Theory of volume transition in polyelectrolyte gels with charge regularization

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We present a theory for polyelectrolyte gels that allow the effective charge of the polymer backbone to self-regulate. Using a variational approach, we obtain an expression for the free energy of gels that accounts for the gel elasticity, free energy of mixing, counterion adsorption, local dielectric constant, electrostatic interaction among polymer segments, electrolyte ion correlations, and self-consistent charge regularization on the polymer strands. This free energy is then minimized to predict the behavior of the system as characterized by the gel volume fraction as a function of external variables such as temperature and salt concentration. We present results for the volume transition of polyelectrolyte gels in salt-free solvents, solvents with monovalent salts, and solvents with divalent salts. The results of our theoretical analysis capture the essential features of existing experimental results and also provide predictions for further experimentation. Our analysis highlights the importance of the self-regularization of the effective charge for the volume transition of gels in particular, and for charged polymer systems in general. Our analysis also enables us to identify the dominant free energy contributions for charged polymer networks and provides a framework for further investigation of specific experimental systems. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.3698168>]

I. INTRODUCTION

Volume transitions in charged polymer gels have attracted considerable attention during the past several decades.^{1–4} While this transition is also present in neutral polymer gels, it is markedly more pronounced in systems of polyelectrolyte gels. The transition in a charged gel is accompanied by a reversible, discontinuous volume change which can be as large as 100 to 1000 times the collapsed state volume. This discontinuous transition can be induced as a function of a number of experimental parameters, such as temperature, pH, ionic concentration, and the solvent composition.

The theory of neutral polymer gels is well understood in terms of the variational free energy as derived by Flory.¹ The relevant physical factors in this case are the mixing free energy and the elasticity of the gel network. However, the introduction of charges on the polymer considerably complicates this simple picture of a gel. The long range nature of the chain connectivity of polymeric systems and of electrostatic interactions, in addition to the nonlinear coupling between the polymer and its dissociated counterions, has made a theoretical formulation of polyelectrolyte systems a considerable challenge. With respect to uncharged systems, there are now two additional length scales in the system, the Bjerrum length, l_B , which sets a length scale for the Coulomb interaction at a temperature T in a medium of dielectric constant ϵ , and the Debye screening length κ^{-1} , which sets the length scale for the range of electrostatic interactions between charges.

The major factor that is responsible for the dramatic transition in polyelectrolyte gels is the osmotic pressure of the dissociated counterions from the polymer backbone. The earliest theory that attempts to explain the behavior of a charged gel was provided by Flory, who considered a fixed ionic charge for the polymer gel and hence calculated the entropy due to the counterions. The effect of electrostatics is computed through the criterion of the Donnan equilibrium, which gives an equilibrium distribution of ions between the gel and the solution. The basic assumption of this approach is that the number of free counterions is independent of the conformation of the polymer backbone.

It is however abundantly clear that the effective charge of a polyelectrolyte cannot remain a constant independent of its environmental conditions. Numerous experiments,^{5–22} computer simulations,^{23–30} and theoretical arguments^{31–49} have established clearly that the effective charge for all polyelectrolyte systems varies as the experimental variables are changed. This effect is known to be present for a variety of polyelectrolyte systems, such as single chains,^{32,46} polyelectrolyte brushes,³⁵ and gels,^{36,49} and in general can be highly nonlinear. In particular, theoretical arguments by Khokhlov and Kramarenko³⁶ have shown that cooperative counterion condensation can lead to a cascade of volume collapse in polyelectrolyte gels. Recent work on the molecular theory of weak polyacid gels has also shown the crucial role of variable charge in understanding such systems.⁴⁹ Thus it is necessary for theoretical formulations of charged polymer systems to take into effect this property of self-regularization of the effective charge, where the effective charge of the polymer, and hence the counterion concentration is determined by a balance between the electrostatic attraction

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between the counterions and the ionized polymer backbone, and the translational entropy of the counterions in the solution.^{46,50–52}

There have been extensive experiments^{4,53–63} and simulations^{64–76} that have studied the volume transition in ionic gels. In particular, Tanaka and co-workers have investigated the effect of added salt concentrations in the volume collapse both for monovalent and divalent salts.⁶¹ They found that the phase transition occurs at much lower salt concentration for divalent salts as compared to monovalent salts, implying that the valency of the ions plays a vital role in the volume collapse. They also found that the solvent quality can play an important role in determining the temperature and extent of the volume transition. There have also been studies which looked at the specific response of a polyelectrolyte gel in the presence of differing species of salt ions, both in the case of monovalent⁵⁶ and divalent salts.⁵⁴ It was found that the response of the system depends on the specific type of ion that is added, implying that other physical characteristics such as ionic size play a significant role in addition to the charge of the ion species. In general, it has proved difficult to address the role of multivalent ions in charged polymer systems. Screening of electrostatic interactions by multivalent ions cannot be described within a mean-field framework,⁷⁷ since they induce attractive forces between non-local segments of the polymer chain through bridging interactions.^{43,47,78} In addition, the role of monovalent and divalent salt ions has also been studied through simulations and continuum theories.^{53,67,68,70} The simulations enable a detailed understanding of the structure of gel networks in the different phases, which is found to differ significantly from features found in polyelectrolyte solutions.

In this paper we present an effective variational free energy of the polyelectrolyte gel which explicitly allows the effective charge of the polymer backbone to self-regulate in response to changes in environmental conditions. The basic framework of the free energy is motivated by the theory of counterion adsorption presented by the one of the present authors.⁴⁶ We have previously examined the effect of charge regularization on salt-free polyelectrolyte solutions,⁵¹ and in this work we investigate how this effect manifests itself for gels which have an additional elastic contribution to the free energy. Our theory is general enough to deal with salt-free solutions, solutions with monovalent counterions, as well as solutions with multivalent counterions.

The rest of the paper is organized as follows: In Sec. II, we write down all the relevant free energy terms that affect the behavior of a polyelectrolyte gel, and thence construct the total effective free energy. The results obtained from the minimization of this variational free energy are discussed in Sec. III. We first demonstrate the importance of charge regularization in Sec. III A. We then investigate the effect on the volume transition of changing crosslink density (Sec. III B), solvent quality (Sec. III C), and counterion size (Sec. III D). Section III E discusses the prediction of our theory for the phenomenon of overcharging in the case of divalent salts, while the relative importance of the different free energy contributions in the collapsed and expanded states of the gel is discussed in Sec. III F. Finally, we summarize

our main results and the various implications as well as shortcomings of our theoretical approach in Sec. IV.

II. THEORY

The present theory is an extension of our earlier work on counterion condensation on flexible polyelectrolytes,⁴⁶ and phase behavior of polyelectrolyte solutions both with fixed effective charge^{50,79} and with self-regularization of charge.⁵¹ The theory of competitive counterion adsorption for polyelectrolyte solutions in the presence of divalent salts has also been worked out previously.⁴⁷ A more extensive derivation of the free energy terms can be found in the above references and we shall only provide a brief discussion below.

A. Polyelectrolyte gel in a salt-free solution

Consider a polyelectrolyte gel composed of N polymer segments of Kuhn length l , and n_s uncharged solvent molecules contained in a total volume Ω . For the purposes of this paper, we assume that the ionizable groups on the polymer backbone are monovalently charged, with each segment carrying a charge of -1 and the corresponding counterion then has a charge of $+1$, in units of the electronic charge, e . The degree of ionization of the chains is denoted by α . To simplify our analysis, we also assume that the polymer segments, solvent molecules, and the counterions all have identical volumes given by l^3 , and that the whole system is incompressible.

The contributions to the total free energy density of the gel, defined as the total Helmholtz free energy per unit volume, in terms of $k_B T$, are given by: (i) translational entropy of the dissociated counterions and the solvent molecules (f_s); (ii) the entropy of adsorbed counterions along the polymer backbone (f_{sa}); (iii) the hydrophobic interaction between the polymer backbone and the solvent molecules (f_χ); (iv) the gain in energy corresponding to the formation of ion-pairs by the adsorbed counterions (f_{ad}); (v) electrostatic interaction among polymer segments (f_{el}); (vi) elastic energy of the gel network (f_{elast}); and (vii) fluctuation of the dissociated counterions ($f_{fl,i}$).

The free energy density due to entropy of mixing of the dissociated counterions and the solvent molecules is given by

$$f_s = \phi_c \log \phi_c + \phi_s \log \phi_s, \quad (1)$$

where ϕ_c and ϕ_s are the volume fractions of counterions and solvent molecules, respectively, and are given by, $\phi_c = \alpha N l^3 / \Omega$ and $\phi_s = n_s l^3 / \Omega$. Under the assumption of incompressibility, these volume fractions are related to the polymer gel volume fraction $\phi (= N l^3 / \Omega)$ by the constraint

$$\phi + \phi_c + \phi_s = 1. \quad (2)$$

Note that this form of the incompressibility constraint assumes that only free counterions contribute to the volume fraction. The effective volume occupied by any species corresponds to the solvated volume, and for a counterion condensed on the polymer backbone, the solvated volume for monomer-counterion complex is assumed to be approximately equal to the solvated volume of the monomer alone.

The net electroneutrality of the system is ensured through the relation between the counterion and polymer volume fractions, $\phi_c = \alpha\phi$. In addition to the dissociated counterions, the counterions adsorbed to the polymer backbone also have a translational entropy along the backbone. The free energy density due to this term is given by

$$f_{sa} = [\alpha \ln \alpha + (1 - \alpha) \ln(1 - \alpha)]\phi. \quad (3)$$

The hydrophobic interaction between the polymer segments and the backbone is modeled via the Flory-Huggins term,

$$f_\chi = \chi\phi\phi_s, \quad (4)$$

where χ is the chemical mismatch parameter representing the local interaction energies. This parameter depends on the particular choice of the system, both on the chemical nature of the polymer gel component and the choice of solvent, and is hence an input parameter for our theory.

The adsorption of counterions on the polymer backbone leads to the formation of ion-pairs, and a consequent reduction in the free energy. The energy due to the formation of a single ion-pair is given by $-e^2/(4\pi\epsilon_0\epsilon_l d)$, where ϵ_l represents the local dielectric constant in the vicinity of the polymer backbone, which is typically much smaller than the bulk value ($\epsilon_{water} = 80$), d is the dipole length between the monomer segment and the counterion, and ϵ_0 is the permittivity of vacuum. As in our earlier work, this energy is parameterized in terms of the quantity

$$\delta = \frac{\epsilon}{\epsilon_l} \frac{l}{d}, \quad (5)$$

the dielectric mismatch parameter. The total free energy associated with all the ion-pairs in the system can then be expressed as

$$f_{ad} = -(1 - \alpha)\phi\tilde{l}_B\delta, \quad (6)$$

where $\tilde{l}_B$ denotes the Bjerrum length scaled by the Kuhn segment length ($\tilde{l}_B = l_B/l = e^2/(4\pi\epsilon_0\epsilon l k_B T)$).

The electrostatic interaction among all polymer segments has previously been calculated using field theoretic arguments.³⁸ In the absence of external salt, the electrostatic screening arises entirely due to dissociated counterions, the volume fraction of which is given by $\phi_c (= \alpha\phi)$. The range of the interaction is then given by the Debye length κ^{-1} , where

$$\tilde{\kappa}^2 = 4\pi\tilde{l}_B\alpha\phi, \quad (7)$$

with $\tilde{\kappa} = \kappa l$. However, as has been previously argued,⁵¹ the electrostatic interaction is a relatively weaker effect, and instead of using the full expression for the corresponding free energy, it is adequate for the purposes of our analysis to use an interpolation formula between the long-range and the short-range limits, respectively, given by the two limits of $\kappa = 0$ and $\kappa R \gg 1$ (where R is the average radius of gyration of the chain). Such an interpolation formula was derived in our earlier work⁵¹ and is given by

$$f_{el} = 2\pi\alpha^2\tilde{l}_B\phi^2 \frac{N^{2/3}}{\frac{3^{4/3}\pi^{7/6}}{2^{5/3}}\phi^{2/3} + \tilde{\kappa}^2 N^{2/3}}. \quad (8)$$

The network structure of the polymer gel is reflected in an associated elastic energy for the gel. This free energy cor-

responding to the expansion of an isotropic network was first calculated from mean-field arguments by Flory¹ and can be expressed in the form

$$f_{elast} = \frac{3}{2}S\phi_0^3 \left[\left(\frac{\phi}{\phi_0} \right)^{1/3} - \frac{\phi}{\phi_0} + \frac{1}{3} \frac{\phi}{\phi_0} \ln \frac{\phi}{\phi_0} \right], \quad (9)$$

where, ϕ_0 represents the volume fraction of an initial reference state, where the cross-linked chains of the unswollen gel are replaced by gaussian chains. This form of the elastic free energy is equivalent to the elastic term used later by Dusek and Patterson⁸⁰ and Tanaka.⁵⁹ The quantity S is an effective crosslinking density, which represents a measure of the number of crosslinks in the gel, and can be written in terms of the number of elastic strands n in the gel as

$$S = \frac{nl^3}{\Omega} \phi_0^{-4}. \quad (10)$$

The final contribution to the free energy comes from the fluctuations in the density of the dissociated counterions and arises due to the Coulomb interaction between the counterions in the cloud around polymer chains. The contribution from this effect has been previously derived by solving the linearized Poisson-Boltzmann equation for a non-neutral charged plasma, as in the Debye-Huckel theory, and is given by⁷⁹

$$f_{fl,i} = -\frac{1}{4\pi} \left[\ln(1 + \tilde{\kappa}) - \tilde{\kappa} + \frac{1}{2}\tilde{\kappa}^2 \right]. \quad (11)$$

This equation is the same as the extended Debye-Hückel expression⁸¹ in the limit of $l \rightarrow 0, f_{fl,i} \rightarrow -(\kappa l)^3/(12\pi)$.³⁸

The parameters in the present model are the Bjerrum length l_B , the Flory-Huggins interaction parameter χ and the dielectric mismatch parameter δ , in addition to the experimental variables of temperature and polymer concentration. The parameters l_B and χ are both temperature dependant, and in keeping with the conventions of our earlier analysis, we combine all the temperature effects by defining a reduced temperature t as^{51,79}

$$t = \frac{l}{4\pi l_B}. \quad (12)$$

For a gel in aqueous media with a Kuhn length of 1nm, room temperature of $T = 300$ K would then correspond to a reduced temperature of $t = 0.1$. The Flory Huggins parameter χ can be expressed in terms of the theta temperature of the solvent as

$$\chi = \frac{\Theta}{2T}, \quad (13)$$

and, as before,^{51,79} we define an effective interaction parameter, a_χ as

$$a_\chi = 20\pi t \chi = \frac{10\pi\epsilon_0 k_B \Theta \ell}{e^2}. \quad (14)$$

The parameter a_χ then provides a measure of the effective hydrophobic interaction between the polymer and the solvent, and is a temperature-dependant quantity, due to the presence of the dielectric constant ϵ in Eq. (14). For physical values of the Flory-Huggins interaction parameter χ , a_χ is roughly of order unity, with $\chi = 0.6$ corresponding to a value

of $a_\chi = 3.8$ in aqueous media. Depending on the case in study, we explore a range of $1 \leq a_\chi \leq 10$ in our present analysis.

The dielectric mismatch parameter δ takes into account the contributions of two important physical effects. First, the local dielectric constant in the vicinity of the polymer backbone can be significantly different from the value of the dielectric constant in the bulk, and this affects the adsorption energy of the counterions on the backbone. Also, depending on the solvent, the length of the dipole in an adsorbed ion-pair is different from the Kuhn segment length l , and this effect leads to species-specific behavior depending on the counterion present in the system. From a theoretical standpoint, the parameter δ can be seen to be related to the negative logarithm of the dissociation constant for the particular ion-pair between the segment and the adsorbed counterion. The value of the local dielectric constant can be calculated using a self-consistent field theory calculation⁸² but for the purposes of our present analysis, both these effects are treated via the single independent parameter δ , which approximately lies within the range $1 < \delta < 10$ depending on the specific solvent used and the ion species under consideration.

The total free energy of a polyelectrolyte gel in a salt-free solution is then given by the sum of these seven contributions

$$f = f_s + f_{sa} + f_\chi + f_{ad} + f_{el} + f_{elastic} + f_{fl,i}. \quad (15)$$

This free energy is then minimized over the two independent variables, the degree of polymerization α , and the volume fraction of the gel phase ϕ , to yield the equilibrium behavior of the gel. The numerical minimization is carried out by the downhill simplex algorithm.⁸³

B. Polyelectrolyte gel in a monovalent salt solution

When a polyelectrolyte gel is immersed in a solvent containing a monovalent salt, the positive and negative ions from the salt can now distribute themselves among the gel phase and the solution phase, and the total free energy can be broadly separated into two contributions, one from the gel phase f_{gel} and one from the solution phase $f_{solution}$. The free energy of the gel phase is similar in form to the free energy of a gel in a salt-free solution and is given by the sum of the same seven contributing factors as given in Eq. (15).

However in this case, the free energy due to the entropy of mixing of the dissociated counterions and the solvent molecules is modified due to the presence of the positive and negative ion species resulting from the dissociation of the salt, and this term is now given by

$$f_s = (\phi_{+g} + \alpha\phi) \ln(\phi_{+g} + \alpha\phi) + \phi_{-g} \ln \phi_{-g} \\ + [(1 - \phi - \alpha\phi - \phi_{+g} - \phi_{-g}) \\ \times \ln(1 - \phi - \alpha\phi - \phi_{+g} - \phi_{-g})], \quad (16)$$

where $\phi_{\{+/-\}g}$ represents the volume fraction of the positive/negative ion species from the dissociated salt in the gel phase, and as before, ϕ is the volume fraction of the polymer gel, and α is the degree of ionization of the gel. In writing this entropy of mixing, we make the assumption that the positive salt ions and the positively charged counterions are chemically indistinguishable.

The remaining contributions have the same form as in the salt-free case and is given by Eqs. (3)–(11). The inverse Debye length ($\tilde{\kappa}$) characterizing the correlation length of the electrostatic interactions, which appears in the f_{el} and $f_{fl,i}$ terms, in this case is modified from the salt-free expression by the presence of the salt ions and is given by

$$\tilde{\kappa}^2 = 4\pi\tilde{l}_B(\alpha\phi + \phi_{+g} + \phi_{-g}). \quad (17)$$

With these modifications, the total free energy of the gel phase f_{gel} is given by Eq. (15) with f_s given by Eq. (16) and $\tilde{\kappa}$ by Eq. (17).

The free energy of the solution phase consists simply of two contributions, the translational entropy of the dissociated salt ions (f_s) and the contributions from Coulomb interactions due to the fluctuations in the density of these ions ($f_{fl,i}$). The translational entropy in this case is given by

$$f_s = \phi_{+s} \ln \phi_{+s} + \phi_{-s} \ln \phi_{-s} \\ + (1 - \phi_{+s} - \phi_{-s}) \ln(1 - \phi_{+s} - \phi_{-s}), \quad (18)$$

where ϕ_{+s} represents the combined volume fraction of all positive ion species, both from dissociated salt and the dissociated counterions, in the solution phase, while ϕ_{-s} represents the volume fraction of negative salt ions in the solution phase. Note that the fluctuation free energy has the same form as before

$$f_{fl,i} = -\frac{1}{4\pi} \left[\ln(1 + \tilde{\kappa}) - \tilde{\kappa} + \frac{1}{2}\tilde{\kappa}^2 \right], \quad (19)$$

where the effective inverse Debye length ($\tilde{\kappa}$) in this case is given by

$$\tilde{\kappa}^2 = 4\pi\tilde{l}_B(\phi_{+s} + \phi_{-s}). \quad (20)$$

The free energy of the solution phase is then given by

$$f_{solution} = f_s + f_{fl,i}. \quad (21)$$

Now if we denote by x_{gel} the fraction of the system separating into the gel phase, then the total free energy density of the system is given by

$$f = f_{gel}x_{gel} + f_{solution}(1 - x_{gel}). \quad (22)$$

As in the salt-free case, we analyze the system in terms of the reduced temperature t (Eq. (12)) and in terms of the effective interaction parameter a_χ and the dielectric mismatch parameter δ . The total salt concentration, or equivalently, the total salt volume fraction (ϕ_{salt}) in the system is an experimental input, and this, in conjunction with the volume fraction of the salt in the gel phase, determines the volume fraction of the salt in the solution phase

$$x_{gel}\phi_{-g} + (1 - x_{gel})\phi_{-s} = \phi_{salt}/2. \quad (23)$$

For monovalent salts, a salt concentration of $c_s = 1\text{M}$ then corresponds to a salt volume fraction of $\phi_{salt} \sim 0.01$. The independent variables in this case are then the volume fraction of the gel ϕ , the degree of ionization α and the volume fraction of the positive ion species in the gel phase ϕ_{+g} , and hence the free energy is determined by a three-dimensional minimization by the downhill simplex algorithm.⁸³

FIG. 1. Schematic diagram of the gel system consisting of the polymer backbone, condensed counterions and dissociated mobile ions in a divalent salt solution. Possible charge complexes for each monomer: (a) Monomer (-1) , (b) monomer-monovalent $(-1,+1)$, (c) monomer-divalent $(-1,+2)$, (d) monomer-divalent-coion $(-1,+2,-1)$, and (e) a bridging configuration of monomer-divalent-monomer.

C. Polyelectrolyte gel in a divalent salt solution

In the presence of a divalent salt, the situation is complicated by the fact that adsorbed divalent counterions can act as bridges which can attract other non-bonded regions of the polymer backbone. In addition, there are now different species of ion-pairs and even ion-triplets that can be formed, and these affect the translational entropy and the adsorption energy terms, in addition to providing a new bridging energy contribution. A detailed analysis of the theory for divalent counterions has previously been worked out for the case of flexible polyelectrolytes,⁴⁷ and we shall extend the free energy results derived there for the case of a polyelectrolyte gel.

In the presence of a divalent salt, the free energy again has two distinct contributions coming from the gel phase (f_{gel}) and from the solution phase ($f_{solution}$), as in the case of monovalent salt solutions. The free energy of the gel phase has contributions from the usual seven terms as given in Eq. (15) and an additional term due to bridging, f_{bridge} (see Fig. 1).

The first contribution we consider is due to the translational entropy of the solvent and dissociated ions. To compute this entropy contribution, we consider a situation where there are N monomers, M_1 adsorbed monovalent ions, M_{2a} number of adsorbed divalent ions without any co-ion condensation that do not participate in bridging, M_{2b} number of adsorbed divalent ions without any co-ion condensation that participate in bridging, and M_3 number of ion triplets. As in the monovalent salt case, we assume that the monovalently charged counterions from the polymer backbone and dissociated ions from monovalent salt, if present, are chemically indistinguishable. We define

$$\alpha_1 = \frac{M_1}{N}, \quad \alpha_{2a} = \frac{M_{2a}}{N}, \quad \alpha_{2b} = \frac{M_{2b}}{N}, \quad \alpha_3 = \frac{M_3}{N}. \quad (24)$$

The effective degree of ionization of the polymer α can then be written in terms of these quantities using the electroneutrality constraint as

$$\alpha = 1 - \alpha_1 - 2(\alpha_{2a} + \alpha_{2b}) - \alpha_3. \quad (25)$$

The translational entropy is then given by

$$\begin{aligned} f_s = & (\phi_{+g} + (1 - \alpha_1)\phi) \ln[\phi_{+g} + (1 - \alpha_1)\phi] \\ & + (\phi_{+2g} - (\alpha_{2a} + \alpha_{2b} + \alpha_3)\phi) \\ & \times \ln[\phi_{+2g} - (\alpha_{2a} + \alpha_{2b} + \alpha_3)\phi] \\ & + (\phi_{-g} - \alpha_3\phi) \ln[\phi_{-g} - \alpha_3\phi] \\ & + (1 - \phi - \phi_{+g} - \phi_{+2g} - \phi_{-g} \\ & - (1 - \alpha_1 - \alpha_{2a} - \alpha_{2b} - 2\alpha_3)\phi) \\ & \times \ln[1 - \phi - \phi_{+g} - \phi_{+2g} - \phi_{-g} \\ & - (1 - \alpha_1 - \alpha_{2a} - \alpha_{2b} - 2\alpha_3)\phi], \end{aligned} \quad (26)$$

where ϕ_{+g} represents the volume fraction of positive ions from dissociated monovalent salt, if present, and ϕ_{+2g} and ϕ_{-g} represent the positive divalent counterions from the divalent salt and negative monovalent co-ions in the gel phase, respectively. The translational entropy of adsorbed counterions on the polymer backbone is given by

$$\begin{aligned} f_{sa} = & [\alpha_1 \ln \alpha_1 + \alpha_{2b} \left(1 - \ln \frac{\phi}{2}\right) \\ & + \alpha_{2a} \ln \alpha_{2a} + \alpha_3 \ln \alpha_3 + \alpha_{2b} \ln \alpha_{2b} \\ & + (1 - \alpha_1 - \alpha_{2a} - \alpha_3 - 2\alpha_{2b}) \\ & \times \ln(1 - \alpha_1 - \alpha_{2a} - \alpha_3 - 2\alpha_{2b})] \phi. \end{aligned} \quad (27)$$

The free energy contribution due to the adsorption of counterions on the polymer backbone, f_{ad} now has three separate contributions coming from adsorption of monovalent counterions, adsorption of divalent counterions, and formation of ion-triplets, respectively. The effect of the local environment can be accounted for by the usual dielectric mismatch parameter for the first two contributions, but it is apparent that a modified parameter must be introduced to model the interaction for the ion triplet, since this involves the formation of two adjacent dipoles. As in our earlier work,⁴⁷ we introduce a parameter δ_2 to model the dielectric mismatch for the polymer-divalent counterion-monovalent co-ion triplet. The adsorption free energy can then be written as

$$f_{ad} = -\delta \tilde{l}_B \alpha_1 \phi - 2\delta \tilde{l}_B \alpha_{2a} \phi - \delta_2 \tilde{l}_B \alpha_3 \phi. \quad (28)$$

Although a precise calculation of the δ_2 parameter requires a detailed microscopic description, we can provide a rough estimate for its value by assuming all the ion species involved to have the same size, and further assuming that the local dielectric constant ϵ_l applies only to the polymer-divalent counterion ion pair, while the dielectric constant for the divalent counterion-monovalent co-ion ion pair is given by the average of the local and the bulk values ($\epsilon = (\epsilon_l + \epsilon_{bulk})/2$). The parameter δ_2 can then be written as⁴⁷

$$\delta_2 = \left(2 + \frac{4}{\delta + 1}\right) \delta. \quad (29)$$

The contributions due to the effects of electrostatic interactions, both due to interactions among the polymer segments (f_{ei}) and due to fluctuations of the dissociated counterions ($f_{fi,i}$) are given by Eqs. (8) and (11), respectively.

However, the typical range of the electrostatic interactions, given by the Debye length ($\tilde{\kappa}^{-1}$) follows from

$$\tilde{\kappa}^2 = 4\pi\tilde{l}_B[(1 - \alpha_1 - 4(\alpha_{2a} + \alpha_{2b}) - \alpha_3)\phi + \phi_{+g} + 4\phi_{+2g} + \phi_{-g}]. \quad (30)$$

Also, the Flory-Huggins interaction energy (f_χ) and the elastic energy due to the polymer network (f_{elast}) are unchanged from the salt-free gel case and are given by Eqs. (6) and (9), respectively. We note that the bridges between polymer segments due to adsorbed divalent counterions can act as physical crosslinks and hence change the effective elastic free energy. However, we verified that this is a comparatively small response that has no appreciable effect on the conclusions of our analysis, and hence for the purposes of this paper, we neglect this term and compute the effective crosslinking density S solely in terms of the number of chemical crosslinks in the polymer gel. The final contribution to the free energy of the gel phase comes from the bridging term, which denotes the attractive energy involved in bridging two non-bonded monomer segments via a divalent cation bridge. The relevant dielectric constant in this case is the local value (ϵ_l) and the energy can be written as

$$f_{bridge} = -\frac{7}{2}\tilde{l}_B\delta\alpha_{2b}\phi. \quad (31)$$

The total free energy of the gel phase in the presence of a divalent salt is then given by the sum of all these individual contributions and can be written as

$$f_{gel} = f_s + f_{sa} + f_\chi + f_{ad} + f_{el} + f_{elast} + f_{fl,i} + f_{bridge}. \quad (32)$$

The free energy of the solution phase, $f_{solution}$, as in the monovalent case, is given by a sum of two contributions, the translational entropy of the dissociated ions (f_s) and the electrostatic interactions due to the fluctuations in the density of these ions ($f_{fl,i}$). The translational entropy in this case is given by

$$f_s = \phi_{+s} \ln \phi_{+s} + \phi_{+2s} \ln \phi_{+2s} + \phi_{-s} \ln \phi_{-s} + (1 - \phi_{+s} - \phi_{+2s} - \phi_{-s}) \ln(1 - \phi_{+s} - \phi_{+2s} - \phi_{-s}), \quad (33)$$

where ϕ_{+s} , ϕ_{+2s} , ϕ_{-s} represent the volume fractions of all positive monovalent ions (including counterions from the polymer backbone), positive divalent ions from dissociated salt and negative monovalent co-ions in the solution phase, respectively. The fluctuation free energy $f_{fl,i}$ is given by Eq. (11) with

$$\tilde{\kappa}^2 = 4\pi\tilde{l}_B(\phi_{+s} + \phi_{-s} + 4\phi_{+2s}). \quad (34)$$

The free energy of the solution phase is then given by

$$f_{solution} = f_s + f_{fl,i}. \quad (35)$$

As in the case of monovalent salts, if we denote by x_{gel} the fraction of the gel phase, then the total free energy of the system is given by

$$f = f_{gel}x_{gel} + f_{solution}(1 - x_{gel}). \quad (36)$$

The total salt concentration is an experimental input, and this controls the distribution of charges in the gel and solution

phase similar to the monovalent salt case. In terms of the negative co-ions volume fraction, the total salt volume fraction is then expressed as

$$x_{gel}\phi_{-g} + (1 - x_{gel})\phi_{-s} = 2\phi_{di-salt}/3. \quad (37)$$

For divalent salts, a salt concentration of $c_s = 1\text{M}$ corresponds to a salt volume fraction of $\phi_{di-salt} \sim 0.02$. The independent variables in this case are the volume fraction of the gel, ϕ , volume fraction of monovalent counterions in the gel phase, ϕ_{+g} , volume fraction of divalent counterions in the gel phase, ϕ_{+2g} , and the four different fractions of counterions, α_1 , α_{2a} , α_{2b} , and α_3 . The free energy minimum is then determined by a seven-dimensional minimization over these variables.

One effect we do not take into account in our theoretical framework is the effect of higher order interactions between the adsorbed ion pairs. In general, the dipoles formed by these ion pairs can attract other dipoles to form multipoles, which can in turn form a hierarchy of multipole clusters. We assume that such higher order interactions are sufficiently weak in the experimental scenarios that we are interested in. Previous studies have indicated that the existence of such avalanche effects might lead to a new supercollapsed state.³⁶ However, since this state has so far not been seen under ordinary experimental conditions, we can safely assume that such higher order terms do not have any appreciable effect on the main physical conclusions of our work.

III. RESULTS AND DISCUSSION

A. Effect of charge regularization

We first illustrate the importance of charge regularization in the polyelectrolyte gel behavior by comparing the results obtained from the minimization of free energy with and without the regularization of charge. This is shown in Fig. 2 for the case of a charged gel without any added salt. First, we consider the discontinuous transition in the gel volume fraction as a function of temperature (solid black curve) and the concomitant variation in the degree of ionization (dashed black curve) as given in Fig. 2(a). For high values of the temperature, the gel is in the expanded state, and the gel volume fraction has a value close to zero. As the temperature is decreased, the gel undergoes a discontinuous volume transition at a transition temperature. For the choice of parameters, $a_\chi = 20.0$, $\delta = 7.6$, and $\ell = 0.9\text{ nm}$, the collapse transition occurs near the room temperature ($\sim 300\text{ K}$), and the gel shrinks abruptly with the volume fraction approaching a value close to unity, corresponding to the completely collapsed gel. Correspondingly, when the gel is expanded, it is favorable for the counterions to be in solution, and hence the degree of ionization has a value close to unity. As the temperature is reduced, the degree of ionization also undergoes a discontinuous change simultaneously with volume transition, as the collapsing gel causes the counterions to condense on the polymer backbone, and the degree of ionization approaches zero. In fact this cooperative collapse of counterions provides the driving force for the volume collapse of the charged gel, highlighting the importance of this phenomenon.

FIG. 2. Gel volume fraction (solid curves) as a function of temperature with (black) and without (red/blue/green) charge regularization for $a_\chi = 20.0$ and $\delta = 7.6$. (a) For the case with charge regularization, the variation of the degree of ionization with temperature (black dashed curve) accompanies the volume transition (black solid curve). (b) In the absence of charge regularization, the transition temperature can vary widely depending on the choice of α , and the gel never reaches the truly collapsed state.

When the degree of ionization of the polymer backbone is allowed to self-regulate, it traverses the entire range between zero and unity in response to the gel conformation (black dashed curve).

In order to compare these results with those obtained from the fixed-charge approximation, we minimize the free energy for three values of effective degree of ionization, $\alpha = 0.1, 0.5$, and 1.0 . The corresponding volume transitions are given in Fig. 2(b), where red, blue, and green curves correspond, respectively, to $\alpha = 0.1, 0.5$, and 1.0 . For a comparison, the volume transition curve (black) with α allowed

to self-regulate is included in Fig. 2(b). As can be seen from the figure, artificially fixing the value of α can result in wildly unphysical collapse temperatures, anywhere between 100 and 600 K for the same choice of the parameters that predicts a collapse near room temperature when the regularization of charge is taken into account. Furthermore, for fixed values of the degree of ionization, the gel never reaches the true collapsed state, equilibrating at moderate values of the volume fraction even when the temperature approaches zero. Thus, consistent with a recent work on weak polyelectrolyte gels,⁴⁹ we conclude that any effective theory of polyelectrolyte gels

FIG. 3. (a) Volume transition temperature (circles) and (b) width of the collapse (diamonds) for charged (red) and neutral (black) gels as a function of the effective crosslink density S , for $a_\chi = 7.0$, $\delta = 7.6$. The trend for polyelectrolyte gels is opposite to that of neutral gels for both cases. Also, as opposed to a neutral gel, there is no critical end-point for polyelectrolyte gels.

should take into account the self-regularization of charge in response to the polymer conformations in order to provide experimentally relevant conclusions.

B. Effect of crosslink density

The elastic response of the gel network to the osmotic pressure due to counterions depends on the effective number of crosslinks in the polyelectrolyte gel. In order to understand the role of the crosslink density, parameterized by the effective parameter S , we have studied its effect on the volume transition temperature (T_c) and the width of the collapse ($\Delta\phi$), as characterized by the difference in the gel volume fraction between the expanded and collapsed states at the transition temperature. The corresponding behavior for

neutral gels has been studied previously,^{2,59} and we compare the neutral gel behavior with that of charged gels in a salt-free solution. The results are shown in Fig. 3. We first consider the dependence of the collapse temperature (T_c) on S (Fig. 3(a)). For a neutral gel, the transition temperature increases with decreasing crosslink density and also there exists a critical endpoint beyond which the discontinuous volume transition disappears and the gel volume changes continuously as a function of temperature. Below a certain critical crosslink density ($S \sim 230$, for our choice of parameters), the volume change is continuous. Interestingly, for charged gels, the behavior of the transition temperature is opposite to that of neutral gels. The transition temperature decreases with decreasing crosslink density, and there is no critical endpoint, with the volume transition persisting even in the limit that

the effective crosslinking density S goes to zero. This limit corresponds to the case of a single polyelectrolyte chain, and the transition corresponds to the coil-globule transition for charged polymer chains. We also considered the width of the volume transition as a function of S as shown in Fig. 3(b). For neutral gels, the width of the collapse ($\Delta\phi$) decreases with decreasing crosslink density, and finally goes to zero at the critical endpoint, at which point the transition becomes continuous. For charged gels, with decreasing crosslinking density, the width of the collapse at the transition point increases and is largest in the limit that S goes to zero. This opposite trend for charged gels can be understood in light of the fact that the elastic network counteracts the swelling pressure provided by the counterions, and hence with decreasing crosslink density, the resistance of the network to swelling decreases, hence increasing the width of the transition. The value of $\Delta\phi$ for $S \rightarrow 0$ corresponds to the coil-globule transition of an isolated flexible polyelectrolyte chain.⁵²

C. Effect of solvent quality

The volume transition of the polyelectrolyte gel is affected by the free energy of mixing between the solvent and polymer molecules. This is characterized in terms of the Flory-Huggins interaction parameter, χ . We have studied the effect of differing solvent quality on the volume transition in terms of the effective interaction parameter a_χ , as defined in Eq. (14), for salt-free, solution with monovalent salt and solution with divalent salt cases. We study the effect on both the transition temperature and also the critical salt concentration for the salty solution cases.

1. Effect on transition temperature

The volume transition temperature is observed to increase as the strength of the Flory-Huggins interaction parameter increases. This is a generic feature and is shown in Fig. 4 for salt-free (Fig. 4(a)), monovalent (Fig. 4(b)), and divalent (Fig. 4(c)) salt cases. In each of these three cases, different values of a_χ were chosen in order to exhibit the salient features of the coupled roles by the Flory-Huggins χ parameter and the salt. In addition, the width of the collapse at the transition increases simultaneously for increasing a_χ , provided the temperature is sufficiently high (Figs. 4(a) and 4(b)). Note that for very low values of the interaction parameter, the transition may become continuous ($a_\chi = 2.0$ curve in Fig. 4(b)), which is in agreement with experimental observation. Also, for the solution with divalent salt, there are two separate transitions for lower values of the interaction parameter. The lower transition (labelled re-entrant transition in Fig. 4(c)) is due to overcharging^{18,44,84–90} which we shall discuss in detail in a subsequent section. For the purposes of this section, we concentrate on the branch of the volume fraction curve with the higher transition temperature, which has the same features as the salt-free and monovalent salt cases.

We have also plotted the corresponding behavior for the effective degree of ionization of the polyelectrolyte gel in all these three cases. This is shown in the insets to Fig. 4. The

degree of ionization mirrors the behavior of the gel volume fraction, and has a large value close to one when the gel is expanded and undergoes a sharp transition to a small value as the gel collapses.

2. Effect on salt concentration

For a gel immersed in a salty solution, the gel volume collapse can be studied as a function of the external salt concentration. We have studied the effect of salt concentration on the volume transition for different values of the Flory-Huggins interaction parameter for both monovalent (Fig. 5(a)) and divalent (Fig. 5(b)) cases. We first consider the case of added monovalent salt. Experimentally, it is known that as the Flory-Huggins interaction parameter increases, the gel volume fraction goes from a continuous to a discontinuous transition. The same behavior is predicted by our theory, with the size of the discontinuity in the gel volume fraction (at the volume transition salt concentration) increasing with larger values of a_χ , in agreement with the experimentally observed trend. The same trend is also observed for added divalent salt, with larger Flory-Huggins interaction strengths corresponding to larger discontinuity at the transition point. Also, for both these cases, the theory predicts that larger interaction strength corresponds to a lower critical salt concentration required for collapse, with the sensitivity for divalent salts being much greater than monovalent salts, again in line with experimental observations. Note that in the case of divalent salts, the volume transition occurs at larger values of the salt concentration than those found experimentally.⁶¹ This is a consequence of our particular choice of the a_χ and δ parameters, and indeed we can observe volume transitions at physically relevant salt concentration regimes by more appropriate choices of the parameters in our theory. However, the minimization algorithm becomes increasingly inefficient at lower volume fractions of salt. Since we are interested in illustrating the qualitative features of the volume collapse, we restrict our computation to higher salt concentrations. In order to connect the results with real experimental systems; however, much lower salt concentrations and experimentally appropriate values of a_χ and δ must be used in our calculations for the system with divalent salt. The behavior of the degree of ionization is shown in Fig. 5 insets, and again they mirror the volume fraction curves, with higher α for expanded gels and lower α for collapsed gels.

D. Effect of counterion size

When a polyelectrolyte gel is immersed in a salt solution, it is observed experimentally that the volume collapse depends not only on the valency of the counterions, but additionally there is a specific response depending on the particular species of the salt ion.⁵⁶ In our variational formulation, this effect is attributed to the different adsorption energy for a particular species owing to its diameter. The diameter, or size of the ion, is encapsulated in the dielectric mismatch parameter δ (Eq. (5)), with a larger value of δ implying a smaller value of the ionic radius. We have studied the effect of varying δ on the volume transition for monovalent and divalent salt ions.

FIG. 4. Temperature vs. gel volume fraction plots for a fixed value of the dielectric mismatch parameter δ and different values of the Flory-Huggins interaction parameter a_χ for (a) salt-free ($\delta = 12.0$), (b) monovalent salt ($c_s = 0.3$ M, $\delta = 7.6$), and (c) divalent salt ($c_s = 0.25$ M, $\delta = 3.0$) cases. The variation of the degree of ionization with temperature is shown in the insets in all three cases. The crosslinking density is taken to be $S = 400$ in all cases.

FIG. 5. Room temperature plots for gel volume fraction as a function of external salt concentration for different Flory-Huggins interaction strengths in the case of (a) monovalent salt ($\delta = 7.6$) and (b) divalent salt ($\delta = 3.0$). The crosslinking density is taken to be $S = 400$ in both cases. The corresponding degree of ionization is shown in the insets of both plots.

This is shown in Fig. 6 as a function of the inverse gel volume fraction for comparison with experimental data. We find that, similar to experimental results, different ion species can be grouped in accordance with their ionic radii, with larger values of δ (or equivalently, smaller ionic radii) causing the volume collapse to occur at lower salt concentrations. For the purpose of this calculation, we fixed the value of the dielectric mismatch parameter for the Na^+ ion arbitrarily as $\delta_{\text{Na}^+} = 7.6$ and the values for all other ions were then computed with reference to this value in accordance with known ionic radii⁹¹ from Eq. (5). Thus although the theory does not predict the exact values, it yields the relative location of the transition for different ionic species.

E. Overcharging and re-entrant transition

For the case of a polyelectrolyte gel immersed in a solution with divalent salts, our theory predicts the phenomenon

of overcharging,^{18,44,84–90} which corresponds to an effective charge reversal of the polymer gel backbone. This effect can be seen in Fig. 4(c) for the two smaller values of the Flory-Huggins interaction parameter, $a_\chi = 2.3$ (black), 3.3 (red), and a fixed salt concentration of $c_s = 0.25\text{M}$. Let us first consider the temperature-volume fraction curve for $a_\chi = 3.3$. At a certain value of the temperature, the gel starts to collapse. However, as the gel collapses, the divalent counterions in the solution competitively adsorb with the monovalent counterions. Negative co-ions also adsorb on the monomer-divalent ion-pair increasingly. As more divalent ions condense on the polymer backbone, the effective degree of ionization decreases and eventually reverses sign, leading to an effective charge reversal for the polymer gel. Beyond the isoelectric point ($\alpha = 0$), the chain however re-swells due to repulsion among the condensed divalent ions. Finally, as increasing number of co-ions condense to neutralize the chain again, the volume fraction collapses again through a

FIG. 6. Room temperature plots for gel volume fraction as a function of external salt concentration for a fixed interaction strength and different values of δ corresponding to different ionic species for a polyelectrolyte gel in a (a) monovalent salt solution ($a_\chi = 5.0$), and (b) divalent salt solution ($a_\chi = 4.3$). This is plotted with inverse of the gel volume fraction to facilitate comparison with experimental data. The δ parameter for Na^+ ions was arbitrarily assigned a value of 7.6 and the values for all other ions were calculated with reference to this value using the known ionic radii.

FIG. 7. (a) Degree of ionization as a function of temperature for different values of the divalent salt concentration for a fixed value of the interaction parameter ($a_\chi = 4.3$) and dielectric mismatch parameter ($\delta = 3.0$). Charge reversal is observed for higher values of the salt concentration. (b) The different constituent degrees of ionization (α , α_1 , α_{2a} , α_{2b} , α_3) for a case with overcharging ($a_\chi = 3.3$, $\delta = 4.0$, $c_s = 0.25$ M).

re-entrant transition. For an even smaller value of $a_\chi (=2.3)$, the overcharging occurs to an even larger extent, and consequently, the chain swells again, soon after the initial collapse. The region of occurrence of the re-entrant transition depends on the coupling between the hydrophobicity-induced volume collapse and the $\delta\ell_B$ -dependent counterion condensation. By varying a_χ , δ , and ℓ_B , the re-entrant volume transition can be shifted around. The phenomenon of charge reversal is more clearly apparent in the temperature-degree of ionization curves, shown in the inset to Fig. 4(c). The reswelling of the charged gel after the initial collapse corresponds to the degree of ionization becoming negative, and as the effective ionization again goes to zero, the gel undergoes the re-entrant collapse.

In terms of the absolute temperature, for this choice of salt concentration ($c_s = 0.25$ M), the initial volume collapse occurs at or near room temperature, while the re-entrant transition occurs at a much lower value of temperature, explaining the difficulty in observing this phenomenon experimentally.¹⁸ The temperature of the re-entrant transition can be varied by varying the external salt concentration, with larger salt concentrations resulting in charge reversal at higher temperatures. This can be seen from Fig. 7(a) where we plot the effective degree of ionization against temperature for a fixed value of $a_\chi = 4.3$ and $\delta = 3$. When the divalent salt concentration is low ($c_s = 0.25$ M), the degree of ionization is large for the expanded gel (higher temperatures) and collapses to near zero below the transition (collapsed gel). As we increase the salt concentration, however, divalent ions increasingly adsorb on the polymer backbone, and beyond a certain critical concentration, can effectively reverse the charge of the polyelectrolyte gel. This is most clearly seen for the salt concentration $c_s = 2.5$ M. Eventually, however, enough of co-ions condense onto the divalent ions to neutralize the excess charge and restore the system to the isoelectric point. The relevant contributions to the different degrees of ionization are shown in Fig. 7(b), for a fixed choice of the a_χ and δ parameters. In the expanded state, the degree of ionization is positive, and the fraction of condensed divalent ions is low, as

can be seen from the α_{2a} , α_{2b} , and α_{2c} plots. As the gel starts to collapse, increasing number of divalent ions condense onto the backbone, reflected in the increase of α_{2a} and α_{2b} values. As the number of condensed divalent ions increases, the overall degree of ionization becomes negative, and the gel re-swells. Beyond a critical reswelling, condensation of co-ions and the consequent formation of ion triplets plays an increasingly important role, as reflected in the increase of the α_3 curves. The co-ion condensation compensates for the excess degree of ionization, and finally the gel collapses again, and the total degree of ionization approaches zero.

The re-entrant volume transition is expected in any low-temperature theory of counterion adsorption.⁸⁴ However, it is so far unobserved experimentally in gels. Our theory (Fig. 4(c)) shows that the re-entrant volume transition in aqueous systems would occur only at impractically low temperatures. The results of Figs. 4(c) and 7 suggest that the re-entrant transition might be experimentally observed by choosing less polar solvents than water and at higher salt concentrations.

F. Free energy contributions

Finally, we have investigated the relative importance of the different free energy terms in the collapsed and expanded states of the polyelectrolyte gel. As a typical illustration, the contributions of the different terms of Eq. (15) are shown in Fig. 8 for the sample case of a polyelectrolyte gel in a monovalent salt solution. Similar general trends are found for the salt-free and divalent salt cases. For the expanded gel at higher temperatures, the dominant contribution is from the entropy of solvent molecules and dissociated small ions (f_s), both in the gel and solution phases. As the gel starts to collapse, other terms begin to play increasingly important roles. In particular, the contribution from the adsorption free energy (f_{ad}) begins to dominate over the other contributions. In the collapsed gel phase, the contribution from f_{ad} is about two orders of magnitude higher than the rest. For completion, contributions from entropy of adsorbed counterions (f_{sa}), the Flory-Huggins interaction energy (f_χ), the network elastic free energy (f_{elast}),

FIG. 8. Contributions of the different free energy terms to the total free energy as functions of temperature for a charged gel in a monovalent salt solution.

counterion fluctuations ($f_{fl,i}$), and electrostatic interaction among the polymer segments (f_{el}) are included in Fig. 8.

IV. CONCLUSIONS

We have computed the phase behavior of charged polymer gels in salt-free, monovalent and divalent salt solutions using a variational calculation that allows the effective charge of the polymer backbone to self-regulate. The degree of counterion condensation is mediated by an interplay between the local dielectric constant, translational entropy of free counterions and gel conformations. Our analysis provides a theoretical framework within which the volume transitions of the gel can be studied. Following our previous work on polyelectrolyte solutions, we also provide a framework to understand the effects of divalent ions, where we introduce an additional free energy term due to bridging segments of the polymer chains which are widely separated along the backbone.

The theory parameterizes the behavior of the gel volume fraction in terms of two quantities, the dielectric mismatch parameter (δ) between the local environment near the polymer backbone and the bulk, and the Flory-Huggins chemical mismatch parameter (a_χ). In general, we find that for a fixed value of δ , the transition temperature and the size of the discontinuity at the transition both increase with increasing values of a_χ , while for fixed a_χ , both decrease with increasing values of δ . This trend holds for salt-free solutions, solutions with monovalent salt and also divalent salts in the absence of overcharging.

For salt-free gels, we have also studied the effect of the gel crosslink density on the volume transition. We find that for charged polymer gels, the volume transition persists even in the limit that the crosslink density goes to zero (the limit of an isolated polyelectrolyte chain). This is in contrast to the neutral gel case where there exists no transition below a certain critical endpoint. The qualitative behavior of the volume transition is also contrary to neutral gels, with the transition temperature decreasing, and the width of the transition increasing with decreasing crosslink density.

For monovalent and divalent salts, we have also computed the volume fraction as a function of the salt concentration. For a fixed value of the dielectric mismatch δ , the critical salt concentration for the volume transition decreases with increasing values of the chemical mismatch parameter a_χ , while the discontinuity at the transition becomes larger. For a fixed value of a_χ , the critical salt concentration increases and the width of the transition decreases with decreasing values of δ .

In addition, for solutions with divalent ions, we find the phenomenon of overcharging above a certain value of the salt concentration c_s . This phenomenon occurs due to the competitive adsorption between monovalent counterions and divalent ions from the salt. The divalent ions can displace the monovalent counterions as the gel shrinks during the volume transition. This can cause the effective charge of the polymer gel to be neutralized completely, and even be reversed, leading to charge reversal. In such a scenario, the gel re-swells due to enhanced repulsion among divalent ions before finally collapsing at a lower critical temperature due to co-ion adsorption.

In agreement with our earlier work^{46,51,52} and a recent work,⁴⁹ our analysis also highlights the importance of the effective polymer charge on the transition. The effective degree of counterion condensation undergoes a discontinuous change simultaneously with gel volume fraction, and effectively functions as a non-conserved order parameter for the transition. Thus this effect should always be taken into account in theoretical descriptions of charged polymer gels, and the fixed effective charge assumption cannot be considered to be a valid representation of such systems.

While our model provides a general framework for the description of charged polymer gels, more work needs to be done in order to critically validate the predictions of the theory with known experimental results. In this paper, we describe qualitative trends as functions of the effective Flory-Huggins parameter (a_χ) and the dielectric mismatch parameter (δ) for different temperatures and salt concentrations. However, the numerical minimization algorithm becomes less efficient at lower salt concentrations and so we have used higher ranges for the purposes of this analysis. The analysis needs to be extended for more experimentally relevant salt concentrations and also for experimentally determined values of the dielectric mismatch and chemical mismatch parameters.

From a theoretical point of view, the variational framework presented here is at the level of a mean field approximation. Further refinements to the theory can be made by accounting for fluctuations beyond the saddle point. Additionally, when the gel is in an extremely collapsed state, multipole electrostatic interactions may play an increasingly important role, which is not accounted for in our present analysis.

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