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Elastic Modulus and Equilibrium Swelling of Polyelectrolyte Gels

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ABSTRACT: We present a scaling theory for the modulus G of polyelectrolyte gels as a function of strand length between cross-links, monomer concentration c, salt concentration c_s, and preparation conditions (monomer concentration c_0 and salt concentration $c_s°$). The theory assumes affine displacement of the junction points when the concentration is changed. With no added salt ($c_s = c_s° = 0$), we predict a new concentration dependence of the modulus $G \sim c^{5/6}$. In the high-salt limit, we predict the usual concentration dependence for uncharged polymers but a novel dependence on salt concentration, $G \sim c^{7/12}c_s^{1/4}$. We also predict the modulus to decrease as charge is added to the gel strands. The predicted effects of added salt and charge on modulus have recently been observed by Candau and co-workers. At low concentrations, we discuss the strong stretching of network strands and its effect on modulus and equilibrium swelling.

1. Introduction

Networks made from charged polymers are quite common in both nature and industry. Polyelectrolyte gels, with a single sign of charge covalently bonded to the polymer chain, are capable of swelling to much greater extents than their uncharged counterparts because of the high osmotic pressure due to dissociated counterions. Thus they are used[1] as superabsorbent materials (e.g., diapers), as ion-exchange resins, and also as the carrier for novel drug delivery that targets specific organs. Early attempts to model the swelling of polyelectrolyte gels[2,3] encompassed much of the important physics, as it was recognized that swelling was determined by a balance between the osmotic pressure of free ions acting to swell the gel and the elasticity of the gel that restricts swelling. The osmotic part has long been understood in terms of the Donnan equilibrium.[4] We use a scaling model for the configuration of intrinsically flexible polyelectrolyte chains in semidilute solution[5−8] and our recent ideas relating network strand configuration and modulus[9] to construct a scaling theory for the modulus and swelling of polyelectrolyte gels.

We consider polyelectrolyte gels, prepared by randomly cross-linking a semidilute solution of linear polyelectrolyte chains (at monomer number density c_0). The solvent must have a high dielectric constant (e.g., water) so that at least some of the counterions dissociate from the charged chain, leaving A monomers between effective charges. We also allow for the possibility of salt in the preparation state, with concentration $c_s°$ (number density). The cross-linking creates a network of charged strands between cross-link junctions, with an average number N of monomers (of size b) per strand. We focus on the limit with many charges per strand ($N \gg A$). The number density of free ions in the preparation state is the sum of the uncondensed counterions (c_0/A) and any dissociated salt ions ($2c_s°$, since we assume, for simplicity, monovalent salt).

The shear modulus of the network in its preparation state is identical to the modulus of an uncharged polymer, simply kT per strand.

$$G_0 \cong \frac{c_0}{N}kT \tag{1}$$

This well-known result holds for all strongly cross-linked gels, independent of the charge on the chain and salt concentration. For weakly cross-linked gels, with a strand length larger than a critical length for entanglement N_e, the modulus is determined by the number density of entanglement strands,[9] and eq 1 holds (roughly) with N replaced by N_e. In what follows, we focus on strongly cross-linked gels, but all results are also valid in the weakly cross-linked regime ($N > N_e$) by merely replacing N with N_e, the entanglement strand length in the preparation state.

We start by reviewing our recent results for the configuration of polyelectrolyte chains in semidilute solution (Section 2). Since we assume cross-linking does not change the chain configurations, these results apply directly to the strands of a polyelectrolyte gel in its preparation state. Section 3 describes stretching a polyelectrolyte chain by pulling its ends, as this happens to the strands of a polyelectrolyte gel when it is swollen. In section 4 we consider the concentration dependence of the modulus of polyelectrolyte gels at fairly high concentrations, where the strands of the network are weakly stretched. Since the strong osmotic pressure arising from counterion entropy can cause polyelectrolyte gels to reach very low concentrations, in sections 5

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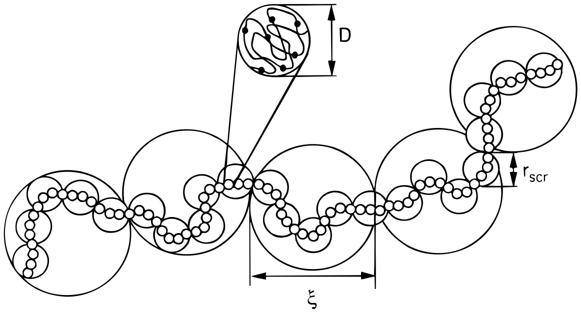

Figure 1. Schematic of a polyelectrolyte chain in semidilute solution with added salt. See text for definitions of length scales.

and 6 we then consider stronger stretching of strands to calculate the modulus at these low concentrations. In section 7 we calculate the swelling of the polyelectrolyte gel in equilibrium with solvent, by finding the concentration at which the osmotic pressure is equal to the modulus. We finish with a discussion of our results and a comparison with experiments in section 8.

2. Semidilute Polyelectrolyte Solutions

We briefly summarize the scaling picture[5−8] of a flexible polymer with salts covalently bonded to it that dissociate in solution leaving charged groups on the chain (a polyelectrolyte). The configuration of a polyelectrolyte chain in semidilute solution with added salt is shown schematically in Figure 1. On sufficiently small length scales (less than the electrostatic blob[5,8] size D), the polymer−solvent interactions dominate over electrostatics, and the configuration of the g_e monomers in each electrostatic blob thus depends on solvent quality.

$$D \cong b g_e^{\nu} \qquad T \geq \Theta \tag{2}$$

The electrostatic blob is a random walk with $\nu = 1/2$ in Θ solvent ($T = \Theta$) and a self-avoiding walk with $\nu \cong 3/5$ in good solvent ($T \gg \Theta$). Following de Gennes et al.,[5] in good and Θ solvent the electrostatic blob is determined as the scale where the electrostatic interaction energy due to charge repulsion within the electrostatic blob $(g_e/A)^2 e^2/(\epsilon D)$ is of order of the thermal energy kT (e is the elementary charge and ϵ is the dielectric constant).

The presence of charges allows polyelectrolytes to be soluble in poor solvents for the uncharged polymer, if the solvent has a high dielectric constant. In poor solvent ($T < \Theta$), we define a reduced temperature $\tau \equiv (\Theta - T)/\Theta$. The electrostatic blob is a collapsed globule[10,11] with a number density of monomers, $\rho \cong g_e/D^3$, determined by the balance of two-body attraction ($\tau b^3 \rho^2$) and three-body repulsion ($b^6 \rho^3$) that depends on temperature $\rho \cong \tau/b^3$.

$$D \cong b(g_e/\tau)^{1/3} \qquad T < \Theta \tag{3}$$

The collapsed electrostatic blob contains some solvent (unless $T \ll \Theta$, making $\tau \cong 1$). The collapsed state is a dense globule of thermal blobs of size ξ_T with g_T monomers. Since the thermal blobs are space-filling ($\rho = g_T/\xi_T^3$) random walks ($\xi_T \cong b g_T^{1/2}$), the thermal blob size is $\xi_T \cong b/\tau$. In poor solvent, the electrostatic repulsion between charges is balanced by the interfacial energy[10] γD^2, with a surface tension[11] γ that is kT per thermal blob on the surface, $\gamma \cong kT/\xi_T^2 \cong \tau^2 kT/b^2$. We can now write expressions for the number of monomers in the electrostatic blob for the three types of solvent.

$$g_e \cong \begin{cases} (A^2/u)\tau & T < \Theta \\ (A^2/u)^{2/3} & T = \Theta \\ (A^2/u)^{5/7} & T \gg \Theta \end{cases} \tag{4}$$

The parameter u is the ratio of the Bjerrum length $l_B = e^2/(\epsilon kT)$ (the scale where the electrostatic interaction energy of two elementary charges in a medium of dielectric constant ϵ is of the order of the thermal energy kT) and the monomer size ($u \equiv l_B/b$). A polyelectrolyte chain in dilute solution with no salt is a linear assembly of electrostatic blobs,[5−8] with length $L \cong DN/g_e \cong Nb/B$, where the second equation effectively defines the parameter B. Note that the electrostatic blob characteristics are independent of salt concentration and polyelectrolyte chain length and concentration, provided that counterion condensation (accounted for by the parameter A) does not change. Thus the electrostatic blobs are simply renormalized monomers, and the contour length of the chain of electrostatic blobs at any concentration is $L \cong Nb/B$. All information about counterion condensation and solvent quality is contained in the parameter B, which can be written[8] in terms of A^2/u and τ.

$$B \cong \begin{cases} (A^2/u)^{2/3}\tau & T < \Theta \\ (A^2/u)^{1/3} & T = \Theta \\ (A^2/u)^{2/7} & T \gg \Theta \end{cases} \tag{5}$$

In semidilute solution, the correlation length ξ separates the small scales, where the chain adopts its dilute solution configuration, from the large scales, where the chain is a random walk. In the absence of salt, this correlation length[5−8] is $\xi \cong (B/cb)^{1/2}$. Recently, we have argued that the electrostatic screening length r_{scr} is essentially equivalent to the correlation length in salt-free semidilute polyelectrolyte solutions.[7,8]

$$r_{scr} \cong \xi \cong (B/cb)^{1/2} \qquad \text{low salt} \tag{6}$$

This electrostatic screening length is proportional to the Debye length, being either larger or smaller depending on the charge on the chain and the quality of solvent.[8]

For weakly charged polyelectrolytes in the presence of added salt, electrostatic interactions are screened at the Debye length.[6,12]

$$r_{scr} \cong (l_B c_S)^{-1/2} \qquad \text{high salt} \tag{7}$$

For arbitrary salt concentration, the electrostatic screening length is approximated as a simple crossover between (6) and (7).

$$r_{scr} \cong (B/cb)^{1/2}(1 + Buc_s/c)^{-1/2} \tag{8}$$

We assume this electrostatic screening length is proportional to the effective persistence length of the chain.[8] On length scales between the electrostatic blob size D and the electrostatic screening length r_{scr}, charge repulsion makes the chain configuration a linear assembly of electrostatic blobs.

Following the reasoning in ref 8, we can write the following expression for the correlation length.

$$\xi \cong (B/cb)^{1/2}(1 + Buc_s/c)^{1/4} \tag{9}$$

Notice that the correlation length becomes larger than the electrostatic screening length when a significant amount of salt is added. Between the electrostatic screening length and the correlation length ξ, the polyelectrolyte chain is a self-avoiding walk. Each correlation blob has g ($\cong c\xi^3$) monomers in it.

$$g \cong (B/b)^{3/2}c^{-1/2}(1 + Buc_s/c)^{3/4} \qquad (10)$$

As in solutions of uncharged polymers, on length scales beyond the correlation length, the chain statistics are Gaussian. The end-to-end distance R of the polyelectrolyte chain is thus determined as a random walk of correlation blobs.

$$R \cong \xi(N/g)^{1/2} \cong (b/cB)^{1/4}N^{1/2}(1 + Buc_s/c)^{-1/8} \quad (11)$$

We summarize the configuration of a polyelectrolyte chain in semidilute solution in Figure 1. The chain has different fractal statistics on different length scales r. Inside the electrostatic blob (r < D), the chain is unperturbed by the charges, with a configuration that depends on polymer−solvent interaction energetics. Between the electrostatic blob size and the electrostatic screening length (D < r < r_{scr}), electrostatics dominate and there is a linear assembly of electrostatic blobs. With added salt there is a regime between the electrostatic screening length and the correlation length (r_{scr} < r < ξ) where the chain is a self-avoiding walk of electrostatic screening blobs (with no salt $r_{scr} \cong \xi$). On its largest length scales (ξ < r < R), the polyelectrolyte is a random walk of correlation blobs.

3. Stretching a Polyelectrolyte Chain

When polyelectrolyte gels are swollen, the strands of the gel are stretched. We therefore need to consider stretching of polyelectrolyte chains by pulling their ends with force f. The stretching occurs only on the largest possible length scales because this is the way the chain can maximize its configurational entropy in the stretched state. The stretching of a chain was considered by Pincus,[14] who found that a stretched chain is essentially unperturbed on length scales smaller than the stretching scale ξ_P, while on scales larger than ξ_P, the chain adopts a linear (stretched) configuration, with ξ_P determined by the applied force f: $\xi_P \cong kT/f$. Pincus has shown that the energy E required to stretch a chain is kT per stretched blob, hereafter called a Pincus blob.

$$E \cong \frac{N}{g_P}kT \qquad T \geq \Theta \qquad (12)$$

The number of monomers in the Pincus blob g_P depends on the unperturbed configuration of the chain. The size of the stretched chain R' is the product of the Pincus blob size ξ_P and the number of such blobs per chain N/g_P, since the stretched chain is a linear assembly of Pincus blobs.[14]

$$R' \cong \xi_P N/g_P \qquad (13)$$

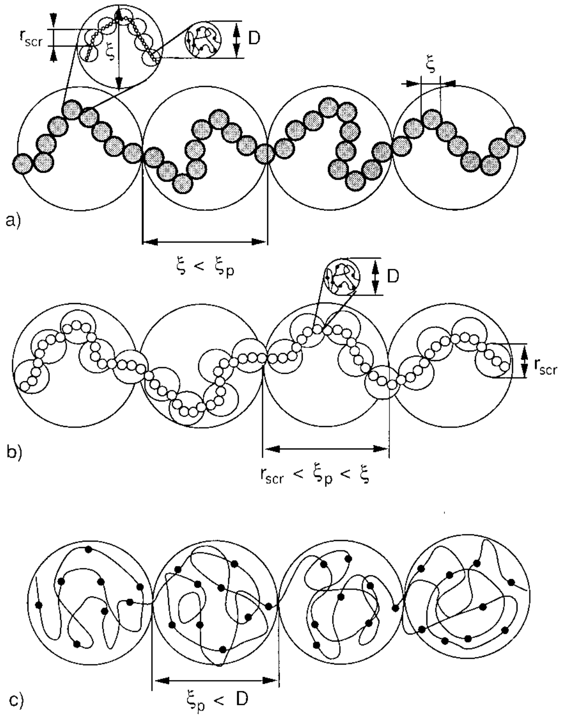

Figure 2. Schematic of a stretched polyelectrolyte network strand: (a) stretching the Gaussian walk of correlation blobs; (b) stretching the self-avoiding walk of electrostatic screening blobs; (c) stretching the electrostatic blobs. Note that the chain is magnified as it is progressively stretched from (a) to (c), in such a way that the Pincus blob size is kept constant, for clarity of illustration in the figures.

The configuration of a stretched polyelectrolyte chain is shown schematically in Figure 2, where we see that there are three possibilities. For weak stretching, where the stretching occurs on length scales larger than the correlation length ($\xi_P > \xi$, Figure 2a), only the random walk is stretched. The polyelectrolyte chain statistics are not perturbed on length scales smaller than ξ_P, so $\xi_P \cong \xi(g_P/g)^{1/2}$. This Gaussian stretching continues until ξ_P reaches the correlation length ξ. Upon further stretching, the self-avoiding walk between the electrostatic screening length r_{scr} and the correlation length ξ must be stretched (Figure 2b). Equation 13 describes the stretched size, with the Pincus blob size $\xi_P \cong r_{scr}(g_P/g_{scr})^{3/5}$, where $g_{scr} \cong r_{scr}B/b$ is the number of monomers inside the electrostatic screening volume r_{scr}^3. The stretching of the self-avoiding walk continues until the Pincus blob size reaches the electrostatic screening length. The configuration is then a linear assembly of electrostatic blobs, which must be stretched for $\xi_P < D$ (Figure 2c, strong stretching), resulting in $\xi_P \sim bg_P^{\nu}$ in good ($\nu \cong {}^3/_5$) and Θ ($\nu = {}^1/_2$) solvents. In each of the three cases, we can solve for the number of monomers in a Pincus blob.

$$g_P \cong \begin{cases} (\xi N/R')^2/g & \xi_P > \xi \quad \text{(weak stretching)} \\ (r_{scr}N/R')^{5/2}/g_{scr}^{\ 3/2} & r_{scr} < \xi_P < \xi \quad \text{(intermediate)} \\ (bN/R')^{1/(1-\nu)} & \xi_P < D \quad \text{(strong stretching)} \end{cases} \qquad (14)$$

Notice that when the Pincus blob size reaches the electrostatic screening length, ξ_P jumps discontinuously from r_{scr} to the electrostatic blob size D. This is because the polyelectrolyte is rodlike on scales between D and r_{scr} (see Figure 1). The consequences of this discontinuous jump are discussed in Appendix B, using an inverse Langevin function.

In a poor solvent for the uncharged polymer, the chain in the strongly stretched regime can be thought of as a cylinder of diameter ξ_P and length R'. The main contribution to elasticity is the creation of new surface area as the cylinder is stretched.[10] The volume of the cylinder is unchanged by stretching, as it is determined by the balance of two-body and three-body interactions, requiring $R'\xi_P{}^2 \cong Nb^3/\tau$, as discussed in section 2. The surface tension in poor solvent is $\gamma \cong \tau^2 kT/b^2$, which leads to the stretching energy per chain.

$$E \cong \gamma R'\xi_P \cong (\tau^3 NR'/b)^{1/2} kT \qquad \xi_P < D, \qquad T < \Theta \quad (15)$$

In all cases, the modulus of a polyelectrolyte gel is the product of the energy for stretching a strand and the number density of strands c/N, where c is the number density of monomers.

$$G \cong \frac{c}{N}E \qquad (16)$$

The modulus is always determined by eq 16. The energy E to stretch a single strand is given by eqs 12 and 14 except in the case of strong stretching in a poor solvent, where the energy is determined by eq 15, because in this case the surface energy controls the stretching. We summarize the modulus predictions in terms of the stretched strand size R' in eq 17.

$$G \cong \frac{ckT}{N}\begin{cases} \left[\dfrac{R'}{\xi(N/g)^{1/2}}\right]^2 & \xi_P > \xi \\ \left[\dfrac{R'}{r_{\mathrm{scr}}(N/g_{\mathrm{scr}})^{3/5}}\right]^{5/2} & r_{\mathrm{scr}} < \xi_P < \xi \\ \left[\dfrac{R'}{bN^{\nu}}\right]^{1/(1-\nu)} & \xi_P < D, \quad T \geq \Theta \\ \left[\dfrac{\tau^3 NR'}{b}\right]^{1/2} & \xi_P < D, \quad T < \Theta \end{cases} \qquad (17)$$

In the next three sections, we use eq 17 to derive explicit predictions for the modulus of polyelectrolyte gels as functions of concentration, salt concentration, effective charge, and preparation conditions.

4. Modulus in the Weak Stretching Regime ($\xi_P > \xi$)

We first consider the modulus in the high-concentration regime depicted in Figure 2a, where the stretching of strands occurs on length scales where the strand is a random walk. Using the $\xi_P > \xi$ case of eq 17, we can write the modulus in a form originally derived by Panyukov[15] and recently applied to the modulus of uncharged gels.[9]

$$G \cong \frac{ckT}{N}\left(\frac{\lambda R_0}{R}\right)^2 \qquad (18)$$

The stretched size of the strand is $R' = \lambda R_0$, where the linear expansion factor is λ and R_0 is the strand size in the preparation state. $R \cong \xi(N/g)^{1/2}$ is the size the strand would have if it were a free chain of N monomers in the new state (eq 11). The linear expansion factor for the strand is assumed to be affinely related to the macroscopic change in the gel size.

$$\lambda \cong \left(\frac{c}{c_0}\right)^{-1/3} \qquad (19)$$

The strand size R_0 in the preparation state is, presumably, unperturbed by the cross-linking and thus identical to a free polyelectrolyte chain of N monomers (eq 11) at polyelectrolyte concentration c_0 and salt concentration $c_s°$ (the subscript or superscript ° denotes preparation state).

$$R_0 \cong (b/c_0B_0)^{1/4}N^{1/2}(1 + B_0uc_s°/c_0)^{-1/8} \qquad (20)$$

The actual size of the network strand in the new state is λR_0.

$$\lambda R_0 \cong (b/B_0)^{1/4}N^{1/2}c_0{}^{1/12}(1 + B_0uc_s°/c_0)^{-1/8}c^{-1/3} \qquad (21)$$

We can now use eq 18 to predict the modulus in the new state.

$$G \cong \frac{kT}{N}c^{5/6}c_0{}^{1/6}\left[\frac{1 + Buc_s/c}{1 + B_0uc_s°/c_0}\right]^{1/4}\left(\frac{B}{B_0}\right)^{1/2} \qquad (22)$$

We allow for the possibility that the effective charge on the chain and/or the solvent quality could change between preparation and testing, i.e., $B \neq B_0$. For example, such changes could be brought about by changing the solvent (affecting both solvent quality and dielectric constant) or by changing the extent of neutralization of a weak polyacid gel. Recent data of Skouri et al.[16] on poly(acrylic acid) gels in water addressed the second case and indicate that as charge is added to the gel, its modulus decreases. This experimental result is qualitatively predicted by eq 22, as $B \cong (A^2/u)^{2/7}$ for polyelectrolytes in good solvent[8] (see eq 5; as charge is added, B decreases and thus G decreases).[17]

In the low-salt limit ($c \gg Buc_s$ and $c_0 \gg B_0uc_s°$), eq 22 takes on a simpler form.

$$G \cong \frac{kT}{N}c^{5/6}c_0{}^{1/6}\left(\frac{B}{B_0}\right)^{1/2} \qquad \text{low salt} \qquad (23)$$

This concentration dependence of modulus ($G \sim c^{5/6}$) is a new prediction that is unique to polyelectrolytes. Unfortunately, we are not aware of any data in the literature to test eq 23.

In the high-salt limit ($c \ll Buc_s$ and $c_0 \ll B_0uc_s°$), eq 22 shows a dependence of modulus on salt concentration.

$$G \cong \frac{kT}{N}c^{7/12}c_0{}^{5/12}\left(\frac{c_s}{c_s°}\right)^{1/4}\left(\frac{B}{B_0}\right)^{3/4} \qquad \text{high salt} \qquad (24)$$

Note that for isoionic dilution of polyelectrolyte gels prepared in high-salt solution (i.e., $c_s = c_s° \gg c_0/(B_0u)$, with $B = B_0$), the expression for the modulus of uncharged gels in good solvent is recovered.[9] This is expected because the high-salt limit of polyelectrolyte solutions is the same as the good solvent limit of solutions of uncharged polymers.[6,8] The prediction of an increase in modulus as salt is added is new and has recently been observed,[16] as will be discussed in section 8. This result is understood in terms of eq 18 because increasing the salt concentration decreases the free chain size R and thus increases the modulus.

5. Modulus in the Intermediate Stretching Regime ($r_{\mathrm{scr}} < \xi_P < \xi$)

In the high-salt regime ($c < Buc_s$), the electrostatic screening length (r_{scr}, eq 8) is smaller than the correla-

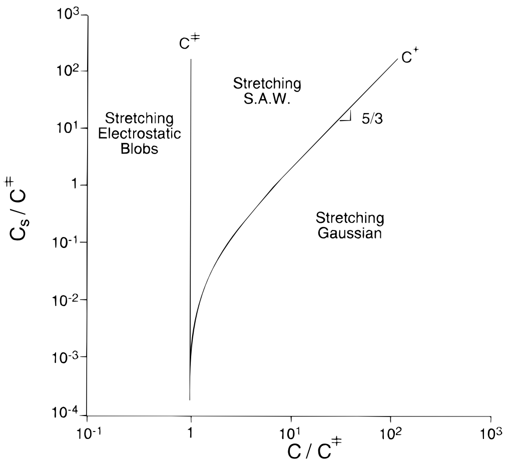

Figure 3. Phase diagram for swelling regimes of a polyelectrolyte gel with $Bu = 20$. Boundaries are $c^{\dagger}$ (eq 25) and $c^{\ddagger}$ (eq 26).

tion length (ξ, eq 9), as depicted in Figure 1. Thus, there are two crossover concentrations, $c^{\dagger}$ and $c^{\ddagger}$, determined from the points where the Pincus blob size reaches the correlation length and the electrostatic screening length, respectively. When $\xi_P \cong \xi$, the stretched strand is a linear assembly of correlation blobs ($\lambda R_0 \cong \xi N/g$), and this is used to calculate $c^{\dagger}$, using eqs 9, 10, and 21.

$$c^{\dagger}(1 + Buc_s/c^{\dagger})^{-3/2} \cong \frac{B^3 c_0^{\ 1/4}}{B_0^{\ 3/4} N^{3/2} b^{9/4}} (1 + B_0 u c_s°/c_0)^{-3/8} \tag{25}$$

The concentration $c^{\ddagger}$ is the point where ξ_P jumps discontinuously from the electrostatic screening length r_{scr} just above $c^{\ddagger}$ to the electrostatic blob size D just below $c^{\ddagger}$. This occurs when the stretched strand size reaches the contour length of the chain of electrostatic blobs ($\lambda R_0 \cong L \cong Nb/B$, with λR_0 given by eq 21).

$$c^{\ddagger} \cong \frac{B^3 c_0^{\ 1/4}}{B_0^{\ 3/4} N^{3/2} b^{9/4}} (1 + B_0 u c_s°/c_0)^{-3/8} \tag{26}$$

The phase diagram for the different regimes of modulus of polyelectrolyte gels is shown in Figure 3 for variables c and c_s and the specific example of $Bu = 20$. For high gel concentration and low enough salt concentration ($c > c^{\dagger}$), the Pincus blobs are larger than the correlation blobs ($\xi_P > \xi$) and the weak stretching results of section 4 apply for the modulus. At very low concentrations ($c < c^{\ddagger}$), the Pincus blobs are smaller than the electrostatic blobs ($\xi_P < D$) and the modulus in this regime of strong stretching will be calculated in section 6. For sufficiently high-salt concentrations, there is an intermediate regime of concentration ($c^{\ddagger} < c < c^{\dagger}$) where the Pincus blobs are self-avoiding walks ($r_{scr} < \xi_P < \xi$). The modulus in this intermediate regime is calculated using the $r_{scr} < \xi_P < \xi$ case of eq 17 with $R' = \lambda R_0$ (eq 21) and r_{scr} given by eq 8.

$$G \cong kT \frac{B c^{2/3} c_0^{\ 5/24} (1 + Buc_s/c)^{1/2}}{B_0^{\ 5/8} N^{5/4} b^{3/8} (1 + B_0 u c_s°/c_0)^{5/16}} \qquad c^{\ddagger} < c < c^{\dagger} \tag{27}$$

As seen in Figure 3, this regime is most important at high salt, where the modulus is predicted to have a weak concentration dependence ($G \sim c^{1/6}$).

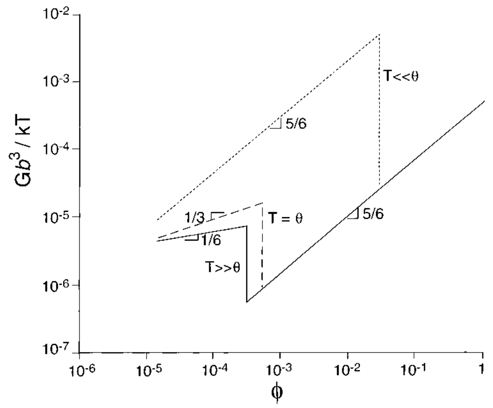

Figure 4. Modulus of polyelectrolyte gels in the low-salt limit ($c \gg Buc_s$) as a function of concentration for different qualities of solvent (solid lines are for good solvent, dashed lines are for Θ solvent, and dotted lines are for poor solvent with $\tau = 1$). Examples use $N = 1000$, $A = 10$, $u = 2.3$, and $c_0 b^3 = 0.1$. The modulus is given by eq 28 below $c^{\ddagger}$ and by eq 23 above $c^{\ddagger}$.

6. Modulus in the Strong Stretching Regime ($\xi_P < D$)

At $c^{\ddagger}$ the strand configuration is a linear assembly of electrostatic blobs. For concentrations lower than $c^{\ddagger}$, this assembly must be stretched (Figure 2c). The $\xi_P < D$ cases of eq 17 apply for the modulus (each with $R' = \lambda R_0$, given by eq 21) for $c < c^{\ddagger}$.

$$G \cong kT \begin{cases} \dfrac{c^{5/6} c_0^{\ 1/24} \tau^{3/2}}{B_0^{\ 1/8} N^{1/4} b^{3/8} [1 + B_0 u c_s°/c_0]^{1/16}} & T < \Theta \\ \dfrac{c^{1/3} c_0^{\ 1/6}}{B_0^{\ 1/2} N b^{3/2} [1 + B_0 u c_s°/c_0]^{1/4}} & T = \Theta \\ \dfrac{c^{1/6} c_0^{\ 5/24}}{B_0^{\ 5/8} N^{5/4} b^{15/8} [1 + B_0 u c_s°/c_0]^{5/16}} & T \gg \Theta \end{cases} \tag{28}$$

For polyelectrolyte gels in the low-salt limit ($c \gg Buc_s$), the concentration dependence of the modulus is described by eq 22 for high concentrations $c > c^{\ddagger}$. As concentration is lowered toward $c^{\ddagger}$, the Gaussian slack is pulled out of the strands, until at $c^{\ddagger}$ the strand is a linear assembly of correlation blobs. However, since each correlation blob is a linear assembly of electrostatic blobs, this means that the strand configuration is a linear assembly of electrostatic blobs at $c^{\ddagger}$. Below $c^{\ddagger}$ the modulus is given by eq 28. In the vicinity of $c^{\ddagger}$, there is a large jump in the modulus (for all three solvents) because of the abrupt change in the Pincus blob size, from $\xi_P \cong r_{scr}$ just above $c^{\ddagger}$ to $\xi_P \cong D$ just below $c^{\ddagger}$. This crossover can be described by non-Gaussian stretching as the strand of correlation blobs becomes fully stretched, via the inverse Langevin function,[18] as discussed in Appendix B. The scaling predictions for the modulus, shown in Figure 4, do not account for this crossover function, and thus at the level of scaling, the modulus is discontinuous at $c^{\ddagger}$. Notice in Figure 4 that $c^{\ddagger}$ decreases as the solvent quality for the uncharged chain improves.

7. Equilibrium Swelling

The driving force for swelling gels with solvent comes from osmotic pressure (a lower free energy when the system has a larger volume). In uncharged gels this osmotic pressure arises from the configurational entropy of chains (kT per correlation blob). In polyelectrolyte gels, this polymer contribution to osmotic pressure is still present, but it is often dominated by the osmotic pressure due to the translational entropy of free ions in the gel. Charge neutrality requires a Donnan equilibrium,[4] with a higher concentration of free ions inside the gel than outside it, leading to a large osmotic component of the free energy acting to swell the polyelectrolyte gel. Equilibrium swelling is determined when the total free energy is minimized with respect to volume. We split this free energy into two parts, an osmotic part F_{os} acting to swell the gel and an elastic part F_{el} that restricts swelling. The volume derivative of the osmotic part ($-\partial F_{os}/\partial V$) is simply the osmotic pressure π of a semidilute polyelectrolyte solution at the same concentration.[4,8,19]

$$\pi \cong \left(\frac{1}{\xi^3} + \frac{c^2}{A(c + 4Ac_s)}\right)kT \qquad (29)$$

The first term is the polymer contribution, and the second term is due to ions. In the low-salt limit ($c \gg 4Ac_s$), the ionic term dominates over the polymer term as long as there is more than one free counterion per blob, and the osmotic pressure reduces to kT per free counterion.

$$\pi \cong \frac{c}{A}kT \qquad c \gg 4Ac_s \qquad (30)$$

In the opposite limit of high salt ($c \ll 4Ac_s$), there are two important cases for the osmotic pressure. At sufficiently low concentrations, the ionic term dominates, and the osmotic pressure has a quadratic concentration dependence.

$$\pi \cong \frac{c^2}{4A^2c_s} \qquad cc_s < B^9u^3/[b^6(2A)^8], \qquad c \ll 4Ac_s \quad (31)$$

At higher concentrations, the polymer term dominates in the high-salt limit, and the osmotic pressure has a stronger concentration dependence.

$$\pi \cong \frac{kT}{\xi^3} \cong b^{3/2}(B^3uc_s)^{-3/4}c^{9/4} \qquad cc_s > B^9u^3/[b^6(2A)^8], \qquad c \ll 4Ac_s \quad (32)$$

The derivative of the elastic term resisting swelling is essentially the modulus ($\partial F_{el}/\partial V \cong G$). Thus, *polyelectrolyte gels swell to the concentration where their modulus equals the osmotic pressure.* This statement is only true when $\partial F_{el}/\partial V$ and G are power laws, and the more general expression for $\partial F_{el}/\partial V$ is derived in Appendix B.

In the low-salt limit, the equilibrium swelling of polyelectrolyte gels always reaches the low concentrations where the configuration of the chain is a linear assembly of electrostatic blobs, and in many cases, the electrostatic blobs are stretched (Figure 2c). The modulus in good and Θ solvents is always determined by $G \cong ckT/g_P$ (from eqs 12 and 16). The equilibrium swelling in good and Θ solvents in the low-salt limit, therefore, requires $g_P = A$. Thus, in the low-salt limit, at equilibrium with either a good or Θ solvent, *polyelectrolyte gels swell until there is a single uncondensed charge per Pincus blob.* The equilibrium swelling is $Q \equiv b^{-3}c^{-1}$ for the gel in equilibrium with pure solvent (Q is the ratio of volumes in the fully swollen and dry states). In all solvents for the low-salt limit, we use eqs 28 and 30 to get the equilibrium swelling.

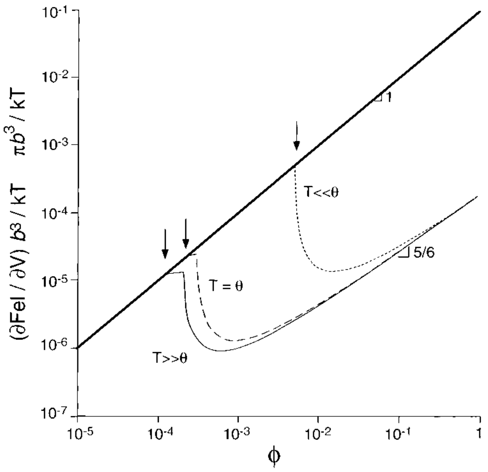

Figure 5. $\partial F_{el}/\partial V$ of a salt-free polyelectrolyte gel in various solvents and osmotic pressure of counterions (thick line is osmotic pressure, thin solid curve is $\partial F_{el}/\partial V$ in good solvent, dashed curve is $\partial F_{el}/\partial V$ in Θ solvent, and dotted curve is $\partial F_{el}/\partial V$ in poor solvent (with $\tau = 1$)). Arrows indicate equilibrium swelling ($cb^3 = 1/Q$ when $\pi = \partial F_{el}/\partial V$). Examples use $N = 1000$, $A = 10$, $u = 2.3$, and $c_0b^3 = 0.1$. At concentrations above $c^\ddagger$, $\partial F_{el}/\partial V$ is given by eq A4 of Appendix B. In good and Θ solvents below $c^\ddagger$, $\partial F_{el}/\partial V$ is approximated as the modulus (eq 28).

$$Q \cong \frac{B_0^{3/4}N^{3/2}}{c_0^{1/4}b^{3/4}} \times (1 + B_0uc_s^\circ/c_0)^{3/8}\begin{cases} A^{-6}\tau^{-9} & T < \Theta \quad (\tau > A^{-1/2}) \\ A^{-3/2} & T = \Theta \quad (\tau < A^{-1/2}) \\ A^{-6/5} & T \gg \Theta \end{cases} \qquad (33)$$

The swelling systematically increases with solvent quality, as A^{-6} (poor solvent) < $A^{-3/2}$ (Θ solvent) < $A^{-6/5}$ (good solvent), because A is always larger than unity. The concentration dependences of $\partial F_{el}/\partial V$ and $\pi = -\partial F_{os}/\partial V$ are shown in Figure 5 for a salt-free polyelectrolyte gel immersed in poor, Θ, and good solvents. The volume derivative of the elastic free energy is calculated in Appendix B. It reduces to the modulus ($\partial F_{el}/\partial V \cong G$) at both low and high concentrations, where the two are power laws in c. The osmotic pressure is the same for all three solvents (eq 30, thick line), and the point where π and $\partial F_{el}/\partial V$ cross determines the equilibrium swelling. It turns out that there is a simple general result for the low-salt limit.

$$Q \geq 1/(c^\ddagger b^3) \qquad \text{for low salt} \qquad (34)$$

When salt is added, the osmotic pressure driving swelling is greatly reduced, and the swelling of the polyelectrolyte gel is considerably less than in the low-salt limit. In the high-salt regime ($c \ll Buc_s$), the osmotic pressure may be dominated either by ions (eq 31) or by polymer (eq 32). At low concentrations, i.e., for $c < B^9u^3/[b^6(2A)^8c_s]$, the osmotic pressure is dominated by ions and we set $\pi = G$ using the high-salt ($c \ll Buc_s$) limit of eq 27 for the modulus and eq 31 for the osmotic pressure of ions in the gel.

$$Q \cong \frac{B_0^{15/44} N^{15/22} (1 + B_0 u c_s^\circ/c_0)^{15/88}}{u^{3/11} B^{9/11} (2A)^{12/11} (c_s b^3)^{9/11} (c_0 b^3)^{5/44}}$$
$$Q > (2A)^8 c_s b^3/(B^9 u^3) \qquad \text{high salt} \quad (35)$$

Notice that in this limit $Q \sim c_s^{-9/11}$, so the swelling is predicted to decrease rather rapidly as salt is added. When sufficient salt is added, the swelling will be low enough that the polymer term in the osmotic pressure dominates over the ionic term. The equilibrium swelling is then determined by setting $\pi = G$, using eqs 27 and 32.

$$Q \cong \frac{B_0^{3/10} N^{3/5} (1 + B_0 u c_s^\circ/c_0)^{3/20}}{B^{9/5} (u c_s b^3)^{3/5} (c_0 b^3)^{1/10}}$$
$$Q < (2A)^8 c_s b^3/(B^9 u^3) \qquad \text{high salt} \quad (36)$$

Most experiments on swelling with added salt appear to be in this regime, as the prediction is $Q \sim c_s^{-3/5}$, while experiments observe[16,20−23] $Q \sim c_s^{-m}$ with $0.3 \leq m \leq 0.6$. The reported slopes less than 0.6 may be explained by a crossover to the low-salt limit (eq 33 has Q independent of c_s).

8. Discussion

Due to the simple fact that the fully swollen state is determined by $\pi = G$, simple relations exist between the fully swollen modulus $G|_{c=1/(Qb^3)}$ and the equilibrium swelling, just as for uncharged networks.[9] In the low-salt limit, the osmotic pressure is particularly simple (kT per counterion; see eq 30), leading to the known result.[24]

$$G|_{c=1/(Qb^3)} \cong \frac{c}{A} kT \cong \frac{kT}{b^3 A Q} \qquad (37)$$

Universal relations, such as eq 37, that are independent of solvent quality and gel preparation details, such as N and c_0, are particularly useful for testing certain aspects of our theory. Equation 37 provides a direct test of the idea that $G = \pi$ determines the equilibrium swelling in the low-salt limit. We test the simple prediction of eq 37 using the data of Ilavsky and Hrouz[25−27] on polyelectrolyte gels made from copolymerization of acrylamide, bisacrylamide, and sodium methacrylate and swollen in water (with no added salt) in Figure 6. These gels were made with variable N, A, and c_0 in the ranges $72 \leq N \leq 11\,000$, $42 \leq A \leq 250$, and $0.7 \leq c_0 \leq 6.3$ M. All data[28] obey the prediction of eq 37, and the solid line has the expected slope of −1, verifying that $G \sim (AQ)^{-1}$. The filled symbols in Figure 6 have constant N and c_0 but variable A.[25] Notice that both the number density of counterions $(AQ)^{-1}$ and the fully swollen modulus G are nearly independent of A. This result is anticipated from our scaling theory, as the good solvent result of eq 33 predicts $Q \sim A^{-6/5}$, and thus, eq 37 predicts the observed very weak dependence of fully swollen modulus on charge density of the gel, $G \sim (AQ)^{-1} \sim A^{1/5}$.

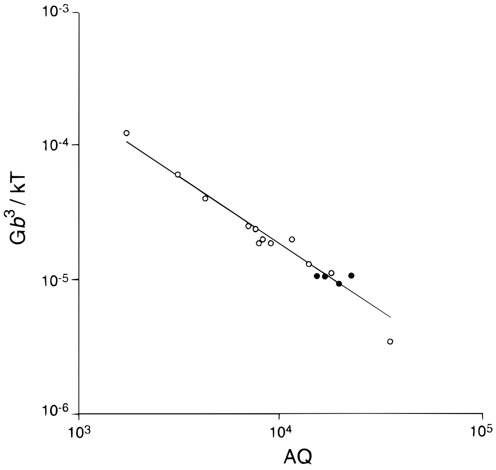

Figure 6. Relation of swollen modulus and swelling for weakly charged gels made from copolymerization of acrylamide, bisacrylamide, and sodium methacrylate (data of Ilavsky and Hrouz[25−27]). Open symbols have $A = 83$, and filled symbols[25] have variable A with $42 \leq A \leq 250$. The solid line has a slope of −1, anticipated by eq 37.

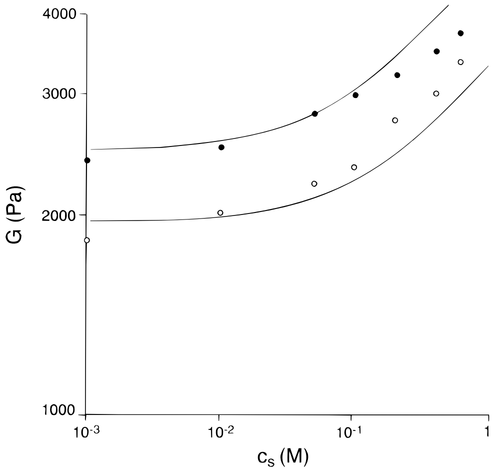

Figure 7. Modulus as a function of salt concentration for two poly(acrylic acid) gels neutralized to different extents (data of Skouri et al.[16]). For all data, $c_0 = 1.11$ M, $c_s^\circ = 0$, $c = 0.916$ M, and N is constant. Filled symbols have $\alpha = 0.4$, and open symbols have $\alpha = 0.8$. Solid curves are the predictions of eq 22 with $kTc^{5/6}c_0^{1/6}/(NB_0^{1/2}) = 1100$ Pa and $c_s^\circ = 0$ for all data and with $B = 5.1$ for $\alpha = 0.4$ and $B = 3.1$ for $\alpha = 0.8$ (see text for details).

Skouri et al.[16] measured the modulus of poly(acrylic acid) gels at concentrations very near the preparation concentration as a function of added salt, enabling us to test eq 22. The gels were prepared with no added salt at a concentration $c_0 = 1.11$ M. The gels were then neutralized with NaOH to two different extents, with the fraction of neutralization α being either $\alpha = 0.4$ or $\alpha = 0.8$. For each neutralization extent, salt solutions were added of varying concentrations, making the gel concentration $c = 0.916$ M. With no added salt, $\alpha = 0.4$ resulted in a modulus of 2300 Pa, while $\alpha = 0.8$ had a modulus of 1800 Pa (both at $c = 0.916$ M). Unfortunately, these neutralization conditions lead to an undetermined amount of counterion condensation,[29] but we can estimate the ratio of B values from the moduli with no added salt using eq 22, resulting in $B(\alpha = 0.4)/B(\alpha = 0.8) \cong 1.64$ (the ratio of salt-free moduli squared). We plot the modulus data as a function of salt concentration in Figure 7 for both neutralization extents. Fitting to eq 22 with $c_s^\circ = 0$ and the ratio of B values above results in the solid curves, with $B = 5.1$ for $\alpha = 0.4$ and $B = 3.1$ for $\alpha = 0.8$. The B values are consistent with some counterion condensation. In the limit of strong counterion condensation, we expect the dipolar attractions between paired charges to force poor solvent chain statistics within the electrostatic blob. Thus we estimate $A \cong B^{3/4}u^{1/2} = 3.5$ for $\alpha = 0.8$ using the poor solvent limit of eq 5. Osmotic pressure measurements on partially neutralized poly(acrylic acid) gels[30] find $A \cong 3$ in the counterion condensation limit, in good agreement with the value extracted from the modulus data.

The modulus of poly(acrylic acid) gels, neutralized with NaOH to varying degrees to change their effective charge, show the qualitative behavior expected from eq 23; the modulus decreases as charge is added to the gel.[16,31] Counterion condensation complications (just discussed above) preclude any quantitative comparison of these data to our theory. At first glance, the prediction of modulus decreasing as charge is added is counterintuitive, because it has long been known that the swelling, and hence the osmotic (bulk) modulus, increases as charge is added to the gel[32] ($\pi \sim 1/A$). The mechanical modulus decreases as charge is added because the free chain size (R in eq 18) increases.

9. Conclusions

Using a simple scaling description of the configuration of a polyelectrolyte chain in semidilute solution,[5-8] together with established ideas about chain stretching,[14] we develop a scaling description of the modulus of polyelectrolyte gels assuming affine displacement of cross-link points. The predictions are in good agreement with two previously unexplainable experimental results on the modulus of polyelectrolyte gels:

(1) The modulus increases as salt is added to the gel.[16] We semiquantitatively predict this increase (see Figure 7).

(2) The modulus decreases as charge is added to the gel.[16] We predict this qualitatively (see eq 22) but the experimental result is a slightly weaker dependence on charge than we predict, possibly because of counterion condensation. For quantitative comparison, the effective charge on the polymer must be measured, using osmotic pressure measurements in un-cross-linked solution at the same concentration, for instance.

Since the dissociated ions contribute a large osmotic pressure, polyelectrolyte gels are capable of swelling a great deal with no added salt. The equilibrium swelling is determined as the concentration where the osmotic pressure of the ions equals the modulus of the gel. This idea leads directly to the simple prediction that $G \sim (AQ)^{-1}$ in the low-salt limit, as observed in literature data (see Figure 6).

Future experiments should determine the concentration dependence of the modulus of polyelectrolyte gels. With no added salt, the high-concentration behavior is predicted to be $G \sim c^{5/6}$, and the full concentration dependence of modulus is predicted to be nonmonotonic (see Figure 4). This would provide a necessary test of the model and, in particular, the affine assumption. The model also predicts a low-concentration regime, where the strands are strongly stretched. This regime should be best seen for weakly charged gels in a good solvent for the uncharged polymer, where Q can be considerably larger than $1/(c^{\ddagger}b^3)$ and we predict $G \sim c^{1/6}$ for $c < c^{\ddagger}$.

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Appendix A. Nomenclature

A	number of monomers between uncondensed charges
b	monomer size
B	dimensionless contour length parameter ($B = Nb/L$)
B_0	dimensionless contour length parameter in preparation state
c	monomer concentration (number density)
c_0	monomer concentration in preparation state
c_s	salt concentration (number density of each monovalent salt ion)
c_s°	salt concentration in preparation state
$c^\dagger$	concentration at which $\xi_p = \xi$
$c^\ddagger$	concentration at which ξ_p jumps from r_{scr} to D
D	electrostatic blob size
e	elementary charge
E	stretching energy for a single strand
f	stretching force on a single strand
F_{el}	elastic part of the free energy of a gel
F_{os}	osmotic part of the free energy of a gel
g	number of monomers in a correlation blob
g_e	number of monomers in an electrostatic blob
g_p	number of monomers in a Pincus blob
g_{scr}	number of monomers in an electrostatic screening volume r_{scr}^3
g_T	number of monomers in a thermal blob
G	mechanical (shear) modulus of a gel
k	Boltzmann's constant
l_B	Bjerrum length
L	contour length of a chain of electrostatic blobs
m	exponent for the dependence of swelling on salt concentration
N	number of monomers in a gel strand
N_e	number of monomers in an entanglement strand
Q	equilibrium swelling (ratio of the fully swollen gel volume and the volume of the dry gel)
r	length scale of observation
r_{scr}	electrostatic screening length
R	size of a gel strand (end-to-end distance)
R'	size of a stretched gel strand
R_0	size of a gel strand in the preparation state
T	temperature
u	ratio of Bjerrum length and monomer size ($u = l_B/b$)
V	volume of a gel strand
α	fraction of monomers that are neutralized (equal to 1/A in the absence of counter-ion condensation)
β	normalized stretching energy in the inverse Langevin function
γ	surface tension of a collapsed globule
ϵ	dielectric constant
λ	linear expansion factor (ratio of final and initial lengths)
λR_0	size of a gel strand
π	osmotic pressure of a semidilute solution at the same concentration as the gel
ν	exponent for the dependence of chain size on mass
ρ	density of collapsed globule
Θ	theta temperature
τ	reduced temperature below Θ ($\tau \equiv (\Theta - T)/\Theta$)
ξ	correlation length (correlation blob size)
ξ_P	Pincus blob size
ξ_T	thermal blob size

Appendix B. Inverse Langevin Function[18]

The stored elastic energy per unit volume (F_{el}/V) of a network of freely jointed strands with N/g random steps of length ξ, each experiencing force f, is written in terms of $\beta \equiv f\xi/kT$.

$$\frac{F_{\mathrm{el}}}{V} \cong \frac{c}{g}kT \ln\left(\frac{\sinh \beta}{\beta}\right) \tag{A1}$$

The strand size λR_0 is also written in terms of β.

$$\lambda R_0 \cong \frac{N}{g}\xi(\coth \beta - 1/\beta) \tag{A2}$$

The low-salt limits of eqs 9, 10, and 21 allow us to write eq A2 in terms of the concentration.

$$c \cong \frac{B^3 {c_0}^{1/4}}{{B_0}^{3/4} N^{3/2} b^{9/4}}(\coth \beta - 1/\beta)^{-3} \tag{A3}$$

One can now calculate the volume derivative of the elastic free energy.

$$\frac{\partial F_{\mathrm{el}}}{\partial V} \cong \frac{kT}{b^3}\left(\frac{\phi}{B}\right)^{3/2}\left[\frac{1}{2}\ln\left(\frac{\sinh \beta}{\beta}\right) - \frac{1}{6}(\beta \coth \beta - 1)\right] \tag{A4}$$

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