

Electrostatic Persistence Length of a Wormlike Polyelectrolyte

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Received April 11, 1977

ABSTRACT: The worm model of Kratky and Porod has been extended to "locally stiff" polyelectrolytes. Neglecting excluded volume effects, the electrostatic persistence length, P_{el} , has been obtained for a continuous, uniform charge distribution in which both charge rearrangements due to bending and fluctuations due to thermal motion are not allowed. Comparisons of experimentally determined dimensions of carboxymethylcellulose in aqueous NaCl with theoretical results reveals good agreement between theory and experiment. In the Appendix, the relationship between the discrete and continuous model is examined. Furthermore we treat the continuous charge distribution with rearrangements with and without fluctuations. If the polyelectrolyte is assumed to be locally stiff, the results of the latter two cases reduce identically to the continuous, uniform case in which the charges are frozen in place.

(I) Introduction

Polyelectrolyte excluded volume theories assume that the unperturbed mean-square end-to-end distance $\langle h_0^2 \rangle$ is independent of the supporting electrolyte concentration, C_s .^{1,2} The basis of this assumption comes either from the use of Stockmayer-Fixman, S-F, plots, which give a slight ionic strength dependence for the unperturbed dimensions,³ even though S-F plots assume $\langle h_0^2 \rangle$ is independent of solvent, or from direct measurements in relatively high salt concentration theta solvents.^{4,5} However, for sufficiently low C_s , one would intuitively expect that local electrostatic forces exert a significant influence on $\langle h_0^2 \rangle$. The model of Rice and Harris⁶ takes account of local electrostatic interactions by considering an equivalent Kuhn chain with charges concentrated at the midpoints of the statistical elements; if nearest neighbor segment interactions are assumed, the polymer behaves as a random chain. Thus, in the absence of long-range interactions, the somewhat artificial Rice-Harris model gives unperturbed chain dimensions that depend in a complicated fashion on C_s .

In the low salt limit, the Debye screening length, κ^{-1} , is much larger than the distance between charges on the polyelectrolyte chain, so that the replacement of a discrete charge distribution by a continuous one should be a good approximation.⁷ The polyelectrolyte can therefore be viewed as a structureless, charged space curve, i.e., a wormlike polymer with a continuous charge distribution.

In this paper, we shall calculate the electrostatic persistence length of a charged wormlike polymer which is sufficiently stiff that no excluded volume effects are present. The electrostatic persistence length, P_{el} , is approximately related to $\langle h_0^2 \rangle$ by:⁸

$$\langle h_0^2 \rangle = 2L(P_0 + P_{el}) = 2LP_T \quad (\text{I.1})$$

where L = contour length of the chain; $P_0 \equiv$ persistence length in the absence of electrostatic forces (i.e., $C_s \rightarrow \infty$); and $P_T \equiv$ total persistence length; P_{el} is obtained for (i) a continuous, uniform charge distribution without charge rearrangements due to bending and without fluctuations due to thermal motion. Our results are then compared with experimental data on carboxymethylcellulose dimensions and reasonably good agreement is demonstrated. Furthermore, in the Appendix we consider three additional calculations relating to P_{el} : (ii) the discrete model with no charge rearrangements or fluctuations; (iii) the continuous charge distribution with charge rearrangements, but no fluctuations; and (iv) the continuous charge distribution with charge rearrangements and fluctuations. The results of case (ii) reduce to the continuous charge distribution result (i) if $\kappa a \rightarrow 0$. (Here a is length of a monomer

unit.) Finally, cases (iii) and (iv) reduce to case (i) if the polymer is assumed to be locally stiff; the exact definition of local stiffness will be presented in the body of the paper.

(II) The Charged Wormlike Polymer

(A) General Formalism. Consider a charged space curve whose infinitesimal elements interact via a screened Coulomb potential. We wish to calculate the electrostatic persistence length, P_{el} . V , the increase in potential energy per unit length due to electrostatic repulsions relative to the reference configuration of a straight rod, is given by:⁸

$$V = \frac{1}{2} \epsilon R_c^{-2} \quad (\text{II.1})$$

ϵ = bending constant of the rod and R_c is the radius of curvature of the element of space curve at which V is evaluated.

It then follows immediately from the worm model that

$$\frac{\langle h_0^2 \rangle}{L} - 2P_0 = 2P_{el} = \frac{2\epsilon}{k_B T} \quad (\text{II.2})$$

k_B is Boltzmann's constant. Thus, we direct our attention to determining the explicit form of $\epsilon = \epsilon(\kappa)$ in eq II.1.

Let us choose the origin at an arbitrary point somewhere in the middle of the space curve, and let us parameterize the space curve by s , the contour length relative to the origin. If $\mathbf{F}(s)$ is the location of a point on the space curve relative to the origin, then

$$\mathbf{F}(s) = f(s)\hat{i} + g(s)\hat{j} + h(s)\hat{k} \quad (\text{II.3})$$

where \hat{i} , \hat{j} , \hat{k} are unit vectors in the x , y , z directions, respectively. Define $\mathbf{F}_0(s)$ to be the location of the point in the straight rod reference configuration. We shall choose the reference configuration to lie along \hat{i} so that we can write

$$\mathbf{F}_0(s) = s\hat{i} = f_0(s)\hat{i} \quad (\text{II.4})$$

Now, the length of the space curve must remain invariant, i.e.,

$$\begin{aligned} s(b) &= \int_0^b [(f'(s))^2 + (g'(s))^2 + (h'(s))^2]^{1/2} ds \\ &= \int_0^b [(f_0'(s))^2]^{1/2} ds \quad (\text{II.5}) \end{aligned}$$

for any arbitrary b . The prime denotes differentiation with respect to s . Hence,

$$(f'(s))^2 + (g'(s))^2 + (h'(s))^2 = (f_0'(s))^2 = 1 \quad (\text{II.6})$$

Setting $f'(s) = 1 - \delta(s)$, where $\delta(s) > 0$, we find on direct substitution into eq II.6 and on solving the quadratic that results

$$\delta(s) = 1 - [1 - \{(g'(s))^2 + (h'(s))^2\}]^{1/2} \quad (\text{II.7})$$

We now introduce the concept of local stiffness; i.e., $g'(s)^2 + h'(s)^2 \ll 1$ (we see later this is equivalent to neglecting terms of order R_c^{-4})

$$f'(s) = 1 - \delta(s) = 1 - \frac{1}{2} \{(g'(s))^2 + (h'(s))^2\} \quad (\text{II.8})$$

Furthermore, the unit tangent vector $\mathbf{u}(s)$ is given by

$$\mathbf{u}(s) = (f'(s), g'(s), h'(s)) \quad (\text{II.9})$$

A general property of unit tangent vectors and their derivatives follows from $\mathbf{u}(s) \cdot \mathbf{u}(s) \equiv 1$.

$$\mathbf{u}(s) \cdot \frac{\partial \mathbf{u}(s)}{\partial s} = f'(s)f''(s) + g'(s)g''(s) + h'(s)h''(s) = 0 \quad (\text{II.10})$$

From eq II.8, it follows that

$$f''(s) = -\{g'(s)g''(s) + h'(s)h''(s)\}$$

and eq II.10 becomes

$$\{g'(s)g''(s) + h'(s)h''(s)\}\{(g'(s))^2 + (h'(s))^2\} = 0 \quad (\text{II.11})$$

This implies that

$$f''(s) = 0 \quad (\text{II.11a})$$

Furthermore, the radius of curvature is related to $\partial \mathbf{u}/\partial s$ by

$$R_c^{-2} = \frac{\partial \mathbf{u}(s)}{\partial s} \cdot \frac{\partial \mathbf{u}(s)}{\partial s} = (h''(s))^2 + (g''(s))^2 \quad (\text{II.12})$$

the last expression follows from eq II.11.

A general property of $g(s)$, $h(s)$, $h'(s)$, and $g'(s)$ is that they must vanish at $s = 0$; i.e., the reference and given configurations have the same tangent vector at the origin. By expanding $g(s)$, $g'(s)$, $h(s)$, and $h''(s)$ in a Taylor series about $s = 0$ and using eq II.12 we find

$$\mathbf{F}(s) = \left(s - \frac{s^3}{6R_c^2(0)}, \frac{g''(0)s^2}{2}, \frac{h''(0)s^2}{2} \right) \quad (\text{II.13})$$

(B) Continuous Charge Distribution with No Rearrangements or Fluctuations. Let $V^* \equiv$ potential at origin, per unit charge, due to electrostatic repulsion relative to the straight rod configuration. We shall neglect intermolecular interactions and assume the polyelectrolyte is a polyacid.

$$V^* = \frac{\sigma_0}{D} \left[\int_0^{L_1} \left\{ \frac{e^{-\kappa|\mathbf{F}(s)|}}{|\mathbf{F}(s)|} - \frac{e^{-\kappa s}}{s} \right\} ds + \int_0^{L_2} \left\{ \frac{e^{-\kappa|\mathbf{F}(s)|}}{|\mathbf{F}(s)|} - \frac{e^{-\kappa s}}{s} \right\} ds \right] \quad (\text{II.14})$$

where $\sigma_0 \equiv$ charge per unit length; $\sigma_0 \equiv \alpha q/a = \alpha \Gamma_0$ ($\Gamma_0 \equiv q/a$); $\alpha \equiv$ degree of ionization; $q \equiv$ charge per monomer unit; $a \equiv$ length of monomer unit; $1/\kappa = (1000Dk_B T/4\pi e^2 N_A \sum_i C_i Z_i^2)^{1/2}$; $e =$ charge on a proton; $C_i =$ concentration of ionic species “ i ” in solution; $Z_i =$ valence of i th species; and $D =$ solvent dielectric constant. L_1 and L_2 are the arc lengths of the curve from the origin to the ends. In what follows, we assume that the interaction is sufficiently short ranged that letting $L_1, L_2 \rightarrow \infty$ does not affect the result.

$$V^* = \frac{2\sigma_0}{D} \int_0^\infty \left\{ \frac{e^{-\kappa|\mathbf{F}(s)|}}{|\mathbf{F}(s)|} - \frac{e^{-\kappa s}}{s} \right\} ds \quad (\text{II.15})$$

Now,

$$|\mathbf{F}(s)| = s \left\{ 1 - \frac{s^2}{12R_c^2(0)} \right\}^{1/2} \quad (\text{II.16})$$

The last step follows from eq II.12.

We expand $|\mathbf{F}(s)|$ and $e^{-\kappa|\mathbf{F}(s)|}$ in a Taylor series about s

$= 0$ to terms of order $1/R_c^2$. (This is the local stiffness approximation.) Hence,

$$\frac{e^{-\kappa|\mathbf{F}(s)|}}{|\mathbf{F}(s)|} = e^{-\kappa s} \left\{ \frac{1}{s} + \frac{s}{24R_c^2(0)} + \frac{\kappa s^2}{24R_c^2(0)} \right\} \quad (\text{II.17})$$

Substitution of eq II.17 into eq II.15 yields

$$V^* = \sigma_0/4\kappa^2 D R_c^2(0) \quad (\text{II.18})$$

Therefore, the potential of an element of length dl is

$$V dl = \frac{1}{2} V^* dq = \frac{1}{2} V^* \sigma_0 dl$$

or

$$V = \alpha^2 \Gamma_0^2 / 8\kappa^2 D R_c^2(0) \quad (\text{II.19})$$

The factor of $1/2$ is introduced to avoid overcounting; i.e., we wish to consider the potential acting on each infinitesimal element only once. Furthermore, we have substituted $\alpha \Gamma_0$ for σ_0 .

Comparing eq II.19 to eq II.1, it is readily seen that

$$\epsilon = \alpha^2 \Gamma_0^2 / 4\kappa^2 D \quad (\text{II.20})$$

Substituting the value of ϵ in eq II.20 into eq II.2 we find

$$2P_{el}^{\text{theo}} = \alpha^2 \Gamma_0^2 / 2\kappa^2 k_B T D \quad (\text{II.21})$$

for the uniformly charged rod without charge rearrangements due to bending and without fluctuations.

(III) Comparison of Theory with Experiment

In the development of the wormlike polyelectrolyte model, it is assumed that (1) $1/\kappa > a$; (2a) excluded volume effects are negligible; and (2b) the polyelectrolyte is locally stiff. Condition (1) can be relaxed by an explicit consideration of the discrete charge nature of the chain (see Appendix). However, the region where P_{el} contributes significantly to P_T is precisely that domain where (1) is valid. Furthermore, condition (1) puts restraints on the range of ionic strengths, I , where our treatment is applicable. For (2a) to hold in general, we must examine the polyelectrolyte in low I , theta solvents. Unfortunately, the existing measurements are in theta solvents at relatively high I ; our theory predicts a very slight dependence on I , as is observed.^{4,5} Hence, we must choose a system at low I in which the polyelectrolyte is sufficiently stiff that excluded volume effects are negligible anyway. Finally, since light scattering gives an unambiguous determination of polyelectrolyte dimensions, it is the method of choice.

On the basis of the above, we decided to compare the experimentally determined dimensions of carboxymethylcellulose, CMC,⁹ in aqueous NaCl solutions with those of our theory in the following way: Schneider and Doty determined b^{exptl} by light scattering.

$$(b^{\text{exptl}})^2 = \langle h^2 \rangle / N \quad (\text{III.1})$$

Here, N is the degree of polymerization and the measurements were corrected for polydispersity.

b^{theo} is obtained from eq I.1, III.1, and $L = Na$ by equating

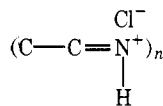
$$2P_T = b^2/a \quad (\text{III.2})$$

We then plot the experimentally determined b vs. $I^{-1} 2P_0^{\text{exptl}}$ is related to the zero intercept of b^{exptl} by eq II.1 and III.2; using eq II.1 and II.21, we have

$$\frac{(b^{\text{theo}})^2}{a} = 2P_0^{\text{exptl}} + \frac{\alpha^2 \Gamma_0^2}{2\kappa^2 D k_B T} \quad (\text{III.3})$$

The experimental and theoretical data are shown in Table I. Agreement between the experimentally determined and theoretical electrostatic persistence lengths is quite good.

One of the surprising results of our literature search to find suitable data is the lack of light-scattering measurements on polyelectrolytes at low ionic strength. Moreover, we were unable to find any light-scattering data on polyethylene imine hydrochloride, PEI(HCl):



PEI(HCl) conforms perfectly to the charged worm model: it has no side chains, and all the charges are located on the backbone of the polymer. Clearly, more experimental work is necessary to test the validity of the proposed model.

IV. Conclusions

In conclusion, the theory of wormlike polymers has been extended to polyelectrolytes. Inherent with the limitations discussed in the previous section, we have been able to demonstrate that $\langle h_0^2 \rangle$ of a charged wormlike chain does in fact depend on C_s . It consequently appears necessary that polyelectrolyte excluded volume theory be reexamined to incorporate $\langle h_0^2 \rangle = \langle h_0^2(C_s) \rangle$. This is an important problem which we hope to treat in the future.

Appendix

The discrete model with no charge rearrangements or fluctuations, case (ii), is treated: Using the approximations employed in case (i), the potential energy, V' , at a given charge site is

$$V' = \frac{q^2}{D} \sum_{j=1}^N \frac{e^{-\kappa ja/\alpha}}{24R_c^2(0)} (ja/\alpha + \kappa j^2 a^2/\alpha^2) \quad (\text{A1})$$

Equation A1 is essentially the discrete version of eq II.14. Here a single sum is employed to correct for overcounting. Consider the sum

$$\psi(\kappa a \alpha^{-1}) = \sum_{j=1}^N e^{-\kappa ja \alpha^{-1}} = \frac{(1 - e^{-\kappa a \alpha^{-1}(N+1)})}{(1 - e^{-\kappa a \alpha^{-1}})} - 1$$

In the limit that $N \rightarrow \infty$

$$\psi(\kappa a \alpha^{-1}) = \{1 - e^{-\kappa a \alpha^{-1}}\}^{-1} - 1 \quad (\text{A2})$$

Furthermore,

$$\frac{-d\psi}{d\kappa} = \sum_{j=1}^{\infty} (ja\alpha^{-1}) e^{-\kappa ja\alpha^{-1}} = \frac{\alpha\alpha^{-1} e^{-\kappa a\alpha^{-1}}}{(1 - e^{-\kappa a\alpha^{-1}})^2} \quad (\text{A3})$$

$$\frac{d^2\psi}{d\kappa^2} = \frac{\alpha^2 \alpha^{-2} e^{-\kappa a\alpha^{-1}}}{(1 - e^{-\kappa a\alpha^{-1}})^2} + \frac{2\alpha^2 \alpha^{-2} e^{-2\kappa a\alpha^{-1}}}{(1 - e^{-\kappa a\alpha^{-1}})^3} \quad (\text{A4})$$

Substituting the expressions of eq A3 and A4 into eq A1, we obtain

$$V' = \frac{q^2}{24R_c^2(0)} \left\{ \frac{(\alpha\alpha^{-1} + \kappa a^2 \alpha^{-2}) e^{-\kappa a \alpha^{-1}}}{(1 - e^{-\kappa a \alpha^{-1}})^2} + \frac{2\kappa a^2 \alpha^{-2} e^{-2\kappa a \alpha^{-1}}}{(1 - e^{-\kappa a \alpha^{-1}})^3} \right\} \quad (\text{A5})$$

To pass from the discrete to the continuum model, we must let $\kappa a \alpha^{-1} \rightarrow 0$ subject to the constraint that $\alpha q/a$ remains fixed. Since V' is the potential energy experienced by a point charge on a segment of length $\alpha\alpha^{-1}$, the potential energy per unit length, V , equals $V' \alpha q a^{-1}$. Expanding the exponentials in eq A5,

$$V = \frac{\alpha^2 q^2}{24R_c^2(0) \alpha^2 D} \left\{ \frac{(1 - \kappa^2 a^2 \alpha^{-2})}{\kappa^2} + \frac{2}{\kappa^2} (1 - 2\kappa a \alpha^{-1}) \right\} \quad (\text{A6})$$

and

$$\lim_{\kappa a \alpha^{-1} \rightarrow 0} V = \frac{\alpha^2 \Gamma_0^2}{8\kappa^2 D R_c^2(0)} \quad (\text{A7})$$

Table I
Comparison of $2P_{el}$ with $2P_{el}^{theo}$ ^a

I	I^{-1}	$b^{exptl}, \text{\AA}$	$2P_T, \text{\AA}$	$2P_{el}, \text{\AA}$	$2P_{el}^{theo}, \text{\AA}$	$b^{theo}, \text{\AA}$
0.5	2	40.2			2.92	
0.05	20	43.1	360.7	27.9	29.2	43.1
0.01	100	49.8	481.6	148.5	146.0	49.6
0.005	200	58.1	655.4	335.6	292.1	56.7

^a For CMC, $\alpha = 5.15 \text{\AA}$, the degree of substitution is 1.15, $\alpha = 0.96$, and $M_w = 4.4 \times 10^5$ (Schneider and Doty^{9a}). Rice and Harris^{9b} give $2P_0 = 335 \text{\AA}$ in agreement with our extrapolated value $2P_0 = 332.8 \text{\AA}$. A value of 80 was used for the dielectric constant D .

In exact agreement with eq II.19.

We now consider case (iii): the continuous charge distribution with charge rearrangements but no fluctuations. The change in free energy of the charged space curve relative to the straight rod configuration, ΔG , can be decomposed into three parts: First, there is the term arising from the excess electrostatic interaction due to bending between various parts of the polyelectrolyte. For definiteness, we shall assume the polymer is a polyacid. Then, there is an entropic contribution arising from the mixing of occupied and unoccupied sites. A site is said to be occupied if it has a net negative charge and unoccupied if the site has no net charge. When the polymer is bent, the fraction of occupied sites will perhaps change; this gives rise to the entropy of mixing term and the third contribution to ΔG , the addition of hydrogen ions from the solution to the polyelectrolyte which acts to reduce the repulsive force between segments.

Before presenting an expression for ΔG , we shall derive an expression for the entropy of mixing. Random mixing is assumed.

For a discrete array of charges

$$\Delta S_{\text{mixing}} = -k_B (N_1^f \ln X_1^f + N_2^f \ln X_2^f - N_1^i \ln X_1^i - N_2^i \ln X_2^i) \quad (\text{A8})$$

Here i and f refer to the initial and final states. N_1 is the net number of sites occupied by a negative charge whose valence is determined by the nature of the individual polyacid. N_2 is the number of sites occupied by H^+ ions.

$$\text{Let } X_j = \frac{N_j}{(N_1 + N_2)}$$

$$\frac{N_1^f}{L} = \sigma, \frac{N_2^f}{L} = \omega - \sigma, \text{ and } \frac{N_1^i}{L} = \sigma_{\text{ref}}$$

(the straight rod configuration is the reference configuration) where ω is the total number of sites per length. Thus

$$X_1^f = \sigma/\omega, X_2^f = 1 - \sigma/\omega, \sigma_{\text{ref}}/\omega = \alpha$$

The continuous version of eq A.8 becomes

$$\Delta S_{\text{mixing}} = -k_B \left[\int_0^L ds \{ \sigma \ln(\sigma/\omega) + (\omega - \sigma) \ln(1 - \sigma/\omega) - \sigma_{\text{ref}} \ln \alpha - (\omega - \sigma_{\text{ref}}) \ln(1 - \alpha) \} \right]$$

Here we have parameterized the arc length from one end of the worm. Thus, ΔG is given by

$$\Delta G = \frac{\Gamma_0^2}{2\omega^2 D} \int_0^L \int_0^L ds ds' \times \left\{ \sigma(s)\sigma(s')U(|s-s'|) - \sigma_{\text{ref}}^2 \frac{e^{-\kappa s}}{s} \right\} - T \Delta S_{\text{mixing}} + k_B T \int_0^L ds (\sigma(s) - \sigma_{\text{ref}}) \ln \alpha_{H^+} \quad (\text{A9})$$

where

$$U(|s - s'|) = e^{-\kappa|s-s'|} \left\{ \frac{1}{|s - s'|} + \frac{|s - s'|}{24R_c^2(s)} + \frac{\kappa|s - s'|^2}{24R_c^2(s)} \right\}$$

a_{H^+} is the activity of the hydrogen ion in solution, i.e., at an infinite distance from the polyelectrolyte. The last term in eq A.9 arises from the free-energy contribution due to H^+ addition caused by the bending of the chain.

We shall now assume that the charge distribution varies slowly on the scale of the range of the interaction, κ^{-1} . At least to lowest order, $\sigma(s)$ and $\sigma(s')$ are functionals of and change on the scale of the variation in R_c^{-2} . In the local stiffness approximation, $R_c^{-2}(s)$ is approximately constant, and as in the derivation of case (i), we implicitly assume the distance over which R_c^{-1} is constant $> \kappa^{-1}$. Hence, setting $\sigma(s) \simeq \sigma(s')$ should be a valid approximation. Thus,

$$\begin{aligned} \Delta G(\sigma) = & \frac{\Gamma_0^2}{2\omega^2 D} \left[\int_0^L ds \sigma^2(s) \int_0^L ds' U(|s - s'|) \right. \\ & \left. - \int_0^L ds \int_0^L ds' \sigma_{\text{ref}}^2 \frac{e^{-\kappa|s-s'|}}{|s - s'|} \right] - T\Delta S_{\text{mixing}} \\ & + k_B T \int_0^L ds (\sigma(s) - \sigma_{\text{ref}}) \ln a_{H^+} \quad (\text{A10}) \end{aligned}$$

Set

$$I \equiv \frac{1}{2} \int_0^L ds' \frac{e^{-\kappa|s-s'|}}{|s - s'|} = \int_{0^+}^{\infty} ds'' \frac{e^{-\kappa s''}}{s''} \quad (\text{A11})$$

s'' denotes the arc length from an origin defined at a point s along the curve. Note that the lower limit of the integral in eq A11 is really not zero but a ; the real lower limit arises from consideration of the discrete nature of the chain. The integral I may be large but it is finite. Furthermore, that the lower limits of the other integrals in (A10) may be replaced by zero follows from our discussion in case (ii).

Similarly,

$$\begin{aligned} H(s) = & \frac{1}{2} \int_0^L ds' e^{-\kappa|s-s'|} \left\{ \frac{|s - s'|}{24R_c^2(s)} + \frac{\kappa|s - s'|^2}{24R_c^2(s)} \right\} \\ & \simeq \frac{1}{8\kappa^2 R_c^2(s)} \end{aligned}$$

For convenience we shall write $R_c^{-2}(s)$ as R_c^{-2} . Substituting the expressions for I and $H(s)$ into eq A10 we obtain

$$\begin{aligned} \Delta G(\sigma) = & \frac{\Gamma_0^2}{\omega^2 D} \int_0^L ds \sigma^2(s) H(s) \\ & + \frac{\Gamma_0^2}{\omega^2 D} \int_0^L ds I (\sigma^2(s) - \sigma_{\text{ref}}^2) - T\Delta S_{\text{mixing}} \\ & + k_B T \int_0^L ds (\sigma(s) - \sigma_{\text{ref}}) \ln a_{H^+} \quad (\text{A12}) \end{aligned}$$

Now, ΔG is a functional of $\sigma(s)$; it can therefore be expanded about the most probable value of σ , $\bar{\sigma}$, as follows:

$$\Delta G(\sigma) = \Delta G(\bar{\sigma}) + \frac{1}{2} \int_0^L ds \left[\frac{\delta^2 \Delta G}{\delta \sigma^2} \right]_{\sigma=\bar{\sigma}} (\sigma - \bar{\sigma})^2 \quad (\text{A13})$$

Here $\delta^2 G / \delta \sigma^2$ is the second functional derivative of G with respect to σ . The second term on the rhs of eq A13 is related to charge fluctuations; we shall consider it further under case (iv). Furthermore by definition,

$$\left[\frac{\delta \Delta G}{\delta \sigma} \right]_{\sigma=\bar{\sigma}} = 0$$

Thus $\bar{\sigma}$ can be calculated from

$$\begin{aligned} \frac{\delta \Delta G}{\delta \sigma} \Big|_{\sigma=\bar{\sigma}} = & \frac{2\bar{\sigma}\Gamma_0^2}{\omega^2 D} \{H(s) + I\} \\ & + k_B T \ln \{\bar{\sigma}/(\omega - \bar{\sigma})\} + k_B T \ln a_{H^+} = 0 \quad (\text{A14}) \end{aligned}$$

If we let $R_c^{-2} \rightarrow 0$ then $\bar{\sigma} = \sigma_{\text{ref}}$, and it follows from eq A.14 that

$$I = \frac{2.303 k_B T D \omega p K_{\text{app}}}{2\alpha \Gamma_0^2} \quad (\text{A15})$$

$$pK_{\text{app}} = \text{pH} - \log \{\alpha/(1 - \alpha)\}$$

Let

$$\bar{\sigma} = \sigma_{\text{ref}} - \frac{A}{R_c^2} \quad (\text{A16})$$

where A is a constant to be determined.

Substituting eq A16 into eq A14 and expanding out logarithmic terms in $\bar{\sigma}$ to order R_c^{-2} , we find that

$$\bar{\sigma} = \sigma_{\text{ref}} - \frac{\alpha^2(1 - \alpha)\Gamma_0^2}{4D\kappa^2 k_B T \{(1 - \alpha)2.303 p K_{\text{app}} + 1\}} \quad (\text{A17})$$

Note that $\bar{\sigma} \rightarrow \sigma_{\text{ref}}$ as $\alpha \rightarrow 0$ and $\alpha \rightarrow 1$ as would be intuitively expected.

Using eq A17 in eq A12 for $\sigma = \bar{\sigma}$ and taking the derivative of $\Delta G(\bar{\sigma})$ with respect to L , one finds to order R_c^{-2}

$$\begin{aligned} \frac{\partial \Delta G(\bar{\sigma})}{\partial L} = & \frac{\partial V(\bar{\sigma})}{\partial L} - \frac{T \partial \Delta S_{\text{mixing}}(\bar{\sigma})}{\partial L} + k_B T (\bar{\sigma} - \sigma_{\text{ref}}) \ln a_{H^+} \\ \frac{\partial V(\bar{\sigma})}{\partial L} = & \frac{\alpha^2 \Gamma_0^2}{8D\kappa^2 R_c^2} - \frac{2.303\alpha^2(1 - \alpha)\Gamma_0^2 p K_{\text{app}}}{4D\kappa^2 \{2.303 p K_{\text{app}}(1 - \alpha) + 1\} R_c^2} \quad (\text{A18}) \end{aligned}$$

$$- \frac{T \partial \Delta S_{\text{mixing}}(\bar{\sigma})}{\partial L} = - \frac{\alpha^2 \Gamma_0^2 (1 - \alpha) \ln \{\alpha/(1 - \alpha)\}}{4D\kappa^2 \{2.303 p K_{\text{app}}(1 - \alpha) + 1\} R_c^2}$$

$$k_B T (\bar{\sigma} - \sigma_{\text{ref}}) \ln a_{H^+} = \frac{2.303\alpha^2(1 - \alpha)\Gamma_0^2 \text{pH}}{4D\kappa^2 \{2.303 p K_{\text{app}}(1 - \alpha) + 1\} R_c^2}$$

Substituting the explicit forms of $\partial V/\partial L$, $-T \partial \Delta S_{\text{mixing}}/\partial L$, $k_B T (\bar{\sigma} - \sigma_{\text{ref}}) \ln a_{H^+}$ to order R_c^{-2} into $\partial \Delta G(\bar{\sigma})/\partial L$,

$$\frac{\partial \Delta G(\bar{\sigma})}{\partial L} = \frac{\alpha^2 \Gamma_0^2}{8\kappa^2 D R_c^2} \quad (\text{A19})$$

Thus, the result of case (iii) is identical with the result of case (i) to terms of order R_c^{-2} .

We now examine (iv): the continuous charge model with charge rearrangements and fluctuations. If we do not assume $\sigma(s) = \sigma(s')$, eq A13 can be rewritten as

$$\begin{aligned} \Delta G(\sigma) = & \Delta G(\bar{\sigma}) + \frac{1}{2} \int_0^L \int_0^L ds ds' \left[\frac{\delta^2 \Delta G}{\delta \sigma(s) \delta \sigma(s')} \right]_{\sigma=\bar{\sigma}} \\ & \times (\sigma(s) - \bar{\sigma}(s)) (\sigma(s') - \bar{\sigma}(s')) \quad (\text{A20}) \end{aligned}$$

It follows directly from eq A9 that

$$\begin{aligned} \frac{\delta^2 \Delta G}{\delta \sigma(s) \delta \sigma(s')} \Big|_{\sigma(s)=\bar{\sigma}(s)} = & \frac{\Gamma_0^2 e^{-\kappa|s-s'|}}{\omega^2 D} \\ & \times \left\{ \frac{1}{|s - s'|} + \frac{|s - s'|}{24R_c^2(s)} + \frac{\kappa|s - s'|^2}{24R_c^2(s)} \right\} + \frac{k_B T \delta(s - s')}{\alpha \omega (1 - \alpha)} \quad (\text{A21}) \end{aligned}$$

So that

$$\begin{aligned} \Delta G(\sigma) - \Delta G(\bar{\sigma}) = & \frac{\Gamma_0^2}{2D} \int_0^L \int_0^L ds ds' e^{-\kappa|s-s'|} \\ & \times \left\{ \frac{1}{|s - s'|} + \frac{|s - s'|}{24R_c^2(s)} + \frac{\kappa|s - s'|^2}{24R_c^2(s)} \right\} \gamma(s) \gamma(s') \\ & + \frac{k_B T \omega}{2\alpha(1 - \alpha)} \int_0^L ds \gamma^2(s) \quad (\text{A22}) \end{aligned}$$

where

$$\gamma(s) = \{\sigma(s) - \bar{\sigma}(s)\}/\omega$$

and $\Delta G(\bar{\sigma})$ is approximated by the value obtained when $\sigma(s) \simeq \sigma(s')$, i.e.,

$$\Delta G(\bar{\sigma}) = \int_0^L \frac{\alpha^2 \Gamma_0^2}{8\kappa^2 D R_c^2(s)} ds$$

Furthermore, we approximate

$$\int_0^L \int_0^L ds ds' \frac{e^{-\kappa|s-s'|}}{|s-s'|} \gamma(s)\gamma(s') \simeq 2 \int_0^L I \gamma^2(s) ds$$

since this term is very short ranged.¹¹ Hence,

$$\begin{aligned} \Delta G(\sigma) - \Delta G(\bar{\sigma}) &= \frac{\Gamma_0^2}{2D} \int_0^L \int_0^L ds ds' \frac{e^{-\kappa|s-s'|}}{24R_c^2(s)} \\ &\times \{|s-s'| + \kappa|s-s'|^2\} \gamma(s)\gamma(s') + \frac{\Gamma_0^2}{D} \int_0^L ds I \gamma^2(s) \\ &+ \frac{k_B T \omega}{2\alpha(1-\alpha)} \int_0^L \gamma^2(s) ds \quad (\text{A23}) \end{aligned}$$

We now expand $\gamma(s)$ and $\phi(r) = e^{-\kappa r}(r + \kappa r^2)$ in a truncated Fourier series

$$\begin{aligned} \gamma(s) &= \sum_{j=0}^{L\omega} c_j \cos [(2\pi j s)/L] + c_j' \sin (2\pi j s/L) \\ c_j &= \frac{2}{L} \int_0^L \gamma(s) \cos [(2\pi j s)/L] ds \\ c_j' &= \frac{2}{L} \int_0^L ds \gamma(s) \sin [(2\pi j s)/L] \quad (\text{A24}) \\ \phi(s) &= \sum_{j=0}^{L\omega} \phi_j \cos (2\pi j s/L) \\ \phi_j &= \left(\frac{2}{L}\right) \int_0^L ds \phi(s) \cos (2\pi j s/L) \end{aligned}$$

If we assume $L \gg$ range of interaction of $\phi(r)$, it follows that^{12,13}

$$\begin{aligned} \Delta G(\sigma) - \Delta G(\bar{\sigma}) &= \frac{\Gamma_0^2 L^2}{96 D R_c^2} \sum_{j=0}^{L\omega} (c_j^2 + c_j'^2) \phi_j \\ &+ \frac{L}{2} \left[\frac{k_B T \omega}{2\alpha(1-\alpha)} + \frac{\Gamma_0^2 I}{D} \right] \left[\sum_{j=0}^{L\omega} c_j^2 + c_j'^2 \right] \quad (\text{A25}) \end{aligned}$$

Furthermore, the excess electrostatic free energy due to bending, G , is given by¹⁴

$$\begin{aligned} \exp(-\beta(G - \Delta G(\bar{\sigma}))) &= L^N \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} dc_0 \\ &\times \prod_{j=1}^{L\omega} dc_j dc_j' \exp W \quad (\text{A26a}) \end{aligned}$$

$$\begin{aligned} W &= -\beta \left\{ \frac{\Gamma_0^2 L^2}{96 D R_c^2} \sum_{j=0}^{L\omega} (c_j^2 + c_j'^2) \phi_j \right. \\ &\left. + \frac{L}{2} \left[\frac{k_B T \omega}{2\alpha(1-\alpha)} + \frac{\Gamma_0^2 I}{D} \right] \left[\sum_{j=0}^{L\omega} (c_j^2 + c_j'^2) \right] \right\} \end{aligned}$$

Evaluating the integrals and taking the logarithm of both sides, we obtain

$$G = \Delta G(\bar{\sigma}) + k_B T \sum_{m=0}^{L\omega} \ln \left(Z + \frac{\Phi_m}{R_c^2} \right) - k_B T L \omega \ln 4\pi k_B T \quad (\text{A26b})$$

where

$$Z = \frac{k_B T}{\alpha(1-\alpha)} + \frac{2\Gamma_0^2 I}{D}$$

$$\Phi_m = \frac{L \Gamma_0^2 \phi_m}{12}$$

To obtain G_{net} , the net electrostatic free energy due to bending, we must let $R_c^{-2} \rightarrow 0$ and subtract that result from eq A26b. Hence,

$$G_{\text{net}} = \int_0^L ds \frac{\alpha^2 \Gamma_0^2}{8\kappa^2 D R_c^2} + \frac{\Gamma_0^2 \alpha(1-\alpha) Y(L\omega, \kappa)}{12\omega D \{2.303 p K_{\text{app}}(1-\alpha) + 1\} R_c^2} \quad (\text{A27})$$

$$Y(L\omega, \kappa) = \sum_{m=0}^{L\omega} \frac{3\kappa^4 - m^4 - 6\kappa^2 m^2}{(\kappa^2 + m^2)^3}$$

Here, the explicit expression for Φ_m has been substituted.

Furthermore, the sum can be evaluated by approximating it as an integral. Then,

$$\begin{aligned} \frac{\partial G_{\text{net}}}{\partial L} &= \frac{\alpha^2 \Gamma_0^2}{8\kappa^2 D R_c^2} \\ &+ \frac{\alpha(1-\alpha) \Gamma_0^2 (3\kappa^2 + 4\pi^2 \omega^2)}{12D(2.303 p K_{\text{app}}(1-\alpha) + 1)(\kappa^2 + 4\pi^2 \omega^2)^2 R_c^2} \quad (\text{A28}) \end{aligned}$$

However, $1/\kappa \gg a = 1/\omega$ or $\omega \gg \kappa$ so that

$$\frac{\partial G_{\text{net}}}{\partial L} \simeq \frac{\alpha^2 \Gamma_0^2}{8\kappa^2 D R_c^2} + \frac{\alpha(1-\alpha) \Gamma_0^2}{12D(2.303 p K_{\text{app}}(1-2) + 1) 4\pi^2 \omega^2 R_c^2} \quad (\text{A29})$$

$$\begin{aligned} 2P_{\text{el}}^{\text{theo}} &= \frac{\alpha^2 \Gamma_0^2}{2\kappa^2 D k_B T} \\ &+ \frac{\alpha(1-\alpha) \Gamma_0^2}{3D k_B T (2.303 p K_{\text{app}}(1-\alpha) + 1) 4\pi^2 \omega^2} \quad (\text{A30}) \end{aligned}$$

By comparing typical experimental data¹⁵⁻¹⁷ for the fluctuating term with calculated values of $\alpha^2 \Gamma_0^2 / 2\kappa^2 k_B T D$, it is readily seen that the charge fluctuation contribution is negligible.

Acknowledgment. One of us, J. S., would like to thank A. Holtzer of Washington University, St. Louis, Mo., for enlightening discussions. This work was supported by NIH Grant No. GM 13556.

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- (11) See discussion preceding eq A10. In fact, even if we do not make the assumption that $\gamma(s) \approx \gamma(s')$, the results of case (iv) will still hold.
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