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Chain Structure in Polyelectrolyte Solutions at Nonzero Concentrations

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ABSTRACT: We present an analytic theory for the structure of intrinsically flexible polyelectrolyte chains in solution at arbitrary concentrations, with or without added salt. We use a self-consistent approach based on an idea suggested by generalized Debye−Hückel theory, namely, that the screening length from polyions is wavevector-dependent, due to chain connectivity. At high wavevectors (short length scales), only counterions contribute to screening, but at lower wavevectors, both polyions and counterions contribute. The results of the theory are in quantitative agreement with molecular dynamics simulations, with no adjustable parameters.

I. Introduction

Polyelectrolytes are long-chain molecules with ionizable groups that can dissociate in solution, leaving ions of one sign bound to the chain and counterions free in solution. Because polyelectrolytes tend to be soluble in highly polar solvents such as water, they are ubiquitous in biological systems and are useful to environmentally-benign polymer processing. In order to understand important properties of polyelectrolyte solutions such as viscoelasticity, however, it is first necessary to understand chain structure, which controls key properties such as the number of entanglements among chains. Chain structure is governed by the electrostatic interactions among the chains and counterions; electrostatic repulsion along a chain tends to stiffen it, and counterions screen this repulsion. It is now fairly straightforward to estimate the electrostatic interaction between a polyelectrolyte of *known* structure, such as a folded protein, and its counterions, by solving the nonlinear Poisson−Boltzmann equation numerically.[1] However, if the structure of the polyelectrolyte chain can adjust in response to the electrostatic interactions, then one must solve *self-consistently* for the structure and the interactions. This is especially difficult because the Coulomb interaction is long-ranged and can be either attractive or repulsive, leading to competing interactions, and so a variety of approaches have been suggested.[2]

Previous theoretical work on chain structure in polyelectrolyte solutions has focused on the structure of a *single*, screened chain in solution,[3−7] while experimental work has necessarily studied polyelectrolyte solutions at nonzero concentrations. To generalize single-chain results to nonzero concentrations, two approaches have been used. The first is scaling theory,[8] which has proven highly successful in describing neutral polymer systems. Unfortunately, the applicability of scaling theory to polyelectrolytes is severely limited by the existence of additional important length scales such as the Debye screening length, the Bjerrum length (the distance at which the electrostatic energy is equal to the thermal energy), the average separation of charges along the chain, and the average separation of counterions. The second approach to polyelectrolyte solutions at nonzero concentrations, the “double screening” theory of Muthukumar,[9] is much closer in spirit to ours. This approach is based on field theoretical calculations and can, in principle, yield predictions for chain structure in the nonasymptotic regime, relevant to simulations and experiments, as well as in the asymptotic scaling regime.

The crux of our approach lies in the nature of polyion screening. One way of deriving Debye−Hückel theory is to integrate over small fluctuations in the local densities of ionic components. If the ions are point particles, this approach leads to the standard Debye screening length. If the ions are connected into chains, however, this changes the correlations and affects the fluctuations. Thus, chain connectivity causes the Debye screening length to become *wavevector-dependent*: it depends on the structure factor of the polymer.[10] This screened electrostatic interaction prefers the chain to be a rigid rod. However, it costs free energy to stretch the chain beyond its intrinsic persistence length. The competition between the electrostatic free energy, which depends on chain structure through the screening length, and the stretching free energy, which also depends on chain structure, leads to an optimal chain structure. In this paper, we describe the interactions between chains using a wavevector-dependent screening length, and we calculate the electrostatic persistence length self-consistently using a technique first introduced by Edwards and Singh to describe the structure of excluded volume chains at nonzero concentrations.[11] Section II contains the derivation of a self-consistent equation for the electrostatic persistence length for arbitrary polyelectrolyte concentration. Finally, section III applies the self-consistent equation to polyelectrolyte solutions at nonzero concentrations. We obtain quantitative agreement with recent molecular dynamics simulations by Stevens and Kremer[12,13] and by Stevens and Plimpton.[14] In comparing our results to the molecular dynamics simulations, we use *no adjustable parameters*.

II. Derivation of the Self-Consistent Equation for the Electrostatic Persistence Length

A. The Random Phase Approximation: Debye−Hückel Theory Generalized to Polyions. We first review the random phase approximation result of Borue and Erukhimovich[10] in order to justify the use of a

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wavevector-dependent screening length. We study a simple model of a salt-free polyelectrolyte solution, in which the ions are monovalent and the charge fraction along the chain is denoted f. We assume that the charge is distributed evenly along the length of the chain and that the particles are otherwise non-interacting. There are n_- negatively-charged polymers made up of M repeat units of length a and volume a^3 and n_+ positively-charged counterions, also of size a and volume a^3, in a volume V. For simplicity, we will work in units where $a = 1$. The whole system is assumed to be neutral, so $n_- fM = n_+$. The microscopic dimensionless number densities of the polyions and counterions are then

$$\hat{\rho}_-(\vec{r}) = \sum_{i=1}^{n_-}\int_0^M \mathrm{d}s\ \delta(\vec{r} - \vec{r}_i^{\,-}(s))$$

$$\hat{\rho}_+(\vec{r}) = \sum_{i=1}^{n_+} \delta(\vec{r} - \vec{r}_i^{\,+}) \tag{1}$$

where $\vec{r}_i^{\,-}(s)$ is the position of the sth monomer and the ith chain and $\vec{r}_i^{\,+}$ is the position of the ith counterion. Hence, the dimensionless charge and total monomer densities are

$$\hat{\rho}(\vec{r}) = f\hat{\rho}_+(\vec{r}) - \hat{\rho}_-(\vec{r})$$

$$\hat{\phi}(\vec{r}) = \hat{\rho}_+(\vec{r}) + \hat{\rho}_-(\vec{r}) \tag{2}$$

The full, unscreened electrostatic interaction Hamiltonian is

$$\beta H_{\mathrm{el}} = \int\int \mathrm{d}\vec{r}\ \mathrm{d}\vec{r}\,'\ \frac{\beta e^2}{4\pi\epsilon|\vec{r} - \vec{r}\,'|}\ \hat{\rho}(\vec{r})\ \hat{\rho}(\vec{r}\,') \tag{3}$$

where ϵ is the dielectric constant of the solvent, e is the electronic charge and $\beta = 1/k_BT$. Finally, we include a Hamiltonian, βH_c, that describes the conformations that individual polyion chains would have if they were neutral. Thus, βH_c describes the *intrinsic* structure of the chain. This could correspond to a Gaussian chain, wormlike chain, or rigid rod, etc. For now, we leave it unspecified. Thus, the total Hamiltonian for the polyelectrolyte system is

$$H = \sum_{n_-} H_c + H_{\mathrm{el}} \tag{4}$$

where the sum over n_- represents the sum over all chains. The free energy resulting from this Hamiltonian can be calculated within the random phase approximation (RPA). This approach assumes that the fluctuations in the local charge densities $\hat{\rho}_+(\vec{r})$ and $\hat{\rho}_-(\vec{r})$ are weak and can be integrated over within the Gaussian approximation. The RPA result for the dimensional Helmholtz free energy density, $F = \mathcal{F}a^3/k_BTV$, expressed in terms of the total average volume fraction $\phi = \rho_+^0 + \rho_-^0$, is

$$F_{\mathrm{RPA}} = \frac{f + 1/M}{1 + f}\,\phi \log \phi + (1 - \phi) \log (1 - \phi) - \frac{\phi}{(1 + f)M} \log Q_0 + \frac{1}{2}\int \frac{d^3k}{(2\pi)^3} \log\left[1 + \frac{\kappa^2(k)}{k^2}\right] \tag{5}$$

The first term in eq 5 represents the ideal gas entropy of mixing of the polyions and the counterions, and the second term contains the entropy of mixing of the solvent molecules. The third term represents the configurational free energy of the chains, where Q_0 is the partition function of a single chain. Finally, the fourth term represents the one-loop electrostatic perturbation to the neutral system; the integral over k represents the energy arising from *screened* Coulomb interactions, where the inverse screening length $\kappa(k)$ depends on the wavevector:

$$\kappa^2(k) = {\kappa_0}^2\frac{f}{1 + f}[fS(k) + 1] \tag{6}$$

Note that $\kappa^2(k)$ is proportional to a charge-weighted average of the structure factors of the polyion, $S(k)$ and counterion, $S_c(k) = 1$. When the polyion is replaced by a point particle, then $f = 1$ and $S(k) = 1$. In that limit, $\kappa^2(k)$ reduces to the well-known Debye–Hückel result for the inverse squared screening length,

$${\kappa_0}^2 = 4\pi l_B\phi \tag{7}$$

in terms of the Bjerrum length, $l_B = \beta e^2/4\pi\epsilon$. Note that we started with unscreened Coulomb interactions in the Hamiltonian (see eqs 3 and 4). Evidently, the screening arises from fluctuations in the charge densities $\rho_\pm(\vec{k})$, which have been included at the Gaussian level. The most important feature of eq 6, however, is that the screening length is wavevector-dependent when the ions have structure.[10] This is physically reasonable: the screening of the electrostatic interaction felt by ions on a polymer should be affected by the shape of the polymer chain. At high wavevectors k, the polyion structure factor $S(k)$ vanishes,[15] so all the screening comes from counterions. In other words, polyions do not screen electrostatic interactions at very short length scales because they cannot “wrap around” counterions to screen them. Instead, polyions contribute to screening only at longer length scales. Thus, both polyions and counterions contribute to screening at small wavevectors k.

We note that it is simple to generalize eq 6 to include salt. If the screening due to salt alone is denoted as ${\kappa_s}^2 = 4\pi l_B\phi_s$, where ϕ_s is the volume fraction of salt ions, then the total wavevector-dependent screening is

$$\kappa^2(k) = {\kappa_0}^2\frac{f}{1 + f}[fS(k) + 1] + {\kappa_s}^2 \tag{8}$$

B. Self-Consistent Calculation. The RPA result in eq 5 represents an estimate of the free energy when the structure of the polyion is known. However, the structure is not known, and our goal is to calculate it. In this paper, we will assume that the structure of the chain is semiflexible and can be characterized by two quantities: the average contour length and a persistence length. This simplifying assumption has also been adopted by Barrat and Joanny[5] and Ha and Thirumalai[6] to describe a single, intrinsically flexible polyelectrolyte chain. However, Li and Witten[7] claim that this assumption leads to erroneous scaling behavior. We will discuss this issue further in section III.

Given the assumption that the structure is characterized by a persistence length, one might be tempted to minimize eq 5 with respect to persistence length to determine the electrostatic persistence length. This is wrong, however, because the RPA result for the free energy is not variational. In other words, we cannot show that the RPA free energy is higher than the true free energy, so we may not minimize it to find the preferred chain structure. Our aim is to calculate the optimal chain structure in a way that retains the beautiful physical result of wavevector-dependent screening. To do so, we have used a self-consistent method introduced by Edwards and Singh[11] to describe the structure of excluded volume chains as a function of polymer concentration in solution. This method has also been used by Ha and Thirumalai[6] to describe the conformations of a single polyelectrolyte chain. The idea is to approximate the mean-square end–end distance of the system of interacting chains with an intrinsic persistence length, l_0, by the mean-square end–end distance of a system of non-interacting chains with a different, electrostatically-stiffened persistence length, l. Thus, the first step in the calculation is to find the Hamiltonians characterizing these two systems, and the second step is to calculate the mean-square end–end distance given these Hamiltonians.

1. Definition of Interacting and Trial Hamiltonians. Our first task is to construct the Hamiltonians for two systems: a solution of interacting chains with intrinsic persistence length l_0 (described by the Hamiltonian H_1) and a solution of non-interacting chains with electrostatic persistence length l (described by the trial Hamiltonian H_t). We will construct the trial Hamiltonian first.

Since the trial Hamiltonian describes a system of non-interacting chains, it is simply the sum over chains of a single-chain Hamiltonian H_c that describes a semi-flexible chain with persistence length l:

$$H_t = \sum_{n_-} H_c(l) \tag{9}$$

where the sum over n_- represents the sum over all chains. We use a semiflexible chain Hamiltonian $H_c(l)$ that is an approximation to the true semiflexible chain, or wormlike chain.[16] If we define $\vec{r}(s)$ as the position vector of a segment of the chain as a function of the contour variable s, where $0 \leq s \leq M$, then the wormlike chain obeys the constraint that the tangent vector $\vec{u}(s) \equiv \partial\vec{r}/\partial s$ has unit length $|\vec{u}(s)|^2 = 1$ for all s. This describes a chain that is not extensible but can bend. The constraint on the tangent vector makes it difficult to solve for the structure factor of the chain. We therefore follow the approach of Ha and Thirumalai[6] and adopt the semiflexible chain Hamiltonian of Lagowski, Noolandi, and Nickel[17] (LNN), which only imposes the constraint on average: $\langle \vec{u}^2(s) \rangle = 1$. The Hamiltonian is

$$\beta H_c(l) = \frac{3}{4l}\left[\int_0^M \mathrm{d}s \left(\frac{\partial \vec{r}}{\partial s}\right)^2 + l^2 \int_0^M \mathrm{d}s \left(\frac{\partial^2 \vec{r}}{\partial s^2}\right)^2\right] + \frac{3}{4}\left[\left(\frac{\partial \vec{r}}{\partial s}\right)^2\bigg|_0 + \left(\frac{\partial \vec{r}}{\partial s}\right)^2\bigg|_M\right] \tag{10}$$

This Hamiltonian yields a mean-square end–end distance

$$\langle R^2 \rangle \equiv \langle (\vec{\mathrm{r}}(M) - \vec{\mathrm{r}}(0))^2 \rangle = 2l^2\left(\frac{M}{l} - 1 + \mathrm{e}^{-M/l}\right) \tag{11}$$

which is identical to the corresponding expression for a wormlike chain.[16]

The system of interacting chains with intrinsic persistence length l_0 is described by the Hamiltonian

$$H_1 = \sum_{n_-} H_c(l_0) + H_{\mathrm{int}} \tag{12}$$

where $H_c(l_0)$ is given by eq 10 with l_0 substituted for l. The second term, H_{int}, is an interaction Hamiltonian that describes the electrostatic interactions between chains. We use the insight provided by the RPA free energy to make an ansatz for the form of the interaction. In terms of wavevector k, the screened Coulomb interaction for chains with charge fraction f with screening length κ^{-1} is described by the Hamiltonian

$$\beta H_{\mathrm{scr}} = 4\pi l_B f^2 \int \frac{d^3k \hat{\rho}(\vec{k})\, \hat{\rho}(-\vec{k})}{(2\pi)^3(k^2 + \kappa^2)} \tag{13}$$

where l_B is the Bjerrum length and $\hat{\rho}(\vec{k})$ is the Fourier transform of the local charge density defined in eq 2. According to the RPA result, however, the screening length is wavevector-dependent. Thus the generalization of eq 13 suggested by the RPA result is

$$\beta H_{\mathrm{int}} = 4\pi l_B f^2 \int \frac{d^3k \hat{\rho}(\vec{k})\, \hat{\rho}(-\vec{k})}{(2\pi)^3(k^2 + \kappa^2(k))} \tag{14}$$

where $\kappa^2(k)$ is given by eq 6 in the case of no added salt, and by eq 8 in the case of added salt.[18] Note from eqs 6 and 8 that the interaction Hamiltonian depends on the single-chain structure factor through $\kappa^2(k)$. The structure factor, in turn, depends on the persistence length of the chains, and can be calculated given the Hamiltonian H_c in eq 10. According to the RPA, the appropriate persistence length would be the intrinsic one, l_0. We provide a more accurate estimate of the interaction by using the electrostatic persistence length, l, instead. This is an uncontrolled approximation, but it improves substantially on the simple RPA result. Thus our final ansatz for the Hamiltonian H_1 of the fully interacting system of charged chains and counterions is given by eq 12 with H_c depending on l_0 and H_{int} depending on l.

In summary, the Hamiltonian for the system of interacting chains with persistence length l_0 is

$$H_1 = \sum_{n_-} H_c(l_0) + H_{\mathrm{int}} \tag{15}$$

and the trial Hamiltonian for the system of non-interacting chains with persistence length l is

$$H_t = \sum_{n_-} H_c(l) \tag{16}$$

where H_c is given by eq 10 and H_{int} by eq 14.

2. Self-Consistent Calculation of $\langle R^2 \rangle$. Now that we have constructed the two Hamiltonians in terms of the electrostatic persistence length l, we can solve for l self-consistently using the method of Edwards and Singh.[11] Given a Hamiltonian H, the mean-square end–end distance is

$$\langle (\vec{r}(s{=}M) - \vec{r}(s{=}0))^2 \rangle \equiv \langle R^2 \rangle \equiv \frac{\int D\vec{r}\, R^2 \mathrm{e}^{-H}}{\int D\vec{r}\, \mathrm{e}^{-H}} \tag{17}$$

We have set $\beta = 1$ here. It is straightforward to calculate $\langle R^2 \rangle_t$, with H in eq 17 given by the trial Hamiltonian H_t in eq 16, because the chains are non-interacting. However, it is not possible to solve for $\langle R^2 \rangle_1$

using the interacting Hamiltonian H_1. Thus, one cannot simply adjust l so that $\langle R^2\rangle_t$ and $\langle R^2\rangle_1$ are identical. However, one can calculate $\langle R^2\rangle_1$ as a perturbation series around $\langle R^2\rangle_t$:

$$\langle R^2\rangle_1 = \frac{\int D\vec{r}\, R^2 e^{-H_1}}{\int D\vec{r}\, e^{-H_1}} = \frac{\int D\vec{r}\, R^2 e^{-H_t} e^{-(H_1-H_t)}}{\int D\vec{r}\, e^{-H_t} e^{-(H_1-H_t)}} = \langle R^2\rangle_t + \Delta R^2 \quad (18)$$

In the last step, the exponential $e^{-(H_1-H_t)}$ is expanded in a power series. Finally, the first-order term in the correction ΔR^2 is set to 0:

$$\langle R^2\rangle_t \langle H_1 - H_t\rangle_t - \langle R^2(H_1 - H_t)\rangle_t = 0 \quad (19)$$

This is a self-consistent equation that can be solved for l. It can be rewritten explicitly in terms of the parameters M, l_0, and l_B :

$$\frac{1}{2}M\left(\frac{1}{l_0} - \frac{1}{l}\right) + \frac{1}{4}\frac{M}{l}e^{-M/l}\left(\frac{l}{l_0} - \frac{l_0}{l}\right) - \frac{1}{4}\left(3\frac{l}{l_0} - \frac{l_0}{l} - 2\right) \times (1 - e^{-M/l}) = \frac{1}{18}\int \frac{d^3k}{(2\pi)^3}\frac{4\pi l_B f^2}{k^2 + \kappa^2(k)}k^2 \int_0^M ds \int_0^M ds' \times \left[s' - s - 2le^{-M/2l}\sinh\frac{s'-s}{2l} \times \cosh\frac{M-s'-s}{2l}\right]^2 e^{-1/3k^2 l[|s'-s|-l(1-e^{-|s'-s|/l})]} \quad (20)$$

This is our final result. In the limit of zero concentration, all the screening comes from salt so $\kappa^2(k) = \kappa_s^2$ and eq 20 becomes identical to eq 14(b) of Ha and Thirumalai.[6] Thus, in the single-chain limit, our theory reduces to theirs. Note that there is a typographical sign error in the last term on the left-hand side of their eq 14(b).

Our theory differs from the double screening theory of Muthukumar[9] in several respects. The double screening theory uses a variational approach, assumes that the swelled chains can be modeled as Gaussian chains, and includes excluded volume screening as well as electrostatic screening. The screening from polyions is not assumed to be wavevector-dependent in the form of eq 6. In contrast, we use a self-consistent approach, assume that the swelled chains can be modeled as semiflexible chains, and ignore excluded volume screening; it is not necessary because electrostatic repulsion generates an effective excluded volume interaction between like ions that is included in our theory.[6] This can be seen from the following argument: consider two points s and s' along the chain that are separated by a contour distance large compared to the screening length κ^{-1}. Because of electrostatic repulsion, the two points will avoid each other. Thus, for $|s' - s| \gg \kappa^{-1}$, the electrostatic repulsion acts like an excluded volume interaction of size κ^{-1}. This swells the chain and changes the chain statistics. The effective excluded volume interaction is longer in range than the true one as long as κ^{-1} exceeds the monomer size. This condition is always met except at very high concentrations. Therefore, it is unnecessary to retain true excluded volume interactions among chains.

III. Results

Our result in eq 20 allows calculation of the electrostatic persistence length for many-chain systems from an analytic theory. Remarkably, our predictions are in quantitative agreement with molecular dynamics simulations by Stevens and Kremer[13] and by Stevens and Plimpton.[13] In the comparisons that follow, there are no adjustable parameters. The parameters that enter into eq 20 are the intrinsic persistence length, l_0, the Bjerrum length, l_B, and the index of polymerization, M. These parameters are all specified within the molecular dynamics simulations. Stevens and Kremer use a freely-jointed, bead-chain polymer model with excluded volume interactions between the beads, and between the beads and counterions.[13] The excluded volume interaction parameter is $\sigma = 1/1.1$ in units of the average bond length, which is 1 in our units. Because the intrinsic chain is a freely-jointed chain, the intrinsic persistence length is half of the average bond length, $l_0 = 0.5$. The simulations were carried out with a Bjerrum length of $l_B = 0.833\sigma = 0.758$. The volume fraction can be expressed in terms of the number density ρ as $\phi = 2(\pi/6)\, \rho\sigma^3$. With these parameters in hand, we can directly compare our results to theirs as a function of the index of polymerization, M, and volume fraction, ϕ. Note that ϕ is the volume fraction of polyelectrolytes and counterions. Thus, in a salt-free solution, the volume fraction of solvent is $1 - \phi$. In a solution with salt, the volume fraction of solvent is $1 - \phi - \phi_s$.

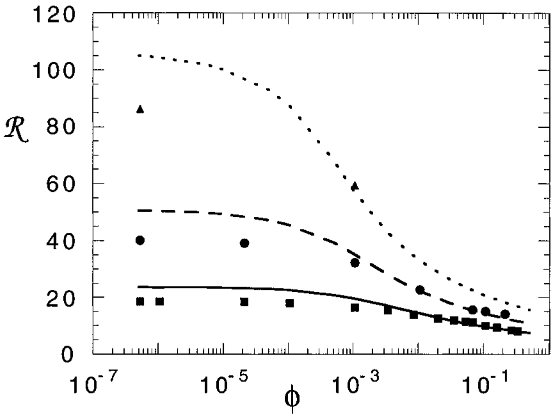

Figure 1. Effect of concentration on chain size in salt-free solutions. We plot the end−end distance, R, as a function of volume fraction, ϕ, for three different chain lengths, M. Our results are the curves (M = 32, solid; M = 64,dashed; M = 128, dotted). The simulation results of Stevens and Kremer[12] are the points (M = 32, squares; M = 64, circles; M = 128, triangles). There are no adjustable parameters in our theory. Note that the agreement is excellent, especially at higher concentrations.

The results of the comparison for salt-free solutions are shown in Figure 1. We have plotted the end−end distance $R \equiv (\langle R^2\rangle)^{1/2}$ as a function of ϕ for three different chain lengths, $M = 32$, $M = 64$, and $M = 128$. Our results are the curves (solid, M = 32; dashed, M = 64; and dotted, M = 128). The simulation results of Stevens and Kremer[13] are the points (squares, M = 32; circles, M = 64; and triangles, M = 128). It is clear from the plot that our theoretical results are in excellent agreement with the simulations, especially at higher concentrations. The results in the dilute, single-chain limit differ by roughly 20%.

The agreement between theory and simulation improves with increasing concentration. This suggests that the discrepancy in the single-chain limit may be due to the crude nature of our semiflexible chain model. Electrostatic repulsion gives rise to effective excluded volume interactions that swell the chain in the dilute limit and lead to a chain structure that is not well-

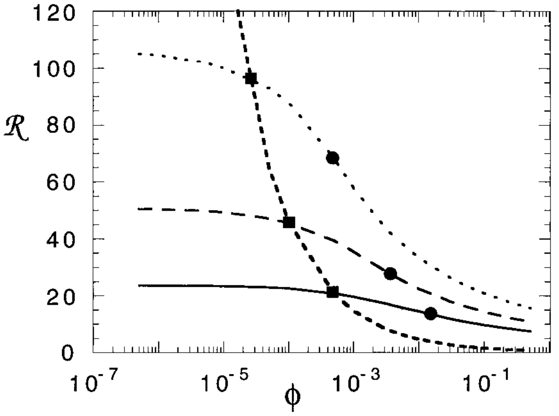

Figure 2. Onset of chain contraction with increasing volume fraction in salt-free solutions. The end–end distance, R, is again plotted as a function of ϕ for $M = 32$ (solid), $M = 64$ (dashed), and $M = 128$ (dotted). In addition, the overlap volume fraction, ϕ^*, is shown for each chain length as a solid circle. Finally, the screening length due to counterions, κ_c^{-1}, is shown as a heavy dashed line. The points where $k_c = R$ are labeled as solid squares. Note that chain contraction occurs at the squares for each of the three chain lengths, at volume fractions almost two orders of magnitude smaller than ϕ^*.

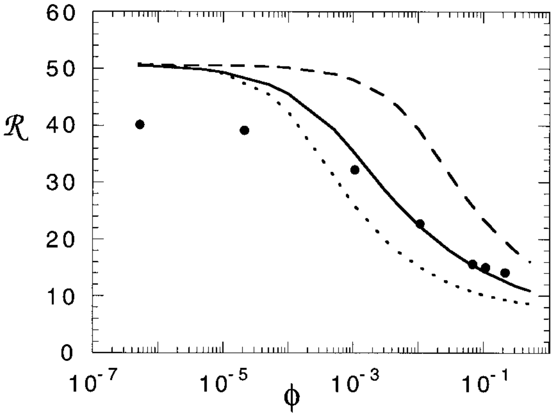

Figure 3. Importance of wavevector-dependent screening in salt-free solutions. The end–end distance R is plotted as a function of ϕ for $M = 64$, using three different models. The first model (solid) assumes that the screening length is wavevector-dependent as in eq 6. The second model (dashed) assumes that κ is given by the high wavevector limit of eq 6; screening is due to counterions alone. The third model (dotted) assumes that κ is given by the low wavevector limit of eq 6. The first model agrees significantly better with the simulation data (circles) of Stevens and Kremer.[12]

approximated by a semiflexible chain with a single persistence length. Instead, the chain is better described by a scale-dependent persistence length, as discussed by Li and Witten.[7] As the concentration increases, however, the effective excluded volume interaction is screened and the polyion structure is better approximated by a semiflexible chain. Another less important reason for the discrepancy between our results and those of Stevens and Kremer lies in our treatment of the counterions. We assume that the only effect of the counterions is to give a contribution to the screening length $\kappa^2(k)$ (see the last term in eq 6). This is known as the Debye–Hückel approximation for counterions. Simulations by Stevens and Kremer[20] show that this approximation works extremely well at higher concentrations. In the dilute limit, however, they find that the Debye–Hückel approximation for counterions yields values of R that are too high by 3–4%. Thus, this approximation is a contributing factor to our high estimate.

Stevens and Kremer[13] found that polyelectrolyte chains contract at volume fractions far below the overlap concentration, ϕ^*. The overlap concentration defines the point where the volume fraction of spheres of diameter $R(\phi)$ reaches the random close packing volume fraction of 0.64. Our calculated values of ϕ^* for $M = 32$, $M = 64$, and $M = 128$ are shown as the circles in Figure 2. The corresponding values for the simulation data are almost identical, since the theory and simulation are in nearly perfect agreement at these volume fractions. Note that our theory yields chain contraction at concentrations that are 2 orders of magnitude below ϕ^*, in agreement with the simulations. This contradicts earlier theories based on scaling considerations,[21–23] which predict that the chains remain rodlike up to ϕ^*. From eq 20, we see that the reason for chain contraction at concentrations below ϕ^* is that screening occurs on scales smaller than the chain size R. If we approximate the screening by the screening length due to counterions, given by the Debye–Hückel expression, $\kappa_c^{-1} = 1/(4\pi l_B\phi_c)^{1/2}$, then chain contraction should occur when the screening length, κ_c^{-1}, becomes smaller than the chain size, R. In Figure 2, we plot κ_c^{-1} (heavy dashed) as a function of ϕ. We also show R for $M = 32$ (solid), $M = 64$ (dashed), and $M = 128$ (dotted). The points where κ_c are marked by solid squares for each M. As expected, the onset of chain contraction is reasonably close to the squares, for all three chain lengths.

The wavevector dependence of the screening length turns out to be quite important. We explore the effect of wavevector dependence by replacing the wavevector-dependent screening, $\kappa^2(k)$, by its high k and low k limits. In Figure 3, we have plotted R as a function of ϕ for $M = 64$. The points are the results of the molecular dynamics simulations,[13] and the solid curve is the result of our full wavevector-dependent calculation (see eq 6). The results of replacing $\kappa^2(k)$ by its high k limit, where only counterions contribute to the screening, are shown in the dashed curve. This is a common approximation used in describing polyelectrolytes, but it clearly overestimates the electrostatic repulsion, which tends to swell the chain. This is not surprising, because polyion screening has been neglected. Another possible approximation is to use the low k limit of $\kappa^2(k)$. The results of this approximation are shown as the dotted curve in Figure 3; this evidently overestimates the amount of screening. Thus, Figure 3 demonstrates that using either the high k or low k limit of $\kappa^2(k)$ is insufficient; the agreement between theory and simulations at higher ϕ relies on using wavevector-dependent screening. In other words, chain connectivity strongly affects the nature of electrostatic screening. This makes intuitive sense, but it implies that scaling theories are inadequate for describing behavior at higher ϕ because the interactions cannot be characterized by a single screening length.

The effect of added salt can also be studied for solutions at arbitrary concentrations. Here, we compare our results to recent molecular dynamics simulation results obtained by Stevens and Plimpton.[14] The simulations were carried out on the same bead-spring model as described above, with the same parameters ($l_0 = 0.5$, $l_B = 0.758$). In all cases, the volume fraction of polyelectrolyte (including counterions) is held fixed at $\phi = 1.05 \times 10^{-3}$. The volume fraction of salt, ϕ_s, is then varied. The comparison is shown in Figure 4, where we have plotted R as a function of the screening length due to salt alone, $\kappa_s^{-1} = 1/(4\pi l_B\phi_s)^{1/2}$. There are simula-

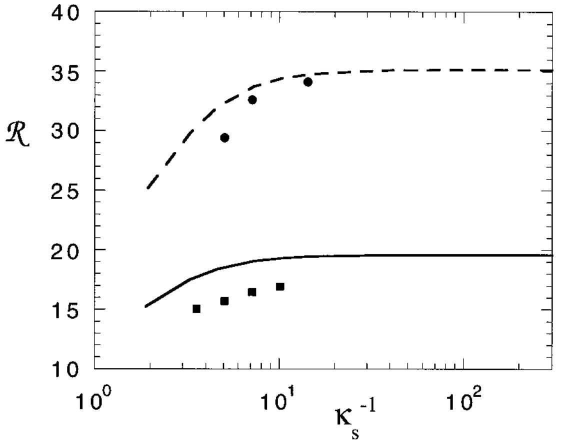

Figure 4. Dependence of chain size on added salt. The end−end distance, *R*, is plotted as a function of the Debye screening length due to salt, κ_s^{-1}, at a fixed volume fraction of polyelectrolyte, $\phi = 1.05 \times 10^{-3}$. Our results are the curves for $M = 32$ (solid) and $M = 64$ (dashed). The results of simulations by Stevens and Plimpton[13] are the points for $M = 32$ (squares) and $M = 64$ (circles). There are no adjustable parameters in our theory, and the agreement is excellent.

tion results for two different chain lengths, $M = 32$ (squares) and $M = 64$ (circles). Our results are also shown for $M = 32$ (solid) and $M = 64$ (dashed). The agreement is quite good; the discrepancy is again around 20%. In our calculations, we assume that the salt contributes only through the Debye screening length κ_s^2, and that the screening due to salt and to counterions and polyions is additive: see eq 8. The excellent agreement between our theory and the simulations implies that these are good approximations. The two sets of results show the same qualitative behavior: as the chain length increases, the chain swells more rapidly as the screening length κ_s^{-1} increases. This is not surprising, since longer chains swell more due to electrostatic repulsion in the salt-free limit. Note that salt does not have an appreciable effect on the chain radius until the screening length is fairly short, near $\kappa_s^{-1} \approx 5$. This corresponds to a concentration of $\phi_s \approx 4 \times 10^{-3}$, comparable to the volume fraction of polyelectrolyte, $\phi = 1.05 \times 10^{-3}$. In other words, salt does not affect the chain radius until the volume fraction of salt exceeds the volume fraction of polyelectrolyte.

We have tried without success to scale the curves shown in Figure 4 for different values of *M* and ϕ. For example, we have tried collapsing the data by plotting R/R_0 as a function of $(\phi_s/\phi)^{1/2}$, where R_0 is the size of the chain at the same ϕ in the absence of salt (the large screening length limit of the curves shown in Figure 4). This scaling is not ruled out by Stevens and Plimpton's data,[14] but is definitely inconsistent with our results. There is another scaling that is possibly consistent with the molecular dynamics simulations,[24] namely, R/R_0 vs $(n_s/n_p)^{1/2}$, where n_s is the number density of salt ions and n_p is the number density of polymer chains, but this scaling is also ruled out by our results. The fact that we have failed to find a way to collapse the data is not surprising, given that the screening due to polyions cannot be described by a single length scale.

In summary, we find that interactions between polyelectrolyte chains can be modeled successfully by a wavevector-dependent screening length. This physically reasonable ansatz leads to results in quantitative agreement with molecular dynamics simulations for salt-free polyelectrolyte solutions, by Stevens and Kremer,[13] and for salt-containing polyelectrolyte solutions, by Stevens and Plimpton.[14] In the dilute, single-chain limit, our theory yields estimates for the chain size *R* that are too large by roughly 20%. We believe that the discrepancy is mostly due to the crude nature of the semiflexible model, which is a poor description of a swelled excluded-volume chain. We are now refining the approach to allow for a scale-dependent persistence length. At higher volume fractions, however, where the chain is well-approximated by a semiflexible model with a single persistence length, the agreement with simulations is nearly perfect. This is an important first step toward closing the gap between theory, which has previously concentrated on the single-chain limit, and experiments, which always operate at nonzero concentrations.

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