Persistence Length of Flexible Polyelectrolyte Chains

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ABSTRACT

We calculate the dependence of the electrostatic persistence length, $l_e$, of weakly charged flexible polyelectrolyte chains using a self-consistent variational theory. The variation of $l_e$ with $\kappa$, the inverse Debye screening length, is controlled by the parameter $l_0l_B/A^2$ where $l_0$ is the bare persistence length, $l_B$ is the Bjerrum length, and $A$ is the mean distance between charges along the chain. Several distinct regimes for the dependence of $l_e$ on $\kappa$ emerge depending on the value of $l_0l_B/A^2$. We show that when $l_0l_B/A^2 \ll 1$ we recover the classical result, $l_e \propto \kappa^{-2}$. For intermediate values of $l_0l_B/A^2$, $l_e \propto \kappa^{-1}$. In this regime one can also get $l_e \propto \kappa^{-y}$ with $y < 1$ depending on the strength of the Coulomb interaction. Qualitative comparisons between our theory and simulations as well as other theories are presented.

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1 Introduction

In recent years, significant attention has been paid to the old problem of the ionic dependence of the size of isolated polyelectrolyte chains [1-4]. The size of the chain is most conveniently expressed in terms of the electrostatic persistence length. The computation of the persistence length of a polyelectrolyte chain is difficult because of the interplay of several length scales. Significant steps in the computation of the size of charged polymers was taken by Odjik [5] and Skolnick and Fixman [6] (OSF), who introduced the concept of the electrostatic persistence length. These authors considered a stiff polyelectrolyte chain near the rod limit so that only small excursions from linear conformations are relevant. By assuming that charges on the rod-like polyelectrolyte interact via the Debye Hückel potential, \( v(r) = l_B e^{-\kappa r}/r \), where \( l_B = e^2/4\pi\epsilon_0 k_B T \) is the Bjerrum length, \( A \) is the average distance between charges, \( \kappa^{-1} \) is the screening length, OSF showed that the total persistence length of the chains can be written as \( l_p = l_0 + l_e \). Here \( l_0 \) is the bare persistence length, and the electrostatic persistence length \( l_e \) in the OSF theory is

\[
l_{OSF} = \frac{1}{4} \frac{l_B}{\kappa^2 A^2}
\]

It is believed that as long as the chain is stiff the dependence of \( l_e \) on \( \kappa \) given above is correct [2]. The above result is exact in large dimensions regardless of the intrinsic stiffness of the chain backbone.

Many experiments on polyelectrolytes have been interpreted using the OSF theory. However, light scattering experiments on some polyelectrolytes systems do show deviations from the OSF theory [7, 8, 9]. The major approximation in the OSF treatment is that the polyelectrolyte is rod-like, and hence deviations from linear configuration is small. If the intrinsic backbone of the polymer chain is flexible, so that large excursions from linearity are possible, it is likely that the OSF result may not be valid. In fact, the validity of Eq. (1.1) for chains that are intrinsically flexible has been questioned using theoretical arguments [7-9] and computer simulations [10, 11]. Starting with the work of Barrat and Joanny [11] (BJ),
several variational calculations [10, 12] show that, when the chains are intrinsically flexible, 
the electrostatic persistence length $l_e \sim \kappa^{-1}$. We had shown earlier [10] that the predicted 
$\kappa^{-1}$ is valid when the controlling parameter $l_0 l_B / A^2 \sim \mathcal{O}(1)$, i.e., when the chain is in the 
so called non-asymptotic regime [10]. Li and Witten [15] argued that, unlike the variational 
theories [10, 11, 12], approximate inclusion of fluctuations still leads to the result predicted 
by OSF even if the backbone is flexible. In other words, the OSF result given in Eq. (1.1) 
is always valid. In the above referenced variational theories it is generally believed that the 
electrostatic interactions generally stiffen the chain significantly so that the trial Hamilton-
nian should consist of terms that account for the electrostatic-mediated interaction rigidity. 
In contrast, Muthukumar has examined the influence of electrostatic interactions on the 
size of the flexible polyelectrolyte chains [16]. This theory, which also emphasize the role of 
excluded volume interactions, has been used to interpret experimental data [18]. A precise 
form of the ionic dependence of the electrostatic persistence length that covers all values of 
stiffness has not emerged from any these studies.

More recently, Micka and Kremer [13] have extracted the persistence length of weakly 
charged polyelectrolytes of varying stiffness using Monte Carlo simulations. They argue that 
there is no apparent simple scaling of $l_e$ with $\kappa$ in all regimes. This raises the possibility that 
a simple concept of electrostatic persistence length may not be useful in determining the size 
of polyelectrolyte chains under diverse conditions. The numerical results can be apparently 
be rationalized using a field-theoretical renormalization group analysis of flexible chains. 
Liverpool and Stapper [17] suggest that the scaling form for the mean square end-to-end 
distance, $\langle R^2 \rangle$, provides a good fit of the computer simulation data.

The preceding survey suggests that we still do not have a simple theory for computing $l_e$ 
for charged polymer chains with arbitrary stiffness. The purpose of this paper is to reexamine 
the variational type theories for computing $l_e$ using the trial Hamiltonian suggested by BJ 
for flexible chains [11]. Rather than compute the approximate free energy using the Gibbs-
Bogoliubov inequality as BJ did, we calculate $\langle R^2 \rangle$ directly using the uniform expansion method \[19\]. We show explicitly that when $l_0l_B/A^2 \ll 1$, the OSF result given in Eq. (1.1) is recovered. The rest of the paper is organized as follows. In Sec. 2, we present the variational theory for the electrostatic persistence length in the asymptotic limit, i.e., when $l_0l_B/A^2 \ll 1$. The case when $l_0l_B \sim \mathcal{O}(1)$, which is most appropriate for examining the crossover regime, is presented in Sec. 3. Comparisons of the theoretical predictions to the simulation result are discussed in Sec. 4. The paper is concluded in Sec. 5 with a few additional remarks.

## 2 Variational Theory: Chain under tension

The flexible polyelectrolyte chain consists of $N$ segments each of length $l_0$ on an average. The charges on the chain are assumed to be a distance $A$ apart. The interaction between the charges on the chain is taken to be given by the Debye-Hückel (DH) potential. In this model the counterions are not explicitly treated. In the continuum limit the partition function of the polyelectrolyte chain is taken to be

$$ Z = \int \mathcal{D}[r(s)] W[r(s)] $$

where the statistical weight associated with a given realization of the polion described in terms of the curve $r(s)$ is

$$ W[r(s)] = W^0[r(s)] \exp \left[ -\frac{l_B}{2A^2} \int_0^L \int_0^L ds ds' e^{-\kappa |r(s') - r(s)|} \frac{1}{|r(s') - r(s)|} \right], $$

and $W^0[r(s)]$ is the weight for the chain backbone in the absence of charges

$$ W^0[r(s)] = \exp \left[ -\frac{3}{2l} \int_0^L \left( \frac{\partial r(s)}{\partial s} \right)^2 \right] $$

with $l = 2l_0$. In order to eliminate the self-interaction in the DH potential we impose the condition that $|s' - s| > s_0$ where $s_0 \sim l_0$. The cut-off dependence vanishes in the variational theory described below.
The direct evaluation of $Z$ in Eq. (2.1a) is not possible due to the non-Markovian nature of the electrostatic interaction term. Consequently, we have to resort to an approximate calculation. Here we use a variational method, first proposed by Edwards and Singh [19] (ES), in their treatment of the standard excluded volume problem in neutral flexible polymers. The basic idea of the ES method is to replace the weight by a simpler trial weight with undetermined parameters. The parameters are chosen so that the size (say the mean square end-to-end distance) calculated using the trial weight, $\langle R^2 \rangle_t$, becomes identical to that given by the true weight, $\langle R^2 \rangle$. The practical implementation of this method requires that the interaction term can somehow be treated as small so that the deviation between $\langle R^2 \rangle_t$ and $\langle R^2 \rangle$ can be computed in powers of the small parameter. The ES method has been successfully used to predict the conformational properties of flexible polyions under a variety of solvent conditions [16, 21].

A word of caution concerning the ES method (and in general variational methods) is in order. Firstly, the results of variational calculations are only as good as the chosen trial Hamiltonian. In polymer problems there is an additional distinction. ES advocate that the variational parameters be chosen to ensure $\langle R^2 \rangle_t = \langle R^2 \rangle$ rather than by employing the Gibbs-Bogoliubov inequality, i.e., by minimizing the free energy. For polymers with short range interactions it has been shown that the ES method is superior to others that minimize the free energy by a suitable variational calculation. For problems with long range interactions the direct minimization of free energy can give reliable results for the scaling of $\langle R^2 \rangle$ with $N$. For the present problem the range of interaction is neither short nor too large. From this discussion it should be clear that the utility of the variational methods should be viewed with some caution.

The choice of the trial weight or Hamiltonian is extremely important. An appropriate trial Hamiltonian is chosen by considering the case of $\kappa = 0$. Here, the weakly charged flexible polyelectrolyte can be considered as an array of blobs of size $D$. The structure of the
chain inside a blob resembles that of a non-interacting (i.e., the electrostatic interactions are unimportant) while there is ordering among the blobs due to the Coulomb repulsion beyond the length scale $D$. The physical picture of the charged chain is that of one under tension \[\text{[4]},\] where the blob size (short length scale effect) is determined by the magnitude of the (as yet undetermined value of the tension), while at long length scales the chain is a free chain with an effective step length different from $l_0$. Thus, in order to determine the structure of such polyions, it is crucial to incorporate the presence of two length scales, namely, $D$ that describes the local ordering and correlations between the semiflexible blobs that gives the effective persistence length. Based on this physically appealing picture, Barrat and Joanny \[\text{[11]}\] proposed a trial probability weight $W_t[\mathbf{r}(s)]$ associated with the configuration $[\mathbf{r}(s)]$ that succinctly captures the conformation of weakly charged polyions described above. In particular they chose

$$W_t[\mathbf{r}(s)] = W^0[\mathbf{r}(s)] \int D[\mathbf{t}(s)]W[\mathbf{t}(s)]\exp \left[ \tau \int_0^L ds \mathbf{t}(s) \cdot \frac{\partial \mathbf{r}(s)}{\partial s} \right], \quad (2.2)$$

where $W^0[\mathbf{r}(s)]$ is the Boltzmann weight for the non-interacting chain (Cf Eq. (2.1c)), $\mathbf{t}(s)$ is the unit vector that gives the direction of the tension at position $s$. The weight $W_t[\mathbf{r}(s)]$ is associated with a particular realization of the direction of the chain tension and is given by

$$W[\mathbf{t}(s)] = \prod_{0 \leq s \leq L} \delta(t(s)^2 - 1) \exp \left[ -\frac{\eta}{2} \int_0^L ds \left( \frac{\partial \mathbf{t}(s)}{\partial s} \right)^2 \right]. \quad (2.3)$$

The weight associated with the tension vector $\mathbf{t}(s)$ is an attempt to capture the physics that the charged chain on a scale $\eta$ behaves as one under tension. On the scale $\eta$ the chain is adequately stiff so that it can be described as worm-like for which the Boltzmann weight is approximately given by Eq. (2.3). The finite range of correlations among the blobs is described by the correlation in $\mathbf{t}(s)$ such that

$$\langle \mathbf{t}(s) \cdot \mathbf{t}(s') \rangle_W = \exp[-|s' - s|/\eta]. \quad (2.4)$$

The trial weight has two parameters namely $\eta$ (the effective persistence length) and the chain
tension $\tau$. Both these are adjusted so that the deviation between $\langle R^2 \rangle$ and $\langle R^2 \rangle_t$ is zero to first order in the interaction (second term in Eq. (2.1b)) term.

From the form of the trial weight $W_t[r(s)]$ it is clear that the blob size $D \simeq \tau^{-1}$. This can be formally established by computing $\langle |r(s') - r(s)|^2 \rangle_{W_t}$ which can be obtained from the generating functional defined by

$$\mathcal{L}(k; s', s) = \left< e^{i k (r(s')-r(s))} \right>_{W_t}.$$  \hfill (2.5)

The evaluation of $\mathcal{L}(k; s', s)$ up to order $k^2$ is given by

$$\mathcal{L}(k; s', s) = e^{-k^2 l|s'-s|/6} \left< e^{i k t(s''|ds''} \right>_{W_t} = -\frac{1}{6} k^2 l|s'-s| \tau^2 \int_s^{s'} ds_1 ds_2 \langle k \cdot t(s_1) k \cdot t(s_2) \rangle_{W_t} = -\frac{1}{6} k^2 l|s'-s| - \frac{1}{18} k^2 l^2 \tau^2 \int_s^{s'} ds_1 ds_2 \langle t(s_1) \cdot t(s_2) \rangle_{W_t}. \hfill (2.6)$$

The mean square internal distance is

$$\langle |r(s') - r(s)|^2 \rangle_{W_t} = -6 \left( \frac{\partial}{\partial k^2} \right)_{k=0} \mathcal{L}(k; s', s) = |s'-s| + \frac{1}{6} k^2 l^2 \tau^2 [2\eta |s'-s| - 2\eta^2 (1 - e^{-|s'-s|/\eta})], \hfill (2.7)$$

where we have used Eq. (2.4). By equating the two terms in Eq. (2.7) we can infer the contour length $S \simeq 1/l^2$ and the blob size $D \simeq (Sl)^{1/2} \simeq \tau^{-1}$. The blob size is naturally expressed also in terms of $l_0, l_B$, and $A$ and is given by Eq. (2.7). For long chains i.e., $L \gg S$ we can neglect the first term in Eq. (3.7), and the size of the chain $\langle R^2 \rangle_{W_t}$ becomes

$$\langle R^2 \rangle_{W_t} = \langle |r(L)| - r(0)|^2 \rangle_{W_t} = 2l_p L' - 2l_p^2 (1 - e^{-L'/l_p}), \hfill (2.8)$$

where $l_p \simeq \eta l \tau$ is the physically observable persistence length and $L'$ is the longitudinal size of the corresponding stretched chain

$$L' \approx l D^{-1} L \approx (l_0 l_B/A^2)^{1/3} L. \hfill (2.9)$$
Note that the notion of stretched blobs is only valid for \( l_p/D \gg 1 \).

In order to set up the calculation of \( l_p \) using the ES method we write

\[
\langle R^2 \rangle = \langle R^2 \rangle_{W_i} + \Delta R^2(l_p, l_B, A, \kappa)
\]  

(2.10)

where \( \langle R^2 \rangle \) is to be computed using the weight given in Eq. (2.1). As explained before the variational parameters \( \eta \) and \( \tau \) are determined from the condition \( \Delta R^2 \equiv 0 \). To obtain an explicit expression for \( \Delta R^2 \) let us write

\[
\langle R^2 \rangle = \frac{\int \mathcal{D}[r(s)] R^2 W[r(s)]}{\int \mathcal{D}[r(s)] W[r(s)]} = \frac{\int \mathcal{D}[r(s)] W_i[r(s)] R^2 \exp\{-B[r(s)]\}}{\int \mathcal{D}[r(s)] W_i[r(s)] \exp\{-B[r(s)]\}}
\]  

(2.11a)

where

\[
B[r(s)] = \frac{l_B}{2A^2} \int_0^L \int_0^L dr' \left( e^{-\kappa |r(s')-r(s)|} \right) + \tau \int_0^L ds \left( \partial r/\partial s \right) \left( \partial r/\partial s \right) - \frac{\eta}{2} \int_0^L ds \left( \partial t/\partial s \right)^2.
\]  

(2.11b)

If \( W_i[r(s)] \) is a good approximation to \( W[r(s)] \) then \( B[r(s)] \) can be treated as small. Consequently up to \( O(B[r(s)]) \) the vanishing of \( \Delta R^2 \) leads to the condition:

\[
\langle R^2 \rangle_{W_i} = \langle R^2 \rangle_{W_i} (B[r(s)])_{W_i}.
\]  

(2.12)

By using the following equations

\[
\eta \frac{\partial}{\partial \eta} \langle R^2 \rangle_{W_i} = \langle R^2 \rangle_{W_i} \eta \int ds \left( \partial t/\partial s \right)^2_{W_i} - \left\langle R^2 \eta 2 \int ds \left( \partial t/\partial s \right)^2 \right\rangle_{W_i}
\]  

(2.13a)

\[
\tau \frac{\partial}{\partial \tau} \langle R^2 \rangle_{W_i} = -\langle R^2 \rangle_{W_i} \tau \int ds \left( \partial r/\partial s \right) + \left\langle R^2 \tau \int ds \left( \partial r/\partial s \right) \right\rangle_{W_i}.
\]  

(2.13b)

eq(2.12) may be written as

\[
l_p \frac{\partial}{\partial l_p} \langle R^2 \rangle_{W_i} \tau \frac{\partial}{\partial \tau} \langle R^2 \rangle_{W_i} = \langle R^2 V \rangle_{W_i} - \langle R^2 \rangle_{W_i} \langle V \rangle_{W_i}
\]  

(2.14)

where \( V \) is the total interaction energy given by the first term in Eq. (2.11b). Using Eq. (2.8) for \( \langle R^2 \rangle_{W_i} \) the L.H.S. of Eq. (2.14) can be easily calculated.

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The computation of $\langle R^2V \rangle_{W_i}$ and $\langle V \rangle_{W_i}$ is somewhat involved. Here we provide of a sketch of the calculation. The details are given in Appendix A. An expression of $\langle R^2V \rangle_{W_i}$ can be obtained in terms of the generating functional

$$\mathcal{L}_1(k; 0, L|q; s, s') = \left\langle e^{i\mathbf{k} \cdot \left(\mathbf{r}(L) - \mathbf{r}(0)\right) + i\mathbf{q} \cdot \left(\mathbf{r}(s') - \mathbf{r}(s)\right)} \right\rangle_{W_i}$$

(2.15)

with the result

$$\langle R^2 \rangle_{W_i} = \frac{l_B}{2A^2} \int \frac{d^3q}{(2\pi)^3} \frac{4\pi}{q^2 + \kappa^2} \left[-6 \frac{\partial}{\partial k^2}\right]_k \mathcal{L}(k; 0, L|q; s, s').$$

(2.16)

Similarly

$$\langle R^2 \rangle_{W_i} \langle V \rangle_{W_i} = \left[-6 \frac{\partial}{\partial k^2}\right]_k \mathcal{L}(k; 0, L) \frac{l_B}{2A^2} \int \frac{d^3q}{(2\pi)^3} \frac{4\pi}{q^2 + \kappa^2} \mathcal{L}(q; s, s')$$

(2.17)

where $\mathcal{L}(q; s, s')$ is given by Eq. (2.5).

In order to obtain a tractable expression for $l_p$ we make an additional, physically motivated, approximation to evaluate Eqs. (2.16) and (2.17). On a scale larger than $\eta$ the chain is effectively Gaussian provided $L/\eta \gg 1$. Thus, the effect of stiffness, arising from stretching due to electrostatic repulsion, is important only on the scale of the order $\eta$. The chain on the scale of $\eta$ can be treated as essentially rod-like with minimal conformational fluctuations. In order to obtain the generating functional $\mathcal{L}$ and $\mathcal{L}_1$ we need to compute terms with the structure $\left\langle e^{iQ \int_0^L t(s)ds} \right\rangle_{W_i}$. With the approximation that on scale of the order of $|s'-s| = \eta$ the chain behaves essentially as rod-like we can write

$$\left\langle e^{iQ \int_0^L t(s)ds} \right\rangle_{W_i} \approx \left\langle e^{iQ (\int_0^L t(s)ds + \int_{s'}^L t(s')ds')} \right\rangle_{W_i} \left\langle e^{iQ \int_s^{s'} t(s')ds'} \right\rangle_{\text{rod}}.$$  

(2.18)

With this physically motivated approximation the generating functional can be calculated. The result for the persistence length can be written as (after considerable algebra)

$$l_p \approx \frac{l_B}{A^2 L} \int \int ds' \int \frac{d^3q}{q^2 + \kappa^2} e^{-q^2|s'-s|/\eta} \left\{q^2 l^2 (s' - s)^2 / \epsilon \right\} \left\langle e^{iQ \int_{s'}^L t(s')ds'} \right\rangle \left\langle e^{iQ \int_0^L t(s)ds} \right\rangle' - \left\langle e^{iQ \int_0^L t(s)ds} \right\rangle \left\langle e^{iQ \int_{s'}^L t(s')ds'} \right\rangle' \left\langle e^{iQ \int_0^L t(s)ds} \right\rangle \left\langle e^{iQ \int_{s'}^L t(s')ds'} \right\rangle'$$

(2.19)
where we have neglected numerical factors. The prime in Eq. (2.19) indicates that the statistical average $\langle e^{iQ \int_0^L t(s) d\ell} \rangle_{\mathcal{W}_t}$ has been performed using the factorization described in Eq. (2.18). The evaluations of various quantities in Eq. (2.19) are given in Appendix A.

We now provide an argument that only the quantity arising from the local interaction, i.e., from the terms with the structure $\langle e^{iQ \int_0^L t(s) d\ell} \rangle_{\text{rod}}$ in Eq. (2.18), contribute to the persistence length. The long length scale term provides an interaction of the excluded volume type and is not relevant in the calculation of $l_p$. In order to show this let us split the integrals in Eq. (3.19) into those arising from $|s' - s| < \eta$ and into the contributions arising from scales larger than $\eta$. The integrals involving the tension term in $t(s)$ are modulated by the Gaussian factor $\exp(-q^2 l |s' - s|/6)$ which accounts for local fluctuations inside a blob. First consider the limit $ql\tau |s' - s| \ll 1$. In this limit we can approximate

$$\langle \exp \left[ \frac{1}{\tau^2} iQ \cdot \int_s^{s'} t(s'') ds'' \right] \rangle_{\mathcal{W}_t} \approx \exp \left[ -\frac{1}{\tau^2} q^2 l^2 \tau^2 (s' - s)^2 \right]$$

(2.20)

for $|s' - s| < \eta$. It is clear from Eq. (2.20) that on scales less than $S (\sim 1/l\tau^2)$ the Gaussian term is more important (see also Eq. (2.7)) while on the scale $S < |s' - s| < \eta$ Eq. (2.20) dominates. On this length scale the segment of the chain behaves as a rod, and hence charges separated by distance $|s' - s| = O(\eta)$ can be assumed to interact via the screened Coulomb interaction. Now consider scales larger than $\eta$. On these long length scales the chain can be pictured as a sequence of rods of length $l_p \sim \eta l\tau$ surrounded by an impenetrable charge cloud of diameter $d$. Two such segments can come arbitrarily close together to a distance of the order of $d$ because the chain is Gaussian on long length scale. The interaction of such rod segments gives rise to a short range excluded volume type terms. Since these interactions are not relevant for describing the local ordering (on scale $\eta$) we only include contributions from short length scales in Eq. (2.19). Polyions on length scale greater than $\eta$ can be considered as flexible chains with an effective step length $l_p$ interacting via an effective excluded volume type interactions.

If we substitute Eqs. (A.5), (A.7), (A.8), and (A.11) into Eq. (2.29) we obtain the result
for $l_p$, which is valid for the screened polyions in the asymptotic limit defined as $l_0 l_B \ll A^2$, 

$$l_p \sim \left(\frac{S}{A}\right)^2 \frac{l_B}{D} \left(D + \frac{1}{D \kappa^2}\right), \quad \kappa L \gg 1$$ (2.21)

where $(S/A)^2(l_B/D) \sim \mathcal{O}(1)$ is the electrostatic energy of a blob. The second term in Eq. (2.21), which varies as $\kappa^{-2}$, can be identified as the electrostatic persistence length while the $\kappa$-independent term $\mathcal{O}(1)D$ can be identified as a renormalized bare persistence length due to the chain fluctuations. Surprisingly, this result is quite similar to the one derived from the OSF result for $l_p$ by replacing $l_0, A$ by the blob size $D$ and the charge per monomer $e$ by the charge $ge$ of a blob, as was done by Khokhlov and Khachaturian [22] (KK) without the benefit of any explicit derivation:

$$l_p = l_0 + \frac{l_B}{4\kappa^2 A^2} \to D + \left(\frac{S}{A}\right)^2 \frac{l_B}{D} \cdot \frac{1}{D \kappa^2} = D + \mathcal{O}(1) \frac{1}{D \kappa^2}.$$ (2.22)

A derivation of the result displayed in Eq. (2.22) was also recently provided by Li and Witten [15] using an entirely different approach. From the preceding calculations, we find that the fluctuations in chain conformations of asymptotic polyions ($l_0 l_B / A^2 \ll 1$) do not invalidate the qualitative aspect of the OSF result. They effectively reduce the direct distances between charges so as to renormalize the bare parameters $l_0, A$ into $D$ and $e$ into $ge$, as was first recognized by KK. In this limit, local fluctuations inside the blobs are strong enough to reduce significantly the direct distance between two consecutive charges by the factor $(l_0 l_B / A^2)^{1/3}$ which is much less than 1. This results in much stronger effective Coulomb repulsion between two consecutive charges. Since the length scale of $l_p$ is much larger than the blob size $D$ and ordering as implied in these cases does not refer to the local structure of blobs, we can expect that the local fluctuations inside a blob not to affect significantly the property of the chain much beyond it. As a result we obtain qualitatively similar dependence of $l_p$ on $\kappa$ as that obtained for stiff polyions. Note that this is relevant only for the asymptotic case where each blob contains a large number of segments which roughly obey Gaussian statistics. Indeed
computer simulations performed by Higgs and Orland [23] correspond to the asymptotic case \((l_0l_B/A^2 = 0.05)\), showing that \(l_p\) is much larger than \(\kappa^{-1}\). Their results support the expression for \(l_p\) given in Eq. (2.22).

The persistence length of unscreened polyions, however, diverges as \(L \to \infty\). This is because all charges on the chain contribute to the chain stiffening. In the OSF theory it is proportional to \(l_BL^2/A^2\). To obtain the corresponding persistence length for unscreened flexible polyions, we replace \(l_B/A^2\) by \(O(1)/D\) and \(L\) by \(L'\)

\[
l_p \sim \frac{L'^2}{D}. \tag{2.23}
\]

It is interesting to contrast the results given in Eq. (2.22) with the calculations of BJ. Our theory and the BJ analysis use exactly the same variational Hamiltonian. The difference is that BJ identified the persistence length by obtaining an upper bound to the free energy of the system using the Gibbs-Bogoliubov inequality. We, on the other hand, have computed \(\langle R^2 \rangle\) using the ES method. The persistence length of the chain is a "local" measure of the size of the polymer. In the formulation of BJ, contributions from these scales are averaged out whereas the ES method, at least approximately, accounts for short length scales effects. We believe this is the major source for differing the conclusions drawn by BJ. This point is further illustrated in Appendix B where we show the deficiencies of the variational theory, using the free energy for computing "local" quantities such as persistence length.

3 Polyions with \(l_0l_B/A^2 \approx O(1)\); Gaussian Chain Model

In the previous section we considered the case of flexible polyelectrolyte in the so called asymptotic limit i.e., when \(A^2 \gg l_0l_B\). If the magnitude of \(A, l_0, l_B\) are similar, then one is in the so called non-asymptotic limit and represents crossover regime from small values to large values of \(l_0l_B/A^2\). In the limit of \(l_0l_B/A^2 \gg 1\), which is the best defined limit, the electrostatic persistence length is given by the Odjik-Skolnick-Fixman theory. When \(l_0l_B/A^2 \sim 1\) then it
is clear that (in all likelihood) the blob size, \(D\), is of the same order as \(l_0\) or \(D/l_0 \sim 1\). In this limit the distinction between the blob size and the bare persistence length is meaningless and the chain becomes ordered on scales greater than \(l_0\) due to electrostatic repulsion. As a result it seems reasonable that one can choose a simpler trial weight in contrast to the polyions in the asymptotic limit which treated in the previous section.

Following the arguments given above, we chose the following trial weight for \(l_0d_B/A^2 \sim 1\)

\[
\mathcal{W}_1 = \exp \left[ -\frac{3}{2l_1} \int \frac{\partial \mathbf{r}(s)}{\partial s} \right]^2 \tag{3.1}
\]

which is a Gaussian (non-interacting) theory with an effective step length \(l_1\). The self-consistent equation using the ES procedure, namely one that gives vanishing \(\Delta R^2\) to first order in

\[
B[\mathbf{r}(s)] = \frac{l_B}{2A^2} \int ds'ds \frac{e^{-\kappa|\mathbf{r}(s')-\mathbf{r}(s)|}}{|\mathbf{r}(s')-\mathbf{r}(s)|} + \frac{3}{2} \left( \frac{1}{l} - \frac{1}{l_1} \right) \int_0^L \left( \frac{\partial \mathbf{r}}{\partial s} \right)^2 ds, \tag{3.2}
\]

for \(l_1\) is

\[
Ll_1 \left( \frac{l_1}{l} - 1 \right) = \langle R^2V \rangle_{\mathcal{W}_1} - \langle R^2 \rangle_{\mathcal{W}_1} \langle V \rangle_{\mathcal{W}_1}. \tag{3.3}
\]

The calculation of the various quantities using the Gaussian weight is straightforward, and using these results Eq. (3.3) becomes

\[
\frac{1}{l} - \frac{1}{l_1} = \frac{1}{18L} \frac{l_B}{A^2} \int ds'ds' (s' - s)^2 \int \frac{d^3q}{(2\pi)^3} \frac{4\pi q^2}{q^2 + \kappa^2} e^{-q^2l_1|s'-s|/\hbar}. \tag{3.4}
\]

The evaluation of the integral in Eq. (3.4) is done by imposing a lower cut-off for \(q = q_0 = l_1^{-1}\). For this choice of \(q_0\) the contribution from charges separated by distance larger than \(l_1\) is exponentially small. Furthermore, since \(l_1\) is the only scale in the Gaussian weight it is reasonable to set \(q_0 = l_1^{-1}\). With this cut-off the evaluation of the integrals in Eq. (3.4) is straightforward and one obtains the following equation for \(l_1\)

\[
l_1^2 \left( \frac{l}{l_1} - 1 \right) = \frac{\alpha l_B}{A^2\kappa^2} \left\{ \frac{1}{l_1\kappa} \left[ \frac{\pi}{2} - \tan^{-1} \left( \frac{1}{l_1\kappa} \right) \right] \right\}, \tag{3.5}
\]

where \(\alpha\) is a numerical constant.
The self-consistent equation can be easily solved if $l_1$ is somewhat larger than the Debye screening length $\kappa^{-1}$. In this case, we can neglect the underlined term in Eq. (3.5). This results in the following solution for $l_p = l_1/2$

$$l_p \sim \begin{cases} l_0 + l_{\text{OSF}}, & \text{if } l_{\text{OSF}} \ll l_0 \\ (l_0 l_B/A^2)^{1/2} \kappa^{-1}, & \text{if } l_{\text{OSF}} \gg l_0 \end{cases}$$

(3.6)

where $l_{\text{OSF}} \sim l_B/A^2 \kappa^2$ is the electrostatic persistence length of stiff chains derived from the variational equation. For the flexible chains ($l_{\text{OSF}} \ll l_0$ or equivalently $l_1 \gg l_0$), the persistence length varies as $\kappa^{-1}$, which is in accord with Barrat and Joanny [13] and our earlier calculation [10]. The result in Eq. (3.6) has also been obtained by others using different methods [20]. These two distinct scaling regions are obtained according to whether the bare persistence length $l_0$ is larger or smaller than $l_{\text{OSF}}$. The dependence of $l_1$ on $l_0$ for the flexible chains ensures the cross-over; namely the value of the electrostatic persistence length for the flexible chain limit crosses over to the Odjik result at $l_0 \simeq l_{\text{OSF}}$.

The result for stiff chains ($l_{\text{OSF}} \ll l_0$) is consistent with the assumption that $l_1 > \kappa$. Thus this is valid for wide range of parameters as long as the inequality $l_{\text{OSF}} \ll l_0$ holds. On the other hand, it is not clear if we can neglect the underlined term in Eq. (3.5) for intrinsically flexible chains. If we include the contribution from the underlined term, $l_p$ may not show simple scaling law exhibited in Eq. (3.6). As long as $l_p \gg l_0$, however, the self-consistent equation (3.5) admits a solution for which $l_p$ varies as $\kappa^{-1}$. This can be easily seen if we rewrite Eq. (3.5) in terms of $x = l_1 \kappa$ as follows

$$x^2 \sim \frac{l_B l_0}{A^2} \left\{ 1 - \frac{1}{x} \left[ \frac{\pi}{2} - \tan^{-1} \left( \frac{1}{x} \right) \right] \right\}, \quad l_p \gg l_0.$$  

(3.7)

This is a transcendental equation for $x$ which cannot be solved analytically. The solution for $x$, however, is a function of $l_0 l_B/A^2$ only which does not assume a simple form except for a case of $l_1 \kappa \gg 1$. In general, we can write

$$l_p = \mathcal{G} \left( \frac{l_0 l_B}{A^2} \right)^{\kappa^{-1}}, \quad l_p \gg l_0$$

(3.8)
where $G$ is a function of $l_0 l_B / A^2$ only. Thus, the behavior of the persistence length which varies as $\kappa^{-1}$ is the general rule for the case of $l_p \gg l_0$ even though its dependence on $l_0 l_B / A^2$ is complicated. Explicitly $G$ satisfies the following equation

$$(2G)^2 \sim \frac{l_0 l_B}{A^2} \left\{ 1 - \frac{1}{2G} \left[ \frac{\pi}{2} - \tan^{-1} \left( \frac{1}{2G} \right) \right] \right\},$$

(3.9)

which can be solved graphically. As mentioned earlier, the above equation allows a simple solution, i.e., $G \sim (l_0 l_B / A^2)^{1/2}$, if $G \gg 1$ or $l_p \gg \kappa^{-1}$. Otherwise we expect a different functional behavior of $G$.

According to the above analysis, the persistence length of polyions in the non-asymptotic limit, which is assumed to be well described by a trial Gaussian weight with an effective step length $l_1$, shows a simple scaling behavior only when $l_p \gg l_0$. On the other hand it is not clear if this is valid for other range of parameters. In order to test this we solved the self-consistent equation (3.38) numerically for a few cases, with $\alpha l_B / A^2$ ranging from 2-6. The values of $A$, $l_B$, and $l$ were chosen to be unity. All lengths are estimated in unit of $l = 1$. In Fig. 1, $\ln l_e$ is plotted against $\ln \kappa^{-1}$. This figure shows that when $\alpha l_B / A^2$ exceeds 3 then $l_e$ has a sub-linear dependence on $\kappa^{-1}$, i.e., $l_e \sim \kappa^{-y}$ with $y$ varying from 0.6-0.9. These results appear to be in accord with the recent simulations performed by Micka and Kremer [13]. The experimental data of S. Förster et al. [7] also suggest that the persistence length does not show a simple power law behavior in certain regimes. When $\alpha l_B / A^2$ is less than about 3 there is no unique scaling behavior, i.e., $l_e$ does not vary as $\kappa^{-y}$.

4 Crossover Conditions and Comparison with Simulations

Based on Monte Carlo simulations for weakly charged polyelectrolytes, Micka and (MK) [13] have arrived at few interesting conclusions. They varied both $\kappa$ and the intrinsic stiffness of the chain. Their principle findings are: (a) In the limit of large stiffness, the electrostatic
persistence length \( l_e \sim \kappa^{-2} \) as predicted by the OSF theory. This is valid when the intrinsic persistence length exceeds the electrostatic persistence length, i.e., \( l_0 \gg l_e \). For flexible chains MK find that \( l_e \sim \kappa^{-y}(y < 1) \), and \( y \to 1 \) as \( l_0 \approx l_e \). (2) MK also showed that \( l_p \) is a strong function of the intrinsic persistence length, \( l_0 \). This implies that \( l_0 \) is altered by balance between the bending rigidity and the electrostatic interactions. They suggest that the contour distance, \( s_c \), at which the contributions from the bending rigidity and electrostatic interactions become comparable goes as \( s_c \sim \kappa^x \) with \( x \geq 0 \).

Our crossover condition for the change in the persistence length goes from the OSF result \((y = 2)\) to \( y = 1 \) is predicted to occur when \( l_{OSF} \approx l_0 \) (See Eq. (3.b)). We will argue that this is not inconsistent with the findings of MK. According to Eq. (3.6), when \( l_{OSF} \approx l_0 \), the persistence length \( l_p \approx l_e \approx \sqrt{l_{OSF}l_0} \approx \kappa^{-1} \). This is the crossover condition for the transition from \( y = 1 \) to \( y = 2 \) reported by MK.

In their paper, MK suggested that the \( \kappa \)-dependence of the contour crossover length from our earlier theory gives \( s_c \sim \kappa^{-2} \). We believe this is an erroneous interpretation of our earlier theory (See Eq. (15) of Ref. [10]). The crossover length for deviation from OSF behavior for \( l_e \) need not be the same as \( s_c \), which describes the contour length scale when electrostatic effects become comparable to rigidity. BJ computed \( s_c \) by considering \( \langle \theta^2(s) \rangle \) where \( \cos \theta(s) = \mathbf{u}(s) \cdot \mathbf{u}(0) \). When \( \langle \theta^2(s) \rangle \) varies as \( 1/(l_0 + l_{OSF}) \), we expect that the bending term is dominant. By identifying the crossover length scale \( s_c \) to be a length scale where the value of \( \langle \theta^2(s) \rangle \) crosses over from \( 1/l_0 \) to \( 1/(l_0 + l_{OSF}) \), BJ showed that \( s_c \sim \kappa^{-1} \).

We can compute \( s_c \) directly using an variational equation for flexible chains when \( l_0 l_B/A^2 \approx O(1) \), i.e., in the so-called non-asymptotic limit. The contour crossover length can be computed by analyzing Eq. (3.4). The condition for computing \( s_c \) is that \( l_e \approx l_0 \), which implies using Eq. (3.4)

\[
\frac{1}{l_0} \approx \frac{1}{18} \frac{l_B}{A^2} \int_0^{s_c} ds s^2 \int \frac{d^3q}{(2\pi)^3} \frac{4\pi q^2}{q^2 + \kappa^2 e^{-q^2 l_1 s/6}}.
\]

This equation is too complicated to solve analytically. However, it is easy to solve Eq. (4.1)
numerically. The resulting solution shows that $s_c$ is an increasing function of $\kappa$. The increase is not very dramatic which suggests that $s_c \sim \kappa^x$ with $x$ being small. The parameters used in solving Eq. (4.1) are $l = A = l_B = 1$. At least in this case our results are consistent with the numerical results of MK. A more detailed comparison between Eq. (4.1) and the simulations would require a thorough mapping of the variables in the theory and the simulation parameters. We believe that, at least qualitatively, the theory is in accord with the computer simulation results.

5 Conclusions

The variation of the electrostatic persistence length of flexible charged polyelectrolytes with $\kappa$ is complicated. Several regimes can emerge depending on the controlling parameter $l_0l_B/A^2$. Here we have identified the limiting behavior in certain regions of the parameter space. The computation of the electrostatic persistence length for flexible chains in the asymptotic limit ($l_0l_B/A^2 \ll 1$) suggests that the original OSF result is valid. These results were obtained by a trial Hamiltonian mimicking a semiflexible chain under tension [11] together with the uniform expansion method [19]. It appears that by focusing directly on the calculation of the mean square end-to-end distance effects that are relevant on the length scale on the order of persistence length can be implicitly taken into account using Edwards-Singh method. The results presented here together with our earlier theory [10] give a rather complicated picture of the dependence of the electrostatic persistence length on the inverse Debye screening length. We predict that in the regime when $l_0l_B/A^2$ is very large or very small the essential features of the OSF result is valid. In the limit of small $l_0l_B/A^2$ the blob picture suggested by Khokhlov and Khachaturian [22] appears to be valid. In this case, the mean distance between the charges is roughly a $\kappa$-independent blob size with each blob carrying a renormalized charge. In the non-asymptotic regime the scaling of $l_e$ with $\kappa$ is more complicated. Here we can expect fractional power for the dependence of $l_e$ on $\kappa$ or in some instances
complete absence of simple scaling laws. Since $l_0$ and $A$ can be experimentally varied over a large regime it may not be possible to analyze the data on the dependence of the persistence length of polyelectrolytes using simple scaling laws (Cf. Beer et al. [18]).

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**Appendix A**

In this appendix, we describe the evaluation of the quantities appearing in Eq. (3.18). We have argued in the text of the paper that the contributions on large length scale (greater than $\eta$) induce an interaction of the excluded volume type, and does not affect the local ordering which is described in terms of a persistence length. The average of $\langle \exp[i(k + q)l\tau/3 \cdot \int s' t(s'')ds''] \rangle'$ on the short length scale can be approximated as

$$\frac{l_B}{A^2 L'} \int \int_{|s' - s| \leq \eta} \left[ -\frac{\partial}{\partial k^2} \right]_{k=0} \int \frac{d^3q}{(q - k)^2 + \kappa^2} e^{-(q-k)^2l||s' - s||/6} \left< e^{iql\tau/3 \cdot \int s' t(s'')ds''} \right>'$$

$$\approx I_1 + I_2 + I_3 \quad (A.1)$$

where

$$I_1 = \frac{l_B}{A^2 l\tau} \int_0^S ds \left[ -\frac{\partial}{\partial k^2} \right] \int \frac{d^3q}{q^2 + \kappa^2} e^{-q^2ls/6} \quad (A.2)$$

$$I_2 = \frac{l_B}{A^2 l\tau} \int_0^S ds' \int \frac{q^2d^3q}{q^2 + \kappa^2} e^{-q^2ls/6} \quad (A.3)$$

$$I_3 = \frac{l_B}{A^2 L'} \int \int_{S \leq |s' - s| \leq \eta} dsds' \left[ -\frac{\partial}{\partial k^2} \right] \int \frac{d^3q}{q^2 + \kappa^2} \left< e^{iql\tau/3 \cdot \int s' t(s'')ds''} \right>_{\text{rod}} \quad (A.4)$$

The first term in Eq. (A.1), $I_1$ can be expanded in powers of $\kappa^2 Sl$ (which is much smaller than 1)

$$I_1 = \frac{l_B}{A^2 L'} \left[ -\frac{\partial}{\partial k^2} \right] \frac{1}{\kappa} \left\{ 1 - \Phi(\kappa \sqrt{ls/6}) e^{\kappa^2ls} \right\}$$

$$\approx (SA)^2 l_B [1 + O(\kappa^2 ls)] \quad (A.5)$$
where $\Phi(x)$ is the error function defined by

$$\Phi(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2} dt. \quad (A.6)$$

Similarly, $I_2$, (Eq. (A.2)) can also be computed. In this case we set $\kappa$ to zero right at the outset without any loss of generality. Since this integration involves length scale which is much smaller than $\kappa^{-1}$, the interaction between charges within this length scale can be assumed to be unscreened. Thus $I_2$ is approximately given by

$$I_2 = \frac{l_B l}{A^2 l'^2} \int_0^S dss' \int d^3 q e^{-q^2 l^2 s'/6} \approx (S/A)^2 l_B. \quad (A.7)$$

Finally $I_3$ can be approximated as

$$I_3 = \frac{l_B D^2}{A^2 l'^2} \left[ -\frac{\partial}{\partial \kappa^2} \right] \frac{1}{L'} \int_{D \leq |x' - x| \leq l_p} dx dx' \int \frac{d^3 q}{q^2 + \kappa^2} \left< e^{i\mathbf{q} \cdot \mathbf{s}'} t(x') dx'' \right> \approx \left( \frac{S}{A} \right)^2 \frac{1}{\kappa^2} \int_{D} dx e^{-\kappa x} \quad (A.8)$$

By following exactly the same procedure the first term in Eq. (3.19) can be approximated as sum of two terms, namely,

$$I_4 = \frac{l_B l^2}{A^2 l'^2} \int_{S \leq |s' - s| \leq \eta} ds' \int d^3 q \frac{q^2 (s' - s)^2 e^{-q^2 l^2 |s' - s|/6} \left< e^{i\mathbf{q} \cdot \mathbf{s}'} t(x') dx'' \right>}{q^2 + \kappa^2} \approx I_4 + I_5 \quad (A.9)$$

where $I_4$ is the contribution to Eq. (A.9) coming from the scale $|s' - s| < S$ and is given by

$$I_4 \approx \frac{l_B S^2}{A^2}. \quad (A.10)$$

The term $I_5$ arises from contributions on the large length scale $S \leq |s' - s| \leq \eta$ and can be approximated as followed

$$I_5 \approx \frac{l_B D^4}{A^2 l'^2} \int_{D \leq |x' - x| \leq l_p} dx dx' \int \frac{\partial^2}{\partial x'^2} e^{-\kappa x} \quad (A.11)$$
To illustrate the limitation of the Gibbs-Bogoliubov variational approach in the computation of persistence length, let us consider a simplified system which is described by the following Hamiltonian

\[
\mathcal{H}_{kB} = \frac{l_0}{2} \int_0^L \dot{\theta}^2(s) ds + \frac{1}{2} \int_0^L \int_0^L \dot{\theta}(s) K(s, s') \dot{\theta}(s') ds ds',
\]

where \(\cos \theta(s) = \mathbf{u}(s) \cdot \mathbf{u}(0)\) and \(\dot{\theta}(s) = \frac{\partial \theta(s)}{\partial s}\). The kernel \(K(s, s')\) describes interaction between charges on the chain and has yet to be specified. If the kernel \(K(s, s')\) is

\[
K(s, s') = \frac{1}{A^2} \int_{s + \frac{L}{2}}^{s' + \frac{L}{2}} ds_1 \int_{s + \frac{L}{2}}^{s' + \frac{L}{2}} dv \frac{(s_2 - s)(s' - s_1)}{(s_2 - s_1)},
\]

then the Hamiltonian in Eq. (B.1) corresponds to a polyelectrolyte chain near the rod limit. For the present purpose, we use a simpler form of \(K(s, s')\) whose Fourier transform is given by \(K_q = \frac{\kappa^2}{\kappa^2 + 2q^2} l_{OSF}\):

\[
\mathcal{H}_{kB} \approx \frac{1}{2} \sum_q \theta_q \theta_{-q} \left[ l_0 + K_q \right].
\]

Since the Hamiltonian in Eq. (B.3) is quadratic in the variables \(\theta_q\) all quantities with reference to Eq. (B.3) may be exactly computed. The efficacy of the approximate methods can be assessed by comparing to the exact result. In the following, we adopt three different trial Hamiltonians in the computation of the persistence length to illustrate possible limitations in each case.

(a) First, let us use a trial Hamiltonian

\[
\mathcal{H}_{t} = \frac{1}{2} \sum_q q^2 \tilde{K}_q \theta_q \theta_{-q}.
\]
Within the Gibbs-Bogoliubov variational approach, the best choice for $\tilde{K}_q$ is obtained by minimizing the variational free energy $F_v = F_t + \langle H - H_t \rangle_t$. Performing the Gaussian integration over $\theta(s)$, we have

$$\frac{F_v}{k_B T} = \frac{1}{2} \sum_q \log \left( \frac{q^2 \tilde{K}_q}{\pi} \right) + \frac{1}{2} \sum_q \left( \frac{l_0 + K_q}{K_q} - 1 \right). \quad (B.5)$$

Minimization of the variational free energy with respect to $\tilde{K}_q$ leads to

$$\tilde{K}_q = l_0 + l_{OSF} \frac{\kappa^2}{\kappa^2 + 2q^2}. \quad (B.6)$$

When a general form of variational kernel is used, the variational model produces the same result as the original Hamiltonian.

(b) As a second example, let us choose a bending model as a trial system which is described by

$$H_t = \frac{l_p}{2} \sum_q q^2 \theta_q \theta_{-q}. \quad (B.7)$$

This is such that $\langle \theta^2(s) \rangle = s / l_p$. In this case, the variational free energy is given by, neglecting numerical prefactors,

$$\frac{F_v}{k_B T} \sim \frac{L l_0}{\Lambda l_p} + \frac{L}{l_p} l_{OSF} \quad (B.8)$$

where $\Lambda^{-1}$ is the upper bound for $q$. Minimization of the variational free energy results in

$$l_p \sim l_0 + \frac{\Lambda l_B}{A^2 \kappa}. \quad (B.9)$$

When a bending model is used, the Gibbs-Bogoliubov variational approach leads to a wrong result for the electrostatic persistence length of a polyelectrolyte chain near the rod-limit which scales as $\kappa^{-1}$. This is because the free energy of the bending model cannot be made mimic the free energy on scales on the order of the persistence length. In other words, short length scale ($l_p$) properties in the original system are washed out by minimizing the variational free energy with respect to $l_p$.

(c) Let us now compute the persistence length of a polyelectrolyte chain described by $\mathcal{H}$ in Eq. (B.1) using the Edward-Singh's self-consistent method. The following derivation is
analogous to that given in the text (Cf. Eq. (3.11)). To this end, we write
\[
\frac{\mathcal{H}}{k_B T} = l_p \sum_q q^2 \theta_q \theta_{-q} + \left(\frac{l_0}{2} - \frac{l_p}{2}\right) \sum_q q^2 \theta_q \theta_{-q} + \frac{1}{2} \sum_q K_q q^2 \theta_q \theta_{-q}
\] (B.10)
and compute \(\langle \theta^2(L) \rangle\) self-consistently by considering the underlined term to be small. Up to the first order in the underlined term, the bending model can be made the same as the real system by requiring
\[
(l_0 - l_p) \frac{\partial}{\partial l_p} \langle \theta^2(L) \rangle_t = \langle \theta^2(L) \rangle_t \frac{1}{2} \sum_q K_q q^2 \theta_q \theta_{-q} - \langle \theta^2(L) \rangle_t \frac{1}{2} \sum_q K_q q^2 \theta_q \theta_{-q}.
\] (B.11)
A little algebra leads to the following equality from the Eq. (B.11)
\[
(l_0 - l_p) \frac{\partial}{\partial l_p} \langle \theta^2(L) \rangle = \frac{2}{l_p} \sum_q K_q \frac{\sin^2(qL/2)}{q^2}.
\] (B.12)
For large \(L\) most of contribution to the sum on r.h.s of Eq. (B.12) is from \(q \simeq 0\). This results in
\[
l_p \approx l_0 + l_{OSF}.
\] (B.13)
Thus the ES method provides a reliable way of calculating the persistence length \(l_p\). The result using this method agrees with the exact answer for the simple Hamiltonians of the form given in Eq. (B.3). By focusing directly on the local quantity the ES method implicitly includes effects on the scale of the persistence length. Such fluctuations are integrated out when the free energy is computed. Consequently, the persistence length needs not be accurately given by minimization of an approximate free energy.

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Figure Caption

Fig. (1). Plot of the electrostatic persistence length, $l_e$, as a function of $\kappa^{-1}$. Both quantities are expressed in natural logarithm values. The various curves correspond to different values of the parameter $\alpha l_B l/A^2$ (See Eq. (3.5)). The values of $\alpha$ from the top to the bottom curves are 6, 4, 3, 2.5, and 2 respectively. For $\alpha l_B l/A^2 \geq 2.5$, $l_e \propto \kappa^{-y}$ and the exponent can be obtained from the slope of the displayed curves. The exponent $y$ varies from 0.6-0.9. For $\alpha l_B l/A^2 \leq 2.5$, there appears to be no simple power law describing the dependence of $l_e$ on $\kappa$. 