Electrostatic Persistence Length of Semiflexible and Flexible Polyelectrolytes

Andrey V. Dobrynin

Polymer Program, Institute of Materials Science and Department of Physics, University of Connecticut, Storrs, Connecticut 06269-3136

ABSTRACT: I have calculated the dependence of the electrostatic persistence length on the Debye screening length for semiflexible, strongly and weakly charged flexible polyelectrolytes. For semiflexible and strongly charged flexible polyelectrolytes the electrostatic part of the chain persistence length is proportional to the Debye screening length. This result is obtained by evaluating the bending angle fluctuations and in the framework of the Gaussian variational principle. A polyelectrolyte chain with linear dependence of the electrostatic persistence length on the Debye screening length has a lower free energy than that of a chain with the Odijk−Skolnick−Fixman electrostatic persistence length. In the case of weakly charged chains the electrostatic persistence length has a sublinear dependence on the Debye screening length which is due to inverse logarithmic dependence of the linear charge density of the chain of electrostatic blobs on the Debye screening length. This result was derived by applying a coarse-graining procedure to an initially flexible polyelectrolyte chain by representing it as a chain of electrostatic blobs. The blob size and chain persistence length are then found self-consistently by minimizing the chain's variational free energy.

1. Introduction

The problem of the electrostatic persistence length in solutions of charged polymers is one of the most controversial subjects of polymer physics. The formulation of the problem is relatively simple since it considers conformational properties of a single polyelectrolyte chain with ionizable groups interacting via the screened Debye−Huckel potential. This is a crude model of dilute polyelectrolyte solutions in the presence of added salt where electrostatic interactions are exponentially screened by salt ions at the length scales larger than the Debye screening length κ^{-1}. However, despite the exponential decay of the strength of the electrostatic interactions, the covalent bonding of ionic groups into polymer chains seems to be able to extend their range beyond the Debye screening length leading to strong orientational correlations between chain segments. Thus, a bond's orientational memory could propagate far beyond the Debye screening length κ^{-1} inducing extra chain stiffening.

The concept of the electrostatic persistence length was introduced by Odijk[1] and by Skolnick and Fixman[2] (OSF), who considered a weak perturbation in conformations of a stiff polyelectrolyte chain near a rodlike conformation. They have showed that the persistence length of a polyelectrolyte chain with the fraction of charged monomers f in a salt solution in which the charged monomers on polymer backbone interact with each other through the screened Debye−Huckel potential with the Debye screening length κ^{-1} can be written as a sum of the bare persistence length l_0 and the electrostatic persistence length l_p^{OSF}

$$l_p \approx l_0 + l_p^{OSF} \approx l_0 + \frac{l_B f^2}{4(\kappa b)^2} \qquad (1)$$

where b is the bond length and l_B is the Bjerrum length ($l_B = e^2/\epsilon k_B T$ is the distance at which the Coulomb interaction between two elementary charges e in a dielectric medium with the dielectric constant ϵ is equal to the thermal energy $k_B T$). This equation shows that chain flexibility could be adjusted by varying the salt concentration.

The OSF approximation for the screened Debye−Huckel interactions between charged monomers was removed by Le Bret[3] and Fixman.[4] In these papers the Poisson−Boltzmann equation describing distribution of the electrostatic potential was solved numerically for a curved, cylindrical polyelectrolyte of a finite thickness. For conducting boundary conditions these numerical calculations have shown perfect agreement with the OSF result. However, in the case of a toroidal polyion with a nonconducting surface the results for the electrostatic persistence length deviate from the OSF expression (eq 1) at high ionic strengths.[3] The results of numerical calculations by Le Bret[3] for nonconducting polyions are in better agreement with the experimental data than the original OSF expression (eq 1) but still overestimate the electrostatic persistence length at low salt concentrations in comparison with experimental data by Hagerman[5] while underestimate it at higher ionic strengths as compared to the data of Kam et al.[6]

Odijk[7] used eq 1 to describe solution properties of flexible strongly charged polyelectrolytes with the electrostatic interaction parameter $uf^2 \approx 1$, where u is the ratio of the Bjerrum length l_B to the bond size b, $u = l_B/b$. In this case the electrostatic contribution to the chain persistence length l_p^{OSF} is the main factor controlling a chain's bending rigidity. For these polyelectrolytes the additional chain stiffening could occur at distances substantially larger than the Debye screening length κ^{-1}. The Odijk result was extended to flexible weakly charged polyelectrolytes with $uf^2 \ll 1$ by Khokhlov and Khachaturian[8] by considering electrostatic blobs of size D_e with g monomers[9,10] as new effective monomers

$$l_p^{KK} \approx \frac{1}{\kappa^2 D_e} \qquad (2)$$

These unexpected results for the quadratic dependence of the electrostatic persistence length on the Debye screening length had a significant impact on the development of the theory of polyelectrolytes[11] over the past three decades and influenced our understanding of dynamics and thermodynamics of polyelectrolyte solutions, adsorption of charged polymers, complexation of DNA with proteins, and colloid stabilization by polyelectrolytes.

Since 1977 there have been a series of attempts to derive an expression for the electrostatic persistence length, l_p^{OSF}, using different methods.[12–20] Schmidt[17] used a variation of the Flory approach to calculate the chain size and persistence length. In this approach the electrostatic energy of the chain was evaluated using the wormlike chain distribution function for the average mean-square distance between monomers. The numerical minimization shows a weaker than κ^{-2} dependence without a pure scaling regime. At high salt concentrations the electrostatic persistence length seems to approach asymptotically a κ^{-1} dependence. Barrat and Joanny[18] applied the variational approach with a trial function describing a chain under tension. They found a κ^{-1} dependence for the electrostatic persistence length. In a series of papers,[19,20] Ha and Thirumalai applied the Edwards and Singh[21] variational principle which utilizes the optimization of the error in the chain mean-square end-to-end distance between trial chain and actual polymer chain. The results of the minimization procedure depend on the value of the parameter uf^2. For weakly charged chains with $uf^2 \ll 1$ the electrostatic persistence length is proportional to κ^{-2}. However, in the limit $uf^2 \sim 1$ the κ^{-1} dependence of the electrostatic persistence length was recovered. Manghi and Netz[12] have recently argued that Ha and Thirumalai's result[19,20] for the κ^{-1} dependence of the electrostatic persistence length is a result of incorrect elimination of divergence in the chain's entropy term. The κ^{-1} dependence of the electrostatic persistence length was also derived by Muthukumar et al.[22,23] Netz and Orland[15] and Manghi and Netz[12] have applied a Gaussian variational principle considering electrostatic persistence length as an adjustable parameter. This approach leads to κ^{-2} dependence of the electrostatic persistence length, and for weakly charged chains Khokhlov–Khachaturian's result[8] is reproduced. Computer simulations of weakly charged polyelectrolyte chains[24–30] and some experiments[31–37] indicate that the exponent for the dependence of the electrostatic persistence length on the Debye screening length is closer to 1 rather than to 2. The recent computer simulations[38–40] have shown that, in order to distinguish between two expressions for the electrostatic persistence length, one has to go to very long chains ($N > 512$). For shorter chains there is no significant difference between quadratic and linear dependence of the electrostatic persistence length on salt concentration. For longer chains there is deviation from the linear dependence but not sufficient to rule it out completely. However, the analysis of the data was done by assuming two pure asymptotic regimes for electrostatic persistence length $l_p^{OSF} \sim \kappa^{-2}$ and κ^{-1} neglecting logarithmic corrections. The origin of logarithmic correction to the chain size dependence on Debye screening length appears because of chain stretching at length scales smaller than the Debye screening length and due to the effective excluded volume between sections of the chain of length l_p interacting through the
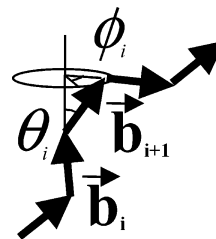
Figure 1. Conformation of a chain with the arbitrary distribution of torsion angles ϕ_i and bending angles θ_i.

screened Coulomb potential. The logarithmic corrections could be important for longer chains with $N = 1024$, 2048, and 4096 repeat units. The importance of logarithmic corrections due to local chain stretching was recently confirmed by molecular simulations of dilute salt-free polyelectrolyte solutions by Liao et al.[41] These simulations have established that the chain size grows faster than linear with chain degree of polymerization N.

In this paper I will show that the origin of the additional chain rigidity appearing in the OSF and KK expressions for the electrostatic persistence length is circular conformation used for evaluation of the chain bending energy. This deformation mode overestimates electrostatic energy penalty due to chain bending. There are other, softer, deformation modes with lower electrostatic energies that lead to linear dependence of the electrostatic persistence length on the Debye screening length. This solution corresponds to the lower chain free energy than that obtained for a polyelectrolyte chain with the OSF persistence length. The rest of the paper is organized as follows. In section 2, I will overview discrete model of a semiflexible chain. Section 3 presents critique of the OSF derivation of the electrostatic persistence length and alternative derivation based on the average electrostatic energy fluctuations. This method leads to linear dependence of the electrostatic persistence length on the Debye screening length. In section 4, I apply the Gaussian variational principle to the case of weakly charged flexible polyelectrolytes. In this case the local stretching of a polyelectrolyte chain leads to an additional logarithmic correction to the electrostatic persistence length weakening its linear increase with the Debye screening length.

2. A Brief Overview of the Discrete Model of Semiflexible Chain

Consider a semiflexible chain with degree of polymerization N and with bond length b. Chain conformations are described by a set of bond angles θ_i and torsion angles ϕ_i (see Figure 1). The potential energy of a semiflexible chain in a given conformation with a set of torsion and bond angles $\{\phi_i, \theta_i\}$ is given by

$$U_{bend}^0(\{\theta_i\}) = k_B T \tilde{\epsilon}_{bend} \sum_{i=1}^{N-1} (1 - \cos(\theta_i)) \qquad (3)$$

where $\tilde{\epsilon}_{bend}$ is a bending energy in terms of the thermal energy $k_B T$. A bending potential (eq 3) imposes restrictions on the accessible values of the bond angles θ_i but allows torsion angles to assume any value from the interval $-\pi \le \phi_i \le \pi$. The partition function of a polymer chain with this bending potential is written as follows:

$$Z_{SF} =$$

$$\int \prod_{i=1}^{N-1} \frac{\sin(\theta_i)\, d\theta_i\, d\phi_i}{4\pi} \exp\left(-\frac{U_{bend}^0(\{\theta_i\})}{k_B T}\right) = Z_1^{N-1} \quad (4)$$

where Z_1 is the single bond partition function.

$$Z_1 = \frac{1}{2}\int_0^\pi d\theta\, \sin(\theta) \exp(-\tilde{\epsilon}_{bend}(1 - \cos(\theta))) =$$

$$\frac{\exp(-\tilde{\epsilon}_{bend})\,\sinh(\tilde{\epsilon}_{bend})}{\tilde{\epsilon}_{bend}} \quad (5)$$

For a polymer chain with the bending potential given by eq 3 the orientational memory between two vectors $\mathbf{b}_i$ and $\mathbf{b}_{i+n}$ is passed along the chain of bonds connecting bonds $\mathbf{b}_i$ and $\mathbf{b}_{i+n}$. Because of free rotations of the torsion angle ϕ_{i+n} the component of the vector $\mathbf{b}_{i+n}$ normal to the vector $\mathbf{b}_{i+n-1}$ averages out to zero. The only correlation between the bond vectors being transmitted is the component of the bond vector $\mathbf{b}_{i+n}$ along the vector $\mathbf{b}_{i+n-1}$. It is equal to $b\langle\cos(\theta)\rangle$. Again vector $\mathbf{b}_{i+n-1}$ passes correlations down to vector $\mathbf{b}_{i+n-2}$, but again only projection of the bond vector $\mathbf{b}_{i+n-1}$ onto $\mathbf{b}_{i+n-2}$ survives due to free rotation of torsion angle ϕ_{i+n-1}. This reduces correlations between vector $\mathbf{b}_{i+n}$ and vector $\mathbf{b}_{i+n-2}$ by the factor $\langle\cos(\theta)\rangle^2$. Thus, the correlations between bond vectors $\mathbf{b}_i$ and $\mathbf{b}_{i+n}$ are reduced by the factor $\langle\cos(\theta)\rangle^n$ due to independent rotation of n torsion angles between them

$$\langle(\mathbf{b}_i \cdot \mathbf{b}_{i+n})\rangle = b^2\langle\cos(\theta(n))\rangle = b^2(\langle\cos(\theta)\rangle)^n \approx$$

$$b^2 \exp(-n\langle\theta^2\rangle/2) \quad (6)$$

where brackets $\langle\ \rangle$ denote the average over torsion angles ϕ_i and bond angles θ_i, and the average value of the $\cos(\theta)$ is equal to

$$\langle\cos(\theta)\rangle = \coth(\tilde{\epsilon}_{bend}) - \tilde{\epsilon}_{bend}^{-1} \underset{\tilde{\epsilon}_{bend}\gg 1}{\approx} 1 - \tilde{\epsilon}_{bend}^{-1} \quad (7)$$

In the derivation of eq 6 it is assumed that the typical values of the bond angle θ are small such that $\cos(\theta)$ can be approximated by its power series, $\cos(\theta) \approx 1 - \theta^2/2$. This assumption is true for large values of the bending energy $\tilde{\epsilon}_{bend}$ (see eq 7). In this approximation the correlations between bond vectors $\mathbf{b}_i$ and $\mathbf{b}_{i+n}$ decay exponentially with the number of bonds n between them. The characteristic length scale of the orientational correlations is equal to $2/\langle\theta^2\rangle$. The mean-square average value of the angle $\theta(n)$ between any two bond vectors separated by n bonds along the polymer backbone is equal to $n\langle\theta^2\rangle$ ($\langle\theta(n)^2\rangle \approx n\langle\theta^2\rangle$) which is a direct result of the randomness in the distribution of the torsion angles. One can say that the bond vectors of a semiflexible polymer chain perform a random walk in the bond orientational space with a step length equal to $\sqrt{\langle\theta^2\rangle}$.

The mean-square average distance between two monomers of this chain separated by n bonds is

$$\langle\mathbf{r}(n)^2\rangle \approx \frac{8b^2}{\langle\theta^2\rangle^2}\left(\exp\left(-\frac{n\langle\theta^2\rangle}{2}\right) + \frac{n\langle\theta^2\rangle}{2} - 1\right) \quad (8)$$

At short distances along the polymer backbone, $n\langle\theta^2\rangle \ll 1$, the conformation of the chain for small angles θ is close to rodlike with average mean-square distance

$$\langle\mathbf{r}(n)^2\rangle \approx b^2 n^2 \quad (9)$$

At larger distances along the polymer backbone, $n\langle\theta^2\rangle \gg 1$, the orientational memory is lost, and the mean-square distance between two monomers scales linearly with the number of bonds n between them

$$\langle\mathbf{r}(n)^2\rangle \approx \frac{4b^2 n}{\langle\theta^2\rangle} \approx 2l_0 bn \quad (10)$$

At these length scales a chain behaves as an ideal chain with the persistence length

$$l_0 = \frac{2b}{\langle\theta^2\rangle} \approx b\tilde{\epsilon}_{bend} \quad (11)$$

The persistence length of a chain with the bending potential energy given by the eq 3 scales linearly with the reduced bending energy $\tilde{\epsilon}_{bend}$ and is proportional to the bond length b. Thus, in the case of small deformations, $\theta \ll 1$, the chain persistence length can be estimated from the coefficient in front of the θ^2 term in the power series of the chain's potential energy (eq 3) with respect to the bond angle θ. In the case of the large bending energies the discrete chain model reduces to the wormlike model of a semiflexible chain.

The free energy of the polymer chain as a function of a bending energy is equal to

$$F_{SF} = -k_B T(N-1)\ln(Z_1) \underset{\tilde{\epsilon}_{bend}\gg 1}{\approx} k_B TN \ln(\tilde{\epsilon}_{bend}) \approx$$

$$k_B TN \ln\left(\frac{l_0}{b}\right) \quad (12)$$

It depends logarithmically on the value of the reduced bending energy $\tilde{\epsilon}_{bend}$ or on the ratio of the chain persistence length l_0 to the bond length b. This logarithmic dependence is a result of the constraints imposed on the values of the bond angles by the bending potential eq 3. One can obtain expression 12 by evaluating the change of the bond orientational entropy due to its localization within the solid angle $\pi\theta_{max}^2$. The value of the bond angle θ_{max} can be estimated from the condition that the typical energy fluctuations of the bending energy per bond $k_B T\tilde{\epsilon}_{bend}\theta_{max}^2$ are on the order of the thermal energy $k_B T$. This leads to the typical value of the bond angle θ_{max} to be on the order of $1/\sqrt{\tilde{\epsilon}_{bend}}$. The number of states $\Omega(\theta)$ available to a bond is proportional to the solid angle $\pi\theta_{max}^2$ and is inversely proportional to the reduced bending energy $\tilde{\epsilon}_{bend}$, $\Omega(\theta) \approx \pi/\tilde{\epsilon}_{bend}$. Using the relation between the number of states and the bond orientational entropy, $S_{bond} \propto k_B \ln \Omega(\theta)$, and multiplying it by the number of bonds per chain $N-1$, one arrives at eq 12.

In the next sections I will use this discrete model of a semiflexible chain to obtain an expression for the electrostatic persistence length.

3. Electrostatic Persistence Length of Semiflexible and Strongly Charged Flexible Polyelectrolytes

Let us now consider a semiflexible polyelectrolyte chain with the degree of polymerization N and with the value of the electrostatic interaction parameter $uf^2 \leq 1$. Once again, chain conformations are described by a set of bond θ_i and torsion ϕ_i angles (see Figure 1). The potential energy of a semiflexible polyelectrolyte chain
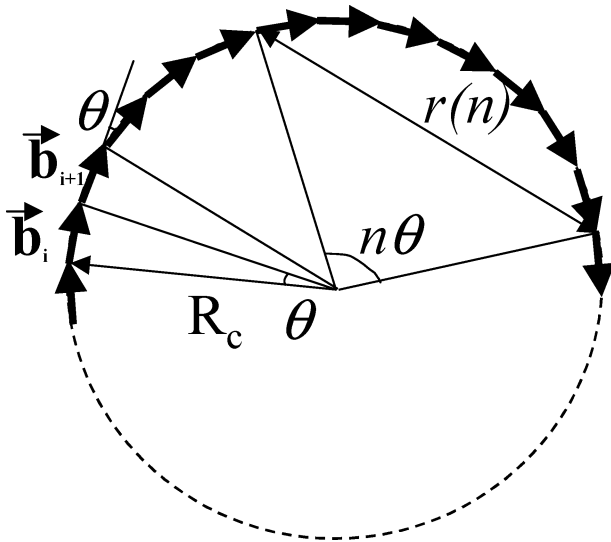
Figure 2. Schematic representation of conformation of polyelectrolyte chain for calculation of OSF electrostatic persistence length.

in a given conformation includes the bending energy given by eq 3 and the electrostatic energy

$$\frac{U_{\text{electr}}(\{\phi_i,\theta_i\})}{k_{\text{B}}T} = \frac{l_{\text{B}}f^2}{2}\sum_{i\neq j}^{N}\frac{\exp(-\kappa|\mathbf{r}_{ij}(\{\phi_i,\theta_i\})|)}{|\mathbf{r}_{ij}(\{\phi_i,\theta_i\})|} \quad (13)$$

where $|\mathbf{r}_{ij}|$ is the distance between monomers i and j on the polymer backbone and the Debye screening length κ^{-1} depends on the parameters of the system as $\kappa^2 = 8\pi l_{\text{B}}c_{\text{s}}$, where c_{s} is the salt concentration.

The calculation of the chain's persistence length is based on the evaluation of the correlation function $\langle\mathbf{b}_i\cdot\mathbf{b}_{i+n}\rangle$ describing the decay of the orientational memory between bond vectors $\mathbf{b}_i$ and $\mathbf{b}_{i+n}$ separated by n bonds along the polymer backbone. The averaging of the correlation function $\langle\mathbf{b}_i\cdot\mathbf{b}_{i+n}\rangle$ should be done over all orientations of the bond vectors with corresponding Boltzmann weights. The exact analytical calculation of this correlation function for the system with long-range electrostatic interactions is an impossible task. The theoretical evaluation of the persistence length of the polyelectrolyte chain is usually done by one of two different methods. In the first approach the chain persistence length is evaluated from the deformation energy fluctuations in the chain conformation for which it is easy to obtain the dependence of the deformation energy on the magnitude of the bond angle θ. In the second approach, the chain with electrostatic interactions and bending rigidity is mapped into a semiflexible chain with an effective bending potential energy. The effective bending energy is then found self-consistently using either Gaussian or Edwards–Singh variational methods.

The approach based on the evaluation of the chain deformation energy was introduced by Odijk[1] and by Skolnick and Fixman[2] (OSF). In this method[1,2] one estimates the change of chain electrostatic energy as its conformation deviates from a straight line. This is done by bending a polyelectrolyte chain into a circle with radius $R_{\text{c}} = b/(2\sin(\theta/2))$ (see Figure 2). In such a conformation all torsion angles are equal to π, and the distance between two monomers separated by n bonds along the polymer backbone is

$$r(n) = 2R_{\text{c}}\sin(n\theta/2) = \frac{b\,\sin(n\theta/2)}{\sin(\theta/2)} \underset{\theta\ll 1}{\approx}$$
$$bn(1 - n^2\theta^2/24) \quad (14)$$

The difference between the chain electrostatic energy per monomer in the circular and rodlike conformations is

$$\frac{\Delta U_{\text{electr}}(\theta)}{k_{\text{B}}T} \approx$$
$$l_{\text{B}}f^2\sum_{n=1}^{\infty}\left(\frac{\exp(-\kappa r(n))}{r(n)} - \frac{\exp(-\kappa bn)}{bn}\right) \underset{\kappa b\ll 1}{\approx} \frac{uf^2}{8\kappa^2 b^2}\theta^2 \quad (15)$$

Equation 15 is obtained by substituting the expression for $r(n)$ (eq 14) into the right-hand side of eq 15 and expanding it into a power series over the bond angle θ. For a semiflexible polyelectrolyte chain there is an additional bending energy contribution $\Delta U_{\text{bend}}(\theta)$ to the chain's deformation energy per bond

$$\Delta U_{\text{bend}}(\theta) = k_{\text{B}}T\tilde{\epsilon}_{\text{bend}}(1 - \cos(\theta)) \underset{\theta\ll 1}{\approx} k_{\text{B}}Tl_0\theta^2/2b \quad (16)$$

where l_0 is the bare persistence length of a chain without electrostatic interactions (see eq 11). The total deformation energy per bond is equal to

$$\frac{\Delta U_{\text{bond}}}{k_{\text{B}}T} \approx \frac{l_0\theta^2}{2b} + \frac{uf^2\theta^2}{8\kappa^2 b^2} \quad (17)$$

In the OSF derivation it was assumed that the persistence length of the semiflexible polyelectrolyte chain is proportional to the coefficient in front of the θ^2 term in the chain deformation energy per bond eq 17. This leads to the following expression for the persistence length

$$l_{\text{p}} \approx l_0 + \frac{l_{\text{B}}f^2}{4(\kappa b)^2} \quad (18)$$

In a circular conformation there is a directed walk in the bond orientational space with the angle $\theta(n)$ between two bond vectors separated by n bonds along the polymer backbone being equal to $\theta(n) \approx n\theta$. Thus, a chain makes a turn after $n_{\text{p}} \propto \theta^{-1}$ steps instead of $n_{\text{p}} \propto \theta^{-2}$ as it is in the case of unrestricted torsion angles (see section 2). Using the relations $n_{\text{p}} \propto \theta^{-1}$ and $l_{\text{p}} \approx bn_{\text{p}}$, one can show that for the OSF persistence length (eq 18) the change of the electrostatic and bending energy per persistence length, $n_{\text{p}}\Delta U_{\text{bond}}(\theta)$, is on the order of the thermal energy $k_{\text{B}}T$ and the optimal value of the bond (bending) angle θ in a circular conformation is equal to $(l_0/b + uf^2/(4\kappa b)^2)^{-1}$. This shows that the OSF approach is only dealing with the energy optimization in a particular conformation and completely ignores the change in the chain conformational entropy associated with the additional penalty for the bond alignment on the length scales smaller than the chain persistence length.

The circular conformation is only one of many possible conformations of the chain with the fixed bond angles. While the values of the bond angles are fixed, the values of the torsion angles can assume any value from the interval $-\pi \leq \phi_i \leq \pi$ (see Figure 1). In fact, the electrostatic part of the chain deformation energy at given value of the bond angle θ depends on the particu-

lar set of the torsion angles $\{\phi_i\}$. To make it only a function of the deformation (bond) angle θ, one has to average electrostatic energy over the torsion angles at fixed value of the bond angle θ. Let us perform averaging of the electrostatic energy per bond over the distribution of torsion angles at a given value of the bond angle θ.

$$\frac{\langle U_{\text{electr}}(\theta)\rangle_\phi}{k_B T} = l_B f^2 \sum_{n=1}^{\infty} \left\langle \frac{\exp(-\kappa r(n))}{r(n)} \right\rangle_\phi \approx$$
$$l_B f^2 \sum_{n=1}^{\infty} \frac{\exp(-\kappa\sqrt{\langle \mathbf{r}(n)\rangle_\phi^2})}{\sqrt{\langle \mathbf{r}(n)\rangle_\phi^2}} \quad (19)$$

In averaging the electrostatic interactions in eq 19 over the torsion angles, I use the integral representation for the screened Coulomb potential.

$$\left\langle \frac{\exp(-\kappa r)}{r} \right\rangle \approx \frac{2}{\pi^{1/2}} \int_0^\infty dy \left\langle \exp\left(-y^2 r^2 - \frac{\kappa^2}{4y^2}\right) \right\rangle \approx$$
$$\frac{2}{\pi^{1/2}} \int_0^\infty dy \, \exp\left(-y^2 \langle r^2\rangle - \frac{\kappa^2}{4y^2}\right)$$

In the case of unrestricted torsion angles and fixed value of the bond angle θ the mean-square average distance $\langle r(n)^2\rangle_\phi$ between two monomers separated by n bonds along the polymer backbone is given by eq 8 where one has to substitute $\langle \theta^2 \rangle$ by θ^2. In this case the distance between these two monomers is approximated as

$$\sqrt{\langle r(n)^2\rangle_\phi} \underset{n\theta^2 \ll 1}{\approx} bn\left(1 - \frac{n\theta^2}{12}\right) \quad (20)$$

Substituting eq 20 into eq 19, evaluating the sum over n, and extracting the term proportional to θ^2, one obtains the following expression for the difference between the average electrostatic energy per bond with a given value of the bond angle θ and that for a polyelectrolyte chain in a rodlike conformation

$$\frac{\langle \Delta U_{\text{electr}}(\theta)\rangle_\phi}{k_B T} \approx$$
$$l_B f^2 \sum_{n=1}^{\infty} \left(\frac{\exp(-\kappa\sqrt{\langle \mathbf{r}(n)\rangle_\phi^2})}{\sqrt{\langle \mathbf{r}(n)\rangle_\phi^2}} - \frac{\exp(-\kappa bn)}{bn} \right) \underset{\kappa b \ll 1}{\approx}$$
$$0.16 \frac{l_B f^2 \theta^2}{\kappa b^2} \quad (21)$$

By comparing eq 21 and eq 15, one can see that the circular conformation has stronger dependence of the electrostatic energy (see eq 15) on the Debye screening length than the average electrostatic energy (see eq 21), and for similar bending angles θ it has a larger value of the electrostatic energy. The weaker dependence of the average electrostatic energy on the Debye screening length (see eq 21) indicates that there are other, softer, deformation modes that have lower electrostatic energies and provide dominant contributions to the chain partition function. Thus, by allowing fluctuations of the torsion angles, one increases the separation between

ionic groups and lows chain electrostatic energy. The circular conformation used in the OSF approach overestimates the electrostatic energy penalty due to chain deformation.

The average electrostatic energy in eq 21 does not depend on the values of the torsion angles ϕ_i. In this case one can use the relation between the chain deformation energy per bond and the persistence length l_p. The typical mean-square average bond angle fluctuations $\langle \theta^2 \rangle$ correspond to the values of the chain deformation energy per bond

$$\frac{\langle \Delta U_{\text{bond}}\rangle_\phi}{k_B T} \approx \frac{l_0 \theta^2}{2b} + 0.16 \frac{uf^2\theta^2}{\kappa b} \quad (22)$$

to be on the order of the thermal energy $k_B T$. Therefore, the persistence length of semiflexible polyelectrolyte chain is estimated as

$$l_p^{\text{WLC}} = \frac{2b}{\langle \theta^2 \rangle} \approx l_0 + 0.32 uf^2 \kappa^{-1} \quad (23a)$$

The electrostatic part of the chain persistence length (the second term on the right-hand side of eq 23a) shows a linear dependence on the Debye screening length instead of the quadratic dependence as it is in the OSF expression. There is very simple interpretation of the electrostatic contribution to the chain persistence length. It is proportional to the reduced energy of electrostatic interactions between two chain segments with length on the order of the Debye screening length κ^{-1} carrying $f/(\kappa b)$ charged monomers and separated by a typical distance κ^{-1}, $\tilde{\epsilon}_{\text{elect}} \approx l_B(f/(\kappa b))^2 \kappa \approx uf^2/(\kappa b)$. Thus, both terms in eq 23a can be rewritten as the bond length b times the typical energy penalty in terms of thermal energy $k_B T$ for chain bending, $l_p^{\text{WLC}} \approx b(\tilde{\epsilon}_{\text{bend}} + \tilde{\epsilon}_{\text{elect}})$. The chain persistence length is controlled by the electrostatic repulsion between charged monomers if the Debye screening length κ^{-1} is larger than l_0/uf^2.

$$l_p^{\text{WLC}} \approx 0.32 uf^2 \kappa^{-1} \quad (23b)$$

This expression is also applicable to the case of strongly charged flexible polyelectrolytes with $uf^2 \approx 1$ and $\tilde{\epsilon}_{\text{bend}} = 0$.

It is interesting to point out that one can derive eq 23 for the chain persistence length by optimizing entropic and energetic penalties for the chain bending. By imposing the angular constraint, one changes the number of available states in the bond's orientational space. For a chain with the bare persistence length b the entropy change due to imposed angular constraint depends logarithmically on the value of angle θ (see discussion after eq 12)

$$S_{\text{bond}}(\theta) \approx k_B \ln(\theta^2) \quad (24)$$

Thus, the free energy change per bond of a chain with electrostatic and bending interactions is equal to

$$\frac{F(\theta)}{k_B T} \approx -\ln(\theta^2) + \frac{l_0 \theta^2}{2b} + 0.16 \frac{uf^2\theta^2}{\kappa b} + \text{const} \quad (25)$$

Minimization of this expression with respect to angle θ leads to the typical values of the bending angle θ to be on the order of $(l_0/2 + 0.16uf^2/\kappa)^{-1/2}$ and to eq 23 for the

chain persistence length. The optimization of the bond conformational entropy and bending energy is a basis of the Gaussian variational principle for calculation of the bending rigidity of a polyelectrolyte chain. The details of this method are described in Appendix A.

To choose between linear and quadratic dependences of the chain's persistence length on the Debye screening length, one has to establish which one corresponds to lower chain free energy. The energetic contribution to the chain free energy for a polyelectrolyte chain with OSF persistence length is on the order of the thermal energy $k_B T$ per each persistence length (see discussion after eq 18) while for the chain model with unrestricted torsion angles (WLC) it is on the order of $k_B T$ per each bond (see eq 22). The conformational part of the chain free energy is associated with the penalty for the bond alignment on the length scales smaller than the chain persistence length and depends logarithmically on the chain persistence length (see eq 12). Combining together conformational and energetic contributions, one can write the total free energy of a semiflexible polyelectrolyte chain as follows

$$\frac{F}{Nk_B T} \approx \ln(l_p/b) + \frac{\Delta U_{bond}}{k_B T} \approx$$
$$\begin{cases} \ln(l_0/b + 0.25uf^2/(\kappa b)^2) & \text{for OSF} \\ \ln(l_0/b + 0.32uf^2/(\kappa b)) & \text{for WLC} \end{cases} \quad (26)$$

where one has to use eqs 18 and 23 for the persistence length l_p and eqs 17 and 22 for ΔU_{bond}. In both cases the chain free energy is dominated by its conformational part (logarithmic term on the right-hand side of eq 26). By comparing expressions in eq 26, one can see that the polyelectrolyte chain in a circular configuration used in the OSF calculation of the electrostatic persistence length has higher chain free energy due to an additional factor $(\kappa b)^{-1}$ in front of the electrostatic part of the persistence length than that for polyelectrolyte chain with unrestricted torsion angles (WLC). This should not be surprising because in the OSF approach one only optimizes chain deformation energy while for the chain deformation modes with unrestricted torsion angles the optimal value of the bond angle corresponds to the minimum of the free energy per bond. Thus, the bending of a polyelectrolyte chain will occur in such a way to optimize both entropic and energetic penalties due to chain bending leading to linear dependence of the chain persistence length on the Debye screening length (eq 23). In the next section I will describe bending rigidity of the weakly charged flexible polyelectrolyte chain.

4. Weakly Charged Flexible Polyelectrolytes

The weakly charged flexible polyelectrolyte chain has a zero bending energy $\tilde{\epsilon}_{bend}$ and the value of the interaction parameter uf^2 being much smaller than unity, $uf^2 < 1$. In this case a polyelectrolyte chain can be viewed as an array of electrostatic blobs. At the length scales smaller than the electrostatic blob size D_e the electrostatic interactions between charged monomers are too weak to perturb chain conformations while at the length scales larger than the electrostatic blob size the electrostatic interactions control chain deformation.[9,10] For a θ-solvent for the uncharged polymer backbone, the relation between the electrostatic blob size and the number of original monomers in it is expected to be $D_e \approx bg^{1/2}$.[9,10] These blobs represent new
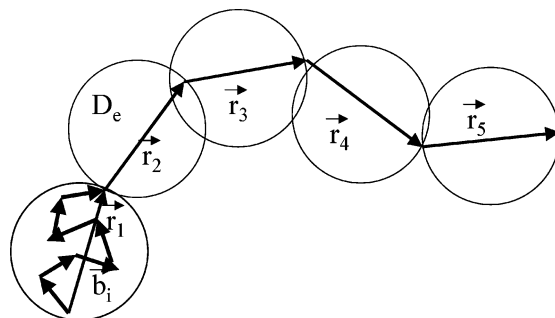
Figure 3. Schematic representation of weakly charged polyelectrolyte chain as chain of blobs.

effective "monomers" (see Figure 3). In salt solutions when the Debye radius becomes smaller than the chain size, the middle of the polyelectrolyte chain is under constant tension created by electrostatic repulsion between charged monomers. These electrostatic blobs have the same size. However, the blobs start growing in size close to the ends of the polyelectrolyte chain within the distance of the order of the Debye screening length from both ends of a chain. Below, I will ignore these weak variations in the number of monomers inside the electrostatic blob and will assume that all blobs have the same size. In this approximation the number of blobs per chain is equal to $k_g = N/g$.

By representing a weakly charged polyelectrolyte chain as chain of electrostatic blobs, one separates two different length scales. At the length scales smaller than electrostatic blob size the orientational correlations between bonds decay very fast. However, at the length scales larger than the electrostatic blob size the contour of chain of blobs weakly fluctuates allowing description of these fluctuations in terms of the bending rigidity of the effective bond vectors—end-to-end vectors of the electrostatic blobs (see Figure 3). This separation of the length scales is done by coarse-graining polyelectrolyte chain and representing it as a chain of electrostatic blobs. This procedure reduces the integration over the original monomers in the chain partition function

$$Z = \int \prod_{i=1}^{N} \frac{\sin(\theta_i)\,d\theta_i\,d\phi_i}{4\pi} \exp\left(-\frac{U_{elect}(\{\phi_i,\theta_i\})}{k_B T}\right) \quad (27)$$

to integration over the coordinates describing the chain of electrostatic blobs. The details of this procedure are given in Appendix B. Here I will only present the final result for the chain free energy as the function of the electrostatic blob size D_e and the variational parameter λ describing the bending rigidity of the chain of electrostatic blobs.

$$\frac{F(D_e,\lambda)}{k_B T} \approx k_g\left[\frac{3}{2}\frac{D_e^2}{b^2 g} - \frac{3}{2}\ln\left(\frac{eD_e^2}{b^2 g}\right) + \ln(\lambda) + \right.$$
$$\left. 0.32\frac{l_B f^2 g^2}{D_e^2 \kappa \lambda} + \frac{l_B f^2 g^2}{D_e}\ln\left(\frac{1}{\kappa D_e}\right)\right] \quad (28)$$

The optimal values of the electrostatic blob size D_e and the variational parameter λ are obtained by minimizing eq 28 with respect to both of them. Minimization of eq 28 with respect to the parameter λ leads to

$$\lambda \approx 0.32 \frac{l_B f^2 g^2}{D_e^2 \kappa} \tag{29}$$

By minimizing eq 28 with respect to electrostatic blob size D_e, one obtains

$$\frac{3D_e}{b^2 g} - \frac{3}{D_e} - 0.64 \frac{l_B f^2 g^2}{D_e^3 \kappa \lambda} - \frac{l_B f^2 g^2}{D_e^2} \ln\left(\frac{1}{\kappa D_e}\right) \approx$$
$$\frac{3D_e}{b^2 g} - \frac{5}{D_e} - \frac{l_B f^2 g^2}{D_e^2} \ln\left(\frac{1}{\kappa D_e}\right) \approx 0 \tag{30}$$

To transform eq 30, I substitute optimal value of the variational parameter λ from eq 29. All terms in eq 30 are of the same order of magnitude when

$$D_e \approx bg^{1/2} \quad \text{and} \quad D_e \approx b(uf^2)^{-1/3}\left[\ln\left(\frac{1}{\kappa D_e}\right)\right]^{-1/3} \tag{31}$$

The electrostatic blob size D_e has additional logarithmic correction in comparison with the expression for the electrostatic blob size obtained in the framework of the scaling model.[9,10] The smaller blob size is a result of the electrostatic repulsion between charged monomers within the Debye screening length leading to stronger chain stretching. These interactions are ignored in the scaling model of the polyelectrolyte chain. The electrostatic persistence length in the case of weakly charged polyelectrolyte is equal to

$$l_p^{WC} = \lambda D_e \approx 0.32 \frac{l_B f^2 g^2}{D_e \kappa} \approx \kappa^{-1} \ln^{-1}((\kappa D_e)^{-1}) \tag{32}$$

It is still proportional to the Debye screening length κ^{-1} but with a logarithmic correction. This logarithmic correction is a difference between eq 32 and Barrat–Joanny result.[18] A logarithmic correction becomes significant at low salt concentrations and should show slower than linear increase of the chain stiffness with decreasing the salt concentration. The explanation of the weaker than linear dependence of the electrostatic persistence length on the Debye screening length is very simple. With decreasing salt concentration, the tension of the chain increases leading to a decreasing of the number of monomers in the electrostatic blobs. This results in lower linear charge density along the polymer backbone fg/D_e and weaker electrostatic interactions between blobs. However, the presented above calculation of the electrostatic persistence length is only correct if there is more than one monomer in the electrostatic blob, $g > 1$. In the case of $g \sim 1$ and $D_e \sim b$ the electrostatic persistence length scales linearly with the Debye screening length (see eq 23b). The crossover between these two regimes takes place at

$$\kappa_{cr}^{-1} \approx b \exp(1/uf^2)$$

The size of weakly charged polyelectrolyte chain with persistence length given by eq 32 is equal to

$$R_e^{WC}(\kappa) \approx \sqrt{l_p^{WC} N D_e/g} \approx$$
$$(uf^2)^{1/6} N^{1/2} b(\kappa b)^{-1/2} \ln^{-1/3}\left(\frac{1}{\kappa D_e}\right) \tag{33}$$

With decreasing salt concentration (increasing of the

Debye screening length) chain becomes stiffer which leads to increasing of the chain size. The crossover from wormlike chain regime to salt-free regime occurs when the chain size $R_e^{WC}(\kappa)$ becomes comparable with size of the weakly charged polyelectrolyte chain in a salt-free regime

$$R_e \approx (uf^2)^{1/3} Nb[\ln(eN/g)]^{1/3} \tag{34}$$

This occurs at the value of the Debye screening length

$$(\kappa_{SF} b)^{-1} \approx (uf^2)^{1/3} N \ln^{2/3}\left(\frac{1}{\kappa_{SF} D_e}\right) \ln^{2/3}\left(\frac{N}{g}\right) \tag{35}$$

With increasing salt concentration, the wormlike chain regime continues until the electrostatic repulsion between remote along polymer backbone persistence segments start swelling the chain. To take into account the electrostatic interactions between remote along the polymer backbone chain segments, I will treat polyelectrolyte chain as a chain of $ND_e/(gl_p^{WC})$ segments of thickness κ^{-1}. The excluded volume between segments is on the order of $v \approx (l_p^{WC})^2 \kappa^{-1}$ and square root of the mean-square end-to-end distance of the chain with this excluded volume is estimated as

$$R_e^F(\kappa) \approx l_p^{WC}\left(\frac{v}{(l_p^{WC})^3}\right)^{1/5}\left(\frac{ND_e}{gl_p^{WC}}\right)^{3/5} \approx$$
$$(uf^2)^{1/5} N^{3/5} b(\kappa b)^{-2/5} \tag{36}$$

The weakly charged polyelectrolyte chain begins to swell when the interaction parameter z_{int} becomes on the order of unity.

$$z_{int} \approx \left(\frac{v}{(l_p^{WC})^3}\right)\left(\frac{ND_e}{gl_p^{WC}}\right)^{1/2} \approx$$
$$(uf^2)^{1/6} N^{1/2}(\kappa b)^{1/2} \ln^{5/3}\left(\frac{1}{\kappa D_e}\right) \approx 1 \tag{37}$$

Thus, the weakly charge polyelectrolyte chain exhibits wormlike chain behavior within the narrow interval of the Debye screening lengths

$$(uf^2)^{1/3} N \ln^{10/3}\left(\frac{1}{\kappa D_e}\right) \leq (\kappa b)^{-1} \leq$$
$$(uf^2)^{1/3} N \ln^{2/3}\left(\frac{1}{\kappa D_e}\right) \ln^{2/3}\left(\frac{N}{g}\right) \tag{38}$$

Outside of this interval the chain size follows either the salt-free dependence given by eq 34 or the swollen chain dependence given by eq 36. Note that for strongly charged polyelectrolyte chains with $uf^2 \approx 1$ this interval of wormlike chain behavior disappears and with increasing salt concentration chain directly enters the swollen chain regime as soon as the Debye screening length becomes comparable with the chain size.

However, in the case of semiflexible polyelectrolytes discussed in section 3 there is a wide enough interval of wormlike chain behavior. To show this, let us consider the case when electrostatic interactions only slightly perturb the bare persistence length l_0, $l_0 > uf^2 \kappa^{-1}$. In this case the electrostatic excluded volume between chain's segments of length l_0 is on the order of $v \approx l_0^2 \kappa^{-1}$. The interaction parameter z_{int} for semiflexible polyelectrolyte chain is equal to

$$z_{int} \approx \left(\frac{v}{l_0^3}\right)\left(\frac{Nb}{l_0}\right)^{1/2} \approx N^{1/2} b^{1/2} l_0^{-3/2} \kappa^{-1} \qquad (39)$$

In the wormlike chain regime the interaction parameter z_{int} is smaller than unity. This leads to the following inequality for the Debye screening length

$$(\kappa b)^{-1} \leq (l_0/b)^{3/2} N^{-1/2} \qquad (40)$$

Thus, below this threshold value a semiflexible polyelectrolyte chain can be viewed as wormlike chain with the persistence length given by eq 23a.

5. Conclusions

In this paper I have shown that the quadratic dependence of the electrostatic persistence length of semiflexible and strongly charged flexible polyelectrolytes on the Debye screening length is a specific feature of the circular deformation mode with bending angles θ_i being equal to θ and torsion angles $\phi_i = \pi$ utilized in the OSF derivation. Effectively, the OSF approach corresponds to evaluation of the electrostatic persistence length of a 2-D polyelectrolyte, which charged monomers interact via screened Coulomb potential. In this conformation the charges on polymer backbone are in the closest possible proximity from each other and chain has the largest possible increase in the electrostatic energy with increasing the value of the bending angle θ. This extremely high electrostatic penalty for chain bending is counterbalanced by small values of the equilibrium bending angles, resulting in larger than necessary persistence length. By allowing fluctuations of the torsion angles ϕ_i, the distances between charged monomers can be increased and electrostatic energy penalty for chain bending can be lowered (see eqs 15 and 21). This results in shorter persistence length and lower chain free energy than that of a chain with the OSF persistence length (see eq 26).

In the case of a weakly charged chain, the electrostatic persistence length has a sublinear dependence on the Debye screening length which is due to the variation of the linear charge density of a chain of electrostatic blobs with salt concentration. This result was derived by applying a coarse-graining procedure to initially flexible polyelectrolyte chain by representing it as a chain of electrostatic blobs. The blob picture of weakly charged polyelectrolyte chain is a way to separate two different length scales at which a chain contour is strongly and weakly fluctuating. At the distances larger than the electrostatic blob size the contour of the chain of blobs is weakly fluctuating. Thus, it can be described in terms of the effective bending rigidity. The blob size and chain persistence length are then found self-consistently by minimizing the chain's free energy.

This dependence of the electrostatic persistence length on the Debye screening length is also in disagreement with quadratic dependence derived in refs 12 and 15. It is important to point out that the expression in eqs 21 and 28 for the average value of intrachain electrostatic energy per monomer (or per blob in the case of weakly charged chain) has the same scaling dependence on the variational parameter λ and the Debye screening length κ^{-1} as one derived in ref 12. The difference in the chain's variational free energy appeared to be in the expression for the chain's orientational entropy. The discrete model of the polymer chain used in this paper leads to a logarithmic dependence of the chain confor-

mational free energy on the variational parameter λ instead of a power law dependence, $-k_B T \lambda^{-1/2}$, as advocated in ref 12 (see eq 32 in ref 12 in which one has to substitute $l_e/\xi = \lambda$). The logarithmic dependence of the free energy of an ideal semiflexible chain on the chain's persistence length is obtained by direct calculation of chain's free energy (see eq 12). A discrete model of a semiflexible polymer chain or discrete chain of blobs is free from the divergences that appear in the continuous chain models at small length scales. Thus, the logarithmic dependence of the chain's free energy on the persistence length is not a result of short length scales cutoff but a property of the discrete chain model. The absence of the logarithmic term in the expression of the free energy obtained in refs 12 and 15 is due to incorrect normalization of the functional integrals describing a polymer chain with effective bending rigidity. Without correct normalization factor the continuous and discrete models of an ideal semiflexible chain results in different expressions for the chain partition function. In fact, the correct normalization of the functional integral is usually obtained by matching results for discrete and continuous models (see for discussion of this subject refs 43 and 44). It is important to remember that a continuous chain model is only an approximation of a discrete chain model. Furthermore, in the case of semiflexible polyelectrolyte chain the authors of ref 12 incorrectly eliminated divergence in the conformational part of the chain free energy (see eq 39 of ref 12).

Another inconsistency of the results of ref 12 that I would like to point out here is associated with the electrostatic energy penalty per electrostatic blob due to chain bending, $\Delta U_{bend} \propto k_B T \kappa D_e \ll k_B T$, which is much smaller than the typical energy fluctuations on the scale of the electrostatic blob. Thus, one should expect that the fluctuations in the chain tension and bending on these length scales destroy such energetically weak chain alignment. Note that the electrostatic energy penalty per electrostatic blob due to chain bending obtained in this paper is on the order of the thermal energy $k_B T$, $\Delta U_{bend} \approx k_B T (l_B f^2 g^2 / D_e^2 \kappa \lambda) \approx k_B T$ (see eq 29 for equilibrium λ) and chain stiffening occurs at the length scales larger than the electrostatic blob size.

The linear dependence of the electrostatic persistence length is in agreement with the results of variational calculations that introduce internal chain stiffening by considering a polyelectrolyte chain as semiflexible polymer with adjustable persistence length. All these methods based on optimization of conformational and electrostatic contributions to chain's free energy. It is also important to point out that the Gaussian and the Edwards–Singh's variational principles are utilized in the PRISM[45−48] and field-theoretical[49,50] theories of polyelectrolytes. In these methods a multichain system is approximated by a system of chains in the effective medium. In this medium monomers on the polymer chain interact via the bare interaction potential and self-consistently determined medium-induced interaction potential. Thus, the chain persistence length in the PRISM method is proportional to the screening length of the effective medium potential.

In this paper I have ignored the effect of counterion condensation, which is important at high linear charge densities along the polymer backbone. The crossover to the counterion condensation regime occurs when the linear charge number density becomes larger than l_B^{-1}.

For higher charge densities the effective charge on the chain is reduced to its crossover value. The fraction of condensed counterions depends on both salt and polymer concentrations, thus leading to an additional concentration-dependent factor in the electrostatic persistence length and further weakening the net concentration dependence of the electrostatic persistence length. I will address this problem in future publications.

Appendix A

The variational approach to calculation of the electrostatic persistence length of semiflexible strongly charged polyelectrolytes utilizes a trial function method to evaluate a chain partition function

$$Z = \int \prod_{i=1}^{N} \frac{\sin(\theta_i)\, \mathrm{d}\theta_i\, \mathrm{d}\phi_i}{4\pi} \times$$
$$\exp\left(-\frac{U_{\text{elect}}(\{\phi_i, \theta_i\}) + U_{\text{bend}}^0(\{\theta_i\})}{k_B T}\right) \quad (A1)$$

Since electrostatic interactions between monomers lead to additional stiffening of the polyelectrolyte chain, the trial function should describe the additional energy penalty associated with deviation of the chain contour from the straight line (directional memory effect). To impose a restriction on the chain bending, I will assume that combination of bending and electrostatic interactions can be reduced to the effective chain with the bending rigidity described by the potential energy

$$\frac{U_{\text{bend}}(\{\theta_i\})}{k_B T} = \lambda \sum_{i=1}^{N-1}(1 - \cos(\theta_i)) \quad (A2)$$

where $k_B T \lambda$ is the bending energy and θ_i is the angle between bond vectors $\mathbf{b}_i$ and $\mathbf{b}_{i+1}$ (see Figure 1). For large λ values the typical θ-angle fluctuations about zero are small, and $\cos(\theta_i)$ can be approximated by its power series up to quadratic term. In this case eq A2 reduces to the well-known expression for the bending energy in the wormlike chain model with mean-square value of the bending angle $\langle \theta^2 \rangle$ equal to $2/\lambda$. The chain partition function is evaluated as follows

$$Z(\kappa, \lambda) \approx Z_{\text{bend}}(\lambda) \times$$
$$\exp\left(-\frac{\langle U_{\text{elect}}(\{\phi_i, \theta_i\}) + U_{\text{bend}}^0(\{\theta_i\}) - U_{\text{bend}}(\{\theta_i\})\rangle_{\text{bend}}}{k_B T}\right)$$
$$(A3)$$

where the brackets $\langle\ \rangle_{\text{bend}}$ denote the angular average with the Boltzmann weights of the chain with the potential energy given by eq A2 and $Z_{\text{bend}}(\lambda)$ is the partition function of a chain with bending rigidity

$$Z_{\text{bend}}(\lambda) = \left(\frac{\exp(-\lambda)\sinh(\lambda)}{\lambda}\right)^N \quad (A4)$$

The parameter λ is an adjustable parameter which value minimizes the difference between the actual electro-
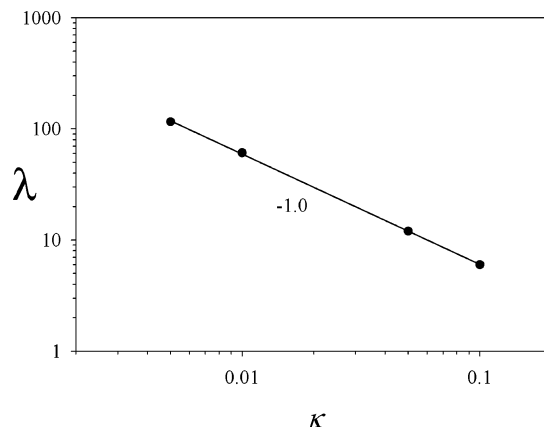
Figure 4. Dependence of the parameter λ corresponding to a minimum of the chain free energy (eq A.5) on the value of the Debye screening length for $l_B = b$, $\epsilon_{\text{bend}} = 0$, and $f = 1$.

static energy of the chain, the bending energy, and entropy loss due to chain stiffening. The averaging of the electrostatic energy is similar to the averaging in eq 19. The expression for the variational free energy of semiflexible polyelectrolyte chain is written as

$$\frac{F(\lambda)}{Nk_B T} \approx -\ln(Z_{\text{bend}}(\lambda)) + (\tilde{\epsilon}_{\text{bend}} - \lambda)(\lambda^{-1} - \coth(\lambda) +$$
$$1) + l_B f^2 \sum_{n=1}^{N}\left(1 - \frac{n}{N}\right)\frac{\exp(-\kappa\sqrt{\langle\mathbf{r}(n)^2\rangle_{\text{bend}}})}{\sqrt{\langle\mathbf{r}(n)^2\rangle_{\text{bend}}}} \quad (A5)$$

The expression for $\langle\mathbf{r}(n)^2\rangle_{\text{bend}}$ is identical to eq 8 if one substitutes $\langle\theta^2\rangle/2$ by λ^{-1}. The expression for the chain free energy can be simplified in the limit of large values of the parameter λ ($\lambda \gg 1$)

$$\frac{F(\lambda)}{Nk_B T} \propto \ln(\lambda) + 0.32\frac{l_B f^2}{\kappa b^2 \lambda} + \frac{\tilde{\epsilon}_{\text{bend}}}{\lambda} + \frac{U_{\text{elec}}^{\text{rod}}}{k_B T} \quad (A6)$$

where the last term describes the electrostatic interactions in the reference rodlike state of the chain which does not depend on the value of the variational parameter λ. There is a very simple interpretation of the first two terms in the chain free energy (eq A6). The first term describes an entropic penalty experienced by the polymer chain due to imposed bending constraints, and the second one is the excess of the average intrachain electrostatic interactions of a chain with given bending rigidity. The optimal value of the parameter λ corresponds to a minimum of the chain free energy. Minimization of the eq A6 with respect to parameter λ leads to a linear relation between the optimal value of this parameter and the Debye screening length κ^{-1}.

$$\lambda \approx \tilde{\epsilon}_{\text{bend}} + 0.32uf^2(\kappa b)^{-1} \quad (A7)$$

It is interesting to point out that in the case of neutral polymer chain with $u = 0$ the variational parameter λ is equal to $\tilde{\epsilon}_{\text{bend}}$, and the variational principle reproduces expression eq 11 for chain persistence length, $l_p = b\lambda \approx b\tilde{\epsilon}_{\text{bend}}$.

Figure 4 shows the result of numerical minimization of the chain free energy (eq A5) with respect to the parameter λ at different values of the parameter κ and $\tilde{\epsilon}_{\text{bend}} = 0$. As one can see, the value of the optimal

parameter λ scales linearly with the Debye screening length κ^{-1}. For these calculations we choose $N = 10\,000$ to minimize the finite N effect. The persistence length for this chain model is defined as $l_p = \lambda b$ which leads to

$$l_{\mathrm{p}}^{\mathrm{WLC}} = b\lambda = b\tilde{\epsilon}_{\mathrm{bend}} + 0.32uf^2\kappa^{-1} \tag{A8}$$

Thus, the Gaussian variational principle gives the same linear dependence of the electrostatic persistence length on the Debye screening length as the method based on evaluation of the bending angle fluctuations discussed in the previous section (see eqs 23).

Appendix B

Let us introduce a set of radius vectors $\mathbf{r}_m$ that are end-to-end vectors connecting sections of the chain with the original g monomers starting from an end of the chain (see Figure 3). In these new variables the chain partition function is written as

$$Z = \int \prod_{m=0}^{k_g-1} d\mathbf{r}_m\, \delta\!\left(\mathbf{r}_m - \sum_{k=1}^{g}\mathbf{b}_{mg+k}\right) \int \prod_{i=1}^{N}\frac{\sin(\theta_i)\,d\theta_i\,d\phi_i}{4\pi} \times$$
$$\exp\!\left(-\frac{U_{\mathrm{elect}}(\{\mathbf{r}_m\})}{k_{\mathrm{B}}T}\right) \tag{B1}$$

where $U_{\mathrm{elect}}(\{\mathbf{r}_m\})$ is the electrostatic energy of the chain written in terms of coordinates of electrostatic blobs. By performing integration over orientations of the original bonds, one has

$$Z \approx \left(\frac{3}{2\pi b^2 g}\right)^{3k_g/2}\int \prod_{m=0}^{k_g-1} d\mathbf{r}_m \times$$
$$\exp\!\left(-\sum_{m=0}^{k_g-1}\frac{3\mathbf{r}_m^{\,2}}{2b^2 g} - \frac{U_{\mathrm{elect}}(\{\mathbf{r}_m\})}{k_{\mathrm{B}}T}\right) \tag{B2}$$

To evaluate the partition function eq B2, I will use a variational approach. The interaction between blobs leads to stiffening of the chain at length scales larger than the blob size. This constraint can be introduced by imposing an additional energy penalty associated with deviation of the contour of chain of blobs from the straight line. I also will assume that each electrostatic blob has an average size D_{e}, $\langle|\mathbf{r}_m|^2\rangle = D_{\mathrm{e}}^2$. The potential energy of a trial chain of electrostatic blobs with size D_{e} and with bending rigidity has the following form

$$\frac{U_{\mathrm{trial}}(\{\mathbf{r}_m\})}{k_{\mathrm{B}}T} = \lambda\sum_{m=0}^{k_g-2}(1 - (\mathbf{n}_m\cdot\mathbf{n}_{m+1})) + \frac{3}{2D_{\mathrm{e}}^{2}}\sum_{m=0}^{k_g-1}\mathbf{r}_m^{\,2}$$
$$\tag{B3}$$

where $\mathbf{n}_m$ is a unit vector pointing along the direction of the blob end-to-end vector $\mathbf{r}_m$. Using the trial function

eq B3, one can estimate the chain partition function eq B2 as follows

$$Z = \left(\frac{3}{2\pi b^2 g}\right)^{3k_g/2}\int \prod_{m=0}^{k_g-1} d\mathbf{r}_m\, \exp\!\left(-\sum_{m=0}^{k_g-1}\frac{3\mathbf{r}_m^{\,2}}{2b^2 g} - \right.$$
$$\left.\frac{U_{\mathrm{elect}}(\{\mathbf{r}_m\}) + U_{\mathrm{trial}}(\{\mathbf{r}_m\}) - U_{\mathrm{trial}}(\{\mathbf{r}_m\})}{k_{\mathrm{B}}T}\right) =$$
$$\left(\frac{3}{2\pi b^2 g}\right)^{3k_g/2}Z_{\mathrm{trial}}(\lambda,D_{\mathrm{e}})\left\langle \exp\!\left(-\sum_{m=0}^{k_g-1}\frac{3\mathbf{r}_m^{\,2}}{2b^2 g} - \right.\right.$$
$$\left.\left.\frac{U_{\mathrm{elect}}(\{\mathbf{r}_m\}) - U_{\mathrm{trial}}(\{\mathbf{r}_m\})}{k_{\mathrm{B}}T}\right)\right\rangle_{\mathrm{trial}} \approx$$
$$\left(\frac{3}{2\pi b^2 g}\right)^{3k_g/2}Z_{\mathrm{trial}}(\lambda,D_{\mathrm{e}})\,\exp\!\left(-\left\langle\sum_{m=0}^{k_g-1}\frac{3\mathbf{r}_m^{\,2}}{2b^2 g} + \right.\right.$$
$$\left.\left.\frac{U_{\mathrm{elect}}(\{\mathbf{r}_m\}) - U_{\mathrm{trial}}(\{\mathbf{r}_m\})}{k_{\mathrm{B}}T}\right\rangle_{\mathrm{trial}}\right) \tag{B4}$$

where the brackets $\langle\;\rangle_{\mathrm{trial}}$ denote averaging over all orientations and amplitude of the vectors $\mathbf{r}_m$ with Boltzmann weights of the chain with potential energy given by eq B3 and $Z_{\mathrm{trial}}(\lambda,D_{\mathrm{e}})$ is the partition function of the chain of blobs with bending rigidity

$$Z_{\mathrm{trial}}(\lambda,D_{\mathrm{e}}) = \int \prod_{m=0}^{k_g-1} d\mathbf{r}_m\, \exp\!\left(-\frac{U_{\mathrm{trial}}(\{\mathbf{r}_m\})}{k_{\mathrm{B}}T}\right) =$$
$$\left(\frac{2\pi D_{\mathrm{e}}^2}{3}\right)^{3k_g/2}\left(\frac{\exp(-\lambda)\,\sinh(\lambda)}{\lambda}\right)^{k_g-1} \tag{B5}$$

The parameters λ and D_{e} are adjustable parameters which values minimize the difference between the actual energy of the polyelectrolyte chain and the energy of a chain of electrostatic blobs with bending rigidity. The variational free energy of a polyelectrolyte chain is written as follows

$$\frac{F(D_{\mathrm{e}},\lambda)}{k_{\mathrm{B}}T} \approx k_g\left[-\ln(Z_{\mathrm{trial}}(\lambda,D_{\mathrm{e}})) + \frac{3D_{\mathrm{e}}^{\,2}}{2b^2 g} - \frac{3}{2} + \right.$$
$$\lambda(\coth(\lambda) - \lambda^{-1} - 1) + \frac{l_{\mathrm{B}}f^2 g^2}{D_{\mathrm{e}}} +$$
$$\left.l_{\mathrm{B}}f^2 g^2 \sum_{s=1}^{k_g}\left(1 - \frac{sg}{N}\right)\frac{\exp(-\kappa\sqrt{\langle\mathbf{r}(s)^2\rangle_{\mathrm{trial}}})}{\sqrt{\langle\mathbf{r}(s)^2\rangle_{\mathrm{trial}}}}\right] \tag{B6}$$

where the expression for $\langle\mathbf{r}(s)^2\rangle_{\mathrm{trial}}$ is identical to eq 13 in which one has to substitute b by $\langle r_m\rangle$. For the trial function eq B3 this average $\langle r_m\rangle$ is equal to $(4/\sqrt{6\pi})D_{\mathrm{e}} \approx 0.92D_{\mathrm{e}}$. Since discussion below is done on the scaling level, I will ignore this factor and use $\langle r_m\rangle \approx D_{\mathrm{e}}$. In the limit when the Debye screening length κ^{-1} is much

larger than the electrostatic blob size D_e eq B6 can be simplified

$$\frac{F(D_e,\lambda)}{k_B T} \approx k_g \left[\frac{3}{2}\frac{D_e^2}{b^2 g} - \frac{3}{2}\ln\left(\frac{eD_e^2}{b^2 g}\right) + \ln(\lambda) + \right.$$
$$\left. 0.32\frac{l_B f^2 g^2}{D_e^2 \kappa \lambda} + \frac{l_B f^2 g^2}{D_e}\ln\left(\frac{1}{\kappa D_e}\right) \right] \quad (B7)$$

References and Notes

(1) Odijk, T. *J. Polym. Phys., Part B: Polym. Phys.* **1977**, *15*, 477.
(2) Skolnick, J.; Fixman, M. *Macromolecules* **1977**, *10*, 944.
(3) Le Bret, M. *J. Chem. Phys.* **1982**, *76*, 6243.
(4) Fixman, M. *J. Chem. Phys.* **1982**, *76*, 6346.
(5) Hagerman, P. J. *Biopolymers* **1981**, *20*, 251.
(6) Kam, Z.; Borochov, N.; Eisenberg, H. *Biopolymers* **1981**, *20*, 1503.
(7) Odijk, T. *Macromolecules* **1979**, *12*, 658.
(8) Khokhlov, A. R.; Khachaturian, K. A. *Polymer* **1982**, *23*, 1793.
(9) de Gennes, P.-G.; Pincus, P.; Brochard, F.; Velasco, R. M. *J. Phys. (Paris)* **1976**, *37*, 1461.
(10) Dobrynin, A. V.; Colby, R. H.; Rubinstein, M. R. *Macromolecules* **1995**, *28*, 1859.
(11) Barrat, J. L.; Joanny, J. F. *Adv. Chem. Phys.* **1996**, *94*, 1.
(12) Manghi, M.; Netz, R. R. *Eur. Phys. J. E* **2004**, *14*, 67.
(13) Li, H.; Witten, T. A. *Macromolecules* **1995**, *28*, 5921.
(14) Liverpool, T. B.; Stapper, M. *Europhys. Lett.* **1997**, *40*, 485.
(15) Netz, R. R.; Orland, H. *Eur. Phys. J. B* **1999**, *8*, 81.
(16) Zandi, R.; Rudnick, J.; Golestanian, R. *Eur. Phys. J. E* **2002**, *9*, 41.
(17) Schmidt, M. *Macromolecules* **1991**, *24*, 5361.
(18) Barrat, J. L.; Joanny, J.-F. *Europhys. Lett.* **1993**, *24*, 333.
(19) Ha, B. Y.; Thirumalai, D. *Macromolecules* **1995**, *28*, 577.
(20) Ha, B. Y.; Thirumalai, D. *J. Chem. Phys.* **1999**, *110*, 7533.
(21) Edwards, S. F.; Singh, P. *J. Chem. Soc., Faraday Trans. 2* **1979**, *75*, 1001.
(22) Muthukumar, M. *J. Chem. Phys.* **1996**, *105*, 5183.
(23) Ghosh, K.; Carri, G. A.; Muthukumar, M. *J. Chem. Phys.* **2001**, *115*, 4367.
(24) Bratko, D.; Dawson, K. A. *J. Chem. Phys.* **1993**, *99*, 5352.
(25) Reed, C. E.; Reed, W. F. *J. Chem. Phys.* **1991**, *94*, 8479.
(26) Seidel, C. *Ber. Bunsen-Ges. Phys. Chem. Chem. Phys.* **1996**, *100*, 757.
(27) Schafer, H.; Seidel, C. *Macromolecules* **1997**, *30*, 6658.
(28) Ullner, M.; Jonsson, B.; Peterson, C.; Sommelius, O.; Soderberg, B. *J. Chem. Phys.* **1997**, *107*, 1279.
(29) Micka, U.; Kremer, K. *J. Phys.: Condens. Matter* **1996**, *8*, 9463.
(30) Micka, U.; Kremer, K. *Phys. Rev. E* **1996**, *54*, 2653.
(31) Tricot, M. *Macromolecules* **1984**, *17*, 1698.
(32) Reed, C. E.; Reed, W. F. *J. Chem. Phys.* **1992**, *97*, 7766.
(33) Forster, S.; Schmidt, M.; Antonietti, M. *J. Phys. Chem.* **1992**, *96*, 4008.
(34) de Nooy, A. E. J.; Besemer, A. C.; van Bekkum, H.; van Dijk, J.; Smit, J. A. M. *Macromolecules* **1996**, *29*, 6541.
(35) Nishida, K.; Urakawa, H.; Kaji, K.; Gabrys, B.; Higgins, J. S. *Polymer* **1997**, *38*, 6083.
(36) Tanahatoe, J. J. *J. Phys. Chem. B* **1997**, *101*, 10442.
(37) Beer, M.; Schmidt, M.; Muthukumar, M. *Macromolecules* **1997**, *30*, 8375.
(38) Nguyen, T. T.; Shklovskii, B. I. *Phys. Rev. E* **2002**, *66*, 021801.
(39) Everaers, R.; Milchev, A.; Yamakov, V. *Eur. Phys. J. E* **2002**, *8*, 3.
(40) Ullner, M.; Woodward, C. E. *Macromolecules* **2002**, *35*, 1437.
(41) Liao, Q.; Dobrynin, A. V.; Rubinstein, M. *Macromolecules* **2003**, *36*, 3386.
(42) Rubinstein, M.; Colby, R. H. *Polymer Physics;* Oxford University Press: New York, 2003.
(43) Freed, K. F. *Adv. Chem. Phys.* **1972**, *22*, 1.
(44) Feynman, R. P.; Hibbs, A. R. *Quantum Mechanics and Path Integrals;* McGraw-Hill: New York, 1965.
(45) Yethiraj, A.; Shew, C. Y. *Phys. Rev. Lett.* **1996**, *77*, 3937.
(46) Yethiraj, A. *Phys. Rev. Lett.* **1997**, *78*, 3789.
(47) Yethiraj, A. *J. Chem. Phys.* **1998**, *108*, 1184.
(48) Yethiraj, A. *J. Chem. Phys.* **1999**, *111*, 1797.
(49) Muthukumar, M. *J. Chem. Phys.* **1996**, *105*, 5183.
(50) Muthukumar, M. *J. Chem. Phys.* **1987**, *86*, 7230.