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An Asymptotic Self-Consistent Field Theory of Polyelectrolyte Expansion

James M. Bailey

Department of Chemistry and Biochemistry, Southern Illinois University, Carbondale, Illinois 62901.

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ABSTRACT: A theory of polyelectrolyte expansion is proposed based on a self-consistent field approach which minimizes the free energy of the molecule. The self-consistent field formalism is that developed by Reiss, as modified by Yamakawa. The electrostatic interaction is taken to be the Debye–Hückel potential and counterion binding is assumed, as described by the Manning theory. The theory should strictly be applicable only in the limit of increasing chain length. However, the results prove to be in at least semiquantitative agreement with experiment.

The theoretical treatment of the chain statistics of polyelectrolytes is a subject that has received attention for a number of years.[1,2] (The subject is reviewed thoroughly in these first two references.) Several theories have been proposed although most have been found to suffer from some deficiency. Typically adjustable parameters are required or the polymer model is clearly unrealistic or the predicted results do not even qualitatively agree with experimental data. In many cases it has been difficult to see how the particular theory of polyelectrolyte expansion could be realistically formulated within the framework of the more rigorous theories of general polymer chain statistics.

It is well-known that there are a number of theories for the prediction of α^2 (the ratio of the mean-square end-to-end vector of the polymer to that of an equivalent ideal Gaussian chain) for nonionic polymers.[3] One of the most rigorous, for large α, is the self-consistent field method of Reiss, as modified by Yamakawa.[4,5] In this paper we wish to demonstrate how a theory of polyelectrolyte expansion can be derived within the framework of this self-consistent field method. The advantage of this formalism is that it enables us to more clearly identify the assumptions and approximations used and to more fully understand the physical meaning of these approximations. Because of the assumptions used in deriving our basic result it is only strictly applicable to locally extended but globally compact polymers in an asymptotic limit.

Theory

The model adopted here to generally describe polyelectrolytes is an equivalent Gaussian chain consisting of $N + 1$ charged sites joined by N bond vectors $\mathbf{s}_i$. The bond vectors are random variables distributed according to a Gaussian function

$$P(\mathbf{s}_i) = \left[\frac{3}{2\pi a^2}\right]^{3/2} exp[-3\mathbf{s}_i{}^2/2a^2] \tag{1}$$

where a is the mean square length of each bond vector. The origin is placed at a terminal charged site, vectors from the origin to the jth charged site will be denoted as $\mathbf{r}_j$ and vectors from the kth to lth charged sites will be denoted as $\mathbf{r}_{kl}$.

It will be assumed that the interaction W_{kl} of the kth and lth charged sites can be described by the Debye–Hückel potential

$$W_{kl} = (z^2/D)\exp(-\kappa r_{kl})/r_{kl} \tag{2}$$

where D is the dielectric constant, κ is the Debye–Hückel screening parameter, and z is the electronic charge on each site. In applying this model we will assume that the charged sites that exist on each equivalent segment of the real molecule can, for the sake of calculation, be localized at the segment joints of the model. Hence z would be the total charge localized on the equivalent segment of the molecule.

Given this model the probability of finding any particular configuration $\mathbf{r}_1\mathbf{r}_2\ldots\mathbf{r}_N$ is

$$\begin{gathered} P(\mathbf{r}_1\mathbf{r}_2\ldots\mathbf{r}_N) = Z^{-1}\prod_{i=1}^{N}\left(\frac{3}{2\pi a^2}\right)^{3/2} \\ \times \exp(-3\mathbf{s}_i{}^2/2a^2)\exp[-\overline{W}/kT] \\ \overline{W} = \tfrac{1}{2}\sum_{i=1}^{N+1}\sum_{\substack{j=1 \\ i\neq j}}^{N+1} W_{ij} \\ \mathbf{s}_i = \mathbf{r}_i - \mathbf{r}_{i-1} \\ Z = \int d\mathbf{r}_1\ldots\int d\mathbf{r}_N\prod_{i=1}^{N}\left(\frac{3}{2\pi a^2}\right)^{3/2} \\ \times \exp(-3\mathbf{s}_i{}^2/2a^2)\exp[-\overline{W}/kT] \end{gathered} \tag{3}$$

Also the probability of some end-to-end vector $\mathbf{R} \equiv \mathbf{r}_N$ is given by

$$P(\mathbf{R}) = \int d\mathbf{r}\ldots\int d\mathbf{r}_N\, P(\mathbf{r}_1\mathbf{r}_2\ldots\mathbf{r}_N)\,\delta\left(\mathbf{R} - \sum_{i=1}^{N}\mathbf{s}_i\right) \tag{4}$$

The self-consistent field seeks to evaluate $P(\mathbf{R})$ by first assuming that

$$\exp[-\overline{W}(\mathbf{r}_1\mathbf{r}_2\ldots\mathbf{r}_N)/kT] = \prod_{i=1}^{N}\exp[-\phi_i(\mathbf{r}_i)/kT] \tag{5}$$

where the $\phi_i(\mathbf{r}_i)$ are functions chosen to minimize the error incurred by the assumption. These functions are determined by the minimization of the Helmholtz free energy. By this procedure they are shown to be given by[5]

$$\phi_j(\mathbf{r}_j) = \sum_{\substack{i=1\\ i\neq j}}^{N+1} \int W_{ij} P(\mathbf{r}_{ij}|\mathbf{r}_j)\,\mathrm{d}\mathbf{r}_i \tag{6}$$

where $P(\mathbf{r}_{ij}|\mathbf{r}_j)$ is the probability that segments i and j are separated by the vector $\mathbf{r}_{ij}$ upon the condition that the jth segment is found at vector $\mathbf{r}_j$ from the origin.

The conditional probability $P(\mathbf{r}_{ij}|\mathbf{r}_j)$, which refers to the charged molecule, is itself unknown. However, it can be approximated by making the uniform expansion assumption. It is noted that $P(\mathbf{r}_{ij}|\mathbf{r}_j)$ is a function of a, the mean square segment length. The parameter α is defined as

$$\alpha^2 = \langle R^2\rangle/\langle R^2\rangle_0 = \langle R^2\rangle/Na^2 \tag{7}$$

where $\langle R^2\rangle_0$ is the mean-square end-to-end vector of the uncharged chain. It is then assumed that $P(\mathbf{r}_{ij}|\mathbf{r}_j)$ is given by the function $P_0(\mathbf{r}_{ij}|\mathbf{r}_j)$, the above defined conditional probability for an uncharged molecule, but with the substitution of αa for a, i.e., $P(\mathbf{r}_{ij}|\mathbf{r}_j) = f(\alpha a)$ where $f(a) = P_0(\mathbf{r}_{ij}|\mathbf{r}_j)$. With this expression the potential $\phi_j(\mathbf{r}_j)$ can be evaluated. However, it still remains a function of the unknown parameter α (since $\langle R^2\rangle$ is unknown). To proceed further the self-consistent field assumption is again invoked to derive a differential equation which allows the evaluation of $P(\mathbf{R})$. From this $\langle R^2\rangle$, and hence α, can be determined as a function of known parameters.[3-5]

We begin the application of this method to polyelectrolytes by evaluating $P(\mathbf{r}_{ij}|\mathbf{r}_j)$. We note that

$$P(\mathbf{r}_{ij}|\mathbf{r}_j) = P(\mathbf{r}_{ij}, \mathbf{r}_j)/P(\mathbf{r}_j) \tag{8}$$

where $P(\mathbf{r}_{ij}, \mathbf{r}_j)$ is the joint probability of vectors $\mathbf{r}_{ij}$ and $\mathbf{r}_j$ and $P(\mathbf{r}_j)$ is the probability of $\mathbf{r}_j$ alone. Because of the uniform expansion approximation $P(\mathbf{r}_{ij}, \mathbf{r}_j)$ can be determined by the Wang–Uhlenbeck method,[3] which considers any vector set $\{\mathbf{q}_m\}$ of a Gaussian chain, where

$$\mathbf{q}_i = \sum_{j=1}^{N} \psi_{ij}\mathbf{s}_j \qquad i = 1, 2, \ldots, m \tag{9}$$

The distribution of the vector set is then given by

$$P_0[\{\mathbf{q}_m\}] = \left(\frac{3}{2\pi a^2}\right)^{3m/2} |C|^{-3/2} \times \exp\left\{-\frac{3}{2a^2}|C| \sum_{k=1}^{m}\sum_{l=1}^{m} C^{kl}\mathbf{q}_k\cdot\mathbf{q}_l\right\} \tag{10}$$

where

$$C_{kl} = \sum_{j=1}^{N} \psi_{kj}\psi_{lj}$$

and C^{kl} is the cofactor of the element C_{kl} of the $m \times m$ matrix C and $|C|$ is the determinant of this matrix.

In this case $m = 2$ and

$$\begin{array}{ll} \mathbf{q}_1 = \mathbf{r}_j = \Sigma\psi_{1k}\mathbf{s}_k & \psi_{1k} = 1, k \leq j \\ & \psi_{1k} = 0, k > j \\ \mathbf{q}_2 = \mathbf{r}_{ij} = \Sigma\psi_{2k}\mathbf{s}_k & \left.\begin{array}{l}\psi_{2k} = 1, i < k \leq j \\ \psi_{2k} = 0, k < i\end{array}\right\} \begin{array}{l}\text{for}\\ j > i\end{array} \\ & \left.\begin{array}{l}\psi_{2k} = 1, j < k \leq i \\ \phi_{2k} = 0, k < j\end{array}\right\} \begin{array}{l}\text{for}\\ i > j\end{array} \end{array}$$

Stipulating that the larger of the two indices be denoted as j it is simple to show that

$$P[\mathbf{r}_{ij}, \mathbf{r}_j] = \left(\frac{3}{2\pi\alpha^2a^2}\right)^3 [1/i(j-i)]^{3/2} \exp\left\{\left(\frac{-3}{2\alpha^2a^2}\right)(1/i(j-i))\,[(j-i)\mathbf{r}_j^{\,2} - 2(j-i)\mathbf{r}_j\cdot\mathbf{r}_{ij} + j\mathbf{r}_{ij}^{\;2}]\right\} \tag{11}$$

Also note that

$$P[\mathbf{r}_j] = \left(\frac{3}{2\pi\alpha^2a^2}\right)^{3/2} (1/j)^{3/2} \exp[-3\mathbf{r}_j^{\,2}/2\alpha^2a^2j] \tag{12}$$

Inserting eq 11 and 12 into eq 8 we obtain, after simplification

$$P(\mathbf{r}_{ij}|\mathbf{r}_j) = \left(\frac{3}{2\pi \mathrm{j}\alpha^2a^2}\right)^{3/2} [1/\epsilon(1-\epsilon)]^{3/2} \times \exp[-A\mathbf{r}_j^{\,2}]\exp[-B\mathbf{r}_j\cdot r_{ij}]\exp[-C\mathbf{r}_{ij}^{\,2}] \tag{13}$$

where

$$\begin{aligned} \epsilon &= |j-i|/j \\ A &= \left(\frac{3}{2j\alpha^2a^2}\right)(\epsilon/(1-\epsilon)) \\ B &= (3/j\alpha^2a^2)(1/(1-\epsilon)) \\ C &= \left(\frac{3}{2j\alpha^2a^2}\right)(1/\epsilon(1-\epsilon)) \end{aligned} \tag{14}$$

Define

$$\phi_{ji}(\mathbf{r}_j) = \int \mathrm{d}\mathbf{r}_i\, W_{ij}P(\mathbf{r}_{ij}|\mathbf{r}_j) \tag{15}$$

such that

$$\phi_j(\mathbf{r}_j) = \sum_{\substack{i=1\\ i\neq j}}^{N+1} \phi_{ji}$$

With this definition and eq 2

$$\phi_{ji}(\mathbf{r}_j)/kT = \left(\frac{3}{2\pi j\alpha^2a^2}\right)^{3/2}[1/\epsilon(1-\epsilon)]^{3/2} \times (z^2/DkT)\exp[-A\mathbf{r}_j^{\,2}]\int \mathrm{d}\mathbf{r}_{ij}\,(\exp[-\kappa r_{ij}]/r_{ij}) \times \exp[-B\mathbf{r}_j\cdot\mathbf{r}_{ij}]\exp[-C\mathbf{r}_{ij}^{\,2}] \tag{16}$$

After considerable simplification it can be shown that

$$\phi_{ji}(\mathbf{r}_j)/kT = (\mathcal{F}/r_j)\exp[-A\mathbf{r}_j^{\,2}][I_1 - I_2] \tag{17}$$

$$\mathcal{F} = (z^2/DkT)\left[\frac{3}{2\pi j\alpha^2a^2}\right]^{1/2}((1-\epsilon)/[\epsilon(1-\epsilon)]^{3/2}) \tag{18}$$

$$I_1 = \int_0^\infty \mathrm{d}r_{ij}\exp[-Cr_{ij}^{\,2}]\exp[-r_{ij}(\kappa - Br_j)]$$

$$I_2 = I_1(-B) = \int_0^\infty \mathrm{d}r_{ij}\exp[-Cr_{ij}^{\,2}] \times \exp[-r_{ij}(\kappa + Br_j)] \tag{19}$$

It is simple to further demonstrate that the integrals can be defined in terms of the complementary error function as

$$I_1 = (\pi/4C)^{1/2}\exp[(\kappa - Br_j)^2/4C]\,\mathrm{erfc}[(\kappa - Br_j)/2(C)^{1/2}] \tag{20}$$

$$I_2 = I_1(-B)$$

such that

$$\phi_{ji}/kT = (\mathcal{F}/r_j)\exp(-Ar_j^{\,2})(\pi/4C)^{1/2}J \tag{21a}$$

with

$$J = \exp[(\kappa - Br_j)^2/4C]\,\mathrm{erfc}[(\kappa - Br_j)/2(C)^{1/2}] - \exp[(\kappa + Br_j)^2/4C]\,\mathrm{erfc}[(\kappa + Br_j)/2(C)^{1/2}] \tag{21b}$$

To proceed further important approximations must be made. We must first consider the relative magnitudes of κ and Br_j. We assume that N, the degree of polymerization, is large and hence for most cases $j \gg 1$, i.e., we will ignore end effects. From its definition

$$Br_j = (3r_j/j\alpha^2a^2)(1/(1-\epsilon))$$

For the sake of rough calculation we assume that r_j is of the order of $j^{1/2}\alpha a$ and hence

$$Br_j \simeq (1/r_j)[1/(1-\epsilon)]$$

Thus for $\epsilon \ll 1-(\kappa r_j)^{-1}$

$$\kappa \gg Br_j$$

and

$$\kappa \pm Br_j \simeq \kappa \tag{22}$$

In evaluating the sum of $\phi_{ji}(\mathbf{r}_j)$ over i we will assume that $\kappa \gg Br_j$ for every term. This is clearly not valid for those terms for which $\epsilon \geq 1-(\kappa r_j)^{-1}$. However, these terms make a very small contribution to the total sum. The function $\phi_{ji}(\mathbf{r}_j)$ is a decreasing function of ϵ, i.e., the potential of interaction of near neighbors exceeds that due to segments separated by a greater contour length. Thus the *maximum* contribution (relative to the total potential) of terms for which $\kappa \leq Br_j$ is $1-\epsilon = 1/\kappa r_j$. Since $\kappa r_j \gg 1$ for most indices j this is a small term. Furthermore this is a considerable overestimate since it is made by assuming that ϕ_{ji} is independent of ϵ and then replacing the sum over i with an integral over ϵ. In reality ϕ_{ji} is a decreasing function of ϵ and the integral over the region where $\epsilon \geq 1-(\kappa r_j)^{-1}$ will be much smaller than the above estimate.

If we do assume that $\kappa > Br_j$ then it is possible to use the following expansion for the error functions of eq 21

$$\operatorname{erfc} X = \pi^{-1}X\exp(-X^2)\sum_{k=1}^{\infty}(-1)^{k+1}\Gamma(k-\tfrac{1}{2})X^{-2k}$$

This is a divergent asymptotic series. The error incurred by using a finite number of terms is less than the magnitude of the last term used in the series. We will use only the first two terms. Clearly the validity of this approximation improves as X increases. For $X = 1$ the relative error is 6.5% and for $X > 1$ it is even less. However, when X falls below unity the error increases very rapidly.

Using the approximation

$$\operatorname{erfc}[(\kappa \pm Br_j)/2(C)^{1/2}] \simeq \pi^{-1/2} \times \exp[-(\kappa \pm Br_j)^2/4C][2(C)^{1/2}/(\kappa \pm Br_j)]$$

it is trivial to demonstrate that

$$J \simeq 4C^{1/2}\pi^{-1/2}Br_j\kappa^{-2} \tag{23}$$

(where we again assume $\kappa \gg Br_j$, as discussed above).

It will be useful for later discussion to also derive this result in a slightly different manner. From eq 17 and 21

$$J = (4C/\pi)^{1/2}[I_1 - I_2]$$

where I_1 and I_2 are defined by eq 19. From the definition of I_1 and I_2 we note that J is a function of $\kappa \pm Br_j$. As discussed above, $\kappa \gg Br_j$ for significant values of ϵ. We thus express J as a Taylor's series in Br_j. It is simple to show that to first order

$$J = (4(C/\pi)^{1/2})Br_j\int_0^{\infty}\mathrm{d}r_{ij}r_{ij} \times \exp[-Cr_{ij}^2]\exp[-\kappa r_{ij}] \tag{24}$$

This is identical with the linear dependence on r_j predicted by eq 23, regardless of the relative values of κ and $(C)^{1/2}$. Thus to the extent that the series truncation used to derive the above result is valid, eq 23 is in error by no more than some constant factor.

It is now simple to also show that

$$\int_0^{\infty}\mathrm{d}r_{ij}r_{ij}\exp(-Cr_{ij}^2)\exp(-\kappa r_{ij}) = -(\mathrm{d}/\mathrm{d}\kappa)[(\pi/2C)^{1/2}\exp(\kappa^2/4C)\operatorname{erfc}(\kappa/2(C)^{1/2})]$$

If one uses the asymptotic expansion for $\operatorname{erf}(x)$, retaining only the first-order term, the result is

$$J = 4(C/\pi)^{1/2}(Br_j/\kappa^2)$$

in agreement with eq 23.

Returning now to the expression for ϕ_{ji} we insert eq 23 into eq 21 and simplify to obtain

$$\phi_{ji}(\mathbf{r}_j)/kT = \beta\left[\left(\frac{3}{2\pi\alpha^2a^2}\right)(j/(j-i)(i)\right]^{3/2} \times \exp[(-3r_j^2/2\alpha^2a^2)(j-i)/ij)] \tag{25}$$

$$\beta = 4\pi z^2/DkT\kappa^2$$

This result is very interesting. Returning to eq 13 and 15 we note that if the original interaction had been a delta-function potential $\beta\delta(r_{ij})$ rather than the Debye–Hückel potential the result would be identical with eq 25. Hence the assumptions embodied in eq 23 and 24 are equivalent to assuming that

$$z^2/DkT\exp(-\kappa r_{kl})/r_{kl} \approx \beta\delta(\mathbf{r}_{kl})$$

With this result the remainder of the calculation is trivial. The self-consistent field method was originally developed for a delta-function potential.[3-5] The self-consistent asymptotic solution for α with such a potential is

$$\lim_{\beta N^{1/2}\to\infty}\alpha^5 = (2\pi/3)^{1/2}\left(\frac{3}{2\pi a^2}\right)^{3/2}\beta N^{1/2} \tag{26}$$

For our problem, from the definition of β, we obtain

$$\alpha^5 = (6z^2/DkT)(N^{1/2}/\kappa^2a^3) \tag{27}$$

As implied, this result can be obtained also by assuming that the pair correlation function is given by $1 - \beta\delta(\mathbf{r}_j)$ where β, the binary cluster integral, is evaluated as[3]

$$\beta = \int_0^{\infty}\mathrm{d}r4\pi r^2\{1 - \exp[-(z^2/DkTr)\exp(-\kappa r)]\}$$

If one assumes that the first exponential within the brackets can be expanded to first order, the definition of β in eq 25 is obtained. This first-order expansion was the approach used by Ptitsyn in his theory of polyelectrolyte expansion.[6] However, this expression was then used in a completely different theory of polymer expansion and thus the results are not similar to those found in this report.

As pointed out by Noda et al., the results expressed in eq 26 can also be more simply derived by applying the uniform expansion approximation to the Katchalsky–Lifson theory and using the Hermans–Overbeek method to evaluate the integral defining α.[7-9] We have gone through the formalism of the self-consistent field method, because we believe it enables one to more clearly understand the physical nature of the approximation and better judge their validity, and also to see the relationship of their approach to the self-consistent field method.

Discussion

The major assumptions of the preceding theoretical development are: (1) the assumptions embodied in eq 22 and 23; (2) the use of the Debye–Hückel interaction with the localization of all charges at the segment joints.

The basic assumptions needed to reach eq 22 are that for most single charge-site potentials, $\phi_j(\mathbf{r}_j)$, r_j is large and the major contribution to $\phi_j(r_j)$ is due to interactions with sites for which $\epsilon < 1 - (\kappa r_j)^{-1}$. Since ϕ_{ji} is a decreasing function of ϵ the maximum contribution of terms for which $\epsilon < 1 - (\kappa r_j)^{-1}$ is $(\kappa r_j)^{-1}\phi_j$. For large j, $\kappa r_j \gg 1$, and this is a very small contribution and is negligible.

Equation 23 is another major approximation. The error incurred by approximating the error function with the first two terms of its expansion is relatively small when the argument is greater than or equal to unity. Thus we might expect this approximation to be acceptable when

$$\kappa/2(C)^{1/2} = (\kappa\alpha a/6^{1/2})[(j-i)i/j]^{1/2} \geq 1$$

For example for a hypothetical polyelectrolyte with $N = 10\,000$, $j = 5000$, and $\kappa = 2.33 \times 10^6$ (0.005 M univalent salt) the minimum value ($i = \mathrm{j} - 1$) of $\kappa/2C^{1/2}$ is 0.91. The error incurred by approximating the error function of an argument of this magnitude by the first two terms of expansion is about 9%. However, the error in this expansion is not strictly a measure of the final error in the potential ϕ_j. For example, consider the above hypothetical polymer with $r_j^2 = j\alpha^2a^2$. Straightforward calculation reveals that the use of eq 23 results in an error in ϕ_j of about 30%. Thus the imprecision in the evaluation of the potential ϕ_j exceeds the imprecision in the evaluation of the error function.

This error in ϕ_j is significant. However, it should be noted that it stems largely from the term $\phi_{j,j-1}$. In the Appendix we show that terms ϕ_{ji} for which $j \simeq i$ are essentially constant (independent of r_j) relative to the total potential ϕ_j. Since constant terms are omitted from the differential equation leading to the final result,[5] error in these terms should not alter the final expression for α. Of course approximations were used to reach the conclusion of the Appendix, such as the series truncation needed to derive eq 24, the replacement of the sum over i by an integral, and the extension of the limits of this integral to derive eq A5 and A6. However, these operations seem to be well-founded and we conclude that for $(\kappa\alpha a(6)^{1/2} \geq 1$ the use of the truncated error function expansion is acceptable.

The use of Debye–Hückel interaction must also be viewed as a major approximation. It is obvious, and has been obvious for many years, that the Debye–Hückel is itself not acceptable. However, it has been also noted many times that if one could assume counterion binding, reducing the net polymer charge, the Debye–Hückel theory is useful. In recent years Manning has given rigorous justification for an assumption of counterion binding and has shown how the extent of binding is calculated.[10] Although this theory is based on a cylindrical polyelectrolyte model, it has been remarkably successful in predicting the properties of a number of polyelectrolytes. Manning has pointed out that the theory should be applicable to locally extended by globally flexible polyelectrolytes. More quantitatively, the theory should be applicable whenever κ^{-1} is less than the average length of a rodlike segment, which is consistent with the error function expansion leading to eq 23. We also note that the Manning theory is strictly applicable only in the limit of zero ionic strength. However, as discussed above we require that $(\kappa\alpha a)/6 \geq 1$ for our other major approximation to be acceptable. For many polymers this will correspond to univalent salt concentrations of 5 mM. Fortunately for such concentrations the Manning theory has been found to be very successful. Hence we believe that the use of the Debye–Hückel interaction, as modified by Manning to include counterion binding, is appropriate in our study. The use of this potential, however, is still an oversimplification. For instance it assumes a uniform dielectric constant and ignores the details of the spacing of charged sites. We have no way of assessing the extent to which this oversimplification affects the final result. We do believe, however, that these effects will be most important in the interaction of close neighbors. Since these terms make an essentially constant contribution to the potential, ϕ_j, the problem might not be so serious.

Table I[a]

Ionic strength	α_+[b]	α_e[c]	(α_+/α_e)
0.11	3.45	2.0	1.61
0.06	3.90	2.18	1.79
0.028	4.54	2.57	1.84
0.019	4.93	2.57	1.91
0.012	5.27	2.67	2.02

[a] Experimental data based on Figure 8 of ref 7, a viscosimetric study of polyacrylate. [b] Theoretical values of α and α_+ were calculated from eq 28 assuming $a = 15$ Å, for a polymer of 10^6 daltons molecular weight. [c] Experimental values of α and α_e were calculated in ref 7 from viscosity data, assuming the Flory–Fox relationship,[15] as a function of $(M/c)^{1/2}$, where M is molecular weight and c is salt concentration. Values of α_e cited above were calculated for a polymer of 10^6 daltons molecular weight. The degree of ionization of the polymer was 0.6.

In discussing the major approximations of this theory we have not mentioned the assumptions of the self-consistent field method itself. These have been discussed elsewhere.[3-5] It must be emphasized that the general method is an asymptotic theory. The final result, as derived by Yamakawa, is valid only as $\alpha \rightarrow \infty$. This is consistent with our application of the theory to polyelectrolytes. In particular we note that the approximations leading to eq 27 improve as N and α increase. However, the question remains as to whether this type of uniform expansion theory is appropriate for polyelectrolytes. Certainly as β increases the expansion of the polyelectrolyte will become less uniform. For example, this approach suggests the distance between segments i and $i + 1$ increases as α increases. This is clearly unrealistic. It is difficult to evaluate how seriously the uniform expansion approximation is in error although to the extent that the final result reflects long-range interactions the uniform expansion approximation is expected to improve somewhat.

In order to determine whether this asymptotic solution is useful, we have calculated theoretical predictions for several experimental studies.[7,12-14] We have computed values for N and α by assuming the experimentally determined value of the unperturbed mean-square end-to-end radius is given by Na^2 and that the contour length of the equivalent chain is identical with that of the molecule. We have restricted the calculations to polyelctrolytes whose charge densities exceed the critical value defined by Manning.[10] We also restrict our consideration to univalent supporting electrolytes to avoid the complications that can occur with divalent metals. In this case it is simple to show that this theory predicts

$$\alpha^5 = 6N^{1/2}/al_c\kappa^2 \tag{28}$$

where l_c is the critical charge separation 7.1 Å (for aqueous solution at 25 °C). Shown in Tables I–V are the ratios of the theoretically predicted to experimentally determined values of α. It can be seen that there is qualitative agreement between theory and experiment. The ratio of the theoretical to experimental values of α never greatly exceeds 2. In every case, however, the agreement between theory and experiment becomes worse as ionic strength decreases. As discussed above we believe this could be due to the inadequacy of the uniform expansion assumption at higher relative values of the excluded volume parameter β.

An excellent experimental system for testing this and other

Table II[a]

Ionic strength	α_+[b]	α_e[c]	(α_+/α_e)
0.25	1.88	1.46	1.26
0.0625	2.49	1.77	1.41
0.028	2.92	2.01	1.45
0.016	3.28	2.19	1.50
0.01	3.58	2.39	1.53

[a] Experimental data based on Figure 5 of ref 7, a viscosimetric study of polyacrylate. [b] Theoretical values of α and α_+ were calculated from eq 28 assuming a = 15 Å, for a polymer of 12.3×10^4 daltons molecular weight. [c] Experimental values of α and α_e were calculated from the parameter B, which was determined by the Stockmayer–Fixman procedure[15] and reported in Figure 5. A molecular weight of 12.3×10^4 daltons was used in the calculation. The degree of ionization for these data is 1.0. The relation between α and β as described in the reference was used to calculate α_e.

Table III[a]

Ionic strength	α_+[b]	α_e[c]	(α_+/α_e)
0.5	1.63	1.56	1.04
0.1	2.28	1.92	1.18
0.05	2.62	2.20	1.22
0.025	3.00	2.47	1.27
0.005	4.14	3.19	1.29

[a] Experimental data based on Table V of ref 12, a viscosimetric study of polyacrylate. [b] Theoretical values of α and α_+ were calculated from eq 28 assuming a = 15 Å, for a polymer of 12.86×10^4 daltons molecular weight. [c] Experimental values of α and α_e were calculated from the parameter β, which was determined by the Stockmayer–Fixman procedure[16] and reported in Table V. A molecular weight of 12.86×10^4 daltons was used in the calculation. The degree of ionization for these data is 1.0. The relation between α and β as described in the reference was used to calculate α_e.

Table IV[a–c]

Ionic strength	$R_+ \times 10^5$	$R_e \times 10^5$	(α_+/α_e)
0.1	0.609	0.552	1.10
0.05	0.700	0.604	1.16
0.02	0.838	0.704	1.19
0.01	0.962	0.791	1.22
0.005	1.11	0.886	1.25
0.001	1.53	1.11	1.38

[a] Experimental data based on ref 13, a viscosimetric study of poly(vinyl alcohol sulfate). [b] Theoretical values of α were calculated from eq 28 assuming a = 17.5 Å for a polymer of 1570 degrees of polymerization. This was used to calculate R_T, the square root of the mean-square end-to-end distance. [c] Experimental values of R and R_e were calculated from viscosity data, assuming the Flory–Fox relation,[15] for a sample of degree of polymerization equal to 1570.

Table V[a,b]

Ionic strength	$(S_+^2 \times 10^{10})$	$(S_e^2 \times 10^{10})$	(α_+/α_e)
1.0	0.39	0.19	1.43
0.5	0.52	0.35	1.22
0.1	1.00	0.51	1.40
0.05	1.31	0.64	1.43
0.02	1.87	0.70	1.64
0.01	2.48	0.75	1.82
0.005	3.30	0.89	1.94

[a] Experimental data taken from Table IV of ref 14, a light-scattering study of poly(styrene p-sulfonate). Experimental values of the radius of gyration, S_e, were reported. The molecular weight of the sample was 15.5×10^5 daltons. [b] Theoretical values of α were calculated from eq 28, assuming a = 15 Å, for a polymer of 15.5×10^5 daltons molecular weight. This was used to calculate a theoretical radius of gyration, S_T.

theories of polyelectrolyte expansion is single-strand DNA. Molecules of very high degrees of polymerization are available and the unperturbed segment length is relatively large.[14] There is one complication in that DNA is capable of intramolecular base pairing. However, this could be overcome by using any of several nonionic DNA denaturants, such as glyoxal, formaldehyde, or methylmercuric hydroxide. Unfortunately such data are not available.

It should be noted that the data presented in Tables I–IV all derive from viscosity measurements. Such data are difficult to interpret. In particular each of these studies assumes the Flory–Fox relationship, i.e., viscosity is proportioned to the third power of the radius of gyration and hence to α^3.[15] It has been pointed out that this assumption is inadequate.[3] Hence experimental values of α calculated directly from the ratios of specific viscosity might be only qualitatively correct.

Noda et al. have calculated the electrostatic contribution to α^3 directly from intrinsic viscosity data for polymers of varying molecular weight at different ionic strengths.[7] They find that the electrostatic contribution to the expansion parameter can be expressed in terms of $(M/c)^{1/2}$ rather than $(M)^{1/2}/c$ as would be predicted by this and most other theories. We are not able to say whether this is due to the use of the Flory–Fox relation or to the failure of theory in the molecular weight and ionic strength range that was considered.

The proportionality of α^5 to the binary cluster integral predicted by this theory is similar to the predictions of several other theoretical approaches. However, a more realistic model of the polymer chain is used here and the formalism of the self-consistent field enables one to more clearly identify the approximations and assumptions that are made. The basic result is one which should be valid only asymptotically. Despite this proviso, however, it can be seen that the theory does predict at least qualitatively correct values for the expansion parameter α.

Appendix

The evaluation of the potential $\phi_j(\mathbf{r}_j)$ requires summation of $\phi_{ji}(\mathbf{r}_j)$ over i.

$$\phi_j(\mathbf{j})/kT = \sum_1^{j-1} \phi_{ji}(\mathbf{r}_j)/kT$$
$$= \beta(3j/2\pi\alpha^2a^2)^{3/2} \sum_1^{j-1} (j-i)^{-3/2}(i)^{-3/2} \times \exp\{(-3r_j^2/2j\alpha^2a^2)(j-i)/i\} \quad \text{(A1)}$$

Following Yamakawa[5] this sum is converted to an integral

$$\phi_j(\mathbf{r}_j)/kT = \beta(3j/2\pi\alpha^2a^2)^{3/2} \int_1^{j-1} \mathrm{d}i\ (j-i)^{-3/2}(i)^{-3/2} \exp\{(-3r_j^2/2j\alpha^2a^2)(j-i)/i\}$$

Changing variables to $x = (j-i)/i$ one can show that

$$\phi_j(\mathbf{r}_j)/kT = (j)^{-1/2}\epsilon \int_{(j-1)^{-1}}^{j-1} \mathrm{d}x\ (x^{-3/2} + x^{-1/2}) \times \exp(-\gamma x) \quad \text{(A2)}$$

where

$$\epsilon = \beta\left(\frac{3}{2\pi\alpha^2a^2}\right)^{3/2}$$
$$\gamma = 3r_j^2/2j\alpha^2a^2$$

Integration by parts leads to

$$\int_{(j-1)^{-1}}^{j-1} \mathrm{d}x\, x^{-3/2} \exp(-\gamma x) = -2x^{-1/2} \exp(-\gamma x)\Big|_{(j-1)^{-1}}^{j-1} - 2\gamma \int_{(j-1)^{-1}}^{j-1} \mathrm{d}x\, x^{-1/2} \exp(-\gamma x)$$

Changing variables to $x = x^2$ we also see that

$$\int_{(j-1)^{-1}}^{(j-1)} \mathrm{d}x\, x^{-1/2} \exp(-\gamma x) = 2 \int_{(j-1)^{-1/2}}^{(j-1)^{1/2}} \mathrm{d}x \exp(-\gamma x^2)$$

It is now assumed that

$$(j - 1)\gamma = 3r_j^2(j - 1)/2j\alpha^2a^2 >>> 1$$

and that

$$\gamma/(j - 1) = 3r_j^2/2j\alpha^2a^2(j - 1) <<< 1$$

The above integrals can then be approximated as

$$\int_{(j-1)^{-1}}^{j-1} \mathrm{d}x\, x^{-3/2} \exp(-\gamma x) \simeq 2(j - 1)^{1/2} - 2\gamma \int_{(j-1)^{-1}}^{j-1} \mathrm{d}x\, x^{-1/2} \exp(-\gamma x) \quad \text{(A3)}$$

and

$$\int_{(j-1)^{-1}}^{j-1} \mathrm{d}x\, x^{-1/2} \exp(-\gamma x) \simeq \int_0^\infty \mathrm{d}x\, x^{-1/2} \exp(-\gamma x) = (\pi/\gamma)^{1/2} \quad \text{(A4)}$$

With these approximations it is simple to derive the following result

$$\phi_j(\mathbf{r}_j)/kT = (2\pi/3)^{1/2}\delta\{(a/r_j\alpha^2) - (3r_j/ja\alpha^4) + (6/\pi)^{1/2}(1 - j^{-1})^{1/2}\alpha^{-3}\} \quad \text{(A5)}$$

$$\delta = \epsilon\alpha^3$$

This is identical with the result derived by Yamakawa[5] although he omitted the term which is independent of r_j.

While it is obvious that each term ϕ_{ji} is a function of r_j, the procedure used to evaluate the total potential ϕ_j can also be used to demonstrate that the terms ϕ_{ji}, for which $i \simeq j$, make a relative contribution to the total potential ϕ_j that is basically independent of r_j. For example, we note that

$$\phi_{j,j-1} = \sum_1^{j-1} \phi_{ji} - \sum_1^{j-2} \phi_{ji}$$

We now evaluate the second sum by the method just described. In this case, however, the integral corresponding to the second sum above has a lower limit of $2(j - 2)^{-1}$ rather than $(j - 1)^{-1}$. If we can assume that $2\gamma/(j - 2) >>> 1$ then insertion of this limit in the appropriate equations and simplification as before leads to the following result

$$\phi_{j,j-1} = 2\epsilon\{(1 - 1/j)^{1/2} - (2)^{-1/2}(1 - 2/j)^{1/2}\} \quad \text{(A6)}$$

a term which is independent of r_j.

Now consider the evaluation of the term $\phi_{j,j-1}$ when the approximation of eq 23 is poor. As demonstrated in the main text eq 23 predicts the proper functional dependence of $\phi_{j,j-1}$ on r_j to a very good approximation and is in error at most by some constant factor (independent of r_j). Thus we can write

$$\phi_{j,j-1}(\mathbf{r}_j)/kT = C_f\beta(3j/2\pi\alpha^2a^2)^{3/2}(j - 1)^{-3/2} \times \exp\{(-3r_j^2/2j\alpha^2a^2)(j - 1)^{-1}\}$$

where C_f is a (somewhat artificial) correction factor which is equal to unity when the approximation of eq 23 is acceptable. Since C_f is a constant we can use the same reasoning applied above to demonstrate that $\phi_{j,j-1}$ makes an essentially constant contribution to the total potential, whether the truncated error function expansion is used or not.

Note that the above derivation depends on extending the integration limits in two equations, i.e., we assume that $j\gamma \gg 1$ and $\gamma/j \ll 1$. Thus the derivation is valid only if $j \gg 1$.

Also note that this result suggests that the final expression for α reflects global interactions since the potential due to near neighbors is essentially constant and independent of r_j.

References and Notes

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