Salt-Induced Swelling and Volume Phase Transition of Polyelectrolyte Gels

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A theoretical model of polyelectrolyte gels is presented to study continuous and discontinuous volume phase transitions induced by changing salt concentration in the external solution. Phase diagrams are constructed in terms of the polymer–solvent interaction parameters, external salt concentration, and concentration of fixed charges. Comparisons with previous experiments for an ionized acrylamide gel in mixed water–acetone solvents are made with good quantitative agreement for a monovalent salt (NaCl) but fair qualitative agreement for a divalent salt (MgCl$_2$), using a simple set of parameters for both cases. The effective polymer–solvent interactions vary with the volume fraction of acetone in the mixed solvent, leading to either continuous or discontinuous volume transitions. The presence of divalent ions (Mg^{2+}) in addition to monovalent ions in the external solution reduces the critical salt concentration for the discontinuous transition by several orders of magnitude. Moreover, a secondary continuous transition is predicted between two highly swollen states for the case of a divalent salt. The present model may be further extended to study volume phase transitions of polyelectrolyte gels in response to other stimuli such as temperature, pH and electrical field. [DOI: 10.1115/1.4036113]

Keywords: gel, polyelectrolyte, volume phase transition

1 Introduction

A polyelectrolyte gel consists of a charged polymer network with ionizable groups on the polymer chains and mobile ions in a fluid solvent [1]. Due to the presence of ionizable groups and mobile ions, polyelectrolyte gels are responsive to many external stimuli such as temperature [2,3], pH [4–6], ionic strength [7], electrical fields [8,9], and light [10,11]. Of particular interest is the volume phase transition, when the gel volume changes enormously in response to a small change of the external environment [12]. A discontinuous volume transition was first predicted theoretically in 1968 by Dusek and Patterson [13]. The first experimental observation of a volume phase transition in a gel was reported in 1978 by Tanaka [14]. Since then, many gel systems have been developed with characteristic volume phase transitions for a wide range of applications, such as sensors and actuators [15], artificial muscles [16], and drug delivery [17,18]. Recent developments of ionic skin [19] and ionic cables [20] have used polyelectrolyte gels as effective ionic conductors, opening doors to new applications in wearable electronics and soft robotics.

Many theoretical models have been developed to understand and predict volume phase transitions in polyelectrolyte gels. Katchalsky et al. [21] first extended the Flory–Rehner model for neutral polymer gels to describe swelling of polyelectrolyte gels. Following a similar approach, Dusek and Patterson [13] predicted the possibility of a discontinuous volume change of a gel based on an analogy of the coil–globule transition of polymers in a solution. Later, Shibayama and Tanaka [12] noted a theoretical analogy between the volume phase transition of a gel and the liquid–gas transition of a van der Waals fluid. While the classical mean-field theory of gels provided a qualitative understanding of the volume phase transition [22,23], improvements in quantitative agreement between the theory and experiments have been made by various modifications to the theoretical formulation [24–26]. To study the kinetics of swelling and inhomogeneous phenomena such as coexisting phases in a polyelectrolyte gel, a continuum field theory

was developed by Hong et al. [27], which couples large deformation and electrochemistry in the constitutive relations along with a system of governing equations and boundary conditions. Alternatively, multiphasic models have also been developed for polyelectrolyte gels, where the polymer network, the solvent and the ions are treated as distinct phases within the framework of mixture theory [28–31].

Volume phase transitions in gels induced by temperature and pH have been studied extensively [5,12]. Less attention has been paid to the effect of salt concentration or salinity on volume phase transitions. Ohmine and Tanaka [32] reported an experimental study on salt-induced volume phase transitions in an ionized acrylamide gel, along with a qualitative explanation based on the classical theory. Their experiments showed intriguing effects due to the valence of the salt ions and composition of a mixed solvent. A direct comparison between the experiments and theoretical predictions would elucidate the capability and limitations of a specific model for a quantitative description of polyelectrolyte gels in both the swollen and collapsed phases. In this paper, we present such a direct comparison based on the continuum theory by Hong et al. [27], slightly reformulated for equilibrium free swelling of a polyelectrolyte gel immersed in a salt solution with a mixed solvent. The theory naturally leads to a balance of osmotic pressures due to elasticity, solvent, and ions in an isotropic, homogeneous state. Under the condition of electroneutrality, the ion concentrations in the gel satisfy the Donnan equilibrium with a Donnan potential, recovering the classical theory for a highly swollen state. Both the salt concentration and solvent composition in the external solution can be varied to induce a discontinuous volume phase transition of the polyelectrolyte gel. Comparisons with the experiments of Ohmine and Tanaka [32] show good quantitative agreement for a monovalent salt (NaCl) but fair qualitative agreement for a divalent salt (MgCl$_2$), which may be further improved by calibrating the model parameters for a specific combination of salt and solvent.

The remainder of this paper is organized as follows: Section 2 presents the theoretical model, including the equations of state for both the polyelectrolyte gel and the external solution as an ionic liquid. Section 3 presents an equilibrium analysis of free swelling, and Sec. 4 discusses the volume phase transition in a general

form. Direct comparisons with experiments are presented in Sec. 5 for both monovalent and divalent salts, followed by a short summary in Sec. 6.

2 Theory

2.1 Kinematic Variables. Take the dry state of the gel (i.e., the polymer network) as the reference configuration, where each material point is labeled by its coordinate $\mathbf{X}$. The location of the material point in the current configuration at a time t is denoted by $\mathbf{x}(\mathbf{X},t)$. The kinematics of deformation is described by the deformation gradient tensor as usual

$$\mathbf{F} = \nabla \mathbf{x} \tag{2.1}$$

With respect to the reference configuration, a nominal electric displacement, $\tilde{\mathbf{D}}(\mathbf{X},t)$, is defined by its relationship with the true electric displacement [33], $\mathbf{D}(\mathbf{x},t)$, as

$$\mathbf{D} = \frac{1}{J}\mathbf{F}\tilde{\mathbf{D}} \tag{2.2}$$

where $J = \det\mathbf{F}$. Similarly, the nominal concentration, C^a, is defined as the number of mobile particles of species a per unit volume of the polymer network in the gel. The true concentration in the current configuration is then $c^a = C^a/J$. The superscript a is used here for all the mobile particles in the gel, including the neutral solvent molecules and the mobile ions. Together, $\mathbf{F}$, $\tilde{\mathbf{D}}$, and C^a constitute a set of kinematic variables that describe the current state of the polyelectrolyte gel.

It is often assumed that the polymer network and the mobile particles are incompressible at the molecular level. Consequently, the volume change of the gel is related to the concentrations of the mobile particles as

$$J = 1 + \sum_a v^a C^a \tag{2.3}$$

where v^a is the molecular volume of each mobile particle a.

2.2 Constitutive Relations. Following Hong et al. [27], the free energy density of the polyelectrolyte gel is written as a function of the deformation gradient $\mathbf{F}$, the nominal electric displacement $\tilde{\mathbf{D}}$, and the nominal concentrations C^a, which consists of four parts

$$W_g\left(\mathbf{F},\tilde{\mathbf{D}},C^1,C^2,\dots\right) = W_g^{\text{net}} + W_g^{\text{sol}} + W_g^{\text{ion}} + W_g^{\text{pol}} \tag{2.4}$$

where W_g^{net}, W_g^{sol}, W_g^{ion}, and W_g^{pol} are the free energy terms associated with stretching of the polymer network, mixing the polymer and the solvent, mixing the solvent and ions, and polarization of the gel, respectively. Note that the free energy density in Eq. (2.4) is per unit volume in the reference configuration (i.e., the dry polymer network); the free energy per unit volume of the gel in the current configuration is simply W_g/J.

The elastic free energy of stretching the polymer network is assumed to be

$$W_g^{\text{net}} = \frac{1}{2}NkT(I - 3 - 2\ln J) \tag{2.5}$$

where $I = tr(\mathbf{F}^{\text{T}}\mathbf{F})$, N is the effective number density of polymer chains in the dry state, kT is the temperature in the unit of energy with the Boltzmann constant k and the absolute temperature T.

The free energy of mixing the solvent and the polymer network is

$$W_g^{\text{sol}} = \frac{kT}{v^s}\left(v^s C^s \ln\frac{v^s C^s}{1 + v^s C^s} + \frac{\chi v^s C^s}{1 + v^s C^s}\right) \tag{2.6}$$

where v^s is the volume of the solvent molecule, C^s is the nominal concentration of the solvent, and χ is the Flory–Huggins parameter for polymer–solvent interactions. Equations (2.5) and (2.6) are identical to those for neutral polymer gels in previous studies [34,35].

Assuming the concentrations of the mobile ions to be low, the free energy of mixing the mobile ions and the solvent is approximately

$$W_g^{\text{ion}} = kT\sum_b C^b\left(\ln\frac{v^b C^b}{J - 1} - 1\right) \tag{2.7}$$

where the superscript b is used here for all the mobile ions, excluding the solvent molecule. Equation (2.7) is slightly different from that in Hong et al. [27], where zero chemical potential was assumed at a reference ion concentration. Here, the free energy of mixing is derived from the statistical mechanics definition of entropy for an ideal solution [36], without explicitly identifying a reference ion concentration. This change leads to some subtle differences in the swelling behavior, as discussed later. By Eq. (2.7), we assume that the free energy due to the mixing between the ions and the polymer network is negligible.

Treating the polyelectrolyte gel as an ideal dielectric, the free energy of polarization in terms of the nominal electric displacement is [33]

$$W_g^{\text{pol}} = \frac{1}{2\varepsilon_g J}|\mathbf{F}\tilde{\mathbf{D}}|^2 \tag{2.8}$$

where ε_g is the effective dielectric constant of the gel. Due to the different dielectric constants of the polymer and the solvent, the effective dielectric constant of the gel in general depends on the concentration of the solvent [37], but is assumed to be a constant here for simplicity.

To impose Eq. (2.3) as a kinematic constraint, the free energy density function is rewritten as

$$\tilde{W}_g = W_g + \Pi_g\left(\sum_a v^a C^a + 1 - J\right) \tag{2.9}$$

where Π_g is a Lagrange multiplier.

With the free energy density function given by Eqs. (2.4)–(2.9), the nominal electric field $\tilde{\mathbf{E}}$ and the electrochemical potential μ^a for each mobile species can then be obtained as [27]

$$\tilde{\mathbf{E}} = \frac{\partial \tilde{W}_g}{\partial \tilde{\mathbf{D}}} \tag{2.10}$$

$$\mu^a = \frac{\partial \tilde{W}_g}{\partial C^a} + ez^a\Phi \tag{2.11}$$

where e is the elementary charge, z^a is the valence of the mobile species a, and Φ is the electric potential so that $\tilde{\mathbf{E}} = -\nabla\Phi$. Substituting Eq. (2.9) into Eqs. (2.10) and (2.11), we obtain

$$\tilde{\mathbf{E}} = \frac{1}{\varepsilon_g J}\mathbf{F}^{\text{T}}\mathbf{F}\tilde{\mathbf{D}} \tag{2.12}$$

$$\mu^s = kT\left[\ln\frac{v^s C^s}{1 + v^s C^s} + \frac{1}{1 + v^s C^s} + \frac{\chi}{(1 + v^s C^s)^2}\right] + \Pi_g v^s \tag{2.13}$$

$$\mu^b = ez^b\Phi + kT\ln\frac{v^b C^b}{J - 1} + \Pi_g v^b \tag{2.14}$$

By Eq. (2.12), the nominal electric displacement is obtained as

$$\tilde{\mathbf{D}} = \left(\varepsilon_g J\mathbf{H}^{\text{T}}\mathbf{H}\right)\tilde{\mathbf{E}} \tag{2.15}$$

where $\mathbf{H} = \mathbf{F}^{-\mathrm{T}}$.

To simplify further calculations, Eq. (2.3) is approximated by neglecting the contribution of the mobile ions due to relatively low concentrations (i.e., $v^b C^b \ll v^s C^s$) so that

$$1 + v^s C^s \approx J \qquad (2.16)$$

Then, by Eq. (2.13), we obtain

$$\Pi_g = \frac{\mu^s}{v^s} - \frac{kT}{v^s}\left(\ln\frac{J-1}{J} + \frac{1}{J} + \frac{\chi}{J^2}\right) \qquad (2.17)$$

which is essentially the osmotic pressure due to polymer–solvent mixing as discussed later (see Eq. (2.22)).

By substituting Eq. (2.17) into Eq. (2.14), the nominal concentration of the mobile ions can be obtained as

$$C^b = \frac{J-1}{v^b}\left(\frac{J-1}{J}\right)^{v^b/v^s}\exp\left\{\frac{\mu^b - ez^b\Phi}{kT} - \frac{v^b}{v^s}\left(\frac{\mu^s}{kT} - \frac{1}{J} - \frac{\chi}{J^2}\right)\right\} \qquad (2.18)$$

Assuming $v^b = v^s = v$, the nominal ion concentration is simplified as

$$C^b = \frac{(J-1)^2}{vJ}\exp\left\{\frac{\mu^b - \mu^s - ez^b\Phi}{kT} + \frac{1}{J} + \frac{\chi}{J^2}\right\} \qquad (2.19)$$

With Eq. (2.18) or Eq. (2.19), the ion concentrations in a polyelectrolyte gel can be obtained explicitly in terms of the electrochemical potentials and the volume swelling ratio ($J = \det\mathbf{F}$).

It is often convenient to rewrite the free energy density as a function of the deformation gradient, the nominal electric field (instead of the electrical displacement), and the electrochemical potentials (instead of concentrations) by a Legendre transform

$$\hat{W}_g(\mathbf{F}, \tilde{\mathbf{E}}, \mu^1, \mu^2, \ldots) = \tilde{W}_g(\mathbf{F}, \tilde{\mathbf{D}}, C^1, C^2, \ldots) - \tilde{\mathbf{E}} \cdot \tilde{\mathbf{D}} \\ - \sum_a C^a(\mu^a - ez^a\Phi) \qquad (2.20)$$

With Eqs. (2.4)–(2.9), (2.15), (2.16), and (2.19), the free energy density function in Eq. (2.20) becomes

$$\hat{W}_g = \frac{1}{2}NkT(I - 3 - 2\ln J) + \frac{kT}{v}(J-1)\left(\ln\frac{J-1}{J} + \frac{\chi}{J} - \frac{\mu^s}{kT}\right) \\ - \frac{kT}{v}\frac{(J-1)^2}{J}\exp\left(\frac{1}{J} + \frac{\chi}{J^2}\right)\sum_{b \neq s}\exp\left(\frac{\mu^b - \mu^s - ez^b\Phi}{kT}\right) \\ - \frac{\varepsilon_g}{2}J|\mathbf{H}\tilde{\mathbf{E}}|^2 \qquad (2.21)$$

The nominal stress in the gel is then obtained as the derivative of the free energy density function with respect to the deformation gradient, namely,

$$\mathbf{P} = \frac{\partial \hat{W}_g}{\partial \mathbf{F}} = NkT(\mathbf{F} - \mathbf{H}) - J\Pi_g\mathbf{H} \\ - \frac{kT}{v}\left(J - 1 + \frac{1-2\chi}{J} + \frac{4\chi-1}{J^2} - \frac{2\chi}{J^3}\right)\exp\left(\frac{1}{J} + \frac{\chi}{J^2}\right) \\ \times \sum_{b \neq s}\exp\left(\frac{\mu^b - \mu^s - ez^b\Phi}{kT}\right)\mathbf{H} \\ + \varepsilon_g J\left(\mathbf{H}\tilde{\mathbf{E}} \otimes \mathbf{H}^{\mathrm{T}}\mathbf{H}\tilde{\mathbf{E}} - \frac{1}{2}\left|\mathbf{H}\tilde{\mathbf{E}}\right|^2\mathbf{H}\right) \qquad (2.22)$$

which includes four parts: the elastic part due to stretching the polymer network, an osmotic part due to polymer–solvent mixing,

another osmotic part due to ionic interactions, and the Maxwell stress due to polarization. In terms of the true stress, $\boldsymbol{\sigma} = \mathbf{P}\mathbf{F}^{\mathrm{T}}/J$, the two osmotic parts are isotropic, yielding two osmotic pressures for the solvent and the mobile ions, respectively. The last term in Eq. (2.22) is the nominal Maxwell stress, with which the true Maxwell stress can be obtained in its usual form: $\boldsymbol{\sigma}_{\mathrm{Maxwell}} = \varepsilon_g(\mathbf{E} \otimes \mathbf{E} - |\mathbf{E}|^2\mathbf{I}/2)$, with the true electrical field $\mathbf{E} = \mathbf{H}\tilde{\mathbf{E}}$.

Therefore, the constitutive relations for the polyelectrolyte gel consist of Eqs. (2.15), (2.19) and (2.22), with which the electrical displacement, ion concentrations, and nominal stress can be determined for given deformation gradient ($\mathbf{F}$), electrical field ($\tilde{\mathbf{E}}$), and electrochemical potentials (μ^a); the solvent concentration can be obtained directly from Eq. (2.16).

2.3 External Solution. In the equilibrium state, the electrochemical potential for each mobile species is a constant in the gel and the external solution. We treat the external solution as an ionic liquid with a mixture of neutral solvent molecules (e.g., water) and ions. The treatment is similar to that for polyelectrolyte gels in Secs. 2.1 and 2.2. Without a polymer network, an arbitrary configuration of the ionic liquid may be used as the reference configuration to define the deformation gradient. Then, the nominal electric displacement is defined by Eq. (2.2) and the nominal concentration is related to the true concentration as $c^a = C^a/J$. Assuming molecular incompressibility, the kinematic constraint for the external solution is

$$\sum_a v^a C^a = J \qquad (2.23)$$

which implies that the entire space is occupied by the solvent molecules and ions in the external solution (i.e., $\sum_a v^a c^a = 1$).

The free energy density function of the external solution contains two parts, due to ion mixing and polarization

$$W_s(\mathbf{F}, \tilde{\mathbf{D}}, C^1, C^2, \ldots) = W_s^{\mathrm{ion}} + W_s^{\mathrm{pol}} \qquad (2.24)$$

Based on the statistical mechanics definition of entropy for an ideal solution [36], the free energy density due to mixing of the ions and the solvent in the external solution is

$$W_s^{\mathrm{ion}} = kT\sum_{b \neq s}C^b\left(\ln\frac{v^b C^b}{J} - 1\right) \qquad (2.25)$$

This expression is slightly different from that for the gel in Eq. (2.7) because the fluid mixture occupies the entire volume of the external solution but only a fraction of the volume in a gel containing the polymer network.

The free energy density of polarization takes the same form as Eq. (2.8) for the gel except with a different dielectric constant, namely,

$$W_s^{\mathrm{pol}} = \frac{|\mathbf{F}\tilde{\mathbf{D}}|^2}{2\varepsilon_s J} \qquad (2.26)$$

where ε_s is the effective dielectric constant of the external solution.

To impose the kinematic constraint in Eq. (2.23), the free energy density function is rewritten as

$$\tilde{W}_s = W_s + \Pi_s\left(\sum_a v^a C^a - J\right) \qquad (2.27)$$

where Π_s is a Lagrange multiplier.

Substituting Eq. (2.27) into Eqs. (2.10) and (2.11), we obtain the nominal electrical field and the electrochemical potentials for the solvent and ions in the external solution

$$\tilde{\mathbf{E}} = \frac{1}{\varepsilon_s J} \mathbf{F}^{\mathrm{T}} \mathbf{F} \tilde{\mathbf{D}} \tag{2.28}$$

$$\mu^s = \Pi_s v^s \tag{2.29}$$

$$\mu^b = ez^b \Phi + kT \ln \frac{v^b C^b}{J} + \Pi_s v^b \tag{2.30}$$

Furthermore, the nominal stress in the external solution is obtained as the derivative of the free energy density function with respect to the deformation gradient, namely,

$$\mathbf{P} = \frac{\partial \tilde{W}_s}{\partial \mathbf{F}} = -\left(J\Pi_s + kT \sum_{b \neq s} C^b \right) \mathbf{H} + \frac{1}{\varepsilon_s J} \left(\mathbf{F}\tilde{\mathbf{D}} \otimes \tilde{\mathbf{D}} - \frac{1}{2} |\mathbf{F}\tilde{\mathbf{D}}|^2 \mathbf{H} \right) \tag{2.31}$$

which consists of an osmotic pressure and the Maxwell stress. More explicitly, in terms of the true quantities, the true stress in the external solution is

$$\boldsymbol{\sigma} = \frac{1}{J} \mathbf{P}\mathbf{F}^{\mathrm{T}} = -\left(\Pi_s + kT \sum_{b \neq s} c^b \right) \mathbf{I} + \frac{1}{\varepsilon_s} \left(\mathbf{D} \otimes \mathbf{D} - \frac{1}{2} |\mathbf{D}|^2 \mathbf{I} \right) \tag{2.32}$$

which is independent of the reference configuration or deformation but includes a hydrostatic term undetermined by the constitutive relation as expected for an incompressible fluid.

Next, we assume an infinitely large reservoir such that the concentrations of the ions are fixed in the external solution far away from the gel. Let c_0^b be the true ion concentration, and use the homogeneous state of the external solution as the reference configuration. The electric potential Φ is set to be zero deep in the solution (far away from the gel), where the solution is electrically neutral and hence $\sum_b c_0^b z^b = 0$. As a result, $\tilde{\mathbf{E}} = 0$ and $\tilde{\mathbf{D}} = 0$. Moreover, the solution is assumed to be stress free so that $\mathbf{P} = 0$. By Eq. (2.31), we obtain

$$\Pi_s = -kT \sum_{b \neq s} c_0^b \tag{2.33}$$

Then, the electrochemical potential is obtained from Eq. (2.30) as

$$\mu^b = kT \ln \left(v^b c_0^b \right) + v^b \Pi_s \tag{2.34}$$

and by Eq. (2.29) the chemical potential of the solvent in the external solution is

$$\mu^s = -v^s kT \sum_{b \neq s} c_0^b \tag{2.35}$$

Therefore, by changing the ion concentrations in the external solution, the chemical potential of solvent and the electrochemical potential of the ions change simultaneously, which would then lead to the change of the equilibrium state of the gel. Since the chemical and electrochemical potentials are set by the external solution in equilibrium with the gel, the only unknown quantities to be determined for the gel are the deformation gradient and the electrical potential.

Note that, based on the statistical mechanics for an ideal solution [36], the chemical potential of each mobile species (including solvent and ions) is zero only when it is not mixed with any other species. Indeed, by Eq. (2.35), the chemical potential of solvent is zero for a pure solvent with zero ion concentrations (i.e., $\sum_{b \neq s} c_0^b = 0$). For ions, however, Eq. (2.34) does not vanish even when $v^b c_0^b = 1$ and $c^s = 0$, because the free energy function in Eq. (2.25) is an approximation for cases with low ion concentrations (e.g., $v^b c^b \ll v^s c^s$) and thus the resulting chemical potential is inaccurate for the case with a high ion concentration.

3 Equilibrium Analysis of Free Swelling

Consider a simple polyelectrolyte gel, with two types of mobile monovalent ions of opposite charges, i.e., $z^+ = +1$ and $z^- = -1$, and monovalent fixed charges ($z_{\text{fix}} = -1$). At equilibrium, the chemical potential of solvent and the electrochemical potentials of the ions in the gel are equal to those in the external solution. Let c_0 be the true concentration of the ions deep in the external solution (electrically neutral and stress free). By Eq. (2.33)–(2.35), we obtain the electrochemical potential for both ions

$$\mu^b = kT \left[\ln \left(v^b c_0 \right) - 2v^b c_0 \right] \tag{3.1}$$

and the chemical potential for the solvent

$$\mu^s = -2kT v^s c_0 \tag{3.2}$$

It is well known that an electrical double layer forms at the interface between the polyelectrolyte gel and the external solution (Fig. 1), with a characteristic thickness proportional to the Debye length [27], which is often much smaller than the size of the gel and the external solution. As a result, the fields of electrical potential, stress, and solvent/ion concentrations are all inhomogeneous near the interface. On the other hand, at a distance much larger than the Debye length from the interface, both the gel and the external solution are electrically neutral, and the fields are homogeneous [27]. Here, we ignore the inhomogeneous fields near the interface and focus on the homogeneous part of the gel. Thus, by electroneutrality the ion concentrations in the gel are related to the concentration of fixed charges as

$$C^+ = C_{\text{fix}} + C^- \tag{3.3}$$

where C_{fix} is the nominal concentration of the fixed charges on the polymer network. For a strong polyelectrolyte gel, C_{fix} is a constant, as is assumed in the present study. For a weak polyelectrolyte gel, C_{fix} may change when the degree of dissociation of the ionizable groups changes in response to the solvent composition or ion concentration [25,37].

Substituting Eqs. (3.1) and (3.2) into Eq. (2.19), we obtain the nominal ion concentrations as

$$C^+ = c_0 \frac{(J-1)^2}{J} \exp \left(\frac{1}{J} + \frac{\chi}{J^2} \right) \exp \left(-\frac{e\Phi}{kT} \right) \tag{3.4}$$
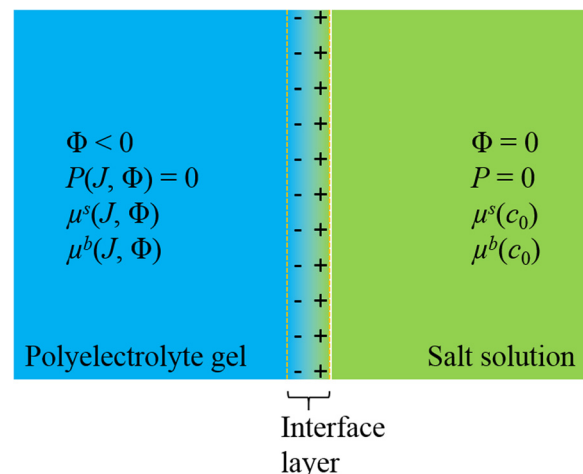

Fig. 1 Schematic of a polyelectrolyte gel in equilibrium with an external salt solution, with an electrical double layer at the interface

$$C^- = c_0 \frac{(J-1)^2}{J} \exp\left(\frac{1}{J} + \frac{\chi}{J^2}\right) \exp\left(\frac{e\Phi}{kT}\right) \qquad (3.5)$$

Substituting Eqs. (3.4) and (3.5) into Eq. (3.3), we obtain

$$\sinh\left(\frac{e\Phi}{kT}\right) = -\frac{JC_{\text{fix}}}{2c_0(J-1)^2} \exp\left(-\frac{1}{J} - \frac{\chi}{J^2}\right) \qquad (3.6)$$

For the case of homogeneous swelling, Eq. (3.6) gives a constant electric potential Φ, which depends on the fixed charge concentration, the ion concentration of external solution, and the volume swelling ratio J. Under this condition, the nominal electric field $\tilde{\mathbf{E}}$ vanishes and the nominal electric displacement $\tilde{\mathbf{D}}$ is zero in the gel.

We note that Eqs. (3.4) and (3.5) satisfy the Donnan equilibrium [7,38,39] with a Donnan potential (Φ) between the gel and the external solvent, namely,

$$\frac{c^+}{c_0} = \frac{c_0}{c^-} \approx \exp\left(-\frac{e\Phi}{kT}\right) \qquad (3.7)$$

where the true ion concentrations ($c^a = C^a/J$) are used instead of the nominal concentrations and the approximation is made for $J \gg 1$ (i.e., highly swollen gels).

Furthermore, by Eq. (2.22), the nominal stress in the gel is obtained as

$$\mathbf{P} = NkT(\mathbf{F} - \mathbf{H}) + \frac{kT}{\upsilon}\left[J\ln\frac{J-1}{J} + 1 + \frac{\chi}{J} + 2\upsilon c_0 J\right]\mathbf{H}$$
$$-2kTc_0\cosh\left(\frac{e\Phi}{kT}\right)\left(J - 1 + \frac{1-2\chi}{J} + \frac{4\chi-1}{J^2} - \frac{2\chi}{J^3}\right)$$
$$\exp\left(\frac{1}{J} + \frac{\chi}{J^2}\right)\mathbf{H} \qquad (3.8)$$

Consider the case of free swelling with an isotropic deformation gradient: $\mathbf{F} = \lambda\mathbf{I}$, where λ is the linear stretch. As a result, $J = \lambda^3$ and the nominal stress in Eq. (3.8) becomes isotropic: $\mathbf{P} = P(\lambda, \Phi)\mathbf{I}$. The static equilibrium requires that the nominal stress vanish for free swelling, thus $P(\lambda, \Phi) = 0$. By Eq. (3.6), the electrical potential is obtained as a function of λ and then Eq. (3.8) becomes

$$P = NkT\left(\lambda - \frac{1}{\lambda}\right) + \frac{kT}{\upsilon}\left(\lambda^2\ln\frac{\lambda^3-1}{\lambda^3} + \frac{1}{\lambda} + \frac{\chi}{\lambda^4}\right)$$
$$+2kTc_0\lambda^2\left(1 - \left(1 - \frac{1}{\lambda^3} + \frac{1-2\chi}{\lambda^6} + \frac{4\chi-1}{\lambda^9} - \frac{2\chi}{\lambda^{12}}\right)\right.$$
$$\left.\exp\left(\frac{1}{\lambda^3} + \frac{\chi}{\lambda^6}\right)\sqrt{1 + \frac{C_{\text{fix}}^2\lambda^6}{4c_0^2(\lambda^3-1)^4}\exp\left(-\frac{2}{\lambda^3} - \frac{2\chi}{\lambda^6}\right)}\right) = 0$$
$$(3.9)$$

Solving Eq. (3.9), we obtain the linear stretch λ of a polyelectrolyte gel in equilibrium with an external solution, which depends on four dimensionless parameters: the effective number density of polymer chains $N\upsilon$, the Flory–Huggins parameter χ, the nominal concentration of fixed charges υC_{fix}, and the normalized ion concentration in the external solution υc_0. Once the stretch is determined, Eq. (3.6) is used to determine the electric potential in the gel. Then, Eqs. (3.4) and (3.5) are used to find the nominal concentrations of the ions in the gel. For example, Fig. 2 shows the results for free swelling of a polyelectrolyte gel with $N\upsilon = 10^{-3}$, $\upsilon C_{\text{fix}} = 0.02$, and $\chi = 0.5$ in an external solution of varying ion concentrations. It can be seen that increasing the ion concentration in the external solution leads to a decrease in the linear stretch and
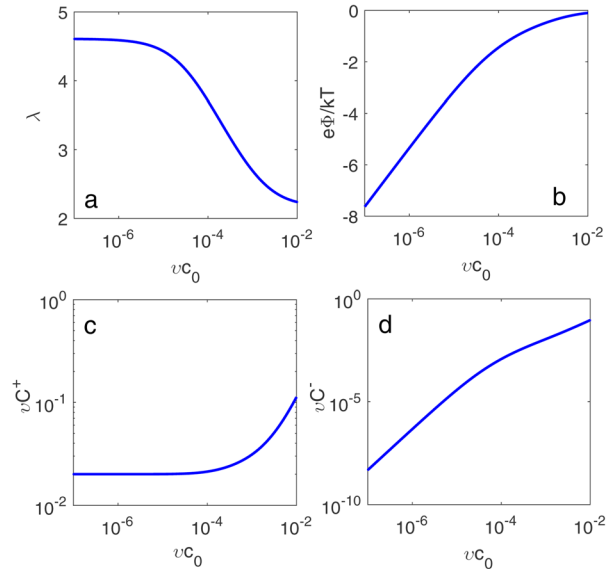
Fig. 2 Free swelling of a polyelectrolyte gel ($N\upsilon = 10^{-3}$, $\upsilon C_{\text{fix}} = 0.02$, and $\chi = 0.5$) immersed in an ionic solution with varying ion concentration. (a) Stretch, (b) electrical potential, (c) and (d) nominal concentrations of counter-ions and co-ions.

thus shrinking of the gel volume. This is a result mainly due to the decrease in the chemical potential of the solvent in the external solution, as given by Eq. (2.35). Meanwhile, the electrochemical potentials of the ions increase, leading to an increase of the ion concentrations in the gel. However, since the ion concentrations are much lower than the solvent concentration ($\upsilon C^{+/-} \ll \upsilon C^s \approx \lambda^3 - 1$), the volume change of the gel is dominated by the change in the solvent concentration. Moreover, with the negative fixed charges in the gel, the electric potential of the gel is negative and increases as the ion concentrations increase in the external solution. These results are similar to those obtained by Hong et al. [27].

Equation (3.9) may be considered as a balance of three osmotic pressures due to elasticity, solvent, and ions, respectively. Similar osmotic pressures were used by Ohmine and Tanaka [32], where the osmotic pressure due to ions was given explicitly for two limiting cases only. First, for a pure solvent without any ions ($c_0 = 0$) or a very low ion concentration ($c_0 \ll C_{\text{fix}}$), Eq. (3.9) becomes

$$P \approx NkT\left(\lambda - \frac{1}{\lambda}\right) + \frac{kT}{\upsilon}\left[\lambda^2\ln\frac{\lambda^3-1}{\lambda^3} + \frac{1}{\lambda} + \frac{\chi}{\lambda^4} - \frac{\upsilon C_{\text{fix}}\lambda^2}{(\lambda^3-1)^2}\right.$$
$$\left. \times \left(\lambda^3 - 1 + \frac{1-2\chi}{\lambda^3} + \frac{4\chi-1}{\lambda^6} - \frac{2\chi}{\lambda^9}\right)\right] = 0 \qquad (3.10)$$

which can be reduced to Eq. (7.10) by Hong et al. [27] if $\lambda^3 \gg 1$. Under the same conditions ($c_0 \ll C_{\text{fix}}$ and $\lambda^3 \gg 1$), the osmotic pressure due to the solvent is negligible, and Eq. (3.10) can be further simplified as

$$P \approx kT\left(N\lambda - \frac{C_{\text{fix}}}{\lambda}\right) = 0 \qquad (3.11)$$

by which the osmotic pressures due to elasticity and ions are balanced. The osmotic pressure due to ions in Eq. (3.11) is proportional to C_{fix}, similar to that in Ref. [32] for $c_0 \ll C_{\text{fix}}$.

For the second limit, if the ion concentrations in the external solution are much higher than the fixed charge concentration in the gel, i.e., $c_0 \gg C_{\text{fix}}$, we have $\Phi \approx 0$ by Eq. (3.6), and Eq. (3.9) becomes

$$P \approx NkT\left(\lambda - \frac{1}{\lambda}\right) + \frac{kT}{\upsilon}\left(\lambda^2 \ln\frac{\lambda^3 - 1}{\lambda^3} + \frac{1}{\lambda} + \frac{\chi}{\lambda^4}\right)$$
$$+ 2kTc_0\lambda^2\left(1 - \left(1 - \frac{1}{\lambda^3} + \frac{1 - 2\chi}{\lambda^6} + \frac{4\chi - 1}{\lambda^9} - \frac{2\chi}{\lambda^{12}}\right)\right.$$
$$\left.\times \exp\left(\frac{1}{\lambda^3} + \frac{\chi}{\lambda^6}\right)\right) = 0 \qquad (3.12)$$

which again can be reduced to the corresponding equation (7.8) in Ref. [27] if $\lambda^3 \gg 1$. Under these conditions ($c_0 \gg C_{\text{fix}}$ and $\lambda^3 \gg 1$), Eq. (3.9) can be further simplified as

$$P \approx kT\left(N\lambda - \frac{C_{\text{fix}}^2}{4c_0\lambda^4}\right) = 0 \qquad (3.13)$$

where the osmotic pressure due to ions is proportional to C_{fix}^2, similar to that in Ref. [32] for $c_0 \gg C_{\text{fix}}$. However, this simplification is problematic, because the condition $\lambda^3 \gg 1$ typically does not hold at high ion concentrations. Hong et al. [27] predicted that the equilibrium swelling ratio is independent of the ion concentration for the limit of a highly concentrated solution. Equation (3.13) predicts that the equilibrium swelling ratio decreases with increasing ion concentration. In contrast, by Eq. (3.12), the equilibrium swelling ratio may increase with increasing ion concentration. Indeed, experiments by Okay and Sariisik [40] found that the equilibrium swelling ratio of a poly(acrylamide-co-sodium acrylate) hydrogel increased with increasing salt (NaCl) concentration in highly concentrated solutions, qualitatively consistent with Eq. (3.12). It should be noted that, with relatively high ion concentrations in the gel, the approximation in Eq. (2.16) may not be applicable, and a more accurate solution can be obtained by solving a system of equations simultaneously.

4   Volume Phase Transition

The Flory–Huggins parameter χ characterizes the polymer–solvent interactions in the gel, which depends on temperature [12,26] and solvent composition [41,42]. A change of χ has a profound effect on the swelling behavior of polyelectrolyte gels. As shown in Fig. 3(a), the equilibrium stretch λ is determined as a function of the ion concentration in the external solution by solving Eq. (3.9) for different values of χ ($N\upsilon = 10^{-3}$ and $\upsilon C_{\text{fix}} = 0.02$). It is found that when χ is small (a good solvent), e.g., $\chi = 0.1$, 0.3, and 0.5, the gel is swollen with a relatively large stretch ($\lambda > 2$) over the entire range of ion concentration, and the equilibrium stretch decreases continuously with increasing ion concentration. However, when χ is larger, e.g., $\chi = 0.7$ (a poor solvent), a discontinuous jump of the equilibrium stretch is predicted at a critical ion concentration, where a transition occurs from a highly swollen gel ($\lambda > 3$) to a collapsed phase ($\lambda < 2$). When χ is even larger, e.g., $\chi = 0.9$, the equilibrium stretch is small ($\lambda \sim 1$) over the entire range of the ion concentration, and thus the gel stays in the collapsed phase. A phase diagram is constructed in Fig. 3(b) in terms of the normalized ion concentration υc_0 and χ, where the two phases (highly swollen and collapsed) are separated by a set of transition lines. The line of the discontinuous transition (the thick solid line) is obtained by plotting the critical ion concentration at the discontinuous transition (if it occurs) versus χ. Apparently, for $N\upsilon = 10^{-3}$ and $\upsilon C_{\text{fix}} = 0.02$, the discontinuous transition occurs only within a narrow range of χ around 0.7. For smaller values of χ, the transition is continuous as indicated by the dashed lines, each corresponding to a constant stretch (e.g., $\lambda = 3$, 2.5, and 2).

To understand the discontinuous transition, we plot the normalized stress–stretch relations (Eq. (3.9)) in Fig. 4(a) for different ion concentrations in the external solution with dimensionless parameters $\chi = 0.7$, $N\upsilon = 10^{-3}$, and $\upsilon C_{\text{fix}} = 0.02$. The equilibrium stretch for free swelling corresponds to the stretch with zero
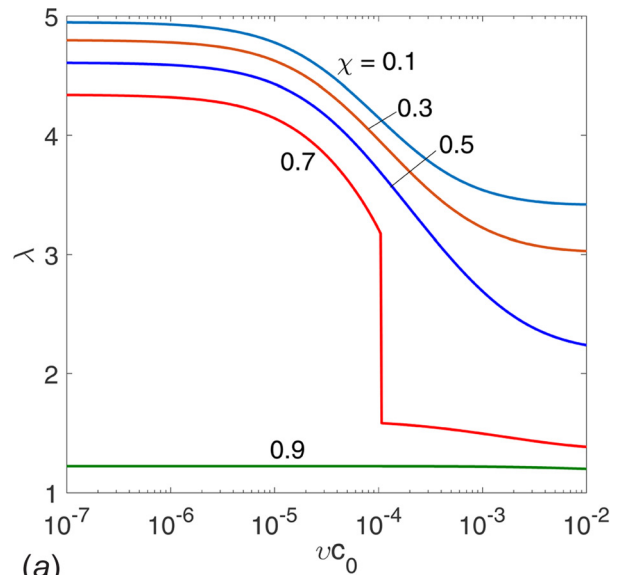
(a)
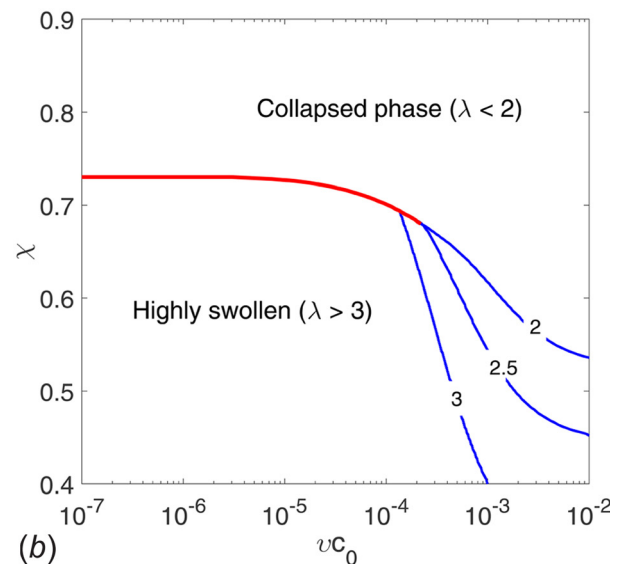
(b)

Fig. 3 (a) Equilibrium stretch as a function of ion concentration in the external solution for polyelectrolyte gels with different values of χ, showing continuous and discontinuous transitions. (b) A phase diagram with two distinct phases, highly swollen and collapsed, and the transition lines in between (thick solid line for discontinuous transition and dashed lines for continuous transition with $\lambda = 3$, 2.5, and 2).

stress, i.e., $P(\lambda) = 0$. When the ion concentration is relatively high (e.g., $c_0/C_{\text{fix}} = 0.02$), there is only one solution for the equilibrium stretch and it is in the collapsed phase. When the ion concentration is relatively low (e.g., $c_0/C_{\text{fix}} = 0.001$), there are three possible solutions for the equilibrium stretch, one in the collapsed phase ($\lambda < 2$), one in the highly swollen phase ($\lambda > 3$), and another in between. To determine which one of these solutions is thermodynamically stable, we compute the mechanical work required to stretch the gel from the collapsed phase to an arbitrary λ as

$$W(\lambda) = \int_{\lambda_1}^{\lambda} P(\lambda')d\lambda' \qquad (4.1)$$

where λ_1 is the stretch in the collapsed phase with $P(\lambda_1) = 0$. As shown in Fig. 4(b), for a relatively low ion concentration, the mechanical work has two local minima and one local maximum, corresponding to the three possible solutions with zero stress in Fig. 4(a). The stretch with the local maximum mechanical work is an unstable solution. The stretch with the lower mechanical work of the two local minima is thermodynamically stable, while the stretch at the other local minimum is metastable. At a critical ion concentration ($c_0/C_{\text{fix}} = 0.0052$), the two local minima are equal in the mechanical work, and the two phases may coexist. If the ion concentration is greater ($c_0/C_{\text{fix}} > 0.0052$) or lower, the stable equilibrium stretch corresponds to the collapsed or highly swollen phase, respectively. The discontinuous transition at the critical ion concentration is thus a first-order phase transition. Alternatively, the critical ion concentration for the discontinuous volume phase

transition can also be determined directly from the stress–stretch relations (Fig. 4(a)) by the Maxwell rule [43,44], equivalent to the energetic consideration.

Interestingly, Fig. 4(a) predicts that a discontinuous volume transition may also be induced by mechanical stress (or pressure) for a fixed ion concentration in the external solution. When the ion concentration is greater than the critical concentration (e.g., $c_0/C_{\text{fix}} > 0.0052$), the gel is in the collapse phase at zero stress. Applying a hydrostatic tension increases the gel volume and induces a discontinuous volume transition to the highly swollen phase at a critical stress. The critical stress can be determined from the stress–stretch diagram by the Maxwell rule. On the other hand, when the ion concentration is lower than the critical concentration (e.g., $c_0/C_{\text{fix}} < 0.0052$), the gel is in the highly swollen phase at zero stress. In this case, the gel volume decreases under a hydrostatic compression and undergoes a discontinuous transition to the collapsed phase at a critical pressure. At the critical ion concentration, the critical pressure (or stress) is zero. Such stress-induced discontinuous volume phase transition has not received much attention and may deserve further studies.

The discontinuous volume phase transition depends sensitively on the concentration of fixed charges in the polyelectrolyte gel. As shown in Fig. 5(a), with increasing concentration of fixed charges, the transition line shifts up and the range of χ values with a discontinuous transition expands. Figure 5(b) shows the upper and lower limits of χ versus the concentration of fixed charges, which may be considered as a diagram of phase transitions. For a polyelectrolyte gel with properties (χ and υC_{fix}) between the two lines, a discontinuous volume phase transition is expected at a critical ion concentration. Below the lower (blue) line, a smooth transition is expected. Above the upper (red) line, the gel is in the collapsed phase with no transition. Interestingly, there exists a critical point where the two lines intersect, with $\chi \approx 0.63$ and $\upsilon C_{\text{fix}} \approx 0.012$ for the case $N\upsilon = 10^{-3}$. The location of the critical point depends on $N\upsilon$. Therefore, a necessary condition for the discontinuous volume phase transition in polyelectrolyte gels requires a relatively large fix charge concentration ($\upsilon C_{\text{fix}} > 0.012$) along with a poor solvent ($\chi > 0.63$). In general, it is known that the presence of fixed charges (by ionization) promotes the discontinuous volume phase transition in many gel systems [12,22].

To explain the discontinuous shrinkage of swollen polymer networks, Erman and Flory [45] considered the effect of gel composition on the solvent–polymer interactions by representing χ as a function of the volume fraction of polymer, namely,

$$\chi = \chi_0 + \frac{\chi_1}{J} + \frac{\chi_2}{J^2} + \cdots \qquad (4.2)$$

Similar forms have been used by others [23,46,47], most commonly with the first two terms on the right hand side of Eq. (4.2). As a result, the nominal stress in Eq. (2.22) contains additional terms associated with the composition dependent interaction parameter $\left((\partial \hat{W}/\partial \chi)(d\chi/dJ)(\partial J/\partial \mathbf{F})\right)$. Following the same procedure in Sec. 3, we obtain an equation slightly different from Eq. (3.9) for the nominal stress

$$P = NkT\left(\lambda - \frac{1}{\lambda}\right) + \frac{kT}{\upsilon}\left(\lambda^2 \ln\frac{\lambda^3 - 1}{\lambda^3} + \frac{1}{\lambda} + \frac{\chi - \chi_1}{\lambda^4} + \frac{\chi_1}{\lambda^7}\right)$$
$$+ 2kTc_0\lambda^2\left(1 - \left(1 - \frac{1}{\lambda^3} + \frac{1 - 2\chi}{\lambda^6} + \frac{4\chi - 1}{\lambda^9} - \frac{2\chi}{\lambda^{12}} - \frac{\chi_1(\lambda^3 - 1)^2}{\lambda^{15}}\right)\right.$$
$$\left.\times \exp\left(\frac{1}{\lambda^3} + \frac{\chi}{\lambda^6}\right)\sqrt{1 + \frac{C_{\text{fix}}^2\lambda^6}{4c_0^2(\lambda^3 - 1)^4}\exp\left(-\frac{2}{\lambda^3} - \frac{2\chi}{\lambda^6}\right)}\right) = 0$$
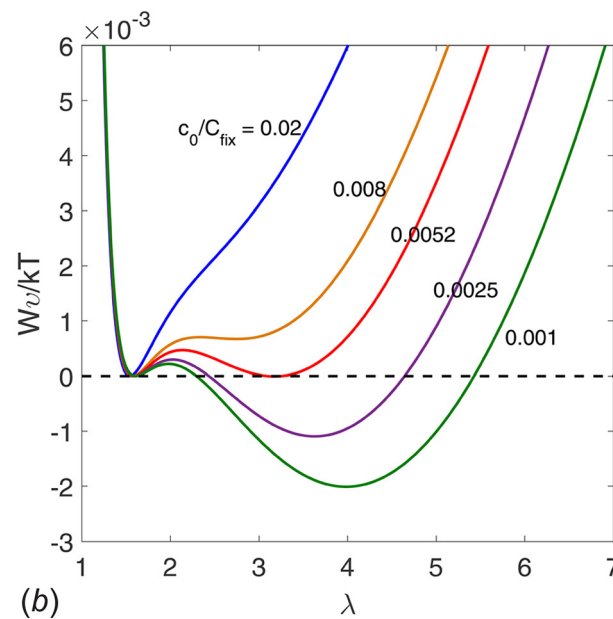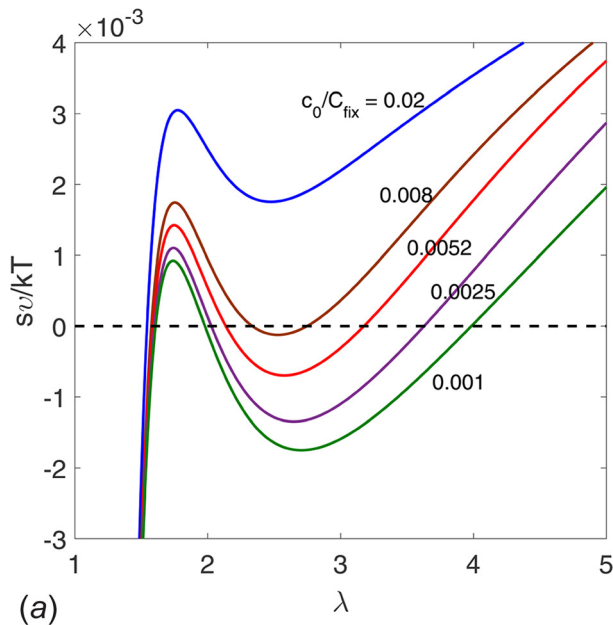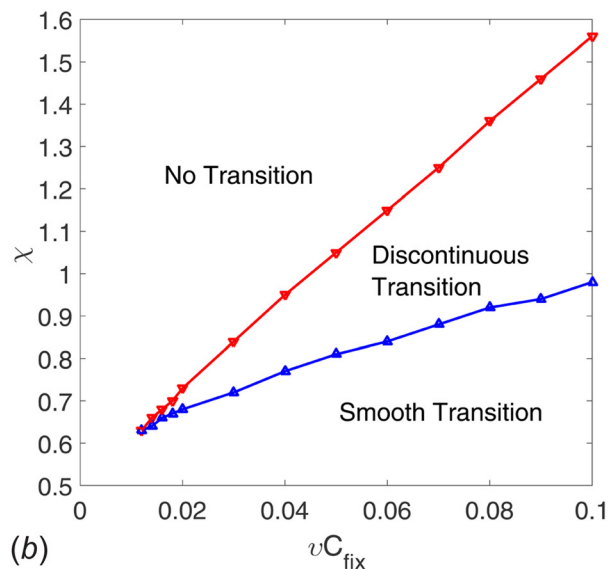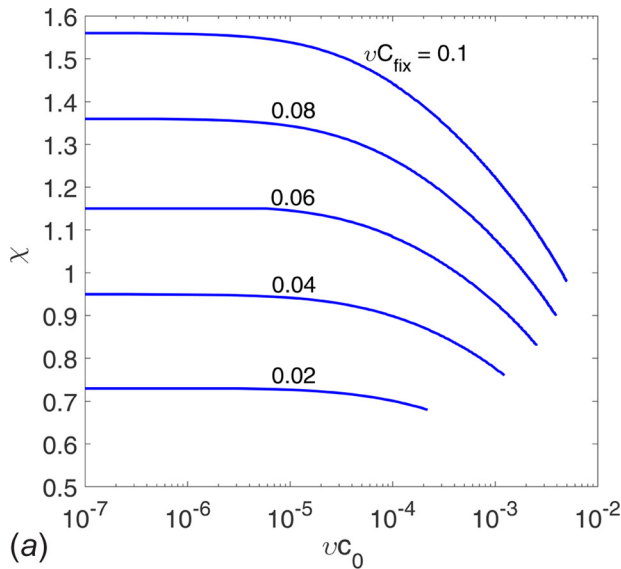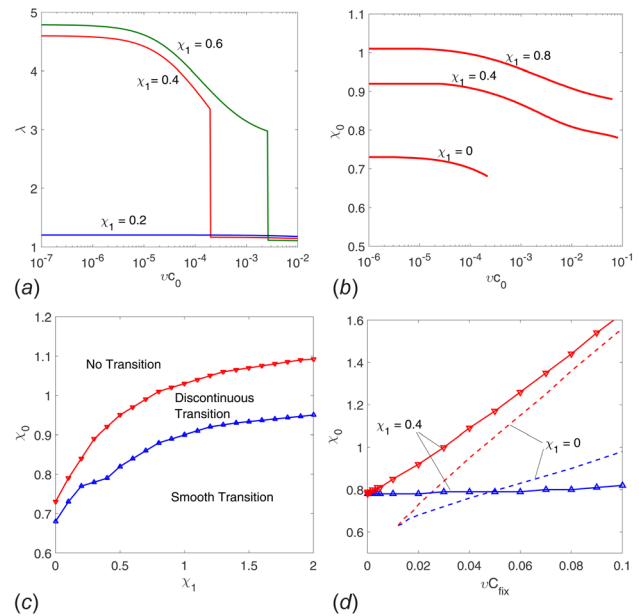
$$(4.3)$$

Fig. 4 (*a*) Normalized stress–stretch relations for a polyelectrolyte gel ($\chi = 0.7$, $N\upsilon = 10^{-3}$, and $\upsilon C_{\text{fix}} = 0.02$) with different ion concentrations, and (*b*) normalized mechanical work

(a)

(b)

Fig. 5 (*a*) Lines of discontinuous transition for different concentrations of fixed charges and (*b*) a diagram of phase transitions for $N\upsilon = 10^{-3}$

Fig. 6 Effects of the composition dependent polymer–solvent interaction. (*a*) Equilibrium stretch for polyelectrolyte gels with $N\upsilon = 10^{-3}$, $\upsilon C_{fix} = 0.02$, and $\chi_0 = 0.9$; (*b*) lines of discontinuous transition ($N\upsilon = 10^{-3}$ and $\upsilon C_{fix} = 0.02$); (*c*) a diagram of phase transitions in terms of the two interaction parameters ($N\upsilon = 10^{-3}$ and $\upsilon C_{fix} = 0.02$); and (*d*) a diagram of phase transitions in terms of υC_{fix} and χ_0 ($N\upsilon = 10^{-3}$ and $\chi_1 = 0.4$), in comparison with the case for composition independent interaction ($\chi_1 = 0$).

The present results suggest that both the degree of ionization (concentration of fixed charges) and the composition-dependent polymer–solvent interaction are important for the discontinuous volume phase transition in polyelectrolyte gels.

5 Comparison With Experiment

In this section, we extend the formulation and analysis in Secs. 2 and 3 to compare with the experiments by Ohmine and Tanaka [32]. In their experiments, acrylamide gels with the ionizable group –COOH were immersed in a mixed solvent of water and acetone with varying salt concentrations of NaCl or MgCl$_2$. The acetone concentration of the mixed solvent plays an important role in the swelling and volume phase transition of the gels [14]. Here, we treat the mixed solvent as one pure solvent with an effective solvent–polymer interaction [41,42] depending on the volume fraction of acetone (φ), namely,

$$\chi = \bar{\chi}_0(\varphi) + \frac{\bar{\chi}_1(\varphi)}{J} \qquad (5.1)$$

where

$$\bar{\chi}_i(\varphi) = \chi_i^a \varphi + \chi_i^w (1 - \varphi) - \chi_i^{aw} \varphi(1 - \varphi) \qquad (5.2)$$

for $i = 0$ and 1. When $\varphi = 0$, the solvent is pure water and the polymer–water interaction is characterized by χ_i^w. When $\varphi = 1$, the solvent is pure acetone and the polymer–acetone interaction is characterized by χ_i^a. In between, a simple rule of mixture is assumed with the parameter χ_i^{aw} as the potential coupling for the mixed solvent. It is assumed that the solvent in the gel has the same volume fraction of acetone as in the external solution. As a result, the gel may undergo a discontinuous volume phase transition upon changing the acetone concentration in the external solution as observed by Tanaka [14], even without adding any salt. As shown in Fig. 5(*a*), for $\upsilon c_0 \to 0$, a discontinuous transition occurs

The effects of the composition dependent interaction parameter on the volume phase transition of polyelectrolyte gels are illustrated in Fig. 6. Most interestingly, the minimum concentration of fixed charges required to have a discontinuous volume phase transition can be reduced to nearly zero with $\chi_1 = 0.4$, as shown in Fig. 6(*d*). As discussed by Erman and Flory [45], the composition dependent polymer–solvent interaction is essential for uncharged polymer networks ($C_{fix} = 0$) to have the possibility of a discontinuous volume phase transition. For ionic gels, the degree of ionization becomes the dominant factor in phase transitions [22]. As shown in Fig. 6(*a*) for polyelectrolyte gels with $N\upsilon = 10^{-3}$, $\upsilon C_{fix} = 0.02$, and $\chi_0 = 0.9$, the equilibrium stretch undergoes a discontinuous transition for $\chi_1 = 0.4$ and 0.6, but no transition for $\chi_1 = 0.2$ or 0. The critical ion concentration for the discontinuous transition depends on both χ_0 and χ_1. As a result, the transition line in Fig. 6(*b*) shifts up as χ_1 increases. A diagram of phase transitions in terms of the two interaction parameters is presented in Fig. 6(*c*) for $N\upsilon = 10^{-3}$ and $\upsilon C_{fix} = 0.02$, where the discontinuous transition is predicted over a range of χ_0 values depending on χ_1.

at a critical value of χ that depends on the concentration of fixed charges in the gel.

Consider an external solution of NaCl with the water–acetone mixed solvent, characterized by the volume fraction of acetone (φ) and the salt concentration (c_0). There exist four types of mobile ions in the gel and the external solution: Na^+, Cl^-, OH^-, and H^+. In addition to the salt ions (Na^+ and Cl^-), dissociation of the ionizable group –COOH in the acrylamide gel leaves fixed charges –COO^- on the polymer network and mobile counter ions (H^+) in the gel, while self-ionization of water yields OH^- and H^+ ions. Strictly, each hydrogen ion (H^+) immediately protonates another water molecule to form a hydronium ion, H_3O^+. Here we do not distinguish H^+ and H_3O^+ under the assumption that its concentration is relatively low compared to the concentration of neutral solvent. With a given salt concentration (c_0), the concentrations of the Na^+ and Cl^- ions in the external solution (far away from the gel) are identically c_0. The concentrations of H^+ and OH^- ions in the external solution are determined by the pH value. Assuming a neutral solution with $pH = 7$, as the case in the experiments by Ohmine and Tanaka [32], the concentrations of H^+ and OH^- are equal and fixed at $c_1 = 10^{-4} N_A$ /m^3 (i.e., $10^{(-7)}$ mol/l), where $N_A = 6.022 \times 10^{23}$ is the Avogadro constant. Taking $v \sim 10^{-28}$ m^3 as a representative volume, we have $vc_1 \sim 6 \times 10^{-9}$, which is a negligibly small portion of the total volume $\left(\sum_a v^a c^a = 1\right)$.

By Eq. (2.35), the chemical potential of the solvent in the external solution is

$$\mu^s = -2kTv(c_0 + c_1) \tag{5.3}$$

By Eq. (2.34), the electrochemical potentials of the Na^+ and Cl^- ions are

$$\mu^{Na^+} = \mu^{Cl^-} = kT\left[\ln(vc_0) - 2v(c_0 + c_1)\right] \tag{5.4}$$

and the electrochemical potentials of the H^+ and OH^- ions are

$$\mu^{H^+} = \mu^{OH^-} = kT\left[\ln(vc_1) - 2v(c_0 + c_1)\right] \tag{5.5}$$

With Eq. (2.19), the nominal concentrations of the mobile ions in the gel are

$$C^{Na^+} = \frac{c_0(J-1)^2}{J}\exp\left\{\frac{1}{J} + \frac{\chi}{J^2} - \frac{e\Phi}{kT}\right\} \tag{5.6}$$

$$C^{Cl^-} = \frac{c_0(J-1)^2}{J}\exp\left\{\frac{1}{J} + \frac{\chi}{J^2} + \frac{e\Phi}{kT}\right\} \tag{5.7}$$

$$C^{H^+} = \frac{c_1(J-1)^2}{J}\exp\left\{\frac{1}{J} + \frac{\chi}{J^2} - \frac{e\Phi}{kT}\right\} \tag{5.8}$$

$$C^{OH^-} = \frac{c_1(J-1)^2}{J}\exp\left\{\frac{1}{J} + \frac{\chi}{J^2} + \frac{e\Phi}{kT}\right\} \tag{5.9}$$

which again satisfy the Donnan equilibrium. The condition of electroneutrality in the gel (far away from the interface) requires that

$$C^{Na^+} + C^{H^+} = C^{Cl^-} + C^{OH^-} + C_{fix} \tag{5.10}$$

Inserting Eqs. (5.6)–(5.9) into Eq. (5.10), we obtain

$$\sinh\left(\frac{e\Phi}{kT}\right) = -\frac{JC_{fix}}{2c_e(J-1)^2}\exp\left(-\frac{1}{J} - \frac{\chi}{J^2}\right) \tag{5.11}$$

which is same as Eq. (3.6) but with $c_e = c_0 + c_1$ as the effective ion concentration in the external solution. Moreover, the interaction parameter χ as given in Eq. (5.1) depends on both the volume

fraction of acetone (φ) in the mixed solvent and the volume fraction of polymer ($1/J$) in the gel. Similarly, the nominal stress is obtained in the same form as Eq. (4.3), which equals zero for free swelling. Therefore, for each external solution with given values of φ (acetone) and c_0 (NaCl), the equilibrium stretch λ can be determined by solving Eq. (4.3).

To compare with the experiment, two dimensionless parameters are needed for the gel, vC_{fix} and Nv, in addition to the interaction parameters (χ_i^w, χ_i^a, and χ_i^{aw}). According to Ohmine and Tanaka [32], the concentration of the –COO^- group was about 0.1 mol/l in the initial state of the gel with $\lambda_0 = 20^{1/3} = 2.7$ (the volume fraction of polymer was 0.05), which can be converted to $vC_{fix} \sim 0.1$ with $v \sim 10^{-28}$ m^3. To determine the other parameters, we first consider the case with pure water as the solvent ($\varphi = 0$), with which we determine Nv and χ_i^w by fitting the theoretical prediction to the experimental data in Ref. [32]. Then, we consider the case with zero salt concentration ($c_0 = 0$) but varying φ, with which we determine χ_i^a and χ_i^{aw}.
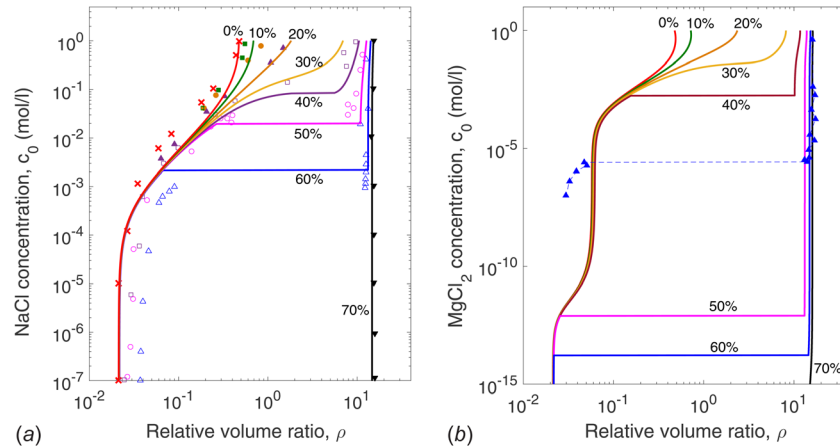
In the experiments by Ohmine and Tanaka [32], when using pure water as the solvent ($\varphi = 0$), the volume of the acrylamide gel varied continuously as the salt concentration changed in the external solution. The equilibrium stretch relative to the dry state ranged from 10 to 3.4, all in the highly swollen state. At extremely low salt concentration ($c_0 \to 0$), the measured volume ratio was $\rho = \lambda_0^3/\lambda^3 \sim 0.022$, corresponding to $\lambda \sim 9.7$. In this case, the osmotic pressure due to the solvent is negligible, and Eq. (4.3) can be approximated by Eq. (3.11), with which we obtain: $Nv = 1.06 \times 10^{-3}$. At this limit ($c_0 \to 0$ and $\lambda \gg 1$), the equilibrium stretch is largely determined by the competition between elasticity of the polymer network and the effect of fixed charges (osmotic pressure of the mobile ions), independent of the interaction parameters. At the other limit, when the salt concentration was high (~ 1 mol/l), corresponding to $vc_0 \sim 0.06$, the volume ratio was $\rho = \lambda_0^3/\lambda^3 \sim 0.5$ and thus $\lambda \sim 3.4$. In this case, Eq. (4.3) can be approximated as

$$P \approx NkT\left(\lambda - \frac{1}{\lambda}\right) + \frac{kT}{v}$$
$$\left[\lambda^2\ln\frac{\lambda^3 - 1}{\lambda^3} + \frac{1}{\lambda} + \frac{\chi_0^w - \chi_1^w}{\lambda^4} + 2vc_0\lambda^2\left(1 - \sqrt{1 + \frac{C_{fix}^2}{4c_0^2\lambda^6}}\right)\right] = 0 \tag{5.12}$$

with which we obtain $\chi_0^w - \chi_1^w \sim 0.1$. For simplicity, we ignore the effect of the gel composition on the solvent–polymer interaction by setting $\chi_1^w = 0$ so that $\chi_0^w \sim 0.1$. With these parameters ($vC_{fix} = 0.1$, $Nv = 1.06 \times 10^{-3}$, $\chi_0^w = 0.1$, and $\chi_1^w = 0$), the theoretical prediction by Eq. (4.3) is in reasonable agreement with the data for the volume swelling ratio ($\rho = \lambda_0^3/\lambda^3$) of the acrylamide gel in a NaCl solution with pure water solvent ($\varphi = 0$) and varying salt concentration from 10^{-7} to 1 mol/l, as shown in Fig. 7(a).

Next consider the case with zero salt concentration ($c_0 = 0$) but varying φ for the water–acetone mixed solvent. In this case, the gel was highly swollen ($\lambda > 7$) when $\varphi < 65\%$ and then underwent a discontinuous transition to the collapsed phase ($\lambda < 2$) for $\varphi > 65\%$ [32]. As shown in Fig. 5, the critical value of χ for the discontinuous transition is ~ 1.55 when $vC_{fix} = 0.1$ and $c_0 = 0$. Assuming $\chi_i^{aw} = 0$ and $\chi_1^a = 0$ in Eq. (5.2), we obtain $\chi_0^a = 2.3$ so that $\chi = 1.55$ for the mixed solvent with $\varphi = 65\%$. As a result, the effective interaction parameter χ varies linearly from 0.1 to 2.3 with the volume fraction of acetone for the mixed solvent. By the phase transition diagram in Fig. 5(b), when $vC_{fix} = 0.1$, a discontinuous volume phase transition is predicted for $0.98 < \chi < 1.55$, corresponding to $0.4 < \varphi < 0.65$, in excellent agreement with the experiment (Fig. 7(a)).

Using the parameters determined above, we calculate the equilibrium stretch by Eq. (4.3) as a function of the NaCl concentration for mixed solvents with various volume fractions of acetone

Fig. 7 (*a*) The relative volume ratio ($\rho = \lambda_0^3/\lambda^3$) versus NaCl concentration for mixed solvents with various volume fractions of acetone, comparing theoretical predictions (lines) with the data (symbols) from the experiments by Ohmine and Tanaka [32]. (*b*) The relative volume ratio versus MgCl$_2$ concentration, with symbols for $\varphi = 60\%$ from the experiments by Ohmine and Tanaka [32]. The same set of parameters are used in the calculations for both (*a*) and (*b*).

and compare directly with the experimental data by Ohmine and Tanaka [32] in terms of the relative volume ratio ($\rho = \lambda_0^3/\lambda^3$ with $\lambda_0 = 2.7$) in Fig. 7(*a*). The overall agreement is remarkable, considering the fact that only a few data points have been used to determine the parameters along with a few assumptions. However, a notable discrepancy between the theoretical and experimental results is for the highly swollen phase at relatively low salt concentrations. As predicted by Eq. (3.11), the theoretical result is independent of volume fraction of acetone at the limit of $c_0 \to 0$ and $\lambda \gg 1$ ($\varphi < 0.65$). In contrast, the experimental data at the same limit shows a slight variation of the relative volume ratio from 0.02 to 0.04 with $0 < \varphi < 0.6$. This may be explained by the change of the fixed charge concentration (υC_{fix}) in the gel. It was noted that the ionizable group (–COOH) is a relatively weak acid and its dissociation in general depends on the dielectric constant of the solvent [37]. The relative dielectric constants of water and acetone at room temperature ($\sim 25\,^\circ$C) are 78 and 21, respectively. For the water–acetone mixed solvent, the effective dielectric constant would depend on the volume fraction of acetone. As a result, dissociation of –COOH would vary with the volume fraction of acetone, yielding different fixed charge concentrations. By Eq. (3.11), decreasing the fixed charge concentration (υC_{fix}) would decrease the equilibrium stretch and increase the relative volume ratio.

Next, consider the polyelectrolyte gel immersed in an external solution of MgCl$_2$. The presence of divalent mobile ions (Mg^{2+}) makes the calculation slightly more complicated. Deep in the external solution, the ion concentrations are different for Mg^{2+} and Cl$^-$, c_0 and $2c_0$, respectively. The concentrations of H$^+$ and OH$^-$ are still the same, $c_1 = 10^{-7}$ mol/l with $pH = 7$. The chemical potential of the solvent is then

$$\mu^s = -kT\upsilon(3c_0 + 2c_1) \tag{5.13}$$

The electrochemical potentials are different for Mg^{2+} and Cl$^-$ ions in the external solution, and they are

$$\mu^{\text{Mg}^{2+}} = kT\left[\ln(\upsilon c_0) - \upsilon(3c_0 + 2c_1)\right] \tag{5.14}$$

$$\mu^{\text{Cl}^-} = kT\left[\ln(2\upsilon c_0) - \upsilon(3c_0 + 2c_1)\right] \tag{5.15}$$

The electrochemical potentials of H$^+$ and OH$^-$ are identical:

$$\mu^{\text{H}^+} = \mu^{\text{OH}^-} = kT\left[\ln(\upsilon c_1) - \upsilon(3c_0 + 2c_1)\right] \tag{5.16}$$

By Eq. (2.19), the nominal concentrations of Mg^{2+} and Cl$^-$ ions in the gel are

$$C^{\text{Mg}^{2+}} = \frac{c_0(J-1)^2}{J}\exp\left\{\frac{1}{J} + \frac{\chi}{J^2} - \frac{2e\Phi}{kT}\right\} \tag{5.17}$$

$$C^{\text{Cl}^-} = \frac{2c_0(J-1)^2}{J}\exp\left\{\frac{1}{J} + \frac{\chi}{J^2} + \frac{e\Phi}{kT}\right\} \tag{5.18}$$

The nominal concentrations of H$^+$ and OH$^-$ ions in the gel remain the same as given in Eqs. (5.8) and (5.9). Again, the Donnan equilibrium is satisfied for all of the ion species. The condition of electroneutrality in the gel (far away from the interface) requires that

$$2C^{\text{Mg}^{2+}} + C^{\text{H}^+} = C^{\text{Cl}^-} + C^{\text{OH}^-} + C_{\text{fix}} \tag{5.19}$$

Inserting Eqs. (5.17), (5.18), (5.8), and (5.9) into Eq. (5.19), we obtain

$$\frac{2c_0}{\gamma^2} + \frac{c_1}{\gamma} - (2c_0 + c_1)\gamma = \frac{JC_{\text{fix}}}{(J-1)^2}\exp\left(-\frac{1}{J} - \frac{\chi}{J^2}\right) \tag{5.20}$$

where $\gamma = \exp(e\Phi/kT)$. Unlike Eq. (5.11) for the case of monovalent ions, Eq. (5.20) does not yield an explicit relationship between the electrical potential in the gel and the volume fraction of polymer ($1/J$), due to the presence of divalent ions (Mg^{2+}). Two limiting cases may be considered. First, when $c_0 \ll c_1 \ll C_{\text{fix}}$, Eq. (5.20) approaches the same form as Eq. (5.11) for $c_0 \to 0$. Second, when $c_0 \sim c_1 \ll C_{\text{fix}}$, Eq. (5.20) is approximately

$$\frac{2c_0}{\gamma^2} = \frac{JC_{\text{fix}}}{(J-1)^2}\exp\left(-\frac{1}{J} - \frac{\chi}{J^2}\right) \tag{5.21}$$

or equivalently

$$\Phi = \frac{kT}{2e}\left[\ln\left(\frac{2c_0(J-1)^2}{JC_{\text{fix}}}\right) + \frac{1}{J} + \frac{\chi}{J^2}\right] \tag{5.22}$$

The nominal stress in the gel is obtained from Eq. (2.22) and is slightly different from Eq. (4.3)

$$P = NkT\left(\lambda - \frac{1}{\lambda}\right) + \frac{kT}{\upsilon}$$

$$\times \left[\lambda^2 \ln\frac{\lambda^3 - 1}{\lambda^3} + \frac{1}{\lambda} + \frac{\chi}{\lambda^4} + \lambda^2(3c_0\upsilon + 2c_1\upsilon) - \frac{\bar{\chi}_1(\lambda^3 - 1)}{\lambda^7}\right]$$

$$-kT\left(\frac{c_0}{\gamma^2} + \frac{c_1}{\gamma} + (2c_0 + c_1)\gamma\right)\left(\lambda^2 - \frac{1}{\lambda} + \frac{1 - 2\chi}{\lambda^4}\right.$$

$$\left. + \frac{4\chi - 1}{\lambda^7} - \frac{2\chi}{\lambda^{10}} - \frac{\bar{\chi}_1(\lambda^3 - 1)^2}{\lambda^{13}}\right)\exp\left(\frac{1}{\lambda^3} + \frac{\chi}{\lambda^6}\right) = 0 \qquad (5.23)$$

Thus, Eqs. (5.20) and (5.23) can be solved simultaneously to obtain γ and λ (or $J = \lambda^3$). Similar to the cases with monovalent ions, multiple solutions may exist when a discontinuous transition occurs. The energetic analysis or the Maxwell rule can then be used to determine the thermodynamically stable solution for the equilibrium state.

Using the same set of parameters as for the acrylamide gels immersed in a NaCl solution with a mixed solvent of water and acetone, we calculate the equilibrium stretch as a function of the MgCl$_2$ concentration for various volume fractions of acetone. To compare with the experimental data by Ohmine and Tanaka [32], the relative volume ratio ($\rho = \lambda_0^3/\lambda^3$ with $\lambda_0 = 2.7$) is shown in Fig. 7(b). In this case, the quantitative agreement is poor as illustrated by the data for $\varphi = 60\%$, where the critical salt concentration for the discontinuous transition differs by several orders of magnitude. Such a discrepancy requires further studies. Nevertheless, the theoretical results are qualitatively consistent with the experiment as the critical salt concentration for the discontinuous transition when $\varphi = 40 - 60\%$ is much lower for the divalent salt (MgCl$_2$) than for the monovalent salt (NaCl). It is also consistent in which no discontinuous transition occurs for $\varphi = 0 - 20\%$. The critical volume fraction of acetone for discontinuous transitions to occur was between 25% and 30% in the experiments, but slightly larger than 30% from the theoretical results. The discrepancy between the theoretical and experimental results for the highly swollen phase at relatively low salt concentrations remains, which may be partly resolved by considering different fixed charge concentrations as discussed for the case of NaCl. Interestingly, the theoretical results for $\varphi \leq 40\%$ show a secondary continuous transition at a very low concentration of MgCl$_2$ ($c_0 \sim 10^{-10}$ mol/l), which did not exist for the case of NaCl. This may be explained theoretically by the two limiting cases for Eq.

(5.20). When $c_0 \ll c_1 \ll C_{\text{fix}}$ and $c_0 \to 0$, Eq. (5.20) approaches the same limit as Eq. (5.11) for the monovalent salt, and as a result, Eq. (5.23) approaches Eq. (3.11) for the highly swollen state with the same equilibrium stretch ($\lambda \sim 9.7$), independent of the salt. However, another limit exists for the case of MgCl$_2$ when $c_0 \sim c_1 \ll C_{\text{fix}}$ and Eq. (5.21) can be used to simplify Eq. (5.23) to obtain

$$P \approx \frac{kT}{\upsilon}\left(\lambda N\upsilon - \frac{\upsilon C_{\text{fix}}}{2\lambda}\right) = 0 \qquad (5.24)$$

which is slightly different from Eq. (3.11). With $N\upsilon = 1.06 \times 10^{-3}$ and $\upsilon C_{\text{fix}} = 0.1$, we obtain $\lambda = 6.9$ and thus $\rho = 0.06$, in close agreement with the numerical results in Fig. 7(b) for $c_0 \sim 10^{-7}$ mol/l and $\varphi \leq 40\%$. Evidently, it is the presence of divalent ions (Mg^{2+}) in addition to monovalent ions in the polyelectrolyte gel and the external solution that leads to the two highly swollen states and the continuous transition. This limit was also noted by Ohmine and Tanaka [32] with an osmotic pressure due to ions similar to that in Eq. (5.24).

To summarize, the comparisons with the experiments in Fig. 7 show quantitative agreement for the monovalent salt (NaCl) and qualitative consistency for the divalent salt (MgCl$_2$), using a simple set of parameters for both cases. It is possible to further improve the quantitative agreement by changing the parameters for different acetone concentrations and different salts. For example, for NaCl in pure water ($\varphi = 0\%$) as the solvent, an excellent agreement can be achieved (Fig. 8(a)) by increasing the concentration of fixed charge to $\upsilon C_{\text{fix}} = 0.3$ and changing the other parameters accordingly: $N\upsilon = 3.18 \times 10^{-3}$, $\chi_0^w = 0.1$, and $\chi_1^w = 0.6$. Similarly, an excellent agreement can be achieved (Fig. 8(b)) for NaCl in a mixed solvent ($\varphi = 60\%$) by slightly increasing $N\upsilon$ so that the equilibrium stretch at $c_0 \sim 10^{-7}$ mol/l is 8.3 instead of 9.7 by Eq. (3.11). As another example, for the case of MgCl$_2$ in a mixed solvent with $\varphi = 60\%$, the critical salt concentration for the discontinuous volume transition can be brought to the same level as the experiment (Fig. 8(b)) by changing the polymer–solvent interaction parameters to $\chi_0^w = 0.43$ and $\chi_0^a = 1.55$. As suggested by Safronov et al. [48], the interaction parameter may depend on the type of the counterions. Meanwhile, to fit the equilibrium stretch ($\lambda \sim 8.7$) at $c_0 \sim 10^{-7}$ mol/l, we obtain $N\upsilon = 0.66 \times 10^{-3}$ for $\upsilon C_{\text{fix}} = 0.1$ by using Eq. (5.24) for the divalent salt instead of Eq. (3.11). The quantitative agreements in Fig. 8 demonstrate the capability of the present model for accurately describing both the continuous and
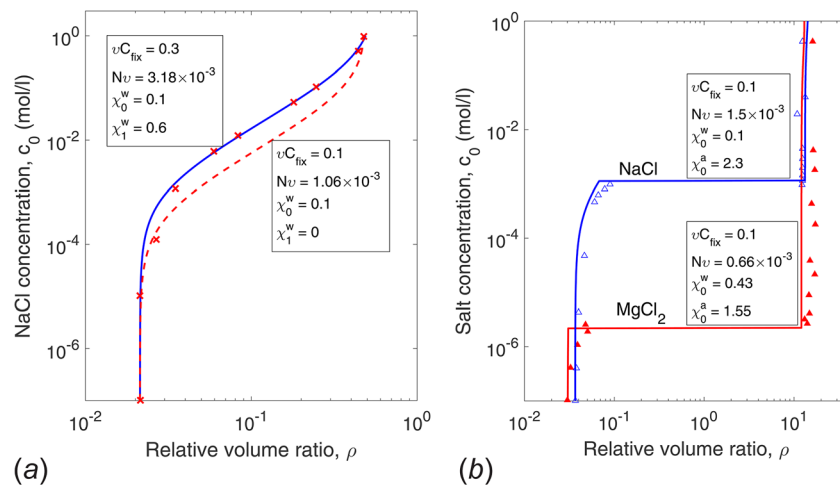

Fig. 8 (a) Improved agreement for continuous volume transition of acrylamide gels in a pure water solvent ($\varphi = 0\%$) with varying NaCl concentrations. (b) Improved agreement for the discontinuous volume transitions of acrylamide gels in a mixed solvent ($\varphi = 60\%$) with either NaCl or MgCl$_2$. Experimental data (symbols) are taken from Ohmine and Tanaka [32].

discontinuous volume phase transitions of polyelectrolyte gels in response to changing salt concentration in the external solution.

6 Summary

In this paper, we present a theoretical model of polyelectrolyte gels to study continuous and discontinuous volume phase transitions induced by changing salt concentration in the external solution. Phase diagrams are constructed in terms of the polymer–solvent interaction parameters, external salt concentration, and concentration of fixed charges. Direct comparisons with previous experiments for an ionized acrylamide gel in mixed water–acetone solvents show good quantitative agreement for a monovalent salt (NaCl) but fair qualitative agreement for a divalent salt (MgCl$_2$), using a simple set of parameters for both cases. The quantitative agreement may be further improved for both cases by calibrating the model parameters for a specific combination of salt and solvent composition. The theory in its present form naturally leads to a balance of osmotic pressures due to elasticity, solvent, and ions in an isotropic, homogeneous state, which can be readily extended to study anisotropic swelling (e.g., under constraint) and inhomogeneous phenomena (e.g., coexisting phases). Under the condition of electroneutrality, the ion concentrations in the gel satisfy the Donnan equilibrium with a Donnan potential that depends on the volume swelling ratio (or the volume fraction of polymer). The present model may be further extended to study volume phase transitions of polyelectrolyte gels in response to other stimuli such as temperature, pH, electrical fields, and pressure (or stress in general).

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