[3] and by Skolnick and Fixman.[4] The Odijk−Skolnick−Fixman (OSF) theory considers the electrostatic energy cost of bending a long wormlike chain. Such a consideration leads to a bending stiffness proportional to the square of the screening length, which in the dilute limit far exceeds the screening length itself.

While the OSF theory has been reasonably verified for stiff polymers such as DNA,[5] there has been quite a controversy over whether the theory can be simply generalized to intrinsically flexible polymers, as was done by Khokhlov and Khachaturian (KK).[6] Such a controversy arises due to a number of reasons: (i) Experimentally, there has been no clear confirmation of the expected scaling in the asymptotic regime of large screening length due to difficulties of probing very dilute solutions. Experiments are also restricted by finite-size effects, since the polymers used are usually not sufficiently long. Several experiments performed in the nonasymptotic regime seem to indicate a deviation from the OSF−KK theory.[7,8] (ii) There are a few recent numerical simulations which seem to suggest a persistence length much smaller than that predicted by OSF−KK formula.[9,10] (iii) OSF theory ignores the fluctuations in the chain conformation, which might add an important contribution to the bending rigidity. It has been argued by Barrat and Joanny (BJ)[11] that the OSF theory is invalidated by fluctuations with wavelengths smaller than the screening length. Using a variational approach, BJ obtained a persistence length proportional to the screening length. Similar conclusions were reached by Bratko and Dawson[12] and also by Ha and Thirumalai[13] using also variational approaches.

In this paper, we calculate the persistence length of charged flexible polymers by explicitly including all fluctuations in the chain conformation. We find that fluctuations do not change the OSF−KK picture qualitatively, although they do modify the persistence length to a slightly smaller value. At length scales much larger than the screening length, the fluctuations are just those epxected in the OSF−KK picture, while at length scales much smaller than the screening length, they become much larger than they would be in a simple wormlike chain characterized by a persistence length. We analyze the numerical simulation data by Barrat and Boyer[9] and show that it is important to consider a local stretching effect which has a logarithmic dependence on the screening length. With both the local fluctuation and the stretching effect included, our theoretical calculation agrees quite well with the simulation data.

II. Fluctuation Correction

In this section we calculate the effect of thermal fluctuations on a flexible polyelectrolyte chain. We exploit the fact that these fluctuations are small for a weakly screened polyelectrolyte. Joanny and Barrat[11] used a similar approach to treat intrinsically rigid polyelectrolytes. For convenience we treat the case of a ring polymer. We first determine the radius variationally, thus fixing the linear charge density. Next we identify the normal modes of fluctuation away from the ring configuration. Finally, we estimate the amount of distortion of the ring owing to these normal modes.

We start by considering a polyelectrolyte consisting of N segments, with segment length a. The charges are A segments apart, with strength q_0. Following refs 9 and 11, we shall not explicitly consider counterions. Instead, we consider counterions as providing a screening, so that the charges on the chain will interact via a screened Coulomb potential,

$$U_{ij} = l_B \frac{\exp(-\kappa r_{ij})}{r_{ij}} \tag{2.1}$$

Here $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ is the distance between two charged monomers, κ is the inverse screening length, and $l_B \equiv q_0^2/(\epsilon k_B T)$ is the Bjerrum length, with ϵ the dielectric constant of the solvent. Hereafter, we shall use the reduced charge $q \equiv q_0/\epsilon^{1/2}$ and measure energy in units of $k_B T$. We assume that the chain has a bare persis-

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tence length l_0. For flexible polymers, $l_0 \approx a$. To focus on the effect of long-range interaction, we shall also neglect the self-avoidance of the monomers. Thus in the absence of the charge interaction, the chain would form a random coil with radius of gyration $R_G \simeq aN^{1/2}$.

Now consider the chain conformation with charge interactions turned on. It is known that for unscreened interaction, the chain consists of linearly stretched blobs of characteristic size ξ;[1,2] within each blob the random walk configuration is not strongly affected. This leads to a radius of gyration proportional to the molecular weight, $R_G \simeq \xi N/N_b$, where N_b is the number of monomers in a blob. When screening is introduced, one expects that this picture of linearly stretched blobs should remain valid within a screening length if $\kappa^{-1} \gg \xi$. More precisely, it should be so within a persistence length l_p with $l_p \gg \xi$. In a simple scaling argument, one obtains blob size by assuming that the electrostatic interaction within a blob is roughly k_BT, giving $\xi \approx \xi_0 = a(l_B/a)^{-1/3}A^{2/3}$.

Here we give an alternative derivation of the blob length using a more careful consideration of balance between the stretching energy (due to entropic effect) and the electrostatic energy. Consider a chain of N monomers in the form of a ring. If the screening is weak, such a chain must form a near-circle of some radius r_0. The radius r_0 is that which minimizes the freen energy $\mathcal{F}$ defined by

$$e^{-\mathcal{F}} = \sum_{\{\mathbf{r}_j\}} \exp(-U\{\mathbf{r}_j\})$$

where $U \equiv {}^1/_2\sum_{i,j} \exp(-\kappa|\mathbf{r}_i - \mathbf{r}_j|)/|\mathbf{r}_i - \mathbf{r}_j|$. It is convenient to use Rouse-mode coordinates $\mathbf{A}_n$ to perform the configuration sum $\{\mathbf{r}_j\}$:

$$\mathbf{r}_j = \mathrm{Re}\,[\sum_{n=0}^{N} \mathbf{A}_n \exp(2\pi i n j/N)]$$

Since the ring has little fluctuation at large scales, we expect the amplitudes $\mathbf{A}_n$ for small index n to be nearly those of a perfect circle. Thus $\mathbf{A}_0 = 0$, $\mathbf{A}_1 = (ir_0,r_0,0)$, and $\mathbf{A}_2 = \mathbf{A}_3 = ... = 0$. We expect the opposite for high-lying models with n of order N. These describe local fluctuations within the chain, at distances where electrostatic effects are minor. We shall treat the two types of modes separately. Accordingly, we first consider a ring in which all the mode amplitudes are fixed to values describing a circle for $n = 0, 1, 2, ..., n_{max}$. For the moment we do not specify n_{max} except to anticipate that $1 \ll n_{max} \ll N$. Then by summing over the modes with $n > n_{max}$, we may obtain an effective free energy $\mathcal{F}_{eff}(r_0)$. By minimizing this $\mathcal{F}_{eff}$ we may find the optimal radius r_0 and hence the thermal blob length ξ and the linear charge density along the chain.

The chief effect of the high-lying modes is to impart an entropic elasticity to the ring. The free energy thus has the form

$$\mathcal{F}_{eff}(r_0) = \frac{(2\pi r_0)^2}{a^2N} + \frac{1}{2}\int d^3r_1\, d^3r_2\, \varrho(\mathbf{r}_1)\varrho(\mathbf{r}_2)\frac{\exp(-\kappa|\mathbf{r}_1 - \mathbf{r}_2|)}{|\mathbf{r}_1 - \mathbf{r}_2|} \quad (2.2)$$

The first term is the familiar elastic free energy of a random-walk polymer. It is unmodified by the constraints on $\mathbf{A}_1, ..., \mathbf{A}_{n_{max}}$, since these represent a vanishingly small fraction of the modes. The second term is the electrostatic energy. In writing it, we exploit the fact that the bulk of the electrostatic energy is that of distant pairs of monomers. At large separations $|\mathbf{r}_1 - \mathbf{r}_2| \gg \xi$, the monomers can be regarded as a ring-shaped cloud of charge with density profile $\varrho(\mathbf{r})$. The width of this ring is the blob size ξ. Using these facts, the second term in the free energy takes the form shown in eq 2.2. At smaller separations $|\mathbf{r}_1 - \mathbf{r}_2| \lesssim \xi$ the charge cannot be treated as a uniform cloud in this way. However, these separations contribute negligibly to the electrostatic energy, as we show in the Appendix. Thus eq 2.2 treats the potential energy adequately at all scales.

Taking the charge density to be that of a ring of radius r_0 and core size ξ, with a smooth distribution inside the core, the second term in the above equation takes the form

$$\langle U\rangle = \frac{Q^2}{2\pi r_0}\left(C_1 \ln\frac{\kappa^{-1}}{\xi} + C_2\right) \quad (2.3)$$

where $Q = Nq$ is the total charge on the chain and C_1 and C_2 are numerical constants. Notice that there is a logarithmic term in the electrostatic energy, depending on an upper cutoff length κ^{-1} and a lower cutoff length ξ.

We now use the relations $2\pi r_0 \simeq \xi N/N_b$ and $\xi/a \simeq N_b^{1/2}$. That is, the chain consists of linearly stretched blobs of size ξ within which the polymer performs a random walk. These two relations combine to give

$$2\pi r_0 = \frac{a^2N}{\xi} \quad (2.4)$$

The equilibrium r_0 is found by minimizing the free energy with the constraint eq 2.4, which yields

$$\frac{\xi}{a}\left(\frac{l_B}{a}\right)^{1/3}A^{-2/3} = \left(C_1 \ln\frac{\kappa^{-1}}{\xi} + C_3\right)^{-1/3} \quad (2.5)$$

In the case where there is no screening, the upper cutoff is provided by the size of the polymer; therefore the screening length κ^{-1} in the above equation should be replaced by r_0. Hence we have

$$\frac{\xi}{a}\left(\frac{l_B}{a}\right)^{1/3}A^{-2/3} = \left(C_1' \ln\frac{a^2N}{\xi^2} + C_3'\right)^{-1/3} \quad (2.6)$$

where C_1' and C_3' are other numerical constants. We see that the result is similar to the one obtained using simple scaling argument, but with logarithmic corrections. These logarithmic corrections can be important in analyzing the simulation data, as we shall discuss later.

The above calculation enables us to determine the local structure of the polymer. On scales much larger than ξ, we can view the chain as a charged loop with core size ξ and linear charge density $\varrho = qN_b/\xi$. This charged loop will have a circular shape with radius r_0 when no fluctuation with $n < n_{max}$ is considered (see Figure 1). In the absence of screening, these fluctuations only slightly distort the circular shape since the chain is very stiff due to the charge interactions. Thus we may treat the fluctuations as a small perturbation. As the screening length is decreased, the persistence length decreases and the fluctuations become stronger. We shall take the circular loop as our base state and consider fluctuations around this base configuration. The persistence length must be proportional to the size of the polymer when the fluctuations completely destroy

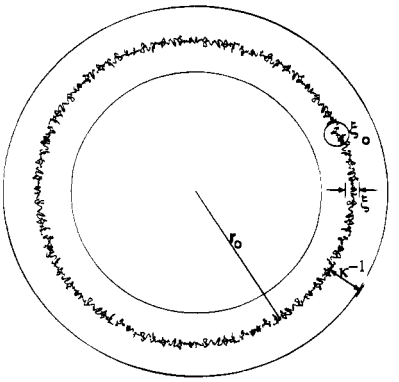

Figure 1. Schematic diagram of the base state, where the chain forms a circular loop with radius r_0 and core size ξ.

the circular loop; i.e., the fluctuation amplitude is comparable to the radius.

To analyze the fluctuation effect, let us consider a loop which can fluctuate only in its own plane; the generalization to out-of-plane fluctuation is straightforward and the effects are minor. In general, an arbitrary fluctuation contains both the deformation of the shape and local stretching. We simplify the consideration by assuming that there is no coupling between stretching and deformation; therefore, any stretching will relax to a uniform value. With this simplification, the configuration of the polymer can be parametrized by

$$r(\theta) = r_0 + \sum_{n=0}^{n_{max}} \Delta_n \cos(n\theta + \phi_n) \tag{2.7}$$

where $r(\theta) = r_0$ is the base state and Δ_n and ϕ_n are the amplitude and phase of the fluctuation of the nth mode. The amplitudes Δ_n are closely related to the Rouse amplitudes $\mathbf{A}_n$ introduced above. Here Δ_0 represents a simple uniform stretching. For a given shape, the electrostatic energy of the system is

$$U_e = \frac{\varrho^2}{2}\int\frac{dl_1\, dl_2}{r_{12}} \exp(-\kappa r_{12}) \tag{2.8}$$

where $\varrho = N_b q/\xi$ is the line charge density,

$$r_{12} = [r^2(\theta_1) + r^2(\theta_2) - 2r(\theta_1)r(\theta_2)\cos(\theta_1 - \theta_2)]^{1/2} \tag{2.9}$$

and the length element dl is given by

$$dl = \left[\left(\frac{dr}{d\theta}\right)^2 + r^2(\theta)\right]^{1/2} d\theta \tag{2.10}$$

We shall calculate the free energy cost due to an arbitrary deformation given by eq 2.7 to quadratic order in Δ_n. Since the free energy is invariant under an arbitrary reparametrization $\theta \to \theta + \delta\theta$, there is no coupling between different modes in the quadratic order, i.e.,

$$\delta\mathcal{F} = \sum_{n=0}^{n_{max}} E_n\left(\frac{\Delta_n}{r_0}\right)^2 \tag{2.11}$$

hence we only need to calculate the free energy change of a single mode $r(\theta) = r_0 + \Delta_n \cos(n\theta)$. Notice that this deformation changes the total length of the loop by $\pi n^2\Delta_n^2/(2r_0)$, so E_n contains contributions from the stretching as well as the electrostatic energy. However, E_n can be calculated by considering only the electrostatic energy change of an n mode that preserves the length of the loop with no stretching cost. This is so because the two deformations differ only by a $\Delta_0 = n^2\Delta_n^2/(4r_0)$, which does not contribute to the quadratic order. It is very convenient to work with length-preserving deformations, since this leaves the core size of the loop and local charge density unchanged. It therefore ensures nice cancellation of the short-distance divergence (depending on the cutoff given by the core size of the loop) when we subtract the electrostatic energy of the base state from the deformed loop.

Consider the electrostatic energy change due to a length-preserving deformation

$$r(\theta) = r_0 - \frac{n^2\Delta_n^2}{4r_0} + \Delta_n \cos(n\theta) \tag{2.12}$$

We shall use the contour length l as the basic variable instead of the angle θ, since the small-length cutoff is uniform in terms of the contour length. The change of variable is accomplished by combining eqs 2.10 and 2.12, and we obtain (to quadratic order in Δ_n)

$$\theta = \alpha - \frac{\Delta_n}{r_0}\frac{\sin(n\alpha)}{n} + \frac{\Delta_n^2}{r_0^2}\left(\frac{1}{2n} + \frac{n}{8}\right)\sin(2n\alpha) \tag{2.13}$$

with $\alpha \equiv l/r_0$. Equations 2.9, 2.12, and 2.13 enable us to express U_e in eq 2.8 in terms of contour variables α_1 and α_2. We then expand eq 2.8 and keep the quadratic terms in Δ_n. After some algebra, we find

$$E_n = \pi r_0\varrho^2\int_0^{\pi/2} dx\, \frac{\exp(-2\kappa r_0 \sin x)}{n^2 \sin^3 x} \times (U^{(0)} + 2\kappa r_0 U^{(1)} + (2\kappa r_0)^2 U^{(2)}) \equiv \pi r_0\varrho^2 I(\kappa r_0, n) \tag{2.14}$$

with

$$U^{(0)} = n^4 \sin^2 x + \sin^2 nx(2 - n^2 - \sin^2 x - n^2 \sin^2 x) - 2n \sin x \sin nx \cos x \cos nx$$

$$U^{(1)} = \sin x[\sin^2 x(n^4 - \sin^2 nx - n^2 \sin^2 nx) + (2 - n^2)\sin^2 nx - n \cos x \sin x \sin 2nx]$$

$$U^{(2)} = \sin^2 x(n \sin x \cos nx - \cos x \sin nx)^2 \tag{2.15}$$

For any given n and κr_0, eq 2.14 gives the free energy cost in terms of the integral $I(\kappa r_0, n)$. The general dependence of $I(\kappa r_0, n)$ on n and κr_0 is complicated but can be obtained numerically. Here we examine a few simple cases.

(i) $\kappa r_0 \ll 1$: this is essentially the unscreened case. The large-n behavior for E_n is

$$E_n \sim \pi r_0\varrho^2 n^2 \ln n \tag{2.16}$$

(ii) $\kappa r_0 \gg 1$ and $n \ll \kappa r_0$: both the size of the loop and the wavelength of the deformation $\lambda = 2\pi r_0/n$ are much larger than the screening length. E_n can be evaluated as a power series in $1/(\kappa r_0)$. We obtain

$$E_n = \pi r_0\varrho^2\frac{(n^2 - 1)^2}{(2\kappa r_0)^2}\left[1 + \mathcal{O}\left(\frac{1}{\kappa r_0}\right)\right] \tag{2.17}$$

This E_n has a natural interpretation. Consider a loop

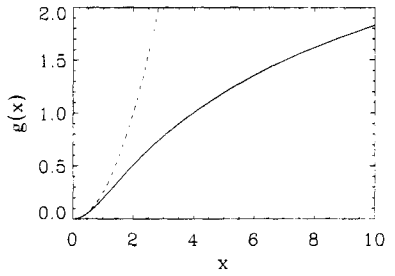

Figure 2. Scaling function $g(x)$ as discussed in the text. The dashed line is a curve given by $y = x^2/4$, which matches $g(x)$ for small x.

with a local bending rigidity B_0. The bending energy U_B is given by $\int dl\ B_0/r_0^2$, where $1/r_0$ is the local curvature. Using this expression, the increase of the bending energy due to an n deformation is computed, $\delta U_B = E_n'\,(\Delta_n/r_0)^2$, with $E_n' = \pi B_0(n^2-1)^2/r_0$. Comparing E_n and E_n', we find that for the charged loop, the electrostatic energy cost for a deformation with wavelength $\lambda \gg \kappa^{-1}$ can be simply calculated by using an effective local bending rigidity

$$B_{\text{eff}} = \frac{\varrho^2}{4\kappa^2} \tag{2.18}$$

which is exactly the one given by the OSF–KK theory. This is expected since the direct charge interaction is limited by the screening length; therefore a deformation with wavelength longer than κ^{-1} should be describable by a local model.

(iii) $n \gg \kappa r_0 \gg 1$: the size of the loop is much larger but the wavelength is much smaller than the screening length.

$$E_n \sim \pi r_0 \varrho^2 n^2 \ln\left(\frac{n}{\kappa r_0}\right) \tag{2.19}$$

This energy can be obtained by considering a deformation of a straight line with wavelength λ. Rewriting the free energy cost $\delta\mathcal{F}$ in terms of λ, we get

$$\delta\mathcal{F} \sim r_0 \frac{\Delta_n^2 \varrho^2}{\lambda^2} \ln\frac{\kappa^{-1}}{\lambda} \tag{2.20}$$

We see that $\delta\mathcal{F}$ is extensive with the size and has the same form as the energy of a stretched string with an effective line tension depending weakly on the wavelength and the screening length. Although the deformation we analyze is restricted to be length preserving, the tension term appears because the effective length within a screening blob has been changed.

Combining (ii) and (iii), we find for $\kappa r_0 \gg 1$ and $n \gg 1$, the energy cost has a simple scaling, $I(\kappa r_0, n) = n^2 g(n/\kappa r_0)$, where $g(x) \approx x^2/4$ for small x and crossed over to $\ln(x)$ for large x (see Figure 2). Thus a deformation with wavelength much smaller than the screening length costs much less energy than that of a bending mode with the OSF bending rigidity.

We now compute the distortion of the loop due to fluctuations. Let us consider the radial fluctuation δr at a given point. With the general deformation given by eq 2.7, we have

$$\frac{\langle(\delta r)^2\rangle}{r_0^2} = \sum_{n=2}^{n_{\max}} \frac{\langle(\Delta_n)^2\rangle}{r_0^2} = \sum_{n=2}^{n_{\max}} \frac{1}{E_n} \tag{2.21}$$

where $n_{\max}$ is related to the short-wavelength cutoff $\lambda_{\min}$: $n_{\max} \approx 2\pi r_0/\lambda_{\min}$. Notice that modes with $n = 0$ and $n = 1$ are excluded from the sum, since they represent merely a dilation and a translation, which do not distort the circular shape.

First let us consider the unscreened case $\kappa^{-1} = \infty$. In this case, since the large-n behavior is $E_n \sim r_0\varrho^2 n^2 \ln n$, the summation in the above equation is nicely converging, leading to $\langle(\delta r/r_0)^2\rangle \simeq a^4/(r_0 l_B \xi^2)$. This implies that for sufficiently large r_0 (much larger than the microscopic lengths), the radial fluctuation will always be small compared to the radius; hence the circular shape of the loop is only slightly distorted. Furthermore, increasing r_0 decreases the relative fluctuation. Thus we conclude that the persistence length in this case is infinity in the asymptotic limit, as it should.

For a finite screening length, the above picture should not change if $\kappa^{-1} \gg r_0$, since the effect of the screening cannot be felt. For $\kappa^{-1} \approx r_0$, the leading behavior for E_n does not change for large n (within a factor of order of unity). The shape of the polymer is still a well-defined circular loop. Therefore we conclude that the persistence length l_p must be much larger than the screening length κ^{-1}.

Next consider $\kappa^{-1} \ll r_0$. The fluctuation contribution from a single long-wavelength mode ($n \ll \kappa r_0$) is

$$\frac{\langle(\delta r)^2\rangle}{r_0^2} = \frac{(2\kappa r_0)^2}{\pi r_0 \varrho^2 (n^2-1)^2} \tag{2.22}$$

which will be order of 1 if $r_0 \simeq \varrho^2/\kappa^2$, giving a $l_p \simeq r_0 \simeq \varrho^2/\kappa^2$, the same as l_{OSF}. This is not a surprise since l_{OSF} is the length where k_BT of energy is needed to bend it by an angle of order of 1.

To calculate the fluctuation correction to the persistence length due to short-wavelength fluctuations, we define $l_p = r_0$ when $\langle(\delta r/r_0)^2\rangle = 1/\pi\sum_{n=2}^{\infty} 1/(n^2-1)^2 = 1.21/(9\pi)$. This definition would give a $l_p = l_{OSF}$ if all the modes could be described by a bending stiffness $B_{\text{eff}} = l_{OSF}$. However, since the modes with wavelength smaller than the screening length are qualitatively softer, the persistence length defined above will be modified to a value smaller than l_{OSF}. Let us examine the aymptotic regime where $\kappa^{-1} \gg \xi$ and $\kappa r_0 \gg 1$ and see the effect of short-wavelength fluctuations. In this regime

$$\frac{\langle(\delta r)^2\rangle}{r_0^2} \approx \sum_{n=2}^{n_c \approx \kappa r_0} \frac{(2\kappa r_0)^2}{\pi r_0 \varrho^2 (n^2-1)^2} + \sum_{n=n_c}^{n_{\max}} \frac{1}{\pi r_0 \varrho^2 n^2 \ln(n/\kappa r_0)}$$

$$\approx \frac{1.21}{9\pi} \frac{4\kappa^2 r_0}{\varrho^2} \left[1 + \mathcal{O}\left(\frac{1}{(\kappa r_0)^3}\right)\right] \tag{2.23}$$

which yield

$$l_p \approx l_{OSF}\left[1 - \mathcal{O}\left(\frac{1}{(\kappa l_{OSF})^3}\right)\right] \tag{2.24}$$

We see that the fluctuations with wavelength smaller than the screening length do not destroy the OSF–KK result. Since the second sum in eq 2.23 converges as $n_{\max} \to \infty$, it does not depend on the detail of the short-wavelength cutoff.

To check if the above calculation is self-consistent, we calculate the fluctuation correction to the distance between any given two points separated by an arbitrary angle. Such a correction must remain small compared to the distance for an undeformed loop in order that the

small-amplitude expansion makes sense. Using eq 2.7, we find that

$$\beta \equiv \left\langle \frac{r^2(\theta_1,\theta_2) - r_0^2(\theta_1,\theta_2)}{r_0^2(\theta_1,\theta_2)} \right\rangle = \sum_{n=2}^{n_{max}} \left\langle \frac{\Delta_n^2}{4r_0^2} \right\rangle \frac{1 - \cos n(\theta_1 - \theta_2)\cos(\theta_1 - \theta_2)}{\sin^2(\theta_1 - \theta_2)/2} \quad (2.25)$$

where the average over the phase angle ϕ_n has already been performed. For $\theta_1 - \theta_2 \sim 1$, $\beta \simeq (\delta r/r_0)^2 \ll 1$ for $r_0 \ll l_p$ as we calculated before. The largest relative fluctuation is for small distance where $\theta_1 - \theta_2 \simeq 1/n_{max}$. In this case the angle-dependent function on the right-hand side of the above equation reaches the maximum n^2, and

$$\beta \simeq \sum_{n=2}^{n_{max}} \frac{1}{\pi r_0 \varrho^2} \frac{1}{g(n/\kappa r_0)} \simeq \sum_{n=2}^{n_c} \frac{4}{\pi r_0 \varrho^2} \frac{(\kappa r_0)^2}{n^2} + \sum_{n_c}^{n_{max}} \frac{1}{\pi r_0 \varrho^2} \frac{1}{\ln(n/\kappa r_0)} \quad (2.26)$$

Notice that the second sum in the above equation depends on the short-wavelength cutoff λ_{min}. Using eq 2.5 (with $A = 1$), we find that for a given cutoff wavelength $\lambda_{min} = \gamma\xi$ (γ blobs),

$$\beta \simeq \frac{k^2 r_0}{\varrho^2} + \frac{a^4}{\gamma l_B \xi^3 \ln(1/\gamma\kappa\xi)} \simeq \frac{\kappa^2 r_0}{\varrho^2} + \frac{C_1 \ln(\kappa^{-1}/\xi) + C_3}{\gamma \ln(1/\gamma\kappa\xi)} \quad (2.27)$$

We see that for $r_0 \ll l_p$ and $\kappa^{-1} \gg \xi$, if we choose $\gamma \gg 1$, then $\beta \ll 1$; i.e., the small-amplitude expansion is self-consistent for deformations with wavelength much larger than the blob length. On the other hand, if γ is chosen to be $\simeq 1$, then eq 2.27 yields $\beta = \mathcal{O}(1)$, indicating that the small-amplitude expansion is no longer valid. This is not a surprise since we expect to see large fluctuations at the scale of a blob length. Indeed, as with the "Pincus blobs" of any stretched chain,[14] we expect to see order of 1 fluctuation of the angle defined by three consecutive blobs.

The above analysis indicates that we can carry out the small-amplitude calculations only down to a length of several blobs. Fortunately, we have already treated the remaining modes; these are the modes that gave rise to the elastic term in eq 2.2. The balance between the elastic term and the electrostatic one simply leads to a stretching effect as expressed in eq 2.5. Such a treatment is valid as long as $\lambda_{min} \ll \kappa^{-1}$ (see Appendix). It is then obvious that a consistent treatment of both long- and short-wavelength modes requires that $1 \ll \gamma \ll \kappa^{-1}/\xi$, which is achievable in the asymptotic limit $\kappa^{-1} \gg \xi$.

As noted before, out calculation for the overall shape fluctuation (as characterized by $\langle(\delta r)^2\rangle$) does not depend on the detail of the short-wavelength cutoff; hence the result regarding the persistence length remains the same with or without the above prescription. Therefore, small-wavelength modes do not change the persistence length qualitatively. However, as we discussed above, these modes contribute significantly to the local fluctuation of the chain.

To analyze further the effect of these short-wavelength modes, we calculate the fluctuation correction to the direct distance of the two points separated by a contour length $\Delta l = l_1 - l_2$ due to all the length-preserving deformations with wavelength $\lambda > \gamma\xi$. The local stretching effect will be included implicitly in the relation $\Delta l = \xi\delta n/N_b$, while δn is the difference of the monomer index between the two points. Combining eqs 2.7, 2.9, and 2.13, the fluctuation correction to the direct distance can be expanded in terms of Δ_n's

$$\langle \delta r(\Delta l) \rangle = 2r_0 \sum_{n=2}^{n_{max}} \frac{\langle \Delta_n^2 \rangle}{r_0^2} H(n,x) = 2r_0 \sum_{n=2}^{n_{max}} \frac{H(n,x)}{E_n} \quad (2.28)$$

where a factor of 2 is included to explicitly count the out-of-plane fluctuations. Here the reduced distance x is defined as $x \equiv \Delta l/r_0$, and the function $H(n,x)$ gives the contribution of mode n at x,

$$H(n,x) = \frac{1}{16n^2 \sin(x/2)}[4n^2 - (8n^4 - 12n^2 + 4)\sin^2(x/2) - 2(n^2 - 1)\cos nx - (n+1)^2 \cos(n-1)x - (n-1)^2 \cos(n+1)x] \quad (2.29)$$

Notice that eq 2.28 is similar to eq 2.25. The crucial difference is that eq 2.28 expresses fluctuations between two points separated by a fixed contour length, while the former expresses that between two points separated by an angle in space.

We are interested in the case where $\Delta l \ll r_0$ or $x \ll 1$ so that the slight curvature due to the circular geometry is negligible. In this limit,

$$H(n,x) = \begin{cases} -\frac{1}{48}(n^2 - 1)^2 x^3, & nx \ll 1 \\ -\frac{1}{4}n^2 x, & nx \gg 1 \end{cases} \quad (2.30)$$

This implies that all modes with wavelength $\lambda \ll \Delta l$ produce a mere uniform contraction.

It is instructive to consider first a simple flexible rod with bending rigidity B_0. As noted above, the mode energies E_n are given by $E_n = \pi B_0(n^2 - 1)^2/r_0$. The summation in eq 2.28 can be divided into two parts where $H(n,x)$ has qualitatively different behavior, $\sum_{n=2}^{n_{max}} = \sum_{n=2}^{n_c=1/x} + \sum_{n_c}^{n_{max}}$; hence

$$\langle \delta r(\Delta l) \rangle \sim \sum_{n=2}^{1/x} \frac{-r_0^2}{24\pi B_0} x^3 + \sum_{1/x}^{n_{max}} \frac{-r_0^2}{2\pi B_0 n^2} x \sim -\Delta l^2/(2\pi B_0) \quad (2.31)$$

We see that the second summation does not depend on the cutoff wavelength. It is also the main contribution to the total fluctuation. An accurate evaluation of the sum in eq 2.28 allows us to determine the coefficient; we find

$$\langle \delta r(\Delta l) \rangle = -\frac{\Delta l^2}{12B_0} \quad (2.32)$$

in agreement with the general formula $\langle r^2 \rangle = 4\Delta l B_0 - 8\Delta l^2[1 - \exp(-\Delta l/2B_0)]$, which predicts $\langle \delta r(\Delta l) \rangle = -\Delta l^2/(12B_0)$ for $\Delta l \ll B_0$.

For a charged loop, E_n behaves like that of a bending mode (with bending stiffness $B_{\text{eff}} = l_{\text{OSF}}$) for $\lambda \gg \kappa^{-1}$ and becomes softer for $\lambda \ll \kappa^{-1}$. Since for a given Δl, the main contribution is from the modes with $\lambda < \Delta l$, we expect to see different behaviors as Δl changes from a distance much smaller to a distance much larger than the screening length.

First let us consider the case where $\gamma\xi \ll \Delta l \ll \kappa^{-1}$. Since E_n and $H(n,x)$ change qualitative behavior for $n \simeq \kappa r_0$ and $n \simeq 1/x$, we divide the summation into three parts, $\sum_{n=2}^{n_{\max}} = \sum_{n=2}^{\kappa r_0} + \sum_{\kappa r_0}^{1/x} + \sum_{n=1/x}^{n_{\max}}$. The summation in eq 2.28 can be estimated using the asymptotic forms for E_n and $H(n,x)$ in the three regions. We obtain

$$\langle \delta r(\Delta l)\rangle \simeq -\sum_{n=2}^{\kappa r_0} \frac{2r_0^{\,2}}{\pi B_{\text{eff}}(n^2-1)^2}\left[\frac{(n^2-1)^2}{48}x^3\right] - \sum_{\kappa r_0}^{1/x} \frac{2r_0}{\pi r_0 \varrho^2 n^2 \ln(n/\kappa r_0)}\left[\frac{(n^2-1)^2}{48}x^3\right] - \sum_{1/x}^{n_{\max}} \frac{2r_0}{\pi r_0 \varrho^2 n^2 \ln(n/\kappa r_0)}\left[\frac{1}{4}n^2 x\right]$$

$$\simeq -\frac{\Delta l^3}{24\pi B_{\text{eff}}\kappa^{-1}} - \frac{a^4}{72\pi l_B \xi^2}\frac{1}{\ln(\kappa^{-1}/\Delta l)} - \frac{\Delta l}{\gamma l_B \xi^3}\frac{a^4}{\ln(2\pi/\gamma\kappa\xi)} \quad (2.33)$$

As anticipated, the results are independent of the radius r_0 in the regime. Thus r_0 can be taken large enough that the loop curvature is negligible.

From the above equation, we see that the short distance fluctuation cannot be characterized by a simple bending model (which predicts a Δl^2 dependence). The main contributions to the direct distance fluctuation are from modes with $\lambda < \kappa^{-1}$, which leads to significant bending at a length of a few blobs.

By similar considerations, we obtain estimates of $\langle \delta r(\Delta l)\rangle$ for $\Delta l \gg \kappa^{-1}$,

$$\langle \delta r(\Delta l)\rangle \simeq -\frac{\Delta l^2}{12 B_{\text{eff}}} - \frac{\Delta l a^4}{\gamma l_B \xi^3 \ln(2\pi/\gamma\kappa\xi)} \quad (2.34)$$

Equation 2.34 indicates that the fluctuation at large distance is in fact characterized by a bending stiffness $B_{\text{eff}} = l_{\text{OSF}}$, except that there is also an overall contraction due to short-wavelength fluctuations, which can be regularized by choosing an appropriate γ.

The above calculations show that for distance smaller than the screening length, the fluctuations get stronger due to softening of small-wavelength modes. If we fit the data in the regime using a pure bending model, we will get a persistence length much smaller than l_{OSF}.

III. Comparison with the Numerical Simulation of Barrat and Boyer

Recently, Barrat and Boyer simulated a simple polyelectrolyte model consisting of charged beads connected by springs. The interaction between charges is simply taken to be a screened Coulomb potential. There seem to be indications that the persistence length comes out much shorter than that predicted by the OSF–KK theory. This simulation shows clearly the chain flexibility that has led to the recent doubts about the OSF–KK theory. Here we shall briefly analyze the simulation

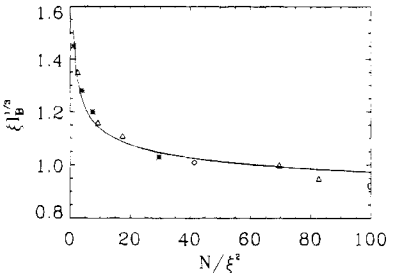

Figure 3. $\xi l_B^{1/3}$ as a function of N/ξ^2 for unscreened chains. Different symbols represent Barrat and Boyer's simulation data with different N(asterisk, $N = 50$; triangle, $N = 100$; diamond, $N = 200$; square, $N = 400$). The solid line is a two-parameter fit using eq 2.6.

data and compare it with our theoretical calculations in the previous section. We find that there are two important factors which could lead a superficially small persistence length: one is the logarithmic stretching effect predicted by eq 2.5; another is the fluctuation effects due to short-wavelength modes as incorporated in eq 2.28. With these effects included, we can give a qualitative account of the simulation data.

In the BB simulation, a crucial quantity studied is $h(n)$, defined as $h(n) = (R^2(n)/a^2 - n)^{1/2}$, where $R^2(n)$ is the mean square distance between two monomers separated by n bonds. For sufficiently large n, this is the same as the $\langle r(\Delta l)\rangle$ we calculated. BB infer a blob length ξ as the inverse of the slope of $h(n)$ at the origin (as predicted by a simple linear chain model). They estimate the persistence length from the point where $h(n)$ starts to deviate from linear behavior.

We first analyze BB's data for the unscreened case. In this case, eq 2.6 predicts that there is a logarithmic dependence of $\xi l_B^{1/3}$ on N/ξ^2 (all lengths are measured in units of a), while simple scaling predicts that $\xi l_B^{1/3}$ is a constant. Figure 3 plots $\xi l_B^{1/3}$ as a function of N/ξ^2 for various N and coupling parameter l_B from the simulation. We see that there is a systematic decrease of $\xi l_B^{1/3}$ with increasing N/ξ^2. Furthermore, data for different N and l_B fall onto the same curve. A two-parameter fit using eq 2.6 gives a good agreement with the numerical data. From the fit, we obtain $C_1 = 0.205$ and $C_3 = 0.217$.

In the presence of screening, the blob length ξ is affected by the screening length κ^{-1} according to eq 2.5. ξ increases with decreasing κ^{-1}, leading to a decrease in the slope of $h(n)$ at the origin. To have an estimate, we take C_1' and C_3' to be the same as C_1 and C_3 obtained above. We find for $N = 200$ and $\kappa^{-1} = 20$, the slope of $h(n)$ decreases by about 14%. Such an decrease of slope at the origin with the decreasing of screening length was observed in the simulation.

To make more comparisons with the simulation, we also compute the function $\langle r(\Delta l)\rangle$ numerically using eq 2.28. The contour length Δl is related to monomer distance δn via $\Delta l = \delta n/\xi$. We take a loop with radius approximately equal to the persistence length. Conveniently, this radius is so large that the loop curvature contributes negligibly. The only input we take from the simulation is the blob length which determines the initial slope of the curve $h(n)$. This blob length is also used to calculate the line charge density. The cutoff wavelength $\lambda_{\min} \equiv 2\pi r_0/n_{\max}$ was chosen at a convenient value larger than ξ, thus in the regime of the validity of our expansion. Figure 4 plots $\langle r(\delta n)\rangle$ as a function of δn for $\kappa^{-1} \gg 20$ and $\kappa^{-1} = 20$. The blob size ξ is taken to be 1.9 and 2.4 for the unscreened and screened cases, respectively. The cutoff wavelength $\lambda_{\min}$ is taken to be

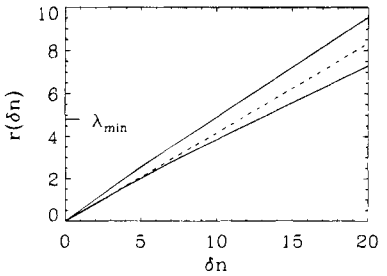

Figure 4. Direct distance $r(\delta n)$ as a function of monomer separation δn calculated using eq 2.28. The two solid lines are for $\kappa^{-1} = \infty$ (upper curve) and $\kappa^{-1} = 20$ (lower curve). The dashed line is a straight line extrapolated from the initial slope of the curve for the screened case. λ_{min} marks the cutoff wavelength. All the lengths are measured in units of a.

$\approx 2\xi$. We observe significant bending of the curve due to short-wavelength fluctuations. A naive fitting using a pure bending model yields $l_{app} \approx 5.6$, much smaller than the true persistence length $l_p \approx l_{OSF} = 58$.

IV. Conclusions

We have seen that the fluctuations of flexible polyelectrolytes have qualitatively different effects depending on the wavelength of the deformation. Deformations with wavelength larger than the screening length are describable by an effective bending model with bending stiffness given by the Odijk length, while those with wavelength smaller than the screening length (but still much larger than the blob length) can be described by an effective line tension depending on the screening length and wavelength. Fluctuations with even smaller wavelengths can be treated by a simple model of stretched random walks. These short-wavelength modes appear to account well for small apparent persistence length reported by Barrat and Boyer. This simulation was designed to mimic experimental polyelectrolytes like those of refs 7 and 8 and detailed simulation like that of ref 10. Thus we believe that these modes are the likely source of flexibility seen in all these systems. However, our systematic calculation gave no support to the conclusions of refs 11–13 that the short-wavelength modes should alter the scaling of the asymptotic persistence length. These authors use a variational ansatz in which the chain at all scales (beyond ξ) is described by a bending model. We believe that this ansatz is not supported by our explicit findings.

The stretching effect we discuss in the previous sections leads to a logarithmic correction to the persistence length given by OSF–KK theory. Since $l_{OSF} = \varrho^2/(4\kappa^2)$, where ϱ is the actual charge density depending on the blob length, we expect to see $l_{OSF} \sim \kappa^{-2}$ with logarithmic correction. Such a correction could be important in the nonasymptotic regime where the screening length is not sufficiently long.

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Appendix

In this appendix, we show that the electrostatic energy within a stretched segment of $N_c = \gamma N_b$ monomers (or γ blobs) is negligible compared to the stretching energy of the segment provided $\gamma \ll \kappa^{-1}/\xi$. Let $R_c = \gamma\xi$ be the linear size of the stretched segment. Using an argument similar to the one which leads to eq 2.3, we find the electrostatic energy within the segment

$$U_e = \frac{Q_c^2}{R_c}\left(C_1 \ln \frac{R_c}{\xi} + C_4\right) \tag{A.1}$$

where C_4 is another numerical constant of order of 1. Given that the segment is described by a stretched random walk, the stretching energy is

$$U_s = \frac{R_c^2}{a^2 N_c} \tag{A.2}$$

Using the relations $Q_c^2 = N_c^2 q^2/A^2 = N_c^2 l_B/A^2$ and $R_c = a^2 N_c/\xi$ (eq 2.4), the ratio of electrostatic and stretching energy is

$$\frac{U_e}{U_s} = \frac{\xi^3 l_B}{A^2 a^4}\left(C_1 \ln \frac{R_c}{\xi} + C_4\right) \tag{A.3}$$

The above equation can be rewritten (using eq 2.5) as

$$\frac{U_e}{U_s} = \frac{C_1 \ln(R_c/\xi) + C_4}{C_1 \ln(\kappa^{-1}/\xi) + C_3} \tag{A.4}$$

which implies $U_e/U_s \ll 1$ for $R_c \ll \kappa^{-1}$ or $\gamma \ll \kappa^{-1}/\xi$; i.e., the electrostatic energy is negligible compared to the stretching energy. This is expected since the stretching effect is due to the charge interactions of all the monomers within a screening length, while U_e has the contributions only from the monomers within the segment.

Since the Coulomb energy within a segment is small compared to the stretching energy, this energy can have only a small effect on the configuration of the segment. In particular, this energy can only have a slight effect on the fluctuations of the end-to-end distance of a segment. In any case, including this energy would be expected to *reduce* these fluctuations.

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