Electrostatic Persistence Length of a Polyelectrolyte Chain

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ABSTRACT: We calculate the electrostatic persistence length l_e both for flexible and for stiff polyelectrolytes using a self-consistent variational theory. For the case of intrinsically rigid polyelectrolytes we recover the classical results due to Odijk, Skolnick, and Fixman (OSF), namely, $l_e \propto \kappa^{-2}$ where κ^{-1} is the Debye screening length. In contrast, l_e for intrinsically flexible polyelectrolytes is found to be proportional to κ^{-1} in the limit of large screening. This is in accord with simulations, experiments, and numerical estimates. We also provide a criterion for the crossover from the OSF result to the behavior observed for intrinsically flexible polyelectrolytes.

1. Introduction

Despite numerous theoretical studies of charged polymers,[1−10] a theory for the description of their conformations, at the level comparable to that for neutral polymer solutions,[11] does not exist. The presence of multiple length scales (six) makes a scaling description of polyelectrolytes difficult to construct. The behavior of a dilute polyelectrolyte solution has been largely analyzed in terms of the electrostatic persistence length advanced by Odijk[3] and independently by Skolnick and Fixman.[4] In the Odijk−Skonick−Fixman (hereafter called OSF) theories, the polyion is described by a semiflexible chain near the rod limit having N charged monomers separated by a distance A along its contour. The electrostatic interaction between the charged segments is assumed to be given the Debye−Hückel potential, $v(r) = l_B e^{-\kappa r}/r$. The strength of the interaction is measured in terms of the Bjerrum length $l_B = e^2/4\pi\epsilon kT$ where e is the charge per segment, and ϵ is the dielectric constant of the solvent. The Debye screening length, $r_D \equiv \kappa^{-1}$, is roughly the distance beyond which the electrostatic interaction is screened. It depends on the total concentration, n, of the counterions (assumed to be monovalent) and any added electrolytes through the relation $\kappa^2 = 4\pi l_B n$.

OSF calculated the increase in free energy due to electrostatic interaction and elastic bending energy for a slightly bent configuration with reference to a rodlike configuration. This was used to analyze the effect of the charges on the chain stiffness, leading naturally to the crucial concept of the electrostatic persistence length, l_e. Following Odijk, the configuration of the polyion is described by the unit tangent vector $\mathbf{u}(s) \equiv \partial\mathbf{r}/\partial s$, $0 \le s \le L$, where $\mathbf{r}(s)$ is the radius vector of a segment of the chain at the curvilinear position s, and L is the contour length of the chain. If the chain is near the rod limit, only those paths which minimize the elastic free energy, i.e., paths for which the angle θ defined by $\cos(\theta(s)) = \mathbf{u}(s)\cdot\mathbf{u}(0)$ varies linearly with s, contribute significantly to the partition function.[12] The electrostatic contribution to the chain stiffness due to the departure from the rod limit allows for the calculation of l_e which in the limit of $\kappa L \gg 1$ is given by[3,4]

$$l_e = l_B/4\kappa^2 A^2 \equiv l_{OSF} \qquad (1)$$

The configurational properties of the chain are determined by the total persistance length which is the sum of l_{OSF} and the bare persistence length l_0.

Odijk's result is based on the assumption that $\theta(s)$ is small, which is appropriate for stiff chains. However, this approximation is expected to break down for intrinsically flexible chains. In this case fluctuations in chain configurations could make a substantial contribution to the free energy, which in turn may result in the alteration of the electrostatic persistence length. Recently, Barrat and Joanny[13] argued that these fluctuations contribute to $\langle\theta(s)^2\rangle$ where $\langle\cdots\rangle$ indicates the average over all paths weighted by the appropriate Boltzmann factor. The criterion for the validity of Odijk's theory can be established by examining the behavior of $\langle\theta(s)^2\rangle$ as a function of s. Barrat and Joanny (BJ) noted that Odijk's estimate for l_{OSF} is valid at length scales larger than a certain crossover length s_c given by[13]

$$s_c \simeq \kappa^{-1} l_0^{1/2}/(l_0 + l_{OSF})^{1/2} \qquad (2)$$

If the chain is intrinsically flexible, then the assumption that $\langle\theta^2\rangle$ be small breaks down at length scales smaller than s_c and Odijk's approach becomes inconsistent. In this case BJ show that the electrostatic persistence length varies as κ^{-1} rather than κ^{-2}. This result is in agreement with the recent Monte Carlo simulations,[14] numerical and several experimental estimates of the electrostatic persistence length of intrinsically flexible polyelectrolytes.[15]

In this paper, we use the model of a stiff chain proposed by Lagowski, Noolandi, and Nickel (LNN)[16] modified to take into account electrostatic interactions between the charges. A variational theory referred to as the "uniform expansion"[17] method is used to calculate the electrostatic persistence length. Our theory is distinct from that of BJ, but we are led to qualitatively similar conclusions. In this sense the present paper is a complement to the work of BJ and further confirms the different scaling behavior expected for the electrostatic persistence length for flexible polyelectrolytes. Here we restrict ourselves mainly to the limit of large κL. For the flexible polyions, we show that the electrostatic persistence length varies as κ^{-1}, while OSF's result is recovered for the rigid chains. A criterion is also provided, which can be used to predict the crossover from the intrinsically rigid chain limit to the flexible chain limit. Thus our theory provides a unified descrip-

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tion for the electrostatic persistence length for semiflexible as well as for flexible chains.

2. Theory for the Semiflexible Chain

Freely jointed chains have the characteristic that the angles $\theta(s_i)$ between two chain segments are unconstrained. Many polymers, however, exhibit internal stiffness restricting the allowed values of the angles between two successive chain bonds. Such stiff chains are semiflexible and are described in terms of both $\mathbf{r}(s)$ and its first derivative $\mathbf{u}(s) = \partial\mathbf{r}/\partial s$. The angles $\theta(s_i)$ in this instance are not uncorrelated, as is the case for flexible chains, but typically exhibit the following correlation

$$\langle \mathbf{u}(s)\cdot\mathbf{u}(s')\rangle = e^{-|s'-s|/l_p} \tag{3}$$

where l_p is the persistence length. For a differentiable curve a geometric constraint is imposed on the derivative,

$$|\mathbf{u}(s)|^2 = |\partial\mathbf{r}/\partial s|^2 = 1 \tag{4}$$

If ϵ is the elastic constant which measures the energetic penalty for bending a curve, the weight assigned with a particular configuration of an unperturbed semiflexible chain is

$$\mathscr{W}_0[\mathbf{u};\mathbf{u}^2=1] \propto \exp\left[-\frac{\epsilon}{2kT}\int_0^L ds\,(\partial\mathbf{u}/\partial s)^2\right]\prod_{\text{all } s,0\le s\le L}\delta(\mathbf{u}^2(s)-1) \tag{5}$$

The variable $\mathbf{u}$ describes the Brownian motion on the unit sphere defined by eq 4. If we let $P(\mathbf{u}_s,\mathbf{u}_{s'};s',s)$ be the probability that $\mathbf{u}(s) = \mathbf{u}_s$ and $\mathbf{u}(s') = \mathbf{u}_{s'}$, then it is possible to show that this function obeys a diffusion equation on the unit sphere[17] the solution of which can be expanded in terms of spherical harmonics. The probability distribution function $P(\mathbf{u}_s,\mathbf{u}_{s'};s',s)$ is, up to the normalization constant, a restricted partition function $\mathscr{Z}(\mathbf{u}_s-\mathbf{u}_{s'};s'-s)$ which can be written as a functional integral over all configurations with $\mathbf{u}(s) = \mathbf{u}_s$ and $\mathbf{u}(s') = \mathbf{u}_{s'}$:

$$\mathscr{Z}(\mathbf{u}_{s'}-\mathbf{u}_s;s'-s) = \int\mathscr{D}[\mathbf{u}]\,\delta(\mathbf{u}(s)-\mathbf{u}_s)\,\delta(\mathbf{u}(s')-\mathbf{u}_{s'})\,\mathscr{W}_0[\mathbf{u};\mathbf{u}^2=1] \tag{6}$$

The dependence of $\mathscr{Z}$ and consequently P only on the differences $\mathbf{u}_{s'} - \mathbf{u}_s, s' - s$ reflects on the translational invariance in $\mathbf{u}$ space for the problem of an ideal semiflexible chain.

With the aid of the probability distribution function P, statistical averages $\langle\cdots\rangle$ can be calculated; $\langle\cdots\rangle = \int\int d\Omega_s\, d\Omega_{s'}(\cdots)P/\int\int d\Omega_s\, d\Omega_{s'}\, P$ where $\Omega = \sin(\theta)\, d\theta\, d\phi$ is the solid angle. For example, we can show that the weight given above yields the correlation in eq 3 with $l_p = l_0 \equiv \epsilon/kT$, where l_0 is the bare persistence length. The correlation, along with the Markovian property of the random variable $\mathbf{u}$, enables one to calculate the mean end-to-end distance $\langle R^2\rangle$:

$$\langle R^2\rangle \equiv \langle(\mathbf{r}(L) - \mathbf{r}(0))^2\rangle = 2l_0L - 2l_0^2(1 - e^{-L/l_0}) \tag{7}$$

The mathematical difficulties associated with the semiflexible chains that include interactions between chain segments are quite formidable. The major difficulty arises because of the presence of the constraint $\mathbf{u}^2 = 1$. In order to obtain a tractable theory, we adopt the semiflexible chain model of LNN in which the constraint in eq 4 is enforced only on an average.

In LNN's work, a relaxed constraint, $\langle\mathbf{u}^2\rangle = 1$ is incorporated into the probability distribution function; the magnitude of the tangent vectors can fluctuate locally, but the average value is held fixed. The corresponding weight associated with a configuration of a single semiflexible chain is given by

$$\mathscr{W}_0[\mathbf{u}] \propto \exp\left[-\frac{3}{2l}\int_0^L ds\,\mathbf{u}^2(s) - \eta\int_0^L ds\,(\partial\mathbf{u}/\partial s)^2 - b(\mathbf{u}_L^2+\mathbf{u}_0^2)\right] \tag{8}$$

where l is the Kuhn length. The relaxed constraint $\langle\mathbf{u}^2(s)\rangle = 1$ is now satisfied by the choice of $\eta = 3l/8$ and $b = 3/4$. It should be noted that the correlation of tangential vectors $\mathbf{u}$ and consequently the mean-squared end-to-end distance $\langle R^2\rangle$ based on this model are the same as that with the exact weight given in eq 5 if we let $l \equiv 2\epsilon/kT = 2l_0$; local fluctuation in the magnitude of the tangent vector $\mathbf{u}(s)$ does not affect the large scale behavior such as $\langle R^2\rangle$.

The probability functional describing the semiflexible chains given in eq 8 was suggested to ensure that $\langle\mathbf{u}^2(s)\rangle = 1$. It turns out that eq 8 can be derived starting from eq 5 using field theoretical methods. The delta function in eq 5 can be exponentiated by introducing an auxiliary field λ.

$$\mathscr{W}_0[\mathbf{u};\mathbf{u}^2 = 1] \propto \int\mathscr{D}[\lambda]\exp[-\int_0^L ds\,(\eta(\partial\mathbf{u}/\partial s)^2 + i\lambda\mathbf{u}^2 - i\lambda)] \tag{9}$$

where the coefficient of the bending term, ϵ/kT, is replaced by η. A saddle-point evaluation of the above functional integral, which corresponds to the most probable value of $\lambda = \tilde{\lambda}$, then leads to the probability functional given in eq 8. For an infinite chain or a ring polymer $\tilde{\lambda}$ is s-independent because of the symmetry of the problem. But for a finite linear chain, $\tilde{\lambda}$ has singularities at both ends of the chain in a continuum limit. These singularities give rise to a factor $\exp[-b(\mathbf{u}_L^2 + \mathbf{u}_L^2)]$ in the weight, which suppresses the end fluctuations. Without this term, the weight in eq 8 gives the same correlation of tangential vectors $\mathbf{u}(s)$ as in eq 3 only when $|s' - s| \gg \eta$ $(0 \ll s, s' \ll L)$. Details of this calculation will be reported elsewhere.

3. Scaling Results for the Persistence Length

As stated earlier, the system considered is a uniformly charged polymer in which the charges interact with each other via screened Coulombic interactions. The weight associated with a configuration of the charged semiflexible chain becomes

$$\mathscr{W}[\mathbf{u}] \propto \mathscr{W}_0[\mathbf{u}]\exp\left(-\frac{\omega_c}{2}\int_0^L\int_0^L ds\,ds'\,\frac{e^{-\kappa|\mathbf{r}(s')-\mathbf{r}(s)|}}{|\mathbf{r}(s')-\mathbf{r}(s)|}\right) \tag{10}$$

where $\mathscr{W}_0[\mathbf{u}]$ is the unperturbed weight given in eq 8 and ω_c is the electrostatic interaction parameter and equal to l_B/A^2. The calculation of averages with the probability measure given by eq 10 is difficult, and hence one has to resort to approximate calculations.

Our goal is to examine the electrostatic contribution to the persistence length. The scattering function $S(\mathbf{k})$ computed with the relaxed constraint gives a good

approximation for small $\mathbf{k}$, and hence for $\langle R^2\rangle$. Se we have calculated $\langle R^2\rangle$ self-consistently using a variational method with the trial weight $\mathscr{W}_1[\mathbf{u}]$ in which l in $\mathscr{W}_0$ is replaced by the new step length l_1. Formally we can write

$$\langle R^2\rangle = \langle R^2\rangle_1 + \Delta R^2(\omega_c,l_1) \tag{11}$$

where $\Delta R^2(\omega_c,l_1)$ is the correction term arising from the replacement of the actual functional in eq 10 with a trial probability functional and depends on ω_c and the trial weight $\mathscr{W}_1[\mathbf{u}]$. The subscript 1 in $\langle\cdots\rangle_1$, from now on, refers to an average taken with $\mathscr{W}_1[\mathbf{u}]$. As ω_c goes to zero, ΔR^2 is expected to vanish. For a nonzero value of the interaction parameter ω_c, the self-consistent equation for l_1 can be obtained by requiring $\Delta R^2(\omega_c,l_1)$ to be zero. This is the method introduced by Edwards and Singh[18] and has been successfully used to obtain the conformations of a flexible polyelectrolyte chain under a variety of solvent conditions.[6,10] Up to first order in ω_c, ΔR^2 is given by

$$\Delta R^2(\omega_c,l_1) \simeq -\langle(\ln \mathscr{W} - \ln \mathscr{W}_1)R^2\rangle_1 + \langle\ln \mathscr{W} - \ln \mathscr{W}_1\rangle_1\langle R^2\rangle_1 \tag{12}$$

In evaluating the averages in eq 12, we encounter the restricted partition function $\mathscr{Z}(\mathbf{r}_L-\mathbf{r}_0,L;\mathbf{r}_{s'}-\mathbf{r}_s,s'-s)$ which is given by

$$\mathscr{Z}_1(\mathbf{r}_L-\mathbf{r}_0,L;\mathbf{r}_{s'}-\mathbf{r}_s,s'-s) = \int \mathscr{D}[\mathbf{u}]\, \delta(\mathbf{r}_L-\mathbf{r}_0-\int_0^L \mathbf{u}\, ds)\, \delta(\mathbf{r}_{s'}-\mathbf{r}_s-\int_s^{s'} \mathbf{u}\, ds'')\mathscr{W}_1[\mathbf{u}] \tag{13}$$

This function can be interpreted as, up to the normalization constant, the *coarse-grained* probability for an ideal semiflexible chain with persistence length $l_1/2$ such that $\mathbf{r}(L) = \mathbf{r}_L$ and $\mathbf{r}(s') = \mathbf{r}_{s'}$ when $\mathbf{r}(0) = \mathbf{r}_0$ and $\mathbf{r}(s) = \mathbf{r}_s$. The term "coarse-grained" refers to the relaxed constraint $\langle\mathbf{u}^2\rangle = 1$ incorporated into the trial weight $\mathscr{W}_1$. Using the Markovian property of $\mathbf{u}$ in the trial weight $\mathscr{W}_1[\mathbf{u}]$, the restricted partition function $\mathscr{Z}_1$ and all other relevant quantities can be computed. By requiring $\Delta R^2(\omega_c,l_1) = 0$, to the first order in ω_c, we obtain

$$\langle R^2\rangle \simeq Ll_1 - \frac{l_1^2}{2}(1 - e^{-2L/l_1}) \tag{14a}$$

where the trial step length l_1 can be determined by the following self-consistent equation

$$L\left(\frac{1}{l} - \frac{1}{l_1}\right) + \frac{L}{2l_1}\left(\frac{l_1}{l} - \frac{l}{l_1}\right)e^{-2L/l_1} + \frac{1}{4}\left(\frac{3l_1}{l} - \frac{l}{l_1} - 2\right) \times (1 - e^{-2L/l_1}) = \frac{1}{18}\int_0^L\int_0^L ds\, ds' \int \frac{k^2\, d^3k}{(2\pi)^3}\frac{4\pi\omega_c}{k^2+\kappa^2} \times [(s'-s) - l_1 e^{-L/l_1}\sinh(s'-s)/l_1 \cdot \cosh(L-s'-s)/l_1]^2 \times \exp\left\{-\frac{k^2}{6}\left[|s'-s|l_1 - \frac{l_1^2}{2}(1 - e^{-2|s'-s|/l_1})\right]\right\} \tag{14b}$$

Here the function $4\pi\omega_c/(k^2+\kappa^2)$ is the Fourier transform of $e^{-\kappa r}/r$.

The complete analysis of eq 14 in terms of the variables ω_c, κ, and l is complicated. Here we focus largely on the limit of large κL, i.e., $\kappa L \gg 1$. The difficulties that arise in the limit of small κL are discussed below. In the limit of $\kappa L \gg 1$, the electrostatic persistence length, at least to leading order in $(\kappa L)^{-1}$, does not depend on the contour length of L of the chain. This is true for the OSF result and can be checked to be true *a posteriori* for the flexible chains. The left-hand side of eq 14b can be simplified considerably by taking a $L \gg l_1$ limit. The right-hand side of eq 14b can be also made more tractable if we split up the integral into two parts;[19] one corresponding to short length scales, $|s'-s| < \lambda$, and the other corresponding to long length scales, $|s'-s| > \lambda$, where λ is a contour length on the order of l_1. More precisely, λ is chosen so that only charges separated by a contour distance smaller than λ contribute significantly to the chain stiffness. Coulombic interaction between charges separated by a large contour distance signifies the excluded-volume effect. For very stiff chains, we can expect that l_1 is appreciably larger than κ^{-1} and the formal splitting is invariant with respect to small changes in λ.[3] This is, however, not necessarily the case for flexible polyions. Unless κ^{-1} is larger than l_1, we can still choose λ to be on the order of l_1. Only the first term gives rise to the electrostatic stiffness. The second term which is proportional to $L^{3/2}$ with a cutoff $s_0 \simeq \lambda$ as a lower bound of the integration gives an interaction of the excluded-volume form. Since our trial probability measure does not contain a term simulating this large distance interaction, we impose an upper bound for $|s'-s|$ in this part to avoid excluded volume type interactions. The polyion then can be viewed as a semiflexible chain with a new persistence length $l_p = l_1/2$ interacting via excluded-volume interactions.

At length scales smaller than λ, the chain resembles a rod. Since only values of s with $|s'-s| < \lambda$ are retained in the integral over a s for reasons explained above, the statistical average on the right-hand side of eq 14b can be computed over rodlike configurations. In this case, charges separated by a distance of $|s'-s| > \lambda$ cannot approach close to each other with appreciable probability and thus interact with each other via the *screened* Coulombic interaction. The integral over s can be evaluated, allowing for all values of s, $0 \le s \le \infty$ without introducing significant errors. Strictly speaking, this procedure is valid only when l_1 is somewhat larger than κ^{-1} as is the case for stiff chains. These approximations lead to two distinct results for l_p, depending on the values of κ and the bare persistence length, $l_0 \equiv l/2$ both for short chains ($L \le \lambda$) on infinitely long chains ($L \gg l_1$):

$$l_p \sim \begin{cases} l_o + l_{OSF}, & \text{if } l_{OSF} \ll l_o \\ (l_o\omega_c)^{1/2}\kappa^{-1}, & \text{if } l_{OSF} \gg l_o \end{cases} \tag{15}$$

where l_{OSF} which is proportional to $\omega_c\kappa^{-2}$ is the electrostatic persistence length derivable from the self-consistent eq 14b for the intrinsically stiff chains. For the flexible chains ($l_{OSF} \gg l_0$ or equivalently $l_p \gg l_0$), the electrostatic persistence length l_e is not different from l_p and varies as κ^{-1}, which is in accord with Barrat and Joanny.[13] These two distinct scaling regions are determined according to whether the bare persistence length l_0 is larger or smaller than l_{OSF}. The dependence of l_p and l_0 for the flexible chains ensures the *crossover*; namely, the value of the electrostatic persistence length for the flexible chain limit crosses over to the Odijk's result at $l_0 \simeq l_{OSF}$.

We believe that the reason for the different behavior seen in l_e for flexible chains is that (in $d = 2$ and $d = 3$) fluctuations play a role. In order to check this, we have calculated l_e in $d > 3$ (see Appendix) for which the

electrostatic term can be treated using perturbation theory. In large enough dimensions such a perturbation series would converge, which is not obviously the case in $d = 2$ or $d = 3$. Furthermore, in large dimensions ($d > 3$) fluctuations are totally suppressed and hence one can investigate the behavior of l_e without regard to the role of fluctuations. In the Appendix we show that l_e for large d always follows the OSF result for $\kappa L \gg 1$. Thus the different behavior seen in eq 15 for flexible chains in $d = 3$ is clearly a result of fluctuations. The variational calculation reported here captures the fluctuations approximately.

There are a few comments concerning eq 15 that are worth mentioning: (1) It is clear that l_p explicitly depends on l_0 and ω_c, which is different from the result of BJ. We believe that the difference is because BJ's analysis is explicitly valid only in the asymptotic limit $(l_0\omega_c)^{1/2} \ll 1$ or equivalently $A \gg (l_0 l_B)^{1/2}$. In this limit, the electrostatic blob concept can be used to construct an appropriate variational Hamiltonian as described by BJ.[13] On the other hand, our analysis is expected to be accurate when $l_0\omega_c \sim \mathcal{O}(1)$. In the asymptotic limit a variational Hamiltonian with a scale-dependent step length l_1 is necessary to capture local ordering implied by the blob picture. Despite this we can show that with a suitable mapping to the blob model the dependence of l_p on l_0 and ω_c disappears in the limit $A \gg (l_0 l_B)^{1/2}$. In this regime, the electrostatic blob size, rather than l_0, should be considered as the effective monomer size. Thus in our theory the value of charge per monomer e should be replaced by the charge ge of one blob, and the blob size D[5] should be used in place of l_0 and A. With this identification our theory can be extended into the regime explicitly treated by BJ. We then find that l_p can be approximated as:

$$l_p \sim \left(\frac{g^2e^2}{4\pi\epsilon D}\frac{1}{kT}\right)^{1/2}\frac{1}{\kappa} \sim \frac{1}{\kappa} \tag{16}$$

where the last equality follows from the fact that the electrostatic energy between two adjacent blobs is on the order of kT. (2) Our theory suggests that when the distance between two adjacent charges is on the order of l_0,l_p decreases as $(l_0\omega_c)^{1/2}$ decreases. This implies that chains with smaller l_0 allow for more fluctuations and the persistence length l_p, which is a measure of local stiffening, depends on l_0. As noted before, because of the local structure of the chain inside a blob (relevant when $A \gg (l_0 l_B)^{1/2}$), we cannot let $l_0\omega_c = 0$ in eq 15 to obtain l_p in this regime. In this limit the modification of our result to account for fluctuations on the scale of the blob size along the lines indicated above becomes necessary.

The qualitative result, namely, the electrostatic persistence length should be proportional to κ^{-1} for chains for which fluctuations in chain configurations are important, is in agreement with the result of BJ. However, the crossover regime between the behavior seen in stiff chains and flexible chains given here differs from that obtained earlier. The formula in eq 2 was used by BJ to distinguish between two distinct scaling regimes for l_p. The criterion for the validity of Odijk's result is that $\langle\theta^2(s_c)\rangle \ll 1$, where s_c is a length scale at which the persistence length l_p crosses over from the bare value l_0 to the OSF value $l_0 + l_{OSF}$. This inequality leads to $l_0(l_0 + l_{OSF}) \gg \kappa^{-2}$. In most of the interesting cases $\kappa^{-1} < l_{OSF}$. Thus BJ's inequality for the validity of Odijk's formula is less stringent than $l_{OSF} \ll l_0$. Now consider the case for the κ^{-1} dependence of l_p. According to BJ, this is the expected result whenever $l_0(l_0 + l_{OSF}) \ll \kappa^{-2}$. According to this inequality, the condition on the allowed values of l_0 becomes more strict as the strength of Coulombic interaction increases. Our variational equation, however, suggests that once $l_p \gg l_0$ is satisfied, a persistence length l_p varying as κ^{-1} is the rule even for the strongly charged polyions for which $A \simeq (l_0 l_B)^{1/2}$. Notice that this condition falls in the crossover regime according to BJ.[13] In this regime we expect the persistence length which depends on l_0 explicitly, as was mentioned in ref 13.

We now discuss the crossover criterion given in eq 15. Our condition, $l_0 \gg l_{OSF}$, for Odijk's result to be valid was obtained by considering a general system with arbitrary values of l_0 and ω_c and examining where the crossover from the flexible chain limit to the stiff chain limit occurs. This is the condition assumed in Odijk's theory to justify, besides the assumption of small θ, that the most probable paths are solely determined by the elastic free energy only.[3] This inequality amounts to requiring $\langle\theta(s=l_{OSF})^2\rangle \ll 1$. Let us now discuss the case when $l_{OSF} \gg l_0$ in eq 15. The notion of the persistence length has physical meaning only as long as $D < r_D \sim l_p$ in the blob model. This inequality, together with $l_0 \ll D$, yields $l_0 \ll D < l_p$. Then our criterion $l_p \gg l_0$ under which $l_p \sim \kappa^{-1}$ amounts to dropping D in the above inequality. This is a minimal modification of BJ's criterion in the sense that the shortest length scale beyond the blob size D is l_p in the limit of $\kappa L \gg 1$. However, since our results are based on some approximations, more studies are necessary to further clarify the criterion for the crossover from the OSF result to the κ^{-1} dependence of the electrostatic persistence length. Some experiments also seem to lend support to our criterion for the scaling behavior of l_e which varies as κ^{-1} for flexible chains. The experimental data of Förster et al. in ref 15 correspond to BJ's crossover region and most likely show κ^{-1} dependence of the electrostatic persistence length. This is especially clear in the work by Tricot, in which the values of the persistence length are provided for various strengths of Coulombic interactions or degrees of ionization. The data show that the linear κ^{-1} dependence of the persistence length is verified for intrinsically flexible polyions, regardless of the strength of Coulombic interactions. This is in accord with the arguments given here.

As κ goes to zero, charges interact with each other via long-ranged Coulombic interactions and thus all charges contribute to the chain stiffening. In this case we expect L-dependent persistence lengths. In the limit of rigid rod, i.e., if l_0 is much larger than the contour length L and the electrostatic contribution to l_p, eq 14b can be simplified to yield the electrostatic persistence length varying as $\omega_c L^2$. This is in agreement with the Odijk's result for the zero screening case. On the other hand, eq 14b does not allow a simple scaling for flexible polyions. For the flexible chains we may assume L is somewhat larger than l_p, which is reasonable.[20] If the statistical average in eq 14b is taken over rodlike configurations (note that $\langle R^2\rangle \sim L^2$ as $\kappa \to 0$), neglecting short-length-scale fluctuations in the chain configurations, then we obtain the persistence length which varies as $(l_0\omega_c)^{1/2}L$. The linear dependence of l_p on the contour length L is in accord with the numerical result of Schmidt.[15] The deviation of the persistence length for the flexible polyions is, however, not complete in the sense that we used two assumptions, i.e., $L > l_p$ and $\langle R^2\rangle \sim L^2$, even though these assumptions are plausible.

At least, we have shown that these assumptions are consistent with the linear dependence of l_p on L.

4. Conclusion

In this paper we have investigated the electrostatic contribution to the persistence length l_p. We have provided the scaling results both for flexible and for stiff polyions. The result of BJ's for l_p obtained for restrictive conditions has been complemented to account for the strongly charged polyions, $A \simeq (l_0 l_B)^{1/2}$. By a suitable modification of our model system, we have shown how the explicit dependence of l_p on l_0 disappears in the asymptotic limit of $A \gg (l_0 l_B)^{1/2}$. Once the chain backbone is flexible, $l_p \gg l_0$, l_p behaves as κ^{-1} even though the polyion falls in BJ's crossover region. In this region we have obtained an expression for l_p which explicitly depends on l_0 and ω_c. Our theory allows for a reasonable distinction between intrinsically flexible and stiff chains depending on the physical parameters, κ, ω_c, and l_0. For nonscreened polyions, we have shown how the electrostatic persistence length depends on the contour length L. The results described in this paper can form the basis for describing the conformations of a polyelectrolyte chain in various solvent conditions.

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Appendix

In this appendix, we show that, in large dimensions $d > 3$, Odijk's result, κ^{-2} dependence of the electrostatic persistence length, is always valid for $\kappa L \to \infty$, based on the perturbative computation of the mean-squared end-to-end distance $\langle R^2 \rangle$. The purpose of this Appendix is the following. It is useful to construct a theory in which the role of perturbation expansion and fluctuations in chain configurations in determining the electrostatic persistence length can be systematically examined. In sufficiently large dimensions the Debye–Hückel potential between charges becomes truely a perturbation, and hence the series for $\langle R^2 \rangle$ is expected to converge. Furthermore, in large dimensions fluctuation effects are unimportant. Thus the theory presented in this Appendix allows us to calculate the electrostatic persistence length in a very well-defined limit. Since the electrostatic contribution is subdominant in d greater than 3, $\langle R^2 \rangle$ can be computed perturbatively:

$$\langle R^2 \rangle \simeq \langle R^2 \rangle_0 + \frac{l^2}{2d^2}\int_0^L\int_0^L \mathrm{d}s\, \mathrm{d}s' \int \frac{\mathrm{d}^d k}{(2\pi)^d} \frac{4\pi^{d/2}\omega_c}{\Gamma(d/2-1)} \times \frac{k^2}{k^2+\kappa^2}[(s'-s) - l\mathrm{e}^{-L/l}\sinh(s'-s)/l \cdot \cosh(L-s'-s)/l]^2 \times \exp\left\{-\frac{k^2}{2d}\left[|s'-s|l - \frac{l^2}{2}(1-\mathrm{e}^{-2|s'-s|/l})\right]\right\} \quad \text{(A-1)}$$

where $\langle R^2 \rangle_0$ is the size of an unperturbed semiflexible chain and $\Gamma(x)$ is the gamma function ($\Gamma(x+1) = x!$). With approximations similar to that described in the text, the above equation can be simplified to yield

$$\langle R^2 \rangle \simeq 2L(l_0 + l_{\mathrm{OSF}}^{(d)}), \quad \kappa L \gg 1 \qquad \text{(A-2)}$$

where $l_{\mathrm{OSF}}^{(d)}$ is the first-order electrostatic contribution to the persistence length in d-dimensional space and is proportional to κ^{-2}. This result for the electrostatic persistence length is a good approximation if l is somewhat larger than κ^{-1} and shows κ^{-2} dependence of the electrostatic persistence length *irrespective* of l_0 and ω_0 for $\kappa L \to \infty$. Because we are working in dimensions where the electrostatic contribution is small, convergence of this series is ensured. However, in the physical dimension, $d = 3$, this perturbation expansion diverges unless the interaction parameter ω_c is small enough. This calculation shows that the reason for the failure of Odijk's result for flexible chains is because fluctuations in chain configurations become important in $d \leq 3$. The variational approach roughly captures the effect of the fluctuations and leads to a modification of the dependence of l_p on κ as indicated in eq 15.

References and Notes

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