

Effect of Counterion Condensation on Rigidity of Semiflexible Polyelectrolytes

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ABSTRACT: I have calculated the effect of counterion condensation on the electrostatic persistence length of semiflexible polyelectrolytes. There are two contributions to the electrostatic persistence length. The first contribution is due to neutralization of the ionized groups by condensed ions that changes the effective linear charge density along the polymer backbone, weakening intrachain electrostatic repulsion. In the case of the monovalent counterions this contribution to the chain persistence length is proportional to the Debye screening length, underlining the fact of the exponential screening of electrostatic interactions on the length scales of the order of Debye screening length. The second contribution is due to correlation/fluctuation-induced attractive interactions between condensed counterions that result in a negative contribution to the chain persistence length. In the case of multivalent ions these interactions are assumed to be due to strong lateral correlations between condensed multivalent ions and were accounted for in the framework of the strongly correlated Wigner liquid approximation.

1. Introduction

Polyelectrolytes are polymers with positively or negatively charged groups.^{1–5} Examples of polyelectrolytes include poly(styrenesulfonate), poly(acrylic acid) and poly(methacrylic acid) and their salts, DNA, and other polyacids and polybases. In dilute solutions electrostatic repulsion between ionized groups on the polymer backbone leads to elongation of the polyelectrolyte chain. With increasing polymer concentration the size of the polyelectrolyte chain decreases. This is a manifestation of the counterion condensation on the polymer backbone.^{3,6–11} The phenomenon of counterion condensation is due to a fine interplay between the electrostatic attraction of counterions to a polymer chain and the loss of the configurational entropy by counterions due to their localization in the vicinity of the polymer backbone. In very dilute polyelectrolyte solutions the entropic penalty for counterion condensation is very high, and almost all counterions leave the polymer chain and stay in a solution. However, as polymer concentration increases, the entropic penalty for counterion localization decreases, resulting in an increase in a number of condensed counterions.

In addition to the reduction of the net polymer charge weakening electrostatic repulsion the condensed counterions also induce effective attractive interactions. There are two different mechanisms that could lead to effective attraction. The first one is the formation of permanent or long-lived ionic pairs between condensed counterions and oppositely charged monomers. In this case, dipole–dipole interactions between ion pairs result in additional attraction between monomers. These extra attractive interactions decrease the value of the second virial coefficient, shifting the position of the θ -temperature. The shift of the θ -temperature in the case of strongly charged flexible polyelectrolytes could be significant, leading to a chain collapse.^{12,13}

Another effect that can give rise to attractive interactions is the correlation-induced attraction between condensed counterions and charged monomers.^{14–19} These interactions are due to heterogeneous distribution of charge density along the polymer backbone. In the case of weak electrostatic attraction the origin of these interactions is similar to the fluctuation-induced

attraction in two-component plasma and is related to the local charge density fluctuations. In the opposite limit of strong electrostatic interactions the effect is due to correlation-induced attraction between the counterions and the oppositely charged polymer backbone (similar to the interactions in strongly correlated Wigner liquid^{14,16,18}).

In solutions of flexible polyelectrolytes the correlation-induced attraction between condensed counterions and charged monomers results in the formation of a necklace structure, consisting of polymeric globules (beads) connected by extended sections of the chain (strings of monomers).²⁰ This structure optimizes the correlation-induced attraction of condensed counterions to charged monomers and electrostatic repulsion between uncompensated charges.

In solutions of semiflexible polymers, such as DNA, F-actin, microtubules, and filamentous viruses, the condensation of multivalent ions triggers an abrupt collapse transition from coillike conformations to compact globular structure.^{18,21–23} The change in the size of the molecule is staggering. For example, the 160 000 base pairs T4 phage DNA with radius of gyration 950 nm fits into a virus capsid 100 nm in diameter, so its volume compression ratio is about 6900 times. The condensation of multivalent ions is also manifested in changes of the chain persistence length. The force–elongation experiments on the λ -bacteriophage DNA in the presence of the multivalent cations revealed that the association of multivalent ions with DNA lead to a dramatic change in the persistence length value by lowering it up to 25–30 nm.²⁴ This is well below the “fully neutralized” value of the persistence length of 45–50 nm observed in the case of monovalent salts. The addition of multivalent ions to the solutions of DNA or microtubules can cause bundle formation and precipitation of charged biomacromolecules.^{25–28}

The effect of the condensed cations on the chain flexibility was studied extensively over the past years. The fluctuation mechanism of the chain softening was considered by Golestanian et al.^{29,30} and by Ariel and Andelman.³¹ Golestanian et al.^{29,30} have shown that the counterion density fluctuations reduce the chain persistence length and could lead to instability

of rodlike chain conformation at the intermediate length scales. Depending on the cation valence, the semiflexible polyelectrolyte chain could be in extended (rodlike) conformation, in a collapsed toroidal or necklace-like conformation. Ariel and Andelman³¹ have used one-loop approximation to calculate the fluctuation corrections to the chain persistence length. In the mean-field approximation they reproduced the Odijk–Skolnick–Fixman expression for the chain persistence length.^{32,33} By taking into account fluctuation corrections, they found strong deviation of the chain's persistence length from the OSF result. In the case of multivalent cations ($Z = 2, 3$, and 4) their theory predicts negative total chain persistence length and chain instability at low salt concentrations. The calculation of the electrostatic persistence length in the strongly correlated Wigner liquid approximation was done by Nguyen et al.³⁴ By representing the condensed ions by strongly correlated ionic liquids, they found that the correlation-induced attractive interactions between condensed ions result in negative contribution to the chain persistence length. However, the decrease in the bending rigidity was very weak and insufficient to explain experimentally observed trends. The correlation effects can be amplified if variations in the local dielectric constant near the polymer backbone are taken into account. Rouzina and Bloomfield³⁵ have used the sigmoidal distance-dependent dielectric constant to calculate the correlation energy of the condensed cations. Their analysis shows that this correction of the local dielectric constant was necessary to qualitatively explain the decrease in the DNA bending rigidity observed for variety of multivalent ions.

While all previous studies of chain bending rigidity were based on the circular chain deformation mode introduced by Odijk³² and by Skolnick and Fixman,³³ my recent paper³⁶ has shown that the circular conformation used in the OSF approach overestimates the electrostatic energy penalty due to chain deformation. In this conformation the charges on the polymer backbone are in the closest possible proximity from each other, and a 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 the chain bending is counterbalanced by small values of the equilibrium bending angles, resulting in larger persistence length. By allowing fluctuations of the torsion angles, the distances between charged monomers can be increased and the electrostatic energy penalty for chain bending can be lowered. This results in shorter persistence length, which scales linear with the Debye screening length, and lower chain free energy than that of a chain with the OSF persistence length.

In this paper I reconsider the effect of condensed counterions on the bending rigidity of semiflexible polyelectrolyte chains by extending approach developed in ref 36. The rest of the paper is organized as follows. In section 2 the Oosawa–Manning condensation theory^{6–8} is applied to the case of semiflexible polyelectrolyte chain. The correlation-induced attractive interactions and their contributions to the chain bending rigidity are calculated in section 3. Finally, section 4 summarizes the results.

2. Renormalization of the Electrostatic Persistence Length by Condensation of Monovalent Counterions

Consider a semiflexible polyelectrolyte chain with degree of polymerization N , fraction of charged monomers f , and bond length b . The fraction β of counterions is condensed on the polymer backbone, reducing the number of ionized groups per chain to $(1 - \beta)fN$. Conformations of semiflexible polyelectrolyte chain are described by a set of bond angles θ_i and torsion angles ϕ_i (see Figure 1). The potential energy of a semiflexible

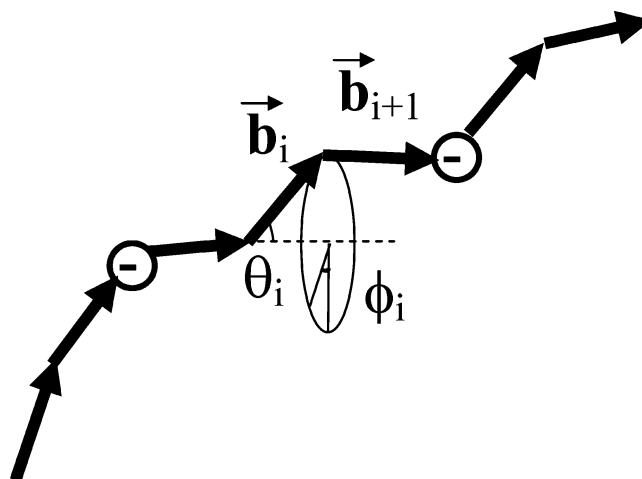


Figure 1. Conformation of a polyelectrolyte with an arbitrary distribution of torsion ϕ_i and bending angles θ_i .

polyelectrolyte chain in a given conformation with a set of torsion and bond angles $\{\phi_i, \theta_i\}$ includes the bending energy

$$U_{\text{bend}}^0(\{\theta_i\}) = k_B T \tilde{\epsilon} \sum_{i=1}^{N-1} (1 - \cos(\theta_i)) \approx \frac{k_B T \tilde{\epsilon} N-1}{2} \sum_{i=1} \theta_i^2 \quad (1)$$

where $\tilde{\epsilon}$ is a bending energy in terms of the thermal energy $k_B T$ and the electrostatic repulsion energy between $(1 - \beta)fN$ ionized groups. In the case of uncorrelated distribution of ionized groups along the polymer backbone each monomer can be considered as carrying an average charge $-e(1 - \beta)f$. The electrostatic energy of such chain is given by the following expression

$$\frac{U_{\text{electr}}(\{\phi_i, \theta_i\})}{k_B T} = \frac{l_B (1 - \beta)^2 f^2}{2} \sum_{i \neq j}^N \frac{\exp(-\kappa |\mathbf{r}_{ij}(\{\phi_i, \theta_i\})|)}{|\mathbf{r}_{ij}(\{\phi_i, \theta_i\})|} \quad (2)$$

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 $\kappa^2 = 8\pi l_B c_s$, c_s is the salt concentration, and l_B is the Bjerrum length ($l_B = e^2/\epsilon k_B T$ —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 $k_B T$).

To estimate the effect of the condensed counterions on the chain rigidity, one has to average eq 2 over distributions of the bond and torsion angles $\{\phi_i, \theta_i\}$. I will use the Flory-like method to perform this averaging (see for details ref 36). In this approximation one assumes that electrostatic interactions do not change the distribution of the torsion angles $\{\phi_i\}$ such that the torsion angles are still distributed with equal probability within the interval $-\pi \leq \phi_i \leq \pi$. However, these interactions results in renormalization of the bond angle θ . Averaging of the electrostatic energy per bond over the distribution of torsion angles $\{\phi_i\}$ at a given value of the bond angle θ yields

$$\begin{aligned} \frac{\langle U_{\text{electr}}(\theta) \rangle_\phi}{k_B T} &= l_B ((1 - \beta)f)^2 \sum_{n=1}^{\infty} \left\langle \frac{\exp(-\kappa r(n))}{r(n)} \right\rangle_\phi \\ &\approx l_B ((1 - \beta)f)^2 \sum_{n=1}^{\infty} \frac{\exp(-\kappa \sqrt{\langle \mathbf{r}(n) \rangle_\phi^2})}{\sqrt{\langle \mathbf{r}(n) \rangle_\phi^2}} \end{aligned} \quad (3)$$

In averaging the electrostatic interactions in eq 3 over the torsion

angles, the integral representation for screened Coulomb potential was used.

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

Note that the substitution $\langle \exp(-y^2 r^2) \rangle$ by $\exp(-y^2 \langle r^2 \rangle)$ is only correct when the parameters $\langle r^{2m} \rangle / \langle r^2 \rangle^m - 1$ are smaller than unity. This is true for chain conformations close to rodlike.³⁷

In the case of unrestricted torsion angles and given 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 (see for details ref 36)

$$\langle r(n)^2 \rangle_\phi \approx \frac{8b^2}{\theta^4} \left(\exp\left(-\frac{n\theta^2}{2}\right) + \frac{n\theta^2}{2} - 1 \right) \quad (5)$$

For the short distances along the polymer backbone, $n\theta^2 \ll 1$, the chain conformation is close to rodlike, and the distance between two monomers can be approximated as

$$\sqrt{\langle r(n)^2 \rangle_\phi} \approx \frac{bn}{n\theta^2 \ll 1} \left(1 - \frac{n\theta^2}{12} \right) \quad (6)$$

Substituting eq 6 into eq 3, evaluating the sum over n , and extracting the terms proportional to θ^2 , one obtains the following expression for the average electrostatic energy per bond with a given value of the bond angle θ :

$$\frac{\langle U_{\text{electr}}(\theta) \rangle_\phi}{k_B T} \approx l_B (1 - \beta)^2 f^2 \sum_{n=1}^{\infty} \left(\frac{\exp(-\kappa bn)}{bn} + \frac{\theta^2 \exp(-\kappa bn)}{12b} (1 + \kappa bn) \right) \quad (7)$$

The summation over n in eq 7 can be carried out exactly leading to

$$\frac{\langle U_{\text{electr}}(\theta) \rangle_\phi}{k_B T} \approx \frac{u((1 - \beta)f)^2}{\kappa b \ll 1} \left(-\ln(\kappa b) + \frac{\theta^2}{6\kappa b} \right) \quad (8)$$

where u is the ratio of the Bjerrum length l_B to the bond length b , $u = l_B/b$.

By imposing the restrictions on the values of the bond angle θ , one changes the number of available states in the bond's orientational space. The number of states $\Omega(\theta)$ available to a bond localized within bond angle θ is proportional to the solid angle $\pi\theta^2$ (see for details ref 36). Using the relation between the number of states and the bond orientational entropy, one arrives at

$$S_{\text{bond}}(\theta) \approx k_B \ln(\Omega(\theta)) \approx k_B \ln(\theta^2) \quad (9)$$

Thus, the free energy per bond of a semiflexible polyelectrolyte chain with fraction of condensed counterions β is equal to

$$\frac{F_{\text{bond}}(\theta, \beta)}{k_B T} \approx -\ln(\theta^2) + \frac{\tilde{\epsilon}\theta^2}{2} + u((1 - \beta)f)^2 \left(-\ln(\kappa b) + \frac{\theta^2}{6\kappa b} \right) \quad (10)$$

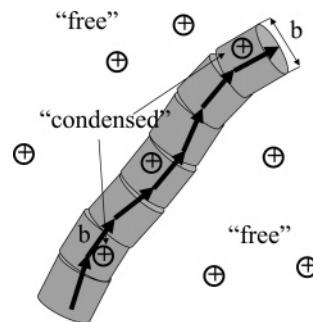


Figure 2. Schematic sketch of a polyelectrolyte chain and definition of different length scales for the two-zone model.

This equation is an analogue of the Flory-like expression for the chain free energy, which includes the entropic penalty for the chain stiffening (the first term on the right-hand side), energetic penalties for chain bending appearing due to initial chain bending rigidity (the second term), and electrostatic interactions between ionized charged groups (the last two terms). The optimal value of the bond angle θ corresponds to the minimum of the free energy (eq 10).

The dependence of the fraction of condensed counterions β on polymer and salt concentration can be evaluated in the framework of the two-zone model for counterion condensation.^{6–8} In this approach (Oosawa–Manning condensation theory^{6–8}) the counterions are separated into “free” and “condensed” (see Figure 2). The volume per chain $V_{\text{ch}} \approx N/c$ (where c is the monomer concentration) is divided into two zones. The first zone is occupied by the polymer chain and has volume of the order of Nv where v is localization volume, assumed to be equal to b^3 . The second zone is the volume free of polymer $V_{\text{ch}} - Nv$. The total number of ions inside the volume V_{ch} is equal to the total number of charged monomers on a polymer chain fN and similarly charged n_s salt ions. The number $n_s + (1 - \beta)fN$ of these ions occupies volume $V_{\text{ch}} - Nv$ and is considered to be free while the number βfN of these ions is localized inside volume Nv . The entropic part of the chain free energy associated with partitioning of ions between two zones has the following form

$$\frac{F_{\text{trans}}(\beta)}{k_B T} \approx (n_s + f(1 - \beta)N) \ln \left[\frac{(c_s + (1 - \beta)fc)b^3}{e} \right] + f\beta N \ln \left[\frac{\beta f}{e} \right] \quad (11)$$

where $c_s = n_s/V_{\text{ch}}$ is the salt concentration and $(1 - \beta)fc$ is the concentration of “free” counterions. In the derivation of the eq 11 it was assumed that the localization volume Nv is much smaller than the volume per chain V_{ch} , which is true for low polymer concentrations. The first term on the right-hand side of eq 11 corresponds to “free” counterions and salt ions in the second zone while the last term accounts for localization of “condensed” counterions near the polymer backbone.

Partitioning of ions between the two zones is obtained by minimizing the total free energy per bond

$$F(\theta, \beta) \approx F_{\text{bond}}(\theta, \beta) + F_{\text{trans}}(\beta)/N \quad (12)$$

with respect to the fraction of condensed counterions β . Note that this minimization corresponds to equality of the chemical potentials of the counterions localized near the polymer backbone and moving “free” in the solution. After minimization one obtains the following equation

$$\ln(\beta) \approx \ln(c_s b^3/f) - 2u(1-\beta)f \ln(\kappa b) + \frac{u(1-\beta)f\theta^2}{3\kappa b} \quad (13)$$

coupling the fraction of condensed counterions β with the value of the bond angle θ . In simplifying eq 13, it was assumed that $c_s > fc$. The minimization of the free energy eq 12 with respect to a bond angle θ leads to

$$\theta^2 \approx \left(\frac{\tilde{\epsilon}}{2} + \frac{u(1-\beta)^2 f^2}{6\kappa b} \right)^{-1} \quad (14)$$

By substituting solution of the eq 14 into eq 13 and keeping only leading terms, one has

$$\ln(\beta) \approx \ln(c_s b^3/f) - 2u(1-\beta)f \ln(\kappa b) + \frac{2u(1-\beta)f}{3\kappa b\tilde{\epsilon}} \quad (15)$$

This equation generalizes Manning's result⁶ for the ion-binding isotherm to the case of semiflexible polyelectrolytes. Equation 15 can be rewritten in a more familiar form

$$\ln(\beta) \approx (1 - \gamma_0(1 - \beta)) \ln(c_s b^3/f) \quad (16)$$

by introducing the Oosawa–Manning counterion condensation parameter

$$\gamma_0 \approx \frac{2uf \ln(\kappa b)}{\ln(c_s b^3/f)} \left(1 - \frac{1}{3\kappa b\tilde{\epsilon} \ln(\kappa b)} \right) \approx \frac{uf \left(1 - \frac{1}{3\kappa b\tilde{\epsilon} \ln(\kappa b)} \right)}{\kappa b \leq 1} \quad (17)$$

where in writing the last equation I have used approximation $2 \ln(\kappa b) \approx \ln(c_s b^3)$, which is correct at salt concentrations for which $\kappa b \ll 1$. The fraction of condensed counterion increases with increasing parameter γ_0 and finally saturates at $\beta \approx 1 - \gamma_0^{-1}$ for the large values of the parameter γ_0 . Thus, there is a counterion condensation phenomenon that is associated with the value of the parameter γ_0 . The crossover to counterion condensation regime occurs at $\gamma_0 \approx 1$. One can rewrite this condition in terms of the interaction parameter u

$$u_{cr} \approx \left[\frac{2f \ln(\kappa b)}{\ln(c_s b^3/f)} \left(1 - \frac{1}{3\kappa b\tilde{\epsilon} \ln(\kappa b)} \right) \right]^{-1} \approx \left[f \left(1 - \frac{1}{3\kappa b\tilde{\epsilon} \ln(\kappa b)} \right) \right]^{-1} \quad (18)$$

The analysis of eq 18 shows that the crossover value of the parameter u is smaller for the semiflexible polyelectrolyte chain than that of a rodlike polymer ($\tilde{\epsilon} \rightarrow \infty$). This should not be surprising since for semiflexible polyelectrolytes the local chain bending reduces the average distance between ionized groups effectively increasing the linear charge density along the polymer backbone.

The persistence length of a semiflexible polyelectrolyte chain is estimated as

$$l_p \approx \frac{2b}{\theta^2} \approx l_0 + l_{elec} \approx b\tilde{\epsilon} + \frac{l_B(1-\beta)^2 f^2}{3\kappa b} \approx b\tilde{\epsilon} + \frac{l_B f^2}{3\gamma_0^2 \kappa b} \quad (19)$$

This equation shows that with increasing the fraction of condensed counterions β the electrostatic contribution (the second term on the right-hand side) tends to zero. Above the counterion condensation threshold $u > u_{cr}$ the fraction of

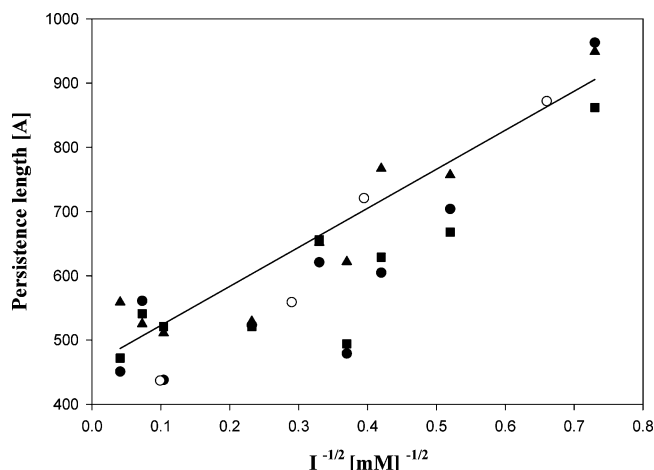


Figure 3. Dependence of the persistence length of the double stranded DNA on the ionic strength of monovalent salt. The filled symbols show the results of persistence length measurements from chain stretching experiments for different chain models: (filled circles) inextensible wormlike chain (WLC) model, (filled squares) strong stretching limit, (filled triangles) extensible WLC model (Baumann, C. G.; Smith, S. S.; Bloomfield, V. A.; Bustamante, C. *Proc. Natl. Acad. Sci. U.S.A.* **1997**, *94*, 6185). The open symbols are results from the diffusion coefficient measurements by D. Porschke (*Biophys. Chem.* **1991**, *40*, 169). The thin solid line is given by the equation $l_p = 461 + 607/\sqrt{I}$.

condensed counterions β is of the order of $1 - 1/\gamma_0$. In this interval of parameters the electrostatic persistence length l_e decreases with increasing the parameter u , $l_e \sim 1/u$.

Figure 3 shows the dependence of the persistence length of DNA on the solution ionic strength, $I = \sum_i z_i^2 c_i$. The chain persistence length was estimated from the chain stretching experiments by analyzing the deformation curves and fitting them to different models of semiflexible polymer chain under applied external force²⁴ and from the chain diffusion coefficient.³⁸ The solid line in Figure 3 corresponds to the best fit to eq 19. As one can see, the experimental data are in good agreement with the prediction of eq 19, confirming the linear dependence of the persistence length on the Debye screening length κ^{-1} .

In the analysis presented above, the electrostatic interactions between condensed counterions were taken into account on the mean-field level by using the average value for counterion density distribution along the polymer backbone. The local counterion density fluctuations lead to an additional negative contribution to the chain persistence length (see Appendix for calculation details). These calculations show that for monovalent ions the fluctuation correction to the chain bending rigidity is small in comparison with the electrostatic contribution due to the repulsion between uncompensated charges and can be safely neglected.

However, in the range of the large values of the interaction parameter u or in the case of the multivalent counterions there is strong lateral repulsion between condensed ions which in turn leads to strong correlations in their positioning along the polymer backbone. These strong lateral correlations between counterions can be taken into account in the framework of the Wigner liquid (WL) model of counterions on the uniformly charged background.¹⁴ In the next section the WL model for condensed counterions is used to describe electrostatic contribution to the chain's persistence length. The presented below approach generalizes the Nguyen et al.³⁴ model to the case of finite salt concentrations and unrestricted torsion angle distributions.

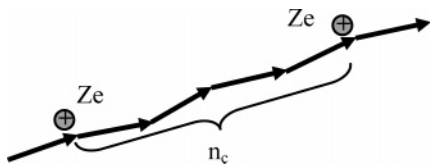


Figure 4. Schematic sketch of a polyelectrolyte chain and definition of different length scales for calculation of the bending rigidity in the presence of multivalent ions.

3. Effect of Multivalent Ions on the Electrostatic Persistence Length

In this section the effect of condensation of multivalent ions with valence $Z > 1$ on chain flexibility is considered. Let us assume that condensed multivalent ions are separated by n_c bonds along the polymer backbone (see Figure 4). The electrostatic energy per bond of a polyelectrolyte chain with condensed multivalent ions includes the electrostatic repulsion between condensed ions

$$\begin{aligned} \frac{\langle U_{ZZ}(\theta, n_c) \rangle_\phi}{k_B T} &\approx \frac{l_B Z^2}{n_c} \sum_{n=1}^{\infty} \left(\frac{\exp(-\kappa b n_c n)}{b n_c n} + \frac{\theta^2 \exp(-\kappa b n_c n)}{12 b} (1 + \kappa b n_c n) \right) \\ &= \frac{u Z^2}{n_c^2} \left(-\ln(1 - \exp(-\kappa b n_c)) + \frac{n_c \theta^2 (1 + \kappa b n_c) \exp(\kappa b n_c) - 1}{12 (\exp(\kappa b n_c) - 1)^2} \right) \quad (20) \end{aligned}$$

electrostatic repulsion between charged monomers

$$\frac{\langle U_{mm}(\theta, n_c) \rangle_\phi}{k_B T} \approx u f^2 \left(-\ln(\kappa b) + \frac{\theta^2}{6 \kappa b} \right) \quad (21)$$

and electrostatic attraction between condensed ions and oppositely charged monomers

$$\frac{\langle U_{mZ}(\theta, n_c) \rangle_\phi}{k_B T} \approx -2 \frac{u Z f}{n_c} \left(-\ln(\kappa b) + \frac{\theta^2}{6 \kappa b} \right) - \frac{l_B Z f}{\sigma n_c} \quad (22)$$

The last term in the eq 22 describes the contact energy of a multivalent ion Z with a monomer on the polymer backbone separated by distance σ .

Combining all terms together, the following expression for the electrostatic energy per bond can be written as

$$\begin{aligned} \frac{\langle U_{\text{electr}}(\theta, n_c) \rangle_\phi}{k_B T} &\approx u \left(f^2 - 2 \frac{Z f}{n_c} \right) \left(-\ln(\kappa b) + \frac{\theta^2}{6 \kappa b} \right) - \frac{l_B Z f}{\sigma n_c} + \\ &\quad \frac{u Z^2}{n_c^2} \left(-\ln(1 - \exp(-\kappa b n_c)) + \frac{n_c \theta^2 (1 + \kappa b n_c) \exp(\kappa b n_c) - 1}{12 (\exp(\kappa b n_c) - 1)^2} \right) \quad (23) \end{aligned}$$

At low salt concentration regime, $\kappa b n_c \ll 1$, this equation can be simplified

$$\begin{aligned} \frac{\langle U_{\text{electr}}(\theta, n_c) \rangle_\phi}{k_B T} &\approx u \left(\frac{Z}{n_c} - f \right)^2 \left(-\ln(\kappa b) + \frac{\theta^2}{6 \kappa b} \right) - \\ &\quad \frac{u Z^2}{n_c^2} \ln(n_c) - \frac{l_B Z f}{\sigma n_c} - \frac{u Z^2 \theta^2}{24 n_c} \quad (24) \end{aligned}$$

There is very simple interpretation of the terms on the right-hand side of eq 24. The first term describes electrostatic repulsion between uncompensated charges. Note that the excess charge could be due to either overcharging or undercharging of the polymer backbone by condensed ions. The second term represents the correlation energy of the multivalent ion with a corresponding neutralizing background, and finally the last term accounts for contribution to the chain bending rigidity due to correlations between multivalent ions.

In the saturation regime, when the number of condensed multivalent ions is stabilized by the electrostatic repulsion between them instead of an entropic penalty for multivalent ion localization near the polymer backbone, the equilibrium distance between condensed ions is obtained by minimizing the electrostatic energy eq 24 with respect to parameter n_c

$$\begin{aligned} -\frac{2uZ}{n_c^2} \left(\frac{Z}{n_c} - f \right) \left(-\ln(\kappa b) + \frac{\theta^2}{6 \kappa b} \right) + \frac{2uZ^2}{n_c^3} \ln\left(\frac{n_c}{\sqrt{e}}\right) + \\ \frac{l_B Z f}{\sigma n_c^2} + \frac{u Z^2 \theta^2}{24 n_c^2} \approx 0 \quad (25) \end{aligned}$$

In the leading approximation for the range of parameters $\kappa b n_c \ll 1$ and $\kappa l_0 \gg 1$ the solution of this equation is

$$n_c \approx \frac{Z}{f} \left(1 + \frac{\ln(Z/(f\sqrt{e}))}{\ln(\kappa b)} \right) \quad \text{low salt} \quad (26)$$

The number of bonds between condensed counterions n_c shows a weak logarithmic dependence on the Debye screening length κ^{-1} . It follows from eq 26 that condensed multivalent ions overcharge a polyelectrolyte chain.

The sum of coefficients in front of the θ^2 terms in eq 24 is equal to half of the ratio of the electrostatic persistence length to the bond size.

$$l_{\text{elec}} \approx \frac{l_B}{3 \kappa b} \left(\frac{Z}{n_c} - f \right)^2 - \frac{l_B Z^2}{12 n_c} \quad \text{low salt} \quad (27)$$

Thus, the electrostatic interactions between charges on the polymer backbone manifest themselves in two different contributions to the chain's persistence length. The positive contribution is due to electrostatic repulsion between excess charges within the Debye screening length. By bending a polyelectrolyte chain, one forces these overcompensated charges closer together, which increases the chain electrostatic energy and results in additional energetic penalty due to chain bending. This positive contribution to the chain persistence length is proportional to the reduced energy of the electrostatic repulsion between two chain segments with length on the order of the Debye screening length κ^{-1} carrying an excess charge $(Z/n_c - f)/(\kappa b)$ and separated by a typical distance κ^{-1} , $\tilde{\epsilon}_{\text{rep}} \approx l_B ((Z/n_c - f)/(\kappa b))^2 \kappa \approx u (Z/n_c - f)^2 / (\kappa b)$. However, the attraction of the condensed multivalent ion to the oppositely charged monomers on the length scales smaller than the distance between multivalent ions favors chain bending. Bending of a polyelectrolyte chain decreases the distance between condensed ion and charged monomers, lowering the chain electrostatic energy. At

low salt concentrations, the negative contribution to the chain persistence length is proportional to the correlation energy describing electrostatic attraction of the multivalent ion with valence Z to the neutralized charged background within correlation hole of size $n_c b \approx bZ/f$. This correlation energy can be estimated as $\tilde{\epsilon}_{\text{cor}} \approx -l_B Z^2/(n_c b) \approx -uZf$. Thus, the strong lateral correlations between condensed multivalent ions result in additional negative contribution to the electrostatic persistence length. Using eq 26 for the equilibrium value of the parameter n_c , one can write the following equation for the electrostatic persistence length of a polyelectrolyte chain with condensed multivalent ions

$$l_{\text{elec}} \approx \frac{l_B f^2}{3\kappa b} \left(\frac{\ln(Zf\sqrt{e})}{\ln(\kappa b)} \right)^2 - \frac{l_B f Z}{12} \left(1 + \frac{\ln(Zf\sqrt{e})}{\ln(\kappa b)} \right)^{-1}, \quad \text{low salt (28)}$$

In the case of high salt concentrations the distance between multivalent ions is of the order of the Debye screening length, $\kappa b n_c \sim 1$, and the sum in eq 20 representing electrostatic repulsion between multivalent ions can be approximated by the first term

$$\frac{\langle U_{ZZ}(\theta, n_c) \rangle_\phi}{k_B T} \approx \frac{l_B Z^2}{n_c} \left[\frac{\exp(-\kappa b n_c)}{b n_c} + \frac{\theta^2 \exp(-\kappa b n_c)}{12b} (1 + \kappa b n_c) \right], \quad \text{high salt (29)}$$

This results in the following modification of the eq 23

$$\frac{\langle U_{\text{electr}}(\theta, n_c) \rangle_\phi}{k_B T} \approx \frac{u}{\kappa b} \left(f^2 - \frac{2Zf}{n_c} \right) \left(-\ln(\kappa b) + \frac{\theta^2}{6\kappa b} \right) - \frac{l_B Zf}{\sigma n_c} + \frac{uZ^2 \exp(-\kappa b n_c)}{n_c^2} + \frac{uZ^2 \theta^2 \exp(-\kappa b n_c)}{12n_c} (1 + \kappa b n_c) \quad (30)$$

As in the case of the low salt concentrations the optimal spacing between multivalent ions is obtained by minimizing eq 30 with respect to the number of bonds between condensed multivalent ions n_c

$$-\frac{2uZf}{n_c^2} \ln(\kappa b) + \frac{l_B Zf}{\sigma n_c^2} - \frac{2uZ^2 \exp(-\kappa b n_c)}{n_c^3} \left(1 + \frac{\kappa b n_c}{2} \right) \approx 0 \quad (31)$$

In writing the last equation θ^2 terms have been neglected because they are small on the parameter $(\kappa l_0)^{-1} \ll 1$. The asymptotic solution of this equation is

$$n_c \approx \frac{1}{\kappa b} \ln \left(\frac{3Z\kappa b}{f(-2 \ln(\kappa b) + b/\sigma)} \right), \quad \text{high salt (32)}$$

The distance between condensed multivalent ions is proportional to the Debye screening length and has a weak logarithmic dependence on the charge valence Z . The electrostatic persistence length in the case of high salt concentrations is equal to

$$l_{\text{elec}} \approx \frac{l_B}{3\kappa b} \left(f^2 - \frac{2Zf}{n_c} \right) + \frac{l_B Z^2 \exp(-\kappa b n_c)}{6n_c} (1 + \kappa b n_c), \quad \text{high salt (33)}$$

Substitution of the solution of eq 32 into eq 33 results in the

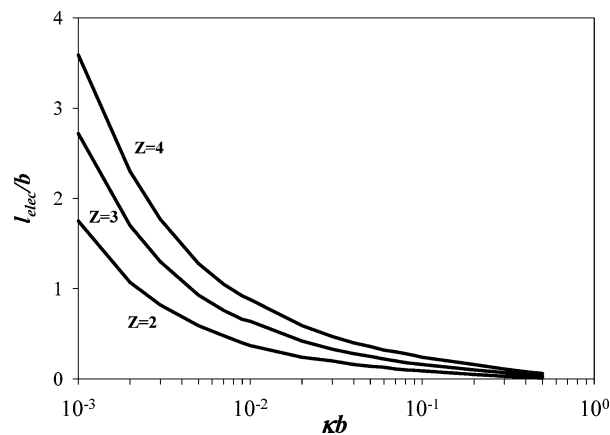


Figure 5. Dependence of the electrostatic persistence length on the Debye screening length for weakly charged chains with $f = 0.2$ and interaction parameter $u = l_B/b = 1$ and $\sigma = b$.

following expression for the electrostatic persistence length in the high salt regime:

$$l_{\text{elec}} \approx \frac{l_B f^2}{3\kappa b} - \frac{2l_B Zf}{3} \left[\ln \left(\frac{3Z\kappa b}{f(-2 \ln(\kappa b) + b/\sigma)} \right) \right]^{-1} + \frac{l_B Zf}{9} (-2 \ln(\kappa b) + b/\sigma) \quad (34)$$

The electrostatic contribution to the chain persistence length that is due to interactions between condensed ions and between condensed ions and neutralized charged background shows only a weak logarithmic dependence on the Debye screening length (the last two terms on the right-hand side of eq 34). Thus, these two contributions can be estimated as $l_B Zf$. They dominate over the electrostatic repulsion between charged monomers on the polymer backbone, $l_B f^2/(\kappa b)$, for the range of the Debye screening lengths, $\kappa b > f/Z$. This corresponds to a crossover into the high salt concentration regime.

Figure 5 summarizes results of this section and shows the dependence of the electrostatic persistence length

$$l_{\text{elec}} \approx \frac{l_B}{3\kappa b} \left(f^2 - \frac{2Zf}{n_c} \right) + \frac{l_B Z^2}{6n_c} \frac{(1 + \kappa b n_c) \exp(\kappa b n_c) - 1}{(\exp(\kappa b n_c) - 1)^2} \quad (35)$$

on the Debye screening length for ions with valence $Z = 2, 3$, and 4. For this plot I have performed numerical minimization of the eq 23 to obtain the optimal number of monomers n_c between condensed multivalent ions. The results show that even in the case of the multivalent ions the electrostatic persistence length is positive. This is an indication of the fact that the electrostatic repulsion between overcompensated charges dominates over the correlation-induced attraction, resulting in positive contribution to the chain's persistence length and additional stiffening of the polyelectrolyte chain. At high salt concentrations the electrostatic persistence length becomes very small. In this range of salt concentrations the correlation-induced attractive interactions become of the same order in magnitude as electrostatic repulsion between overcompensated charges.

The results shown in Figure 5 are qualitatively different from those obtained by Ariel and Andelman.³¹ These authors have shown that the electrostatic persistence length is negative throughout the entire salt concentration range for multivalent ions with $Z = 2, 3$, and 4. The main reason for the differences between the two results is the one-loop approximation used by Ariel and Andelman³¹ for calculation of the fluctuation correc-

tions to the chain persistence length in the case of multivalent ions. This approximation relays on the uniform counterion density distribution along the polymer backbone as the reference state for calculation of the fluctuation corrections to the chain's free energy. However, it was shown by Shklovskii (see for review refs 16 and 18) that in the case of multivalent ions there are strong lateral correlations between condensed ions. These strong lateral correlations can be taken into account in the framework of the strongly correlated Wigner liquid model.^{14,16,18} This approximation could lead to qualitatively different results than those obtained in the framework of the one-loop approximation. For example, in the framework of the strongly correlated Wigner liquid approach one can obtain the object overcharging after condensation or adsorption of multivalent ions. Note that the overcharging is impossible in the framework of the one-loop approximation because it underestimates interactions between condensed ions.

4. Conclusions

In this paper I have shown that the counterion condensation on the polymer backbone results in weakening of the electrostatic contribution to the chain persistence length. There are two different factors that contribute to this effect. The first is due to neutralization of the ionized groups by condensed counterions that decreases the linear charge density along the polymer backbone and weakens the electrostatic repulsions between chain segments. The other one is due to fluctuations/correlations in the counterion density distribution along the polymer backbone. These fluctuation (or correlation) corrections result in the negative contribution to the chain persistence length. However, the magnitude of this correction is not sufficient to make electrostatic contribution to the chain persistence length negative.

The conclusions of this paper seem to contradict the experimental results showing a dramatic change in the DNA persistence length by lowering it up to 25–30 nm.²⁴ Let us estimate the magnitude of the correlation induced attraction to the DNA persistence length. Substitution of the DNA parameters $b = 1.7\text{Å}$, $f = 1$, $l_B = 7\text{Å}$, and salt concentration range used in experiments $1\text{ nm} < \kappa^{-1} < 10\text{ nm}$ into expression

$$l_{\text{cor}} \approx -\frac{l_B f Z}{12} \quad (36)$$

describing contribution of the correlation-induced attractive interactions into chain persistence length (see eq 28) results in a very weak effect of the condensed multivalent ions on the chain rigidity $l_{\text{cor}} \sim -0.05Z\text{ nm}$. Indeed, this contribution to the chain persistence length is too small to cause significant changes in the DNA persistence length.²⁴

The origin of the weak electrostatic interactions is the bulk value of the dielectric constant ϵ used in eq 36. In aqueous solutions the value of the dielectric constant changes with distance from the polymer backbone. At short separations between condensed ions (close to the polymer backbone) the local dielectric constant is of the order of $\epsilon = 2\text{--}4$ and is about 20–40 times lower in comparison with the bulk value, $\epsilon = 80$.^{35,39,40} The variations in the local dielectric constant represent the effect of solvation of the polymer backbone by the water molecules. For the DNA molecule these variations occur at the length scales of the order of 5–10 Å.³⁵ In this case one can envision condensed counterions and ionized phosphate groups on the DNA backbone being surrounded by the dielectric cylinder with radius $\sim 5\text{--}10\text{Å}$. Thus, at distances between ions smaller than the radius of dielectric cylinder the local dielectric constant should be used for evaluation of the electrostatic

interactions between charges. In this case the correlation contribution will be about 40 times larger, $l_{\text{cor}} \sim -2Z\text{ nm}$. Unfortunately, it is still about an order in magnitude too small to explain experimentally observed trend. However, now this difference can be explained by the numerical factor 1/12 in eq 36. Note that the coefficient 1/12 appearing in eq 36 is a result of evaluation of the electrostatic interactions between charges in eqs 20–22. The exact consideration of the effect of the local dielectric constant will require recalculation of the Debye–Hückel interaction potential near the cylindrical dielectric boundary and reevaluation of expressions 20–22 for this interaction potential. Another improvement can be derived from the explicit consideration of the double-helical structure of the DNA molecule.⁴¹ Both these modifications can change numerical coefficients in expressions 28 and 34. I will consider a more general model of DNA bending rigidity in a future publication.

However, the predictions of this paper can be tested in the molecular simulations of the coarse-grain model of semiflexible polyelectrolytes. In such simulations the solvent is modeled by the dielectric continuum with space independent dielectric constant. In this case the value of the dielectric constant will not depend on the proximity to the polymer backbone. I hope this paper will inspire such simulations.

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Appendix

To describe counterion density fluctuations along the polymer backbone, let us introduce the counterion density distribution function

$$\rho(n) = \sum_{i=1}^{f\beta N} \delta_{n,i} \quad (\text{A.1})$$

where $\delta_{s,p}$ is the Kronecker delta which is equal to 1 for $s = p$ and 0; otherwise, the summation in eq A.1 is carried out over all $f\beta N$ condensed counterions. The location of the condensed counterion along the polymer backbone in eq A.1 is associated with the monomer location. In this description the counterion localization volume near the polymer backbone is divided into N cells of size b^3 . Using the counterion density distribution function $\rho(n)$, one can rewrite the energy of electrostatic interactions between condensed counterions as follows

$$\frac{U_{\text{el}}}{k_B T} = l_B \sum_{n=0}^N \sum_{m=0}^{n-1} \frac{\exp(-\kappa r(n,m))}{r(n,m)} \rho(n) \rho(m) \quad (\text{A.2})$$

where $r(n,m)$ is the distance between monomers n and m . In the case of the small bending deformations the electrostatic energy can be expanded around a rodlike conformation and represented as a sum of the electrostatic interactions between counterions condensed on the rodlike polymer and bending correction energy

$$\frac{U_{\text{el}}}{k_B T} = \frac{U_{\text{rod}}}{k_B T} + \frac{U_{\text{bend}}}{k_B T} \quad (\text{A.3})$$

where

$$\frac{U_{\text{rod}}}{k_B T} = u \sum_{n=0}^N \sum_{m=0}^{n-1} \frac{\exp(-\kappa b(n-m))}{(n-m)} \rho(n) \rho(m) \quad (\text{A.4})$$

and

$$\frac{U_{\text{bend}}}{k_B T} = \frac{u\theta^2}{12} \sum_{n=0}^N \sum_{m=0}^{n-1} \exp(-\kappa b(n-m))(1 + \kappa b(n-m))\rho(n)\rho(m) \quad (\text{A.5})$$

In writing eqs A.3–A.5, I have used the expansion eq 6 for the distance $r(n,m)$ between monomers of the polymer chain with the bond angle θ . Introducing the discrete Fourier transform of the function $\rho(n)$

$$\hat{\rho}(p) = \frac{1}{N} \sum_{n=0}^N \rho(n) \exp\left(i \frac{2\pi np}{N}\right) \quad \text{and} \quad \rho(n) = \sum_{p=-N/2}^{N/2} \hat{\rho}(p) \exp\left(-i \frac{2\pi np}{N}\right) \quad (\text{A.6})$$

one can rewrite eqs A.4 and A.5 in terms of the Fourier amplitudes $\hat{\rho}(p)$

$$\frac{U_{\text{rod}}}{k_B T} = -Nu(\beta f)^2 \ln(\kappa b) - uN \sum_{p=1}^{N/2} V_{\text{rod}}\left(\frac{2\pi p}{N}\right) \hat{\rho}(p) \hat{\rho}(-p) \quad (\text{A.7})$$

and

$$\frac{U_{\text{bend}}}{k_B T} = \frac{u(\beta f)^2 \theta^2 N}{6\kappa b} + \frac{u\theta^2 N^{N/2}}{6} \sum_{p=1}^{N/2} V_{\text{bend}}\left(\frac{2\pi p}{N}\right) \hat{\rho}(p) \hat{\rho}(-p) \quad (\text{A.8})$$

where I introduced the Fourier transforms of the interaction potential of the condensed counterions on the rodlike polymer

$$V_{\text{rod}}(q) = \ln((\kappa b)^2 + 2(1 - \cos(q))) \quad (\text{A.9})$$

the electrostatic contribution to the bending potential

$$V_{\text{bend}}(q) = \frac{(1 + \kappa b)(A \cos(q)) - 1}{[(\kappa b)^2 + (1 - \cos(q))]} + \frac{\kappa b A (1 - 2A \cos(q) + A^2 \cos(2q))}{[(\kappa b)^2 + 2(1 - \cos(q))]} \quad (\text{A.10})$$

and the parameter A defined as $A = \exp(\kappa b)$. Note that the value of the Fourier amplitude $\hat{\rho}(0) = \beta f$ corresponds to the average fraction of the condensed counterions. To obtain fluctuation corrections to the electrostatic energy, one has to average the expression eq A.3 over the counterion density distributions $\{\rho(n)\}$. In the Gaussian approximation the effective Hamiltonian describing fluctuations in the system of condensed counterions has the following form:

$$\frac{H(\{\hat{\rho}(p)\})}{k_B T} = \frac{1}{2} N \sum_{p \neq 0}^{N/2} \left(\frac{1}{\beta f} - u V_{\text{rod}}\left(\frac{2\pi p}{N}\right) + \frac{u\theta^2}{6} V_{\text{bend}}\left(\frac{2\pi p}{N}\right) \right) \hat{\rho}(p) \hat{\rho}(-p) \quad (\text{A.11})$$

(The derivation of the effective Hamiltonian was done along the lines described in refs 42–44.) The first term in the brackets corresponds to the ideal gas contribution to the effective Hamiltonian and describes correlations in the system of non-interacting counterions for which $\langle \Delta \rho(n)^2 \rangle = \beta f$. The last two terms describe electrostatic interactions between counterion

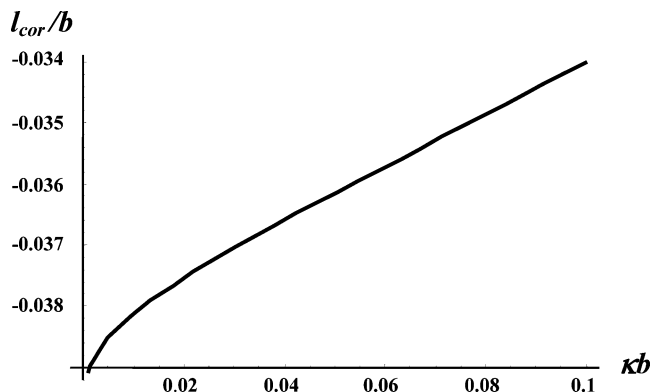


Figure 6. Correlation part of the chain persistence length as a function of κb for the value of the parameter $u\beta f = 0.3$.

density fluctuations. The average value of the density–density correlation function in the Gaussian (quadratic) approximation is

$$\langle \hat{\rho}(p) \hat{\rho}(-p) \rangle = N^{-1} \left(\frac{1}{\beta f} - u V_{\text{rod}}\left(\frac{2\pi p}{N}\right) + \frac{u\theta^2}{6} V_{\text{bend}}\left(\frac{2\pi p}{N}\right) \right)^{-1} \quad (\text{A.12})$$

It is interesting to point out that the eq A.12 shows instability for the large values of the parameter $u\beta f$ for value of the parameter p close to $\pm N/2$. For a rodlike chain, $\theta = 0$, this instability first appears at $u\beta f = 1/(\ln(4) + (\kappa b)^2)$ and indicates ordering of condensed counterions along the polymer backbone with increasing the value of the interaction parameter u . Note that the location of the instability region will depend on the details of the model such as the number of condensed counterions per each ionize group and counterion size.

The averaging of the electrostatic energy with respect to the counterion density fluctuations corresponds to substitution in eqs A.7 and A.8 $\hat{\rho}(p)\hat{\rho}(-p)$ by its average value given by eq A.12. After some algebra one has

$$\frac{\Delta U}{k_B T} \approx -\frac{uN\beta f}{2\pi} \int_0^\pi dq \left[\frac{V_{\text{rod}}(q)}{1 - u\beta f V_{\text{rod}}(q)} \right] + \frac{uN\beta f \theta^2}{12\pi} \int_0^\pi dq \left[\frac{V_{\text{bend}}(q)}{(1 - u\beta f V_{\text{rod}}(q))^2} \right] \quad (\text{A.13})$$

where I substitute summation over p by integration over wavenumber $q = 2\pi p/N$, in the limit of large N , $N \rightarrow \infty$. The first term on the right-hand side of eq A.13 describes the fluctuation corrections to the mean-field chain free energy due to fluctuation of the density of the condensed counterions along the rodlike chain, while the second term provides fluctuation correction to the chain bending rigidity. The fluctuation part of the electrostatic contribution to the chain persistence length is equal to

$$l_{\text{cor}} \approx \frac{l_B \beta f}{6\pi} \int_0^\pi dq \left[\frac{V_{\text{bend}}(q)}{(1 - u\beta f V_{\text{rod}}(q))^2} \right] \quad (\text{A.14})$$

Figure 6 shows the dependence of the fluctuation correction to the electrostatic persistence length on the Debye screening length κ^{-1} , for the value of the parameter $u\beta f = 0.3$. As one can see, fluctuations lead to negative contribution to the electrostatic persistence length. However, the magnitude of this correction is small, less than 4% of the bond length b , and can be neglected in comparison with the mean-field contribution describing

induced rigidity due electrostatic repulsion between uncompensated charges (see eq 19).

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