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Citation: J. Chem. Phys. 94, 8479 (1991); doi: 10.1063/1.460081
View online: http://dx.doi.org/10.1063/1.460081
View Table of Contents: http://jcp.aip.org/resource/1/JCPSA6/v94/i12
Published by the American Institute of Physics.

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Monte Carlo electrostatic persistence lengths compared with experiment and theory

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(Received 19 December 1990; accepted 14 March 1991)

An off-lattice rotational isomeric state model Monte Carlo algorithm for a polyelectrolyte with Debye–Hueckel screening and no hard core repulsion is used to generate short (up to 150 unit) chains at (1) different ionic strengths, (2) varying uniform charge densities, and (3) pH–pK₀ governed ionization. The mean square radii of gyration are related to the apparent total persistence lengths of the polyelectrolytes via the wormlike chain model. Near the random coil limit the apparent electrostatic persistence length varies approximately as the inverse square root of the ionic strength and linearly with charge density. The persistence length behavior is very similar in cases (2) and (3). These approximate power laws agree well with those found experimentally for hyaluronate and variably ionized polyacrylic acid. The original electrostatic persistence length theory, which does not contain excluded volume effects, predicts power law exponents which are twice these. Corrections due to polyelectrolyte excluded volume theories do not consistently yield good fits to the data, but do give “pseudo-” or weakly changing power laws similar to those obtained from the Monte Carlo and experimental data. The similarity between the Monte Carlo and experimental results may indicate that the Debye–Hueckel approximation is reasonable, and that the neglect of hard core repulsion (e.g., zero chain diameter) is insignificant compared to electrostatic effects. This lends strength to the interpretations that electrostatic excluded volume effects explain much of the apparent deviation from the electrostatic persistence length theory and that the approximation of a smeared out line charge works fairly well, even when the actual charges are irregularly spaced.

I. INTRODUCTION

Several reports on apparent persistence lengths of long, flexible polyelectrolytes, obtained from viscosity and light scattering measurements, show the apparent electrostatic persistence length L;*, defined below, varying as the inverse square root of the ionic strength.¹–⁴ One work found L;* approximately proportional to the polyelectrolyte’s linear charge density. In these articles it was argued that since the long polyelectrolytes had contour lengths L much greater than the total persistence length Lₑ, the molecules could be treated in the coil limit of the wormlike chain model relation⁵ between mean square radius of gyration ⟨S²⟩₀ and Lₑ. That is,

\[ ⟨S²⟩₀ = \frac{LLₑ}{3} - \frac{L}{Lₑ} + 2Lₑ/L \]

\[ - 2(Lₑ/L) [1 - \exp(-L/Lₑ)] \]

becomes

\[ ⟨S²⟩₀ = \frac{LLₑ}{3}. \]

(1a)

The subscript on ⟨S²⟩₀ is to emphasize that Eq. (1) does not include excluded volume effects. Here, \( Lₑ = L₀ + Lₑ \), where \( L₀ \) is the intrinsic persistence length and \( Lₑ \) the electrostatic persistence length.⁶–⁷

We now define what we mean by an “apparent electrostatic persistence length” obtained from light scattering data. First we define an apparent total persistence length \( L;* \). Equation (1b) yields \( Lₑ = 3⟨S²⟩₀/L \) for wormlike chains in the Gaussian random coil limit \( L >> Lₑ \), which holds only if there is no excluded volume.⁵ Static light scattering gives \( ⟨S²⟩ \), and \( Lₑ \) can be estimated by combining knowledge of the polymers molecular weight \( M \) from static light scattering, and of the repeating unit of the polymer. (Reference 3 discusses how to deal with polydispersity effects for large polymers.) Thus if the molecular weight of a repeating unit is \( m₀ \), and its contour length is \( L₀ \), \( L = L₀ M/m₀ \). Then, in analogy to Eq. (1b), the apparent total persistence length is defined as

\[ L;* = 3⟨S²⟩₀/L. \]

(2a)

The use of the term “apparent,” indicated by a superscript prime, and the dropping of the subscript zero, are intended as reminders that, due to electrostatic excluded volume effects,⁸–¹¹ Eqs. (1) do not necessarily hold for an electrically charged polymer at low salt concentrations. Indeed, this work contends that electrostatic excluded volume effects can render \( L;* \) much larger than \( Lₑ \). These effects arise because a flexible chain can bend so that units far apart along the chain are placed in close proximity; if they carry the same charge they will then repel.

Following Refs. 6 and 7, it is assumed that the (actual) total persistence length \( Lₑ = L₀ + Lₑ \), where \( L₀ \) is the intrinsic persistence length of the polymer and \( Lₑ \) an electrostatic persistence length⁶–⁷ due to stiffening of the polymer by repulsion of like charges. To estimate \( L;* \) from \( Lₑ \), one first estimates \( L₀ \). This was done³–⁴ by finding the exponent \( β \) in \( L;* = aC^β + d \) which maximized the linearity of \( L;* \) vs \( C \) and extrapolating to \( C = 0 \). This should eliminate ele-
trogenic effects on both the persistence length and the excluded volume because it amounts to an extrapolation to complete electric field screening; nonelectrostatic excluded volume effects, if any, would remain. Then the apparent electrostatic persistence length \( L_* \) is

\[
L_* \equiv L^- - L_{0,\text{estimated}} \quad \text{(light scattering).}
\]

For the Monte Carlo calculations described below, Eq. (2a) was also used to find \( L^- \); however the structure of the model polymer and thus \( L_0 \) were known exactly, and we used

\[
L_* \equiv L^- - L_0 \quad \text{(Monte Carlo).}
\]

Similarly, since \( L \approx k^{-1} \) (\( k \) = the Debye–Hückel screening parameter, and is proportional to \( C^0 \), where \( C \) is the ionic strength), the original prediction of electrostatic persistence length is

\[
L_e = \left(1/12\right) \left(q^2/Dk_B T\right)N^2 \left[3y^2 - 8y^{-3} + e^{-y} \left(y^{-1} + 5y^{-2} + 8y^{-3}\right)\right],
\]

where \( y = \frac{k_B T}{4e^2 \sigma} \) is the dielectric constant of the solute, \( k_B \) is Boltzmann's constant, and \( N \) is the number of charge groups in the polymer, reduces to

\[
L_e = \frac{\xi^3}{4 \pi d_B^2},
\]

where \( d_B = q^2 / Dk_B T \) is the Bjerrum length (about 7.18 Å at 25 °C) and \( \xi \) is the macroion's linear charge density, expressed as number of elementary charges per Bjerrum length. \( L_e \) is thus predicted to show a quadratic dependence on charge density, and a reciprocal first power dependence on ionic strength.

The object of this article is to use a Monte Carlo algorithm to generate polyelectrolyte chains as a function of ionic strength and linear charge density, and to compare the resulting scaling behavior of \( \langle S^2 \rangle \) and the apparent persistence lengths with the previously reported light scattering results, and with Eqs. (1)–(4). The origin of the discrepancy between the predicted power laws for persistence length and the experimental power laws for apparent persistence length is then investigated in terms of the assumptions made in the theory, the Monte Carlo model, and the interpretation of the experimental results.

The apparent persistence lengths \( L^- \) and \( L_* \) deduced via Eqs. (1) and (2) from light scattering or Monte Carlo results for \( \langle S^2 \rangle \) would be the actual persistence lengths \( L^+ \) and \( L_* \) if Eqs. (1) held; i.e., if there were no excluded volume effects, i.e., if \( \langle S^2 \rangle = \langle S^2 \rangle_0 \). Since polyelectrolytes may display significant excluded volume effects at low salt concentrations, an analysis will be attempted in terms of polyelectrolyte excluded volume theories, following the prescription of Odijk and Houwaart. It is usual to define a factor \( \alpha \) by

\[
\langle S^2 \rangle = \alpha^2 \langle S^2 \rangle_0.
\]

The factor \( \alpha^2 \) thus contains excluded volume effects on \( \langle S^2 \rangle \). Previously, several somewhat ad hoc combinations of theories for polyelectrolyte excluded volume were considered; all of them followed Ref. 9 in using the limit (1b) of Eqs. (1) to make contact with excluded volume theories for Gaussian random coils. That is, long linear polyelectrolytes are treated as random coils with excluded volume by choosing their Kuhn segment length \( L_k \) to be \( 2L_T \) and the number of Kuhn segments \( n_k \) to be \( L / L_k \). Overall, the best correction used the Gupta–Forsman form for \( \alpha^2 \),

\[
\alpha^2 - \alpha^2_* = (134/105) \left(1 - 0.885n_{\text{K}}^{-0.463}\right) z,
\]

where \( z \) is the standard excluded volume parameter from perturbation theory;

\[
z = \left(3/2 \pi N \right)^{1/2} \beta n_{\text{K}}^{-1/2}.
\]

The Fixman–Skolnick form for the binary cluster integral \( \beta \) was used;

\[
\beta = 8L_\xi^2 k^{-1} \langle R \rangle(\omega),
\]

where \( \omega = 2\pi^2 d_B^{-1} k^{-1} \exp(-kd), \) \( d_B \) being the cylinder diameter, and

\[
\langle R \rangle(\omega) = \int_0^{\omega/2} \sin^2 \theta \int_0^{\omega/\sin \theta} x^{-1}(1 - e^{-x}) dx \, dx.
\]
polyacid. The change in free energy when a unit is ionized is taken to be $-k_B T (pH - pK_a) \ln(10)$, and is incorporated into the Metropolis Monte Carlo reptation algorithm. That is, an end of the polymer is selected randomly. A trial polymer configuration is generated from the existing one by adding a new unit to that end in one of six ways (3 rotational states times 2 ionization states) with equal probability and removing a unit from the other end, the rest of the polymer staying unchanged. The total change $\Delta F$ in free energy in going to the trial configuration is calculated as the change in electrostatic energy minus $k_B T (pH - pK_a) \ln(10)$ times the change in the number of ionized units. If $\Delta F > 0$ the trial configuration is always accepted and becomes the new configuration; if $\Delta F < 0$ the trial configuration is accepted with probability $\exp(-\Delta F/k_B T)$. The use of a quasithermal initial guess as the starting state keeps the algorithm from getting stuck in metastable initial configurations in which both ends of the polymer are highly charged while the middle was uncharged.

$N^2$ reptation attempts are made between taking “stroscopic profiles” of new chains thus generated. The information stored upon taking the profile includes total electrostatic energy, end-to-end length, radius of gyration, and fractional charge of the chain.

B. Previous investigations

We know of several Monte Carlo simulations of screened linear polyelectrolytes, some of which we have already mentioned. These works investigated counterion screening or Debye–Hückel screening only, on a lattice or off lattice, partially ionized chains, or fully ionized chains. We note two very recent papers. Christos and Carne found that although the simplest combination of Manning’s counterion condensation and Debye–Hückel theory seemed to have considerable merit, it did “not quantitatively agree” with their results. Hooper, Blanch, and Prausnitz compared polion end-to-end lengths to an improvement of a theory of Katchalsky and Lifson, which also predicts electrostatic energies. This end-to-end length prediction includes electrostatic excluded volume effects but not persistence length effects, and is somewhat analogous to our Eqs. (5)–(9). Its agreement with their Monte Carlo results was qualitative.

C. Situations investigated, parameter settings, and correspondence to wormlike chain

Three situations were investigated; the effects, especially on $\langle S^2 \rangle$, of (1) changing ionic strength (via the selectable Debye–Hückel screening length), (2) varying the linear charge density at full ionization (by changing the magnitude of the charge per monomer, each of which is ionized by making pH–pK_a large), and 3) varying the linear charge density via the degree of ionization of the chain (by changing the value of pH–pK_a at fixed charge magnitude per monomer). For convenience, the method of varying linear charge density by maintaining full ionization and reducing the magnitude of the charge per monomer will be denoted by uniform charge density (UCD), whereas the method involving variable ionization through variation of pH–pK_a will be referred to as random charge density (RCD). For all of these situations the bond angle was taken as 70° (as measured from the direction of propagation of the preceding link; 70° is thus close to the tetrahedral bond angle), the bond length was 7 Å, and no hard core excluded monomer volume was used.

Since the experimental results referred to in this work were obtained for long chains (well over 1000 monomers per chain) in the coil limit, it would have been desirable to likewise simulate long polyelectrolytes. As the computer cpu time per chain increases as about $N^3$, however, it was not feasible to do this and still generate enough samples for statistical accuracy. Accordingly, 150 unit chains were the largest investigated; this allowed collecting a fair amount of data on chains near the coil limit.

For uncharged 150 unit chains with the above parameters $\langle S^2 \rangle$ was 2428 ± 150 Å, and the mean square end-to-end length $\langle R^2 \rangle$ was 14.82 Å, in good agreement with the classical expression for a fixed valence angle $\theta$ rotameric state polymer of $N$ links of link length $A$ and without excluded volume effects:

$$\langle R^2 \rangle = 6 A^2 \left[1 + \cos \theta \left(1 + \eta \right) / \left(1 - \cos \theta \right) \left(1 - \eta \right) \right] \cdot$$

where $\eta$ is the thermodynamically averaged cosine of the rotameric angle, and is zero if there is no energy difference between rotameric states, as is the present Monte Carlo model. This also agrees well with the result that for an ideal chain $\langle R^2 \rangle = 6 \langle S^2 \rangle$. In the coil limit of Eq. (1b) this yields an apparent intrinsic persistence length $L_\perp$ of 8.7 Å, agreeing with the manner in which the intrinsic persistence length was calculated in Ref. 8, so as to make the zig-zag chain correspond to the wormlike chain model.

$$L_\perp = A \left[1 + \cos \theta \right] / \left[2 \left(1 - \cos \theta \right) \cos \left( \theta / 2 \right) \right].$$

The contour length was chosen to yield the correct $\langle S^2 \rangle$ in the coil limit while making the wormlike chain model equal to the stretched-out length of the zig-zag rotameric isometric state polymer via

$$L = A \left(N - 1 \right) \cos \left( \theta / 2 \right).$$

This yields $L = 854.38$ Å, compared to the value of 854.39 Å obtained directly from the Monte Carlo program by setting $\kappa \to 1$, $q_1$, and pH–pK_a to large values. Manning showed that in the Debye–Hückel model, if counterions are allowed to approach arbitrarily close to a linear polyelectrolyte modeled as a long straight rod having charge uniformly distributed along its length, the rod cannot have $\xi > 1/V$, $V$ being the valence of the counterions. Otherwise, counterions would condense upon the rod until its net $\xi$ was reduced to 1/V. This result, which also holds as $\kappa \to 0$ for long linear polyelectrolytes with finite diameter or regularly spaced charges, is widely believed to be a good first approximation for linear polyelectrolytes.

We therefore do not want to consider values of $\xi$ much larger than 1. Previously we argued that for the rotational isometric state model it is reasonable to estimate $\xi$ using the net charge on the polion and its maximum stretched out length. That is,
\[
\xi = \text{net charge}/e \times L_B/L_c
\]  
where \( L \) is given by Eq. 12 and \( e \) is the electronic charge. When the chain can be partially ionized, we define \( \xi_0 \) to be the value of \( \xi \) when the chain is fully ionized.

We note that the present model is determined by the dimensionless parameters \( \xi_0, \theta, \text{pH} - \text{pK}_a, \text{and } \xi_0 \), variations of \( T, A, q, \) and \( D \) being significant only as they affect \( \xi_0 \). Thus in situation (2) the quantity being varied is really \( \xi_0 \).

The current results were based on \( T = 298 \text{ K} \) and \( e/e_0 = 78.33 \), appropriate to water at that temperature. Thus for \( A = 7 \text{ A} \) and \( \theta = 70^\circ C \), \( \xi_0 \) is about 1.25, somewhat over the Manning limit, and thus too high. However, the results of the present model are not highly sensitive to \( \xi_0 \), as shown by results obtained on 150 unit chains with \( \xi_0 = 0.75 \). Under the above conditions \( \kappa^{-1} \) is 97 A when \( C_s \) is 1 mM.

III. RESULTS

Figure 1(a) shows \( \langle S^2 \rangle \) for chains with \( \xi = 0.75 \) and 1.25 plotted vs \( C_s^{-0.5} \), where \( C_s \) denotes concentration of monovalent salt in mM (for consistency with Refs. 3 and 4) and is thus equal to ionic strength. The rationale for plotting it in this form was that when the exponent \( b \) for \( \langle S^2 \rangle = aC_s^b + d \) over the coil limit range of \( C_s \) (about 10–5000 mM) was sought so as to maximize the linear correlation coefficient of \( \langle S^2 \rangle \) vs \( aC_s^b \), the value was always close to -0.5 (actual values ranged from -0.43 to -0.57). We thus conclude that \( \langle S^2 \rangle \) has an approximate inverse square root dependence on ionic strength. The weighting for such fits used the error in \( \langle S^2 \rangle \) as estimated from the lag 1 autocorrelation, following Smith and Wells. 31 That is, the estimated variance of the mean is the variance of the \( M \) sample points divided by \( (M - 1) \) and multiplied by \( (1+r_1)/(1-r_1) \), where \( r_1 \) is the lag 1 autocorrelation. 32 This is based on the (dubious) assumption that each sample is generated from the previous one by a first order recursive process. At any rate, it should be better than the assumption of equal weighting.

Figure 1(b) shows \( \langle S^2 \rangle \) vs \( C_s^{-0.5} \) for data on bacterial hyaluronate (BHA) of molecular weight around 1 million, 3 for which \( \xi \approx 0.72 \), and on 7% ionized sodium polyacrylamide (PA) of around 4 million daltons, 4 for which \( \xi \approx 0.2 \). In both cases \( \langle S^2 \rangle \) is quite straight vs \( C_s^{-0.5} \) over the whole range from around 1 mM to 1 M \( C_s \).

Using Eq. (2a) to calculate the apparent total persistence length \( L' \), from the \( \langle S^2 \rangle \) values in Fig. 1(a) and subtracting the intrinsic persistence length \( L_o \) (\( = 8.7 \text{ A} \)) yields the apparent electrostatic persistence length, \( L' \). Log(\( L' \)) vs log(\( C_s \)) is plotted in Fig. 2(a). The unweighted fits give -0.55 and -0.49 for \( \xi = 1.25 \) and 0.75, respectively. Also shown is an estimate of \( L_o \) using Eqs. (5)–(9) from excluded volume theory to find \( \langle S^2 \rangle \) from the \( \langle S^2 \rangle_0 \) given by Eq. (1a), and then Eqs. (2) to find \( L' \). The correction looks fairly good, except that it “sags” somewhat at intermediate ionic strengths, whereas the Monte Carlo results form a relatively straight line. Linear fits to the theoretical curves yield slopes of -0.57 and -0.44 for the \( \xi = 1.25 \) and 0.75 corrections, respectively. The linear correlation coefficients were much lower than for the corresponding Monte Carlo results.

Figure 2(b) shows \( L' \) vs \( C_s \) for the BHA and PA of Fig. 1(b), and the corresponding excluded volume calculations determined as for Fig. 2(a). For BHA 3 \( L \) and \( L_o \) were 27 000 and 87 A, respectively; for PA they were 70 000 and 24 A, 4 The rod diameter \( d_p \) of Eq. 8 was taken as 10 A for BHA and 5 A for PA. The calculations were not very sensitive to \( d_p \). The slopes were -0.56 and -0.49 for the BHA and PA linear fits, respectively, and -0.62 and -0.57 for linear fits to the excluded volume curves. Figure 2(b) also shows \( L_o \) according to Eq. (4); it’s a poor fit.

Figure 3(a) shows Monte Carlo results for \( \langle S^2 \rangle \) vs \( \xi \) for Debye lengths of 10, 24, and 34 A. For all three \( \kappa^{-1} \), RCD results are shown. (The titration behavior resulting from this type of ionization will be dealt with in Ref. 33.) For \( \kappa^{-1} \) of 10 and 34 A, UCD results are also shown. Interestingly, \( \langle S^2 \rangle \) values obtained by both methods overlap quite well. The slopes for the \( \langle S^2 \rangle \) from UCD are slightly lower than those from RCD. Again, the rationale for representing \( \langle S^2 \rangle \) linearly in \( \xi \) comes from maximizing the linear correlation coefficient for \( \langle S^2 \rangle = a + b\xi^c \), giving a best \( c \) near 1, in agreement with Ref. 4.

Figure 3(b) shows \( L' \) vs \( \xi \) for 1.5%, 7%, 17%, and 27% ionized PA (corresponding, respectively, to \( \xi = 0.04, \ldots \)
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0.20, 0.48, and 0.76) at \( C_s \) of 94, 16, and 8.2 mM. \( L_e \), which is proportional to \( \langle S^2 \rangle \) since the molecule is in the coil limit Eq. (1b), is roughly proportional to \( \xi \). The \( L_e \) calculated from the excluded volume discussion above is also shown. The excluded volume calculation is fairly good for \( C_s = 94 \) mM, but quickly deviates from the experimental values for lower \( C_s \).

Figures 4(a) and 4(b) show the \( L_e \) calculated from the \( L_e \) extracted from Fig. 3(a) via Eqs. (2), using \( L_0 = 8.7 \) Å, for \( \kappa^{-1} = 10 \) and 34 Å, respectively. Also shown are the corresponding excluded volume corrections according to the scheme Eqs. (5)-(9). In Fig. 4(b), the predicted \( L_e \) without excluded volume correction is also shown. While the excluded volume calculation is obviously much better than this, its absolute agreement with the Monte Carlo results is only fair. The slopes for the Monte Carlo results in Fig. 4(a) are 0.87 (UCD) and 1.16 (RCD), and in 4(b) they are 1.17 (UCD) and 1.26 (RCD). Linear fits to the excluded volume calculations gave 1.01 and 0.93 for Figs. 4(a) and 4(b), respectively. These latter fits are much less linear than the corresponding Monte Carlo results.

Figure 5 shows total electrostatic energy per monomer vs \( \xi \) for UCD and RCD ionization at \( \kappa^{-1} \) of 10 and 34 Å for 150 unit chains and at \( \kappa^{-1} \) of 10 Å for 20 unit chains. The UCD and RCD results agree closely, the RCD results lying slightly below the UCD results. Second order fits to these results are also shown.

IV. DISCUSSION

The salient feature of the Monte Carlo results is that the functional dependence of \( \langle S^2 \rangle \) on \( C_s \) agrees with the experimental results on different synthetic and biological polyelectrolytes, and its dependence on \( \xi \) roughly agrees with that for variably ionized polyacrylic acid, whereas both these dependencies disagree with the nonexcluded volume \( L_e \) of Eqs. (3)-(4).

That the approximate power laws agree for the experimental and Monte Carlo cases indicates that the approximation of Debye–Hueckel screening in the Monte Carlo model is reasonable, at least over the ionic strength range for which experimental data is available; around 1–1000 mM. Furthermore, setting the hard core excluded volume to zero in the
Monte Carlo model does not impair its agreement with experiment. The numerical solution to the nonlinear Poisson-Boltzmann equation for charge smeared out over a torus of adjustable diameter, within which the dielectric constant could be set to that of the polymer, formed the basis of Le-Bret’s approach to persistence lengths. That model took no account of excluded volume. Others using its results reported an approximate inverse square root dependence on ionic strength for the electrostatic persistence length. Ghosh et al. made electrostatic excluded volume corrections, noting, however, that Le-Bret’s model might also explain the discrepancy between Eqs. (1)–(4) and the experimental results. The current Monte Carlo agreement with experiment strengthens the argument that electrostatic excluded volume effects are a major cause of this discrepancy.

Although the excluded volume correction for varying \( C_e \) [Fig. 2(a)] is encouraging, its slight “sag” in the middle is peculiar. Although it is generally inappropriate to base criticisms of a theory on minor deviations from (inevitably) noisy data, the straightness of the Monte Carlo data [Figs. 2(a), 4(a), and 4(b)] and experimental \( L \) vs \( C_e \) [Figs. 2(b) and 3(b)] data almost suggest that there is something simpler occurring in the experiment than in the theory.

Another interesting aspect of the Monte Carlo results is the good agreement of \( \langle S^2 \rangle \) vs \( \xi \) for polyelectrolytes ionized by RCD and UCD for longer chains, when the two types have the same total net charge. Whereas the UCD chains have evenly spread charges, the RCD chains have wide, irregular gaps between charge groups. That the two ionization types should agree fairly well is not obvious, since not only should interactions between nearby groups be different in the two cases, but average lengths between charge groups at low ionization can stand in totally different proportions to relevant length scales like persistence, contour, and screening lengths than at full ionization. If the results for \( \langle S^2 \rangle \) can be so similar for widely and irregularly spaced charges and uniformly spaced charges, then going from closely spaced uniform charges to a smeared out uniform charge may preserve this agreement; i.e., \( \xi \) may be the most important parameter of a charge distribution. If this is true, the assumption of uniform smeared out charge density used in the persistence length theories behind Eqs. (3) and (4), and other theories such as Manning’s counterion condensation theory, may be well justified.

This idea was investigated by plotting the average electrostatic energy per monomer (Fig. 5) \( \langle E \rangle \) vs \( \xi \) for both UCD and RCD ionization. That these values overlap so closely for several values of \( \kappa^{-1} \) and chain length, suggests that the mean potential \( V \) felt by any monomer in the two ionization modes is the same.

The near equality in \( \langle E \rangle \) for UCD and RCD chains at the same \( \xi \) can be partially explained and interpreted in terms of a third charge distribution which we call the totally random charge distribution or TRCD. In the TRCD, the probability for any given unit to be ionized is exactly \( \langle \alpha \rangle \), independent of the ionization states of the other units and the spatial configuration of the chain. Then it turns out that the \( \langle E \rangle \) vs \( \xi \) curves must be the same in the TRCD and UCD distributions, and the RCD distribution should lie below them. The question then becomes; why does the \( \langle E \rangle \) vs \( \xi \) curve for the RCD lie so little below that for the TRCD (and UCD)? One possible explanation would be that in the RCD the actual distribution of charges is indeed surprisingly random. This could be checked by compiling appropriate stats-
ties on the distributions of charges inside the chains. We have not done so.

That the \( \langle E \rangle \) vs \( \xi \) curves should be the same in the UCD and TRCD models can be seen by considering the expected electrostatic interaction energy \( \langle E' \rangle \) in a particular spatial configuration of the polymer of any two units \( i \) and \( j \). If \( R_{ij} \) is the distance between units \( i \) and \( j \) then \( E'_y \) is \( q^2 \exp(-\kappa R_{ij})/(4\pi R_{ij}) \), when both units are charged in the TRCD model, and zero otherwise. Thus \( \langle E' \rangle \) is \( (\alpha)^2 q^2 \exp(-\kappa R_{ij})/(4\pi R_{ij}) \) in this spatial configuration in the TRCD model, the same as its value in the UCD model, with charges of size \( (\alpha)q \). Since, in a given spatial configuration

\[
\langle E \rangle = \frac{1}{2} \sum \sum \langle E'_q \rangle,
\]

\( \langle E \rangle \) must be the same for UCD and TRCD chains in any given spatial configuration. Since, for both UCD and TRCD chains, the probability for any particular spatial configuration to occur must be proportional to \( \exp(-\langle E \rangle/k_BT) \), that probability is also the same for UCD and TRCD ionization. Thus \( \langle E \rangle \) or \( \langle S^2 \rangle \) averaged over all spatial configurations are the same for the UCD and TRCD ionization, as are all the quantities reported in this work.

Of course in RCD ionization the ionization states of nearby units are not independent; in Fig. 5 the interaction energies of adjacent units are of order \( k_BT \). Also, \( \langle \alpha \rangle \) should be slightly higher in most spatial configurations for units located toward the ends of a chain, and should on average be lower the more compact the spatial configuration. Such variations in \( \langle \alpha \rangle \) should tend to reduce \( \langle E \rangle \), averaged over all configurations, below its value in the TRCD model.

Then, that the \( \langle E \rangle \) in the RCD model lies so little below its value in the TRCD and UCD model curve despite the large ratios of \( E'_q/k_BT \) for adjacent units, suggests that the curve of \( \langle \alpha \rangle \) vs pH–pK \(_0\) might be surprisingly well predicted by a simple mean-field theory using a TRCD type model. This will be investigated further in Ref. 33.

The \( \langle E \rangle \) vs \( \xi \) curves for the UCD and RCD models must coincide in the limits \( \alpha = 0 \) and \( \alpha = 1 \), because there the charge distributions are identical. Indeed, the quadratically fitted curves shown in Fig. 5 appear to obey this rule. In fact, it is also interesting just how closely quadratics do fit the \( E \) vs \( \xi \) curves.

V. SUMMARY

Values of \( \langle S^2 \rangle \) obtained by the present Monte Carlo algorithm yield approximate scaling behavior for apparent electrostatic persistence lengths of \( L'_c \sim \xi/C^{-0.3} \), as opposed to the \( \xi^2/C \) behavior predicted by Eqs. (3) and (4) for the \( L_c \) of unperturbed chains. The \( L'_c \sim \xi/C^{-0.4} \) dependence agrees well with the experimental apparent persistence length scaling behavior found for several different polyelectrolytes. Similar power laws are obtained by using Eqs. (5)–(9) to approximate the excluded volume effect. This makes it probable that the Debye–Hueckel and infinitely thin rod (i.e., neglecting both the polymer’s intrinsic excluded volume and its dielectric constant) approximations are quite adequate in predicting the scaling behavior of polyelectrolyte dimensions using the Monte Carlo technique.

This level of agreement seems sufficient to show that electrostatic excluded volume can cause a rough proportionality of apparent persistence length (as determined by light scattering and by viscosity) to \( \kappa^{-1} \) very similar to that predicted \(^{14,34} \) for actual persistence lengths using the nonlinear Poisson–Boltzmann equation in the limit of low polymer dielectric constant. This shows the importance of considering excluded volume effects when computing \( \langle S^2 \rangle \) using Eqs. 1 and 3, and, conversely, when extracting true persistence lengths from experimental values of \( \langle S^2 \rangle \).

Over a wide range of conditions the values of \( \langle S^2 \rangle \) and \( U \) agree between the two modes of variable ionization treated. This insensitivity of the polyelectrolyte’s dimensions and electrostatic energy to the difference between irregularly spread and uniformly spaced charges (with the same \( \xi \)), supports the approximation of smeared out uniform charges employed in many polyelectrolyte theories, including the persistence length theories \(^{6,7} \) used in this work.

Judging by the linearity of the fits [Figs. 2, 4(a), and 4(b)], the experimental and Monte Carlo behavior of \( L'_c \) may actually be simpler than the present somewhat ad hoc theory predicts. It is unusual for data (which is not very noisy) to show less structure than corresponding theories based on simplifying assumptions. Further experiments to obtain direct evidence of electrostatic excluded volume effects would be interesting, perhaps by high resolution determinations of scattered light intensity \( I(q) = (4\pi\eta/\lambda) \times \sin(\theta/2) \), on coil polyelectrolytes.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the support of the National Science Foundation Grant No. DMB-8803760 for support of this work. We also thank the Tulane Computing Center for its patience and support.

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