Large deformation and electrochemistry of polyelectrolyte gels

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Abstract

Immersed in an ionic solution, a network of polyelectrolyte polymers imbibes the solution and swells, resulting in a polyelectrolyte gel. The swelling is reversible, and is regulated by ionic concentrations, mechanical forces, and electric potentials. This paper develops a field theory to couple large deformation and electrochemistry. A specific material model is described, including the effects of stretching the network, mixing the polymers with the solvent and ions, and polarizing the gel. We show that the notion of osmotic pressure in a gel has no experimental significance in general, but acquires a physical interpretation within the specific material model. The theory is used to analyze several phenomena: a gel swells freely in an ionic solution, a gel swells under a constraint, electric double layer at the interface between the gel and the external solution, and swelling of a gel of a small size.

Keywords: polyelectrolyte, gel, ions, electrolyte, large deformation.

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1. Introduction

Many natural and synthetic macromolecules are polyelectrolytes, long-chained polymers that contain ionizable groups (Fig. 1). When such a polymer is in a solution, the ionizable groups dissociate into *fixed charges* bonded to the polymer and ions mobile in the solution. The solution consists of solvent molecules of a low molecular weight (e.g., water molecules), as well as ions of two types: *counterions* that bear charges of the sign opposite to the fixed charges, and *co-ions* that bear charges of the same sign as the fixed charges.

A large number of flexible polyelectrolytes can form a three-dimensional network by a low density of covalent crosslinks. When immersed in the solution, the network imbibes the solution and swells, resulting in a polyelectrolyte gel. The volume of the gel is typically many times the volume of the dry network. The swelling is reversible, and the amount of the swelling can be regulated by ionic concentrations, mechanical forces, and electric potentials.

Most tissues of plants and animals contain polyelectrolytes (Melody and Mark, 2007). For example, pectin, which has long been used to make jellies and jams, is a polyelectrolyte gel in cell walls of plants. The flow of water in plants is regulated by reversible swelling and shrinking of pectin in response to changes in ionic concentration (Zwieniecki et al., 2001). As another example, articular cartilage consists of collagen fibers and synovial fluid, where ions are essential to maintain low friction in joints (Gong and Osada, 2002). Perhaps the best known synthetic polyelectrolyte gels are those used as ion exchangers (Helfferich, 1962). Recent applications of polyelectrolyte gels include drug delivery (Duncan, 2003), tissue engineering (Lee and Mooney, 2001), and soft actuators (Beebe et al., 2000; Dong et al., 2006; Sidorenko, et al., 2007; Hong et al., 2008a). A large number of biomedical applications of soft active materials are reviewed in the text edited by Carpi and Smela (2009). In many of these applications, gels serve as transducers that convert between changes in mechanical variables (i.e., forces and displacements) and in physiological variables (e.g., slat concentrations, pH, and temperature).

The object of this paper is to develop a field theory of polyelectrolyte gels to couple large deformation and electrochemistry. Recent applications of polyelectrolyte gels have called into attention two aspects of behavior. First, because a gel swells by imbibing solvent molecules, the time to equilibrate is short when the gel has a small size (Ballauff and Lu, 2007; Hirose et al., 1987; Nayak and Lyon 2005; Pelton, 2000; Saunders and Vincent, 1999). When the size of the gel is comparable to the Debye length (Hoogeveen et al., 1996; Zhou and Chu, 1998), assumption of electroneutrality should be re-examined. Second, in applications a gel is often integrated with hard materials, leading to a hybrid structure of soft and hard materials. The hard materials constrain the swelling of the gels, often leading to inhomogeneous deformation even when the gel has reached equilibrium (Zhao et al., 2008; Hong et al., 2009). Constrained swelling also induces in the gel a field of stress, which may damage the gel.

A field theory describes the swelling process in terms of thermodynamics and kinetics. The thermodynamics of swelling dates back to Gibbs (1878), who characterized the state of an element of a swollen solid using the gradient of displacement and the concentration of fluid, deduced the conditions of equilibrium in terms of the nominal stress and the chemical potential, and represented the behavior of materials using a free-energy function. Gibbs, however, did not give any explicit form of the free-energy function. Flory and Rehner (1943) provided a free-energy function for polymeric gels by combining the entropy of stretching the polymer network and the entropy of mixing the polymers with the solvent. Once a free-energy function is specified, the Gibbs theory leads to a boundary-value problem that governs the fields of the deformation of the network and the concentration of the solvent in a gel in equilibrium with external forces and solvent. A growing number of such boundary-value problems have been solved, as reviewed by Hong et al. (2009).

The kinetics of swelling also has a long history. Biot (1941) used Darcy's law to model the migration of a fluid in a porous elastic solid. The resulting theory, known as poroelasticity, has been used to analyze phenomena ranging from compaction of soils to deformation of tissues.

Larche and Cahn (1985) formulated an analogous theory for diffusion of atoms in an elastic crystal. The literature has been updated by, among others, Rice and Cleary (1976), Scherer (1989), Sekimoto (1991), Durning and Morman (1993), Govindjee and Simo (1993), Dolbow et al. (2005), Hui and Muralidharan (2005), Hong et al. (2008b).

Field theories have been formulated specifically for polyelectrolyte gels. Lai et al. (1991) proposed a triphasic theory, where the network, the solvent and the ions are treated as distinct phases with individual velocity fields; for recent developments along this line, see Ateshian et al (2004), Li et al. (2007), and Bufalo et al. (2008). Alternatively, following Gibbs and Biot, one can regard a gel as a single phase, characterized by fields of deformation gradient and composition; for developments along this line see Nemat-Nasser and Li (2000), Xiao and Bhattacharya (2001), De et al. (2002), Baek and Srinivasa (2004), and Swaminathan et al. (2007).

While qualitative principles of the swelling of polyelectrolyte gels have long been understood (e.g., Helfferich, 1962), quantitative representations of these principles have been evolving, as manifested in works cited above. Given that many forms of the theory exist in the literature, with varying notations, assumptions, and degrees of generality, we and many other authors have found it necessary to examine the theory with care, before analyzing specific phenomena. In particular, following a tradition in continuum mechanics, we find it desirable to organize the theory into parts specified by general principles, and parts specified by special models. Such a modularized theory will aid the progress in linking diverse macroscopic phenomena to microscopic processes of the network, solvent and ions.

Along a related line of research, recently we and others have re-formulated the field theory of elastic dielectrics (Dorfmann and Ogden, 2005; McMeeking and Landis, 2005; Suo et al., 2008). A feature of the new formulation is that the effect of electric field on deformation is no longer introduced as the Maxwell stress, but as a part of a material model. This approach allows the theory to readily include more complex electromechanical interactions (Zhao et al.,

2007; Zhao and Suo 2008).

This paper develops a theory of polyelectrolyte gels by combining our previous works on elastic dielectrics (Suo et al., 2008) and on neutral gels (Hong et al., 2008b). Following Gibbs and Biot, we represent a polyelectrolyte gel as a single phase. To account for the coupling between the deformation of the network and the migration of the ions and the solvent, we invoke the procedure of nonequilibrium thermodynamics. This procedure makes it evident that parts of the theory are specified by general considerations such as the laws of thermodynamics and conservation (Sections 2-4), and parts of the theory are specified by special considerations such as models of solution, network and polarization (Sections 5,6). In particular, following Flory and Rehner (1943), we assume that the degree of crosslinks is low, such that the free energy of a gel may be approximated by a superposition of that of the network and that of the solution. From this material model the osmotic pressure and Maxwell stress emerge naturally.

Sections 7-11 apply the theory to analyze several phenomena (Fig. 2). When a gel swells freely in a solution, the amount of swelling is affected by diverse factors, including the density of crosslinks, the concentration of the fixed charges, and the ionic strength of the external solution. When constrained by hard materials, a swelling gel pushes against the constraint. How various factors affect the blocking force is of central significance to the design of transducers. Near an interface between the gel and the external solution, electroneutrality is no longer maintained. For example, when a gel with negative fixed charges is immersed in a dilute ionic solution, the counterions released from the polymers will spill into the external solution. Consequently, near the interface the gel is negatively charged, while the external solution is positively charged. The positive and the negative charges on the two sides of the interface form an electrical double layer. The electroneutrality is recovered inside the gel and the external solution at a distance known as the Debye length. When the size of a gel is comparable to, or smaller than, the Debye length, the behavior of the gel may deviate from that of the gel of a large size. We explore the size effects by analyzing a thin layer of a gel immersed in a solution.

2. Three ways of doing work to a polyelectrolyte gel

Sections 2-4 refine a note posted online (Suo, 2007) and describe parts of the theory specified by general principles. The gel moves in a three-dimensional space, in which places are identified by a set of coordinates. We will use the undeformed dry network as a reference state (Fig. 3). An element of the network occupies a place with coordinate $\mathbf{X}$ when the network is in the reference state, and moves to a place with coordinate $\mathbf{x}$ when the network is in the current state at time t. The function

$$\mathbf{x} = \mathbf{x}(\mathbf{X}, t) \tag{2.1}$$

describes the history of the deformation of the network.

Both the gel and the external solution are included in the domain under consideration. In the reference state, let $dV(\mathbf{X})$ be an element of volume, $dA(\mathbf{X})$ be an element of an interface, and $N_K(\mathbf{X})$ be the unit vector normal to the element of the interface between media labeled as – and +, pointing toward medium +.

Also illustrated in Fig. 3 are three ways in which external agents do work. We will use the word "weight" as shorthand for any external agent that applies a mechanical force to the network. Imagine that every element of the network is attached with a weight. The field of weights applies a field of forces to the gel. In the current state, let the forces due to the weights be $\mathbf{B}(\mathbf{X}, t) dV(\mathbf{X})$ on an element of volume, and be $\mathbf{T}(\mathbf{X}, t) dA(\mathbf{X})$ on an element of interface. When the network deforms by δx_i, the field of weights do work

$$\int B_i \delta x_i dV + \int T_i \delta x_i dA. \tag{2.2}$$

The gel is taken to be an ionic conductor, but an electronic insulator. Imagine that every element of the network is attached with an electrode, and that electrodes of neighboring elements are electrically insulated from one another. We will use the word "battery" as shorthand for any external agent that brings electrons to an electrode from the ground through

an electronic conductor outside the gel. The battery maintains the electric potential Φ of the electrode relative to the ground. The field of batteries prescribes a time-dependent field of the electric potential:

$$\Phi = \Phi(\mathbf{X}, t). \tag{2.3}$$

The field of electrodes bears electronic charges. In the current state at time t, let the electronic charges be $q(\mathbf{X}, t)dV(\mathbf{X})$ on an element of volume, and $\omega(\mathbf{X}, t)dA(\mathbf{X})$ on an element of interface. When small amounts of electrons, $\delta q dV$ and $\delta \omega dA$, are brought to the field of electrodes, the field of batteries do work

$$\int \Phi \delta q dV + \int \Phi \delta \omega dA. \tag{2.4}$$

In practice, many parts of the gel are not attached with electrodes and batteries, and are kept in the open-circuit condition. These parts of the gel have no excess electrons, because we have assumed that the gel itself is an electronic insulator. In formulating the theory, however, it is equivalent to imagine that every element of the network is attached with an electrode and a battery, and ask what the electric potential of the battery needs to be to keep the electrode charge-free.

We will use the word "pump" as shorthand for any external agent that injects mobile particles (i.e., solvent molecules or ions) into the gel. Imagine that every element of the network is attached with a pump, and let μ^a be the electrochemical potential of species a in the pump. The field of pumps prescribes a time-dependent field of the electrochemical potential of every mobile species:

$$\mu^a = \mu^a(\mathbf{X}, t). \tag{2.5}$$

Let t_0 be a fixed time. In the time period from t_0 to the current time t, the pumps inject a total of $r^a(\mathbf{X}, t)dV(\mathbf{X})$ number of particles of species a into an element of volume, and a total of $i^a(\mathbf{X}, t)dA(\mathbf{X})$ number of particles of species a into an element of interface. When small

amounts of mobile species, $\delta r^a dV$ and $\delta i^a dA$, are injected into the gel, the field of pumps do work

$$\sum \int \mu^a \delta r^a dV + \sum \int \mu^a \delta i^a dA.\qquad(2.6)$$

Unless otherwise stated, the sign of summation in this paper implies a sum taken over all mobile species, including both the solvent and ions.

In practice, many parts of the gel are not attached with pumps. In these parts of the gel, mobile species of ions and molecules are not injected from pumps, but migrate to and from neighboring parts of the gel. In formulating the theory, however, it is equivalent to imagine that every element of the network is attached with a pump, and ask what the electrochemical potential of every species in the pump needs to be for not injecting any particles.

3. Free-energy density as a function of field variables

We will focus on isothermal processes, and drop the temperature from the list of variables to be considered. Let WdV be the Helmholtz free energy of an element of volume when the gel is in the current state. We will neglect the free energy of the interface. The Helmholtz free energy of the gel is an integral of the free-energy density over the volume of the gel, namely, $\int WdV$. Following a common practice in formulating field theories, we take this representation to mean that the gel consists of many small volumes, the free energy of the gel is the sum of the free energy of the small volumes, and the field in each small volume is homogeneous in terms of a set of field variables. The choice of the field variables, as well as the functional form of the free-energy density, constitutes a material model. Commonly used field variables are recalled below.

In the current state at time t, the element of the network $\mathbf{X}$ occupies the place $\mathbf{x}$. The deformation gradient is defined as

$$F_{iK}(\mathbf{X}, t) = \frac{\partial x_i(\mathbf{X}, t)}{\partial X_K}. \tag{3.1}$$

The deformation gradient is used as a variable in the free-energy function to model the contractility of the network. The free energy is invariant if the gel rotates as a rigid body. Following a well known result of continuum mechanics, we require that W depend on $\mathbf{F}$ only through the product $F_{iK}F_{iL}$, known as the Green deformation tensor.

The number of particles in each mobile species may not be conserved in practice. For example, at the interface between an electrode and a solution, ions may gain or lose electrons to become a neutral particle. As another example, an acidic group on a polymer chain may dissociate into a fixed charge and a proton, and the fraction of the acidic group dissociated depends on the pH of the solution. While these effects are significant and can be included in the theory, to limit the scope of discussion, we assume in this paper that no chemical reaction occurs, so that the number of particles in each species is conserved. In the current state at time t, let $C^a(\mathbf{X}, t)dV$ be the number of particles of species a in an element of volume. From a fixed time t_0 to the current time t, a total number $I_K^a(\mathbf{X}, t)N_K dA$ of particles of species a crosses an element of area. The conservation of the number of particles in species a requires that

$$C^a(\mathbf{X}, t) - C^a(\mathbf{X}, t_0) + \frac{\partial I_K^a(\mathbf{X}, t)}{\partial X_K} = r^a(\mathbf{X}, t) \tag{3.2}$$

in the volume, and that

$$N_K \left[I_K^a(\mathbf{X}, t) \right]^+ - N_K \left[I_K^a(\mathbf{X}, t) \right]^- = i^a. \tag{3.3}$$

on an interface. Equations (3.2) and (3.3) hold for every mobile species in the gel. The superscript - signifies the value of a quantity in medium - and near the interface, and the superscript + signifies the value of a quantity in medium + and near the interface.

Let $Q(\mathbf{X}, t)dV(\mathbf{X})$ be the total electric charge on an element of volume. The total electric charge is contributed from electrons, ions, and fixed charges. Thus,

$$Q = q + \sum e z^a C^a + z_0 C_0 , \tag{3.4}$$

where z_0 is the valence of the fixed charge, C_0 is the concentration of the fixed charges, e is the elementary charge, and z^a is the valence of species a, with the valence being zero for a neutral mobile species. Equation (3.3) has stipulated that the ions injected into the interface are totally diffused out into the two phases. Thus, the interfacial charge has its contribution only from the electrons, and $\omega(\mathbf{X}, t) dA(\mathbf{X})$ is the total electric charge on an element of interface.

Gauss's law can be expressed in terms of the nominal fields (e.g., Dorfmann and Ogden, 2005; Suo et al., 2008). The nominal electric displacement $\tilde{D}_K(\mathbf{X}, t)$ satisfies the following equations:

$$\frac{\partial \tilde{D}_K(\mathbf{X}, t)}{\partial X_K} = Q(\mathbf{X}, t) \tag{3.5}$$

in the volume, and

$$N_K \tilde{D}_K^+(\mathbf{X}, t) - N_K \tilde{D}_K^-(\mathbf{X}, t) = \omega(\mathbf{X}, t) \tag{3.6}$$

on an interface.

As a part of the specification of a material model, the free-energy density, W, is assumed to be a function of the deformation gradient, the nominal electric displacement, and the composition, namely,

$$W = W\left(\mathbf{F}, \tilde{\mathbf{D}}, C^1, C^2, \cdots\right). \tag{3.7}$$

Associated with small changes in the independent variables, the free-energy density changes by

$$\delta W = \frac{\partial W}{\partial F_{iK}} \delta F_{iK} + \frac{\partial W}{\partial \tilde{D}_K} \delta \tilde{D}_K + \sum \frac{\partial W}{\partial C^a} \delta C^a . \tag{3.8}$$

The significance of the partial derivatives is interpreted in the next section.

4. Equilibrating a gel with weights, batteries and pumps

The gel, weights, batteries and pumps together constitute a thermodynamic system. The

system is held at a fixed temperature by being in thermal equilibrium with a reservoir of energy. The system exchanges energy with the rest of the world, but nothing else. The Helmholtz free energy of the system is the sum over the parts: the change in the free energy of the gel is $\int \delta W dV$, and the change in the free energy of the weights, or batteries, or pumps is the negative amounts of the work listed in Section 2. While the system is in thermal equilibrium with the reservoir of energy, the system may still be not in mechanical, electrostatic or electrochemical equilibrium. Thermodynamics dictates that the Helmholtz free energy of the system should never increase:

$$
\begin{aligned}
&\int \delta W dV - \int B_i \delta x_i dV - \int T_i \delta x_i dA \\
&- \int \Phi \delta q dV - \int \Phi \delta \omega dA \\
&- \sum \int \mu^a \delta r^a dV - \sum \int \mu^a \delta i^a dA \leq 0
\end{aligned}
\tag{4.1}
$$

For this statement to be meaningful, $\delta(\ )$ stands for the value of a quantity in the current state minus the value of the quantity in a state a short time before. The inequality holds when the system is not in equilibrium, and the equality holds when the system is in equilibrium.

Using (3.1)-(3.9) and applying the divergence theorem, we rewrite (4.1) as

$$
\begin{aligned}
&- \int \left(\frac{\partial}{\partial X_K} \left(\frac{\partial W}{\partial F_{iK}} \right) + B_i \right) \delta x_i dV - \int \left(N_K \left(\frac{\partial W}{\partial F_{iK}} \right)^+ - N_K \left(\frac{\partial W}{\partial F_{iK}} \right)^- + T_i \right) \delta x_i dA \\
&+ \int \left(\frac{\partial W}{\partial \tilde{D}_K} + \frac{\partial \Phi}{\partial X_K} \right) \delta \tilde{D}_K dV \\
&+ \sum \int \left(\frac{\partial W}{\partial C^a} + ez^a \Phi - \mu^a \right) \delta r^a dV + \sum \int \left(\frac{\partial W}{\partial C^a} + ez^a \Phi - \mu^a \right) \delta i^a dA \\
&+ \sum \int \frac{\partial}{\partial X_K} \left(\frac{\partial W}{\partial C^a} + ez^a \Phi \right) \delta I_K^a dV \leq 0
\end{aligned}
\tag{4.2}
$$

Each line of (4.2) accounts for the contribution to the change in the Helmholtz free energy of the system made by a distinct process: the first line is due to the deformation of the network, the second due to the redistribution of electric charges, the third due to the injection of mobile species to the gel, the fourth due to the migration of mobile species within the gel.

The rate of swelling is usually limited by the migration of mobile species, so that the first three lines in (4.2) are assumed to vanish, giving rise to three equalities, while the fourth line remains negative. The three equalities are conditions of partial thermodynamic equilibrium with respect to three distinct processes: mechanical equilibrium with respect to the deformation of the network, electrostatic equilibrium with respect to the distribution of charges, and electrochemical equilibrium with respect to the injection of mobile species. We next discuss these conditions of partial equilibrium one by one.

Define the nominal stress by

$$s_{iK} = \frac{\partial W(\mathbf{F}, \widetilde{\mathbf{D}}, C^1, C^2, ...)}{\partial F_{iK}}.$$ (4.3)

To ensure that the first line in (4.2) vanishes for arbitrary field of displacement, $\delta\mathbf{x}$, we obtain that

$$\frac{\partial s_{iK}(\mathbf{X}, t)}{\partial X_K} + B_i(\mathbf{X}, t) = 0$$ (4.4)

in the volume, and

$$N_K s_{iK}^-(\mathbf{X}, t) - N_K s_{iK}^+(\mathbf{X}, t) = T_i(\mathbf{X}, t)$$ (4.5)

on interfaces. In continuum mechanics, (4.4) and (4.5) are usually derived by balancing forces acting on a small volume or a small area. As reviewed by Suo et al. (2008), such a derivation has been open to the criticism as to why only forces due to weights need be balanced by stresses, and not the forces due to electrostatic interaction. The derivation presented here makes it evident that (4.4) and (4.5) are the conditions of mechanical equilibrium, i.e., partial thermodynamic equilibrium associated with the field of displacement.

Define the nominal electric field by

$$\widetilde{E}_K = \frac{\partial W(\mathbf{F}, \widetilde{\mathbf{D}}, C^1, C^2, ...)}{\partial \widetilde{D}_K}.$$ (4.6)

To ensure that the second line in (4.2) vanishes for arbitrary variation in the field of electric

displacement, we obtain that

$$\widetilde{E}_K(\mathbf{X},t) = -\frac{\partial \Phi(\mathbf{X},t)}{\partial X_K}. \tag{4.7}$$

The negative sign conforms to the convention that the electric field points from an element with a high electric potential to an element of a low electric potential. Eq. (4.6) and (4.7) constitute the conditions of electrostatic equilibrium.

To ensure that the third line in (4.2) vanishes for arbitrary small injection of mobile species, we obtain that

$$\mu^a = e z^a \Phi + \frac{\partial W(\mathbf{F}, \widetilde{\mathbf{D}}, C^1, C^2, ...)}{\partial C^a}. \tag{4.8}$$

This set of equations constitutes the conditions of equilibrium for each mobile species in the pump and in the gel. Eq. (4.8) recovers a similar one derived by Gibbs (1878).

Once the above conditions of partial equilibrium are satisfied, only the last line in (4.2) remains and the inequality reduces to

$$\sum \frac{\partial \mu^a}{\partial X_K} \delta I_K^a < 0 \tag{4.9}$$

for arbitrary non-vanishing fluxes of mobile species in the gel. A common way to enforce this inequality is to assume that the flux $J_K^a(\mathbf{X},t) = \partial I_K^a(\mathbf{X},t)/\partial t$ is linear in the gradients of the electrochemical potential, with a negative-definite matrix of the linear transformation.

In the remainder of this paper, we will only consider states of equilibrium, in which the electrochemical potential of each mobile species is uniform throughout the gel and the external solution, namely,

$$\mu^a = \text{constant}. \tag{4.10}$$

This equation is the condition of electrochemical equilibrium.

5. Incompressibility of individual constituents

As the final step to construct a material model, Sections 5 and 6 consider a free-energy function of a specific form. The thermodynamics of polyelectrolyte gels have been studied by, among others, Flory (1953), Katchalsky (1971), Skouri et al. (1995), Rubinstein et al. (1996), and English et al. (1996). Here we do not intend to construct a free-energy function to describe a real gel accurately. Rather, we will construct a free-energy function of an idealized gel to analyze basic phenomena of polyelectrolyte gels, such as those illustrated in Fig. 2.

Because typically the stress in a gel is small and the swelling ratio is large, we assume that individual polymers and mobile particles are incompressible. The ionizable groups on the polymers are taken to be fully dissociated. In the reference state the volume is taken by the dissociated polymers. Imagine a unit volume of the dry network imbibes C^1, C^2, ... numbers of particles and swells to a gel of volume $\det \mathbf{F}$. The mobile particles have the total volume $\sum v^a C^a$, where v^a is the volume per particle of species a, and is taken to be a constant. Because all the constituents are assumed to be incompressible, the sum of the volume of the dry polymers and that of the mobile species equals the volume of the gel:

$$1 + \sum v^a C^a = \det \mathbf{F} . \tag{5.1}$$

Consequently, the incompressibility of the constituents places a constraint between the concentrations of mobile species and the deformation of the network.

The consequence of the constraint (5.1) is studied next. In deriving (4.3) and (4.8), we have assumed that the concentrations of the mobile species and the deformation of the network are independent variables. To modify (4.3) and (4.8), following Hong et al. (2008b), we enforce the constraint by replacing the free-energy density W with

$$W + \Pi \left(1 + \sum v^a C^a - \det \mathbf{F} \right). \tag{5.2}$$

Here $\Pi(\mathbf{X}, t)$ is a field of Lagrange multiplier. Replacing W in (4.2) with (5.2), we find that (4.3) becomes

$$s_{iK} = \frac{\partial W\left(\mathbf{F}, \widetilde{\mathbf{D}}, C^1, C^2, \ldots\right)}{\partial F_{iK}} - \Pi H_{iK} \det \mathbf{F} \, , \tag{5.3}$$

and that (4.8) becomes

$$\mu^a = ez^a \Phi + \frac{\partial W\left(\mathbf{F}, \widetilde{\mathbf{D}}, C^1, C^2, \ldots\right)}{\partial C^a} + \Pi v^a \, . \tag{5.4}$$

In taking partial derivatives in (5.3) and (5.4), we have regarded the concentrations and the deformation gradient as independent variables, and used a mathematical identity

$$\frac{\partial \det \mathbf{F}}{\partial F_{iK}} = H_{iK} \det \mathbf{F} \, , \tag{5.5}$$

where $F_{iK} H_{jK} = \delta_{ij}$ and $F_{iK} H_{iL} = \delta_{KL}$.

The Lagrange multiplier Π may be interpreted as osmotic pressure. For example, (5.4) may be interpreted as follows. When a gel equilibrates with an external solution, the two phases must equalize the electrochemical potential of each mobile species, (4.10). Typically, the two phases have different values of the electric potential Φ, as well as different values of $\partial W / \partial C^a$. Such differences must be compensated for by different values of the osmotic pressure Π in the two phases.

The above interpretation is also consistent with (5.3). It is well known in continuum mechanics that the nominal stress s_{iK} relates to the true stress σ_{ij} as

$$\sigma_{ij} = \frac{s_{iK} F_{jK}}{\det \mathbf{F}} \, . \tag{5.6}$$

Combining (5.3) and (5.6), we obtain an expression for the true stress

$$\sigma_{ij} = \left(\frac{\partial W}{\partial F_{iK}} \right) \frac{F_{jK}}{\det \mathbf{F}} - \Pi \delta_{ij} \, . \tag{5.7}$$

In this expression, the first term results from the contractility of the network, and the second term results from the osmotic pressure. When the gel swells freely under no external stress, $\sigma_{ij} = 0$, the osmotic pressure counteracts the contractile stress.

In general, when the gel swells under mechanical constraint, the deformation in the gel is inhomogeneous even when the gel has reached equilibrium. In such a general case, the osmotic pressure in the gel is also inhomogeneous, and should be determined as a part of the solution to the boundary-value problem.

Even when the deformation is homogeneous and isotropic, the osmotic pressure in the gel is not well defined. The constraint (5.1) will allow us to write the function $W(\mathbf{F}, \tilde{\mathbf{D}}, C^1, C^2, \cdots)$ in many forms. For example, using (5.1) we can express C^1 in terms of the concentrations of other mobile species and $\det \mathbf{F}$, and then use this expression to substitute C^1 appeared in some terms in the function $W(\mathbf{F}, \tilde{\mathbf{D}}, C^1, C^2, \cdots)$, but not other terms. The choice of the terms to be replaced is arbitrary. Subsequently, we regard all variables of W as independent and calculate electrochemical potential from (5.4) or stress from (5.7). Because the electrochemical potential and stress are quantities set by external agents, and are not modified by this partial substitution of a variable, the quantity Π must be modified accordingly.

This ambiguity in defining the osmotic pressure in a gel also has an experimental consequence: the osmotic pressure in a gel is not a measurable quantity. With reference to (5.7), the stress σ_{ij} applied on a uniform gel can be measured in experiments, but no experiments can be devised to measure the contractile stress and the osmotic pressure separately. That is, dividing the stress into contractile stress and osmotic pressure in general has no empirical significance, and is a mathematical artifact. Such a division, however, does have a specific physical interpretation in a class of models described in the next section.

6. An explicit form of the free-energy function

A large number of models describe liquid mixtures of uncrosslinked polymers and solvent molecules. Also a large number of models describe the elasticity of crosslinked polymers. In many gels, the density of the crosslinks is so low that, to a good approximation,

the effect of crosslinks on mixing may be neglected, and one simply writes the free energy of a gel as the sum of the free energy of the network and that of the solution. The best known model of this kind is due to Flory and Rehner (1943) for neutral gels, where the free energy of a gel is assumed to result from two molecular processes: stretching the network of the polymers, and mixing the polymers and the solvent molecules.

When a liquid mixture is separated from a pure solvent by a membrane permeable to the solvent but not to the solute, solvent may cross the membrane to dilute the liquid mixture. This process will continue unless the mixture is subject to a pressure, known as the osmotic pressure. The osmotic pressure can be measured experimentally. The difference between a liquid mixture and a gel is that in the latter polymers are crosslinked. The crosslinks serve the function of the semi-permeable membrane: the solvent can enter the gel, but the polymers cannot leave the gel. As the solvent molecules enter the gel, the network expands. The solvent and the gel equilibrate when osmosis counteracts contractility of the network.

So long as the density of the crosslinks is low enough, and the crosslinks affect the behavior of the individual molecules in the mixture negligibly, we may assume that the osmotic pressure in the gel is the same as that in the liquid mixture. This assumption is tacitly made in nearly entire literature on polymeric gels. The assumption is clearly invalid if the density of the crosslinks is high enough to modify the behavior of the individual molecules in the mixture, in which case, the osmotic pressure is a nebulous notion and cannot be unambiguously separated from contractile stress.

The Flory-Rehner approach has been extended to polyelectrolyte gels (e.g., Ricka and Tanaka, 1984; Hooper et al., 1990; Brannon-Peppas and Peppas, 1991). We further extend this approach by adding a term due to polarization. Specifically, we write the free-energy density of the gel as a sum:

$$W = W_{net} + W_{sol} + W_{ion} + W_{pol} \ , \tag{6.1}$$

where W_{net}, W_{sol}, W_{ion} and W_{pol} are the contributions from stretching the network, mixing the polymers and the solvent, mixing the solvent and ions, and polarizing the gel. We next describe these contributions one by one.

The free energy of stretching the polymer network is taken to be (e.g., Flory, 1953)

$$W_{net} = \frac{1}{2} NkT \left(F_{iK} F_{iK} - 3 - 2 \log(\det \mathbf{F}) \right), \tag{6.2}$$

where N is the number of polymer chains divided by the volume of the dry polymer, and kT is the temperature in the unit of energy. This free energy assumes that contractility of the network is entirely due to the reduction in the entropy caused by stretching the polymer chains, and the configurations of the polymer chains obey the Gaussian statistics. When the deformation does not change volume, $\det \mathbf{F} = 1$, this model recovers the neo-Hookean model. For a swelling gel, of cause, the change in volume is large, $\det \mathbf{F} \gg 1$.

The free energy of mixing the polymers and the solvent takes the form (Flory, 1942; Huggins, 1941):

$$W_{sol} = \frac{kT}{v_s} \left(v^s C^s \log \frac{v^s C^s}{1 + v^s C^s} - \frac{\chi}{1 + v^s C^s} \right), \tag{6.3}$$

where C^s is the nominal concentration of the solvent in the gel, and v^s the volume per solvent molecule. The volume of a swollen gel is predominantly occupied by the solvent molecules, so that $v^s C^s \gg 1$. Eq. (6.3) consists of the entropy of mixing of the polymer chains and the solvent molecules, as well as the enthalpy of mixing, characterized by a dimensionless parameter χ.

The concentrations of the mobile ions are taken to be low, so that their contribution to the free energy is due entirely to the entropy of mixing, namely,

$$W_{ion} = kT \sum_{b \neq s} C^b \left(\log \frac{C^b}{v^s C^s c_0^b} - 1 \right). \tag{6.4}$$

The sum is taken over all species of the mobile ions, excluding the solvent, and C^b is the nominal concentration of ionic species b. To understand this expression, one may consider the

external solution. Let c_0^b be a reference concentration of species b in the solution; at this concentration, the chemical potential of the species is set to be zero. When the concentration changes to c^b, the chemical potential is $kT\log(c^b/c_0^b)$. In the gel, we still assume that the ions and the solvent form a solution independent of the polymer network. The true concentration of the species b is now $c^b = C^b/v^sC^s$.

Following Zhao et al. (2007), we assume that the polyelectrolyte gel is an ideal dielectric, with the free energy of polarization being $D_i D_i/2\varepsilon$ per unit volume in current state, the same as that of a liquid. Here D_i is the true electric displacement, and is related to the nominal electric displacement by

$$D_i = \frac{\tilde{D}_K F_{jK}}{\det \mathbf{F}}.\tag{6.5}$$

We express the free energy of polarization as a function of the nominal fields:

$$W_{pol} = \frac{1}{2\varepsilon}\frac{F_{iK}F_{iL}}{\det \mathbf{F}}\tilde{D}_K\tilde{D}_L.\tag{6.6}$$

Because of the difference in the dielectric properties between the solvent and the network molecules, the permittivity of the gel in general is a function of the solvent concentration, $\varepsilon(C^s)$. A simple estimate would be the volumetric average among the solvent and the network:

$$\varepsilon = \frac{\varepsilon_n + v^sC^s\varepsilon_s}{1 + v^sC^s},\tag{6.7}$$

where ε_n and ε_s are the permittivity of the polymer network and the solvent, respectively. However, often the major part of the gel is occupied by the solvent, $v^sC^s \gg 1$, and we will simply use the permittivity of the solvent for the gel, independent of the composition.

We have now constructed a specific free-energy function. Applying this free-energy function to Eq. (5.7), we obtain that

$$\sigma_{ij} = \frac{NkT}{\det F}\left(F_{iK}F_{jK} - \delta_{ij}\right) + \frac{1}{\varepsilon}\left(D_iD_j - \frac{1}{2}D_mD_m\delta_{ij}\right) - \Pi\delta_{ij}.\tag{6.8}$$

The first term is due to the entropy of the network, the second is the Maxwell stress, and the third is the osmotic pressure. In our formulation of the theory, it is evident that the Maxwell stress can be used to describe the effect of electric field on deformation only for liquid-like dielectrics, but not for more general dielectrics. For a review of other models of electromechanical coupling see Zhao and Suo (2008).

Applying the free-energy function to (4.6), and expressing the resulting equation in terms of the true quantities, we recover the familiar relation

$$D_i = \varepsilon E_i.$$ (6.9)

Applying the free-energy function to (5.4), we obtain the electrochemical potential of each species of ions:

$$\mu^b = e\Phi z^b + kT \log \frac{C^b}{v^s C^s c_0^b} + \Pi v^b.$$ (6.10)

When the external solution equilibrates with the gel, the electrochemical potential of each species of ions is uniform throughout the external solution and the gel, and results from the following effects: a positive ion increases its electrochemical potential when the electric potential is high, an ion increases its electrochemical potential when its concentration is high, and an ion increases its electrochemical potential when both its effective volume v^b and the osmotic pressure are positive.

The solvent molecules are taken to be uncharged. Applying the free-energy function to (5.4), we obtain the chemical potential of the solvent:

$$\mu^s = kT \left[\log \frac{v^s C^s}{1 + v^s C^s} + \frac{1}{1 + v^s C^s} + \frac{\chi}{\left(1 + v^s C^s\right)^2} - \sum_{b \neq s} \frac{C^b}{C^s} \right] + \Pi v^s.$$ (6.11)

When the external solution equilibrates with the gel, the chemical potential of the solvent is uniform throughout the external solution and the gel. Eq. (6.11) is applicable to both the external solution and the gel. In the external solution, the terms due to mixing the polymers and the solvent should be dropped, and the chemical potential of the solvent in the external

solution is due to the presence of ions and the osmotic pressure. The osmotic pressures in the external solution and in the gel are usually unequal.

7. Free swelling

We now explore consequences of the theory by considering several special cases. As the first special case, consider the free swelling of a gel immersed in an external solution (Fig. 2a). Free swelling has been analyzed by many authors by using free-energy functions containing diverse physical effects, as reviewed by Brannon-Peppas and Peppas (1991). Here we will analyze free swelling by using the free-energy function specified in the previous section. The results will be used in the later sections to compare with swelling subject to constraints, and swelling of gels of small sizes.

As discussed in Section 1, an electrical double layer forms at the interface between the gel and the external solution. The characteristic thickness of the double layer, the Debye length, is often much smaller than the size of the gel and of the external solution. At a distance larger than the Debye length from the interface, in either the gel or the external solution, electroneutrality prevails and the electric field vanishes. The electric potential and the osmotic pressure are uniform deep inside the gel, change across the interface, and then are uniform deep inside the external solution. We will study the overall swelling in this section, and then the electrical double layer in the later sections.

We set the electric potential and the osmotic pressure deep inside the external solution to be zero. Let Φ and Π be the electric potential and the osmotic pressure deep inside the gel. To illustrate essential ideas, we assume that only two species of ions, of valences +1 and -1, are mobile in the gel and in the external solution. Let C^+ and C^- be the nominal concentrations of the two species of ions in the gel. The amount of the gel is taken to be much smaller than that of the external solution, so that the concentration of either species of the ions deep inside the

external solution remains at a fixed level c_0, invariant as the gel swells. At the concentration c_0, the electrochemical potentials of the two species of ions in the external solution are set to be zero. When the gel equilibrates with the external solution, the electrochemical potential of each species of the ions is uniform throughout the gel and the external solution, so that (6.10) gives that

$$C^+ = c_0 v^s C^s \exp\left(\frac{-e\Phi - \Pi v^+}{kT}\right),$$ (7.1)

$$C^- = c_0 v^s C^s \exp\left(\frac{e\Phi - \Pi v^-}{kT}\right).$$ (7.2)

Here v^+ is the volume per counterion, and v^- the volume per co-ion.

The chemical potential of the solvent is also uniform throughout the gel and the external solution. Deep inside the external solution, the two species of ions each has a concentration of c_0. We can apply (6.11) to the external solution by dropping the contributions of the network and osmosis, so that the chemical potential of the solvent in the external solution is $\mu^s = -2kTv^s c_0$. Equating the chemical potential of the solvent in the external solution to that in the gel, (6.11), we obtain that

$$\Pi = \frac{kT}{v^s}\left[\frac{C^+ + C^-}{C^s} - 2v_s c_0 - \log\frac{v^s C^s}{1 + v^s C^s} - \frac{1}{1 + v^s C^s} - \frac{\chi}{(1 + v^s C^s)^2}\right].$$ (7.3)

This equation is readily interpreted. The osmotic pressure in the gel, Π, is due to the imbalance of the ions in the gel and in the external solution, as well as due to the mixing of the polymers and the solvent.

The ionizable groups on the polymers are taken to be fully dissociated, with C_0 being the number of the fixed charges divided by the volume of the dry polymer. The fixed charges are taken to have valence -1. Deep inside the gel, electroneutrality prevails. The gel and the external solution are not connected by any electronic conductor, so that no excess electrons and

present in the gel. Consequently, electroneutrality requires that the sum of the number of the fixed charges and the number of the co-ions equals the number of the counterions:

$$C_0 + C^- = C^+ . \tag{7.4}$$

When the gel equilibrates with the external solution, the network expands by an isotropic stretch λ. If the concentration of ions are much lower than that of the solvent, $v^{\pm}C^{\pm} << v^s C^s$, the solvent molecules contribute most to the swelling of the gel. The condition of incompressibility of the polymers and solvent molecules (5.1) becomes that

$$1 + v^s C^s = \lambda^3 . \tag{7.5}$$

Deep inside the gel, both the electric field and the stress vanish, so that (6.8) becomes

$$\Pi = NkT\left(\lambda^{-1} - \lambda^{-3}\right). \tag{7.6}$$

As expected, the osmosis of the gel relative to the external solution counteracts the contractility of the network. Observe that Π decreases as λ increases. This trend is understood as follows. The osmotic pressure enters (6.8) as a part of the true stress. When the network swells, the contractile force increases, but the size of the gel also increases, resulting in a reduction in the true contractile stress.

The six algebraic equations, (7.1)-(7.6), solve the six unknowns $\Phi, \Pi, \lambda, C^+, C^-, C^s$, while all other quantities in these equations are considered known. We note two limiting cases. In the limit of a concentrated solution, when the concentration of ions in the external solution is much higher than the concentration of the fixed charges, $c_0 >> C_0$, the effect of the fixed charges is negligible, and the polyelectrolyte gel behaves the same as the neutral gel. In this limit, the true concentrations of ions in the gel are the same as those in the external solution:

$$\frac{C^+}{v^s C^s} = \frac{C^-}{v^s C^s} = c_0 , \tag{7.7}$$

A combination of (7.3), (7.5) and (7.6) gives

$$\log\left(1 - \lambda^{-3}\right) + \lambda^{-3} + \chi\lambda^{-6} + Nv^s\left(\lambda^{-1} - \lambda^{-3}\right) = 0 . \tag{7.8}$$

This nonlinear algebra equation determines the free swelling ratio of a gel in a concentrated solution.

In the limit of a dilute solution, when the concentration of ions in the external solution is much lower than the concentration of the fixed charges, $c_0 \ll C_0$, inside the gel, the number of the co-ions is negligible, and the fixed charges are fully compensated by the counterions, namely,

$$C^- = 0, \quad C^+ = C_0. \tag{7.9}$$

A combination of (7.3), (7.5) and (7.6) gives

$$\log\left(1 - \lambda^{-3}\right) + \lambda^{-3} + \chi\lambda^{-6} - \frac{v^s C_0}{\lambda^3 - 1} + Nv^s\left(\lambda^{-1} - \lambda^{-3}\right) = 0. \tag{7.10}$$

This nonlinear algebra equation determines the free swelling ratio of a gel in a dilute solution. In this limit, electroneutrality demands that the number of the counterions be the same as that of the fixed changes. Consequently, the concentration of the counterions inside the gel is much higher than that in the external solution, resulting in an additional osmotic pressure that causes the network to imbibe more solvent.

Fig. 4 plots numerical results for free swelling. In these and subsequent numerical calculations, we assume that $v^+ = v^- = v^s$, and write $v^s = v$. We also set $Nv = 10^{-3}$, which means that each polymer chain contains 10^3 monomers; and set $\chi = 0.1$, which means that the polymers and the solvent have a slightly positive enthalpy of mixing.

Fig. 4a and 4b show the expected trend: the swelling ratio increases from the limit of a gel in a concentrated solution to the limit of a gel in a dilute solution. When the ionic concentration of the external solution is high compared to the concentration of the fixed charges on the polymers, ions in the gel are nearly balanced with ions in the external solution and contribute to osmosis negligibly, so that and the polyelectrolyte gel behaves like a nonionic gel. When the ionic concentration of the external solution is low compared to the concentration of the fixed charges on the polymer, electroneutrality demands that the concentration of the

counterions in the gel be equal to the concentration of the fixed charges, and the excess counterions motivate more solvent to enter the gel. In practice, the ionic concentration can be increased by adding slat to the external solution. Thus, polyelectrolyte gels are responsive to the change in the slat concentration (Ricka and Tanaka, 1984; Hooper et al., 1990).

Fig. 4a and 4b also show that the swelling ratio increases with the concentration of the fixed charges. This trend is readily understood: the more fixed charges on the polymers, the more counterions need be inside the gel to maintain electroneutrality. The larger excess of mobile ions in the gel causes more solvent to enter. The concentration of the fixed charges may be varied by the design of the polymer chains. A more intriguing way to vary the concentration of the fixed charges is by an association-dissociation reaction, so that the amount of swelling of the polyelectrolyte gel can be regulated by pH (e.g., Brannon-Peppas and Peppas, 1991).

Figs. 4c and 4d plot the concentrations of the counterions and of the co-ions inside the gel. When the gel is immersed in an external solution of a low ionic concentration, inside the gel the concentration of the counterions is the same as that of the fixed charges, and the concentration of the co-ions is vanishingly small. When the gel is immersed in an external solution of a high ionic concentration, the concentrations of both the counterions and the co-ions in the gel are the same as those in the external solution.

Fig. 4e shows that the osmotic pressure inside the gel increases with the concentration of the ions in the external solution. As indicated by (7.3), the osmotic pressure has two contributions: the imbalance of the ions between the gel and the external solution, and the mixing of the polymers and solvent. The former reduces the osmotic pressure as the concentration of ions in the external solution increases, but the latter increases the osmotic pressure as the concentration of solvent in the gel decreases. The combination gives the overall trend of the osmotic pressure shown in Fig. 4e. This trend is consistent with the trend of the swelling ratio in Fig. 4a, because the osmotic pressure balances the contractile stress, which decreases as the gel swells.

Fig. 4f plots the electric potential of the gel relative to the external solution. The trends are readily understood. From the condition of neutrality, in the gel the counterions always outnumber the co-ions, $C^+ > C^-$, so that the electric potential of the gel is always below that in the external solution. When either the number of fixed charges is large or the external solution is dilute, the ratio C^+ / C^- increases, lowering the electric potential in the gel.

8. Constrained swelling

A gel often swells under constraint. For example, a thin layer of a gel, coated on a substrate of a stiff material, can only swell in the direction normal to the surface, but not in the directions within the surface. As another example, when used as a transducer, a gel needs to push against some hard materials. It is known that constraints markedly modify the amount of swelling of neutral gels (e.g., Treloar, 1950; Hong et al., 2009).

To illustrate constrained swelling of a polyelectrolyte gel, consider a disk of a gel, with the thickness constrained to a fixed value, but the radius allowed to swell freely (Fig. 2b). This example may model a transducer that changes the blocking force associated with a change in the concentrations of ions in the solution. Let λ_0 be the fixed stretch in the thickness direction, and λ be the stretch in the radial direction. Incompressibility of the polymers and solvent molecules relates the solvent concentration and the stretch:

$$1 + v^s C^s = \lambda_0 \lambda^2. \tag{8.1}$$

Deep inside the gel, the electric field vanishes, and so does the stress in the radial direction. Consequently, the osmotic pressure is uniform, and (6.8) becomes that

$$\Pi = \frac{NkT}{\lambda_0 \lambda^2} \left(\lambda^2 - 1 \right). \tag{8.2}$$

Once again, the contractility of the network counteracts the osmosis of the gel.

Eqs. (8.1) and (8.2), along with (7.1)-(7.4), solve the six unknowns $\Phi, \Pi, \lambda, C^+, C^-, C^s$. In

the limit of a gel in a concentrated solution, the swelling ratio λ is determined by

$$\log \frac{\lambda_0 \lambda^2 - 1}{\lambda_0 \lambda^2} + \frac{1}{\lambda_0 \lambda^2} + \frac{\chi}{\left(\lambda_0 \lambda^2\right)^2} + \frac{Nv^s}{\lambda_0 \lambda^2}\left(\lambda^2 - 1\right) = 0 \,. \tag{8.3}$$

In the limit of a gel in a dilute solution, the swelling ratio λ is determined by

$$\log \frac{\lambda_0 \lambda^2 - 1}{\lambda_0 \lambda^2} + \frac{1}{\lambda_0 \lambda^2} + \frac{\chi}{\left(\lambda_0 \lambda^2\right)^2} - \frac{v^s C_0}{\lambda_0 \lambda^2 - 1} + \frac{Nv^s}{\lambda_0 \lambda^2}\left(\lambda^2 - 1\right) = 0 \,. \tag{8.4}$$

Fig. 5 shows that all the trends in the constrained swelling remain the same as those in the free swelling, Fig. 4. The constraint, however, substantially reduces the volume of swelling. The constraint somewhat affects the concentrations of the ions and the electric potential in the gel.

The constraint also causes a blocking stress in the gel along the thickness direction. Specializing (6.8), we obtain this stress:

$$\sigma_0 = \frac{NkT}{\lambda_0 \lambda^2}\left(\lambda_0^2 - \lambda^2\right) . \tag{8.5}$$

When the stretch in the direction of thickness is constrained at a level smaller than the swollen stretch in the radial direction, $\lambda_0 < \lambda$, the blocking stress is compressive, $\sigma_0 < 0$. Note that NkT is the elastic modulus of the dry polymer. Fig. 6 plots the stress as a function of the concentration of ions in the external solution. The magnitude of the stress increases as the concentration decreases. The blocking stress can be changed by varying the concentration of the fixed charges. These observations should be of interest when a gel is used as an actuator.

9. Inhomogeneous field in the external solution

We next examine the inhomogeneous field in the gel and in the external solution near their interface (Fig. 2c). The interface is assumed to be flat, and both the gel and the external solution are large compared to the Debye length. This section describes the field in the external solution, and the next section the field in the gel. The external solution consists of solvent

molecules and ions, and may be considered as a special case of the general theory presented in Section 5, with W_{net} and W_{sol} removed. The field in the solution is well studied (e.g., Russel et al., 1989). The basic equations are listed here for use later in this paper.

Let the x-axis be perpendicular to the interface, with the origin coinciding with the interface, and the direction towards the external solution. Near the interface, the electric potential and the osmotic pressure varies with x, as noted $\Phi(x)$ and $\Pi(x)$. Because no external stress is applied, the stress normal to the interface vanishes, so that Eq. (6.8) gives that

$$\Pi = \frac{\varepsilon}{2}\left(\frac{d\Phi}{dx}\right)^2. \tag{9.1}$$

This equation is interpreted as follows. Consider a small volume of the solution. The osmotic pressure tends to draw solvent into the volume, while the Maxwell stress tends to expel solvent out the volume. In equilibrium, the osmotic pressure counteracts the Maxwell stress. Note that ε represents the permittivity of the solvent. In this paper, however, we assume the same permittivity in the gel and in the solvent.

Denote the concentration of the two species of ions in the external solution by $c^+(x)$ and $c^-(x)$. Deep inside the external solution, the two species of ions have the same value of a fixed concentration, $c^+(\infty) = c^-(\infty) = c_0$, the electrochemical potentials of the two species of the ions are set to be zero, $\mu^+(\infty) = \mu^-(\infty) = 0$, and the electric potential is also set to be zero, $\Phi(\infty) = 0$. In equilibrium, the electrochemical potential of each species is uniform, so that $\mu^+(x) = \mu^-(x) = 0$. The electric potential, however, is nonuniform, and so is the osmotic pressure. Eq. (6.10) gives that

$$c^+ = c_0 \exp\left(-\frac{e\Phi + \Pi v^+}{kT}\right). \tag{9.2}$$

$$c^- = c_0 \exp\left(-\frac{-e\Phi + \Pi v^-}{kT}\right). \tag{9.3}$$

The positive ions concentrate where the electric potential is low, and the negative ions concentrate where the electric potential is high.

Near the interface, the two species of ions no long balance each other, $c^+(x) \neq c^-(x)$. The excess electric change is the source that gives the nonuniform electric potential, governed by Poisson's equation:

$$-\varepsilon \frac{d^2 \Phi}{dx^2} = e(c^+ - c^-). \tag{9.4}$$

Submitting (9.1)-(9.3) into (9.4), we obtain that

$$2 \frac{d^2 \Psi}{d\xi^2} = \exp\left[\Psi - v^- c_0 \left(\frac{d\Psi}{d\xi}\right)^2\right] - \exp\left[-\Psi - v^+ c_0 \left(\frac{d\Psi}{d\xi}\right)^2\right], \tag{9.5}$$

where $\Psi = \Phi e / kT$ is the dimensionless electric potential, and $\xi = x / L_D$ is the dimensionless coordinate, with L_D being the Debye length:

$$L_D = \sqrt{\frac{kT\varepsilon}{2e^2 c_0}}. \tag{9.6}$$

The concentrations of ions in the solution are typically low, $v^\pm c_0 \ll 1$, so that the term containing $(d\Psi/d\xi)^2$ can be neglected from the right-hand side of (9.5). Thus, (9.5) is often written in a more familiar form, i.e., the Poisson-Boltzmann equation:

$$\frac{d^2 \Psi}{d\xi^2} = \sinh \Psi. \tag{9.7}$$

Integrating this second-order ordinary differential equation once subject to the boundary condition $\Psi(\infty) = 0$, we obtain that

$$\frac{d\Psi}{d\xi} = -2 \sinh \frac{\Psi}{2}. \tag{9.8}$$

This first-order differential equation can be integrated subject to the conditions that both the electric displacement and the electric potential are continuous across the interface.

10. Inhomogeneous field in the gel

Now we study the inhomogeneous field in the gel near the interface. An element of the network occupies the place of coordinate X when the gel is in the reference state, and moves to the place with coordinate x when the gel is swollen. The function $x(X)$ describes the deformation of the gel. Near the interface, the gel does not swell homogeneously. The stretch normal to the interface is

$$\lambda_1(X) = dx/dX. \tag{10.1}$$

Constrained by the overall swelling of the gel, the stretches parallel to the interface are equal and uniform in the gel; we designate this uniform stretch by λ_2, which is the same as the stretch due to free swelling.

The assumption of incompressibility relates the nominal concentration of the solvent molecules to the stretches. Typically the concentrations of ions in the gel are low, so that the condition of incompressibility reduces to

$$1 + v^s C^s = \lambda_1 \lambda_2^2. \tag{10.2}$$

Near the interface, the electric charge is no longer neutral. The excess charge, $e(C^+ - C^- - C_0)$, causes an inhomogeneous field of electric potential, $\Phi(x)$, governed by the Poisson equation:

$$\varepsilon \frac{d^2 \Phi}{dx^2} = \frac{e}{\lambda_1 \lambda_2^2}\left(C_0 + C^- - C^+\right). \tag{10.3}$$

Near the interface, the osmotic pressure is also inhomogeneous, $\Pi(x)$. The component of stress normal to the interface vanishes, so that (6.9) gives that

$$\Pi = \frac{NkT}{\lambda_1 \lambda_2^2}\left(\lambda_1^2 - 1\right) + \frac{\varepsilon}{2}\left(\frac{d\Phi}{dx}\right)^2. \tag{10.4}$$

The osmotic pressure is balanced by the contractile stress of the network and the Maxwell stress.

Inserting the expressions for the concentrations of the counterions and co-ions, (7.1) and (7.2), into the Poisson equation (10.3), we obtain that

$$\frac{d^2\Psi}{d\xi^2} = \frac{C_0}{2c_0}\frac{1}{\lambda_1\lambda_2^2} + \left(1 - \frac{1}{\lambda_1\lambda_2^2}\right)\sinh\Psi .$$

(10.5)

Inserting (7.1)-(7.3) and (10.2) into (10.4), we obtain that

$$\left(\frac{d\Psi}{d\xi}\right)^2 + \frac{N}{c_0}\left(\frac{\lambda_1}{\lambda_2^2} - \frac{1}{\lambda_1\lambda_2^2}\right) + \frac{1}{vc_0}\left[\log\left(1 - \frac{1}{\lambda_1\lambda_2^2}\right) + \frac{1}{\lambda_1\lambda_2^2} + \frac{\chi}{\lambda_1^2\lambda_2^4}\right] - 2(\cosh\Psi - 1) = 0 .$$

(10.6)

Eliminating λ_1 from (10.5) and (10.6), we obtain a second-order ordinary differential equation for $\Psi(\xi)$. The equation is subject to the following boundary conditions. Both electric displacement and the electric potential in the gel match those in the external solution, so that Eq. (9.8) holds at $x = 0$. Deep inside the gel, the electric field vanishes, so that $d\Psi / d\xi = 0$ as $\xi \to -\infty$. The differential equation is integrated numerically.

Once the function $\Psi(\xi)$ is determined, the distribution of stretch $\lambda_1(\xi)$ is determined from (10.5), and the distribution of the stress parallel to the interface is determined from

$$\sigma_{22} = \frac{NkT}{\lambda_1\lambda_2^2}(\lambda_2^2 - \lambda_1^2) - \varepsilon\left(\frac{d\Phi}{dx}\right)^2 .$$

(10.7)

This equation is obtained from (6.8).

Fig. 7 plots the numerical results. As expected, at a distance larger than the Debye length in the gel, the field becomes homogeneous, the same as in the overall swelling studied above. To understand various trends in Fig. 7, consider the case of the gel in a dilute ionic solution, $vc_0 = 10^{-5}$. The concentration of the fixed charges is $vC_0 = 0.002$. As discussed above, deep inside the gel, the concentration of counterions is equal to that of the fixed charges. Near the interface, however, the counterions in the gel spill into the external solution to gain entropy. The loss of the counterions causes the gel to be negatively charged near the interface, and the electric potential to bend up. The loss of the counterions also expels some solvent molecules

from the gel, decreasing the swelling ratio near the interface. Because the stretch parallel to the interface is set by the overall swelling of the gel, the loss of solvent molecules near the interface causes a tensile stress in the directions parallel to the interface. The stress peaks at a finite depth from the interface, due to the repulsion between net charges accumulated near the interface.

11. Swelling of a thin layer of a gel

Consider a polyelectrolyte gel of a small characteristic size immersed in a large amount of an external solution of a low ionic concentration. The size of the gel may become comparable to, or even smaller than, the Debye length. The network has a relatively high concentration of the fixed charges. The counterions, however, spill into the external solution to gain entropy. Consequently, the entire gel is charged, and the charge of the gel is screened by counterions in the external solution.

To illustrate this situation, here we study a layer of a polyelectrolyte gel, whose thickness H is comparable to the Debye length L_D (Fig. 3d). The x-axis remains normal to the interfaces, with the origin of the axis now coinciding with the center of the gel. The reference state of the gel occupies the region $-\frac{H}{2} < X < \frac{H}{2}$. The gel swells in the external solution under no external forces. The stretch through the thickness in nonuniform, $\lambda_1(X)$, while stretches in the plane of the layer is uniform, $\lambda_2 = \lambda_3$.

The field equations are the same as those in the last section, except that λ_2 is no longer the stretch of the swelling of a thick gel, but a constant to be determined. No mechanical load is applied. In the direction of thickness, this condition is satisfied by requiring $\sigma_{11} = 0$, which leads to (9.1). In the directions in the plane of the layer, this condition of no external force is enforced by requiring that the integral of the in-plane stress vanish:

$$\int_0^{\frac{h}{2}} \sigma_{22}\, dx = 0 \,, \tag{11.1}$$

where h is the thickness of the swollen gel. Using (6.8), this expression can be rewrite in a dimensionless form:

$$\int_0^{\eta/2} \left[\frac{Nv}{\lambda_1 \lambda_2^2} \left(\frac{\lambda_1^2 + \lambda_2^2}{2} - 1 \right) + \log\left(1 - \frac{1}{\lambda_1 \lambda_2^2} \right) + \frac{1}{\lambda_1 \lambda_2^2} + \frac{\chi}{\lambda_1^2 \lambda_2^4} + 2 v c_0 \left(1 - \cosh \Psi \right) \right] d\xi = 0 \,. \tag{11.2}$$

where $\eta = h / L_D$.

The two unknown functions, $\Psi(\xi)$ and $\lambda_1(\xi)$, and the one unknown constant, λ_2, are determined by three coupled equations (10.5), (10.6) and (11.2), subject the boundary conditions:

$$\left. \frac{d\Psi}{d\xi} \right|_0 = 0 \,, \tag{11.3}$$

$$\left. \frac{d\Psi}{d\xi} \right|_{\frac{\eta}{2}} = -2 \sinh \frac{\Psi\left(\frac{\eta}{2} \right)}{2} \,. \tag{11.4}$$

We solve this set of equations by integrating (10.5) and (10.6) numerically and using a shooting method to determine λ_2.

Fig. 8 plots the numerical solution for the case $h = 2 L_D$. When the concentration of ions in the external solution, c_0, is relatively high, the effect of the fixed charges is negligible, and the swelling ratio of the polyelectrolyte gel is similar to that of a neutral gel. When the concentration of ions in the external solution is low, the swelling of the polyelectrolyte gel becomes inhomogeneous. The stress parallel of the surface is tensile at the center of the gel and compressive at the surface.

Once $\lambda_1(\xi)$ is determined, H is determined by integrating (10.1), or

$$\int_0^{\frac{\eta}{2}} \frac{d\xi}{\lambda_1(\xi)} = \frac{H}{2 L_D} \,. \tag{11.5}$$

To illustrate size-dependent swelling, Fig. 9 plots h/H and λ_2 as functions of H/L_D. The

swelling ratios are low when the thickness of the layer is small, but asymptote to the value of a thick gel when the thickness exceeds several times the Debye length.

12. Concluding remarks

This paper develops a field theory of polyelectrolyte gels by integrating a recent formulation of the theory of elastic dielectrics with the Gibbs theory of swelling elastic solids. The theory is separated into parts specified by general principles, and parts specified by special models. This modularization may aid the further development of the theory. A form of the free-energy function is prescribed to describe idealized behavior of polyelectrolyte gels. The theory is applied to study free and constrained swelling of a polyelectrolyte network immersed in an ionic solution. Swelling is affected not only by the ionic concentration of exterior solution, but also by geometric constraints. A blocking stress against the imposed constraints can be determined readily by the theory. Boundary-value problems are solved to study the inhomogeneous fields near the gel-solution interface and in an ultrathin layer of a gel. The method to construct free-energy function may be applied to study diverse effects, such as pH-sensitive gels and temperature-sensitive gels. The theory may be used to determine inhomogeneous fields in polyelectrolyte gels in nature and in engineering.

Acknowledgements

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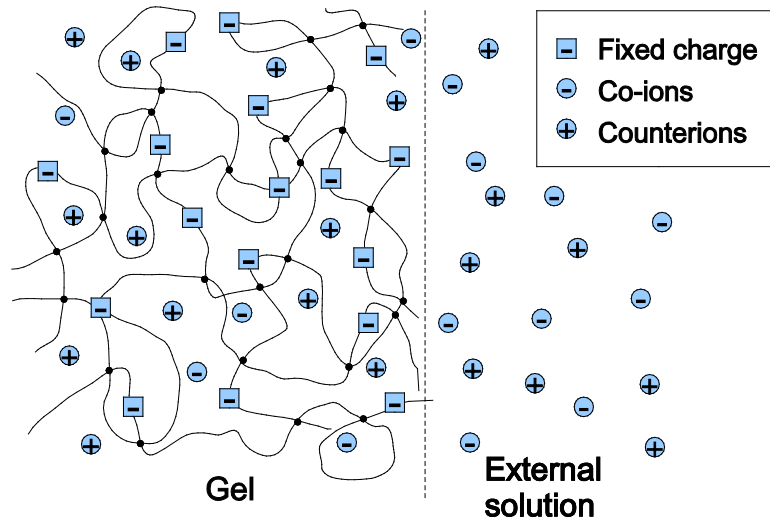
Figure 1. Flexible, long-chained polyelectrolyte polymers are crosslinked by covalent bonds into a three-dimensional network. The network imbibes a solution and swells, resulting in a polyelectrolyte gel. The ionizable groups on the polymers dissociate, so that the polymers carry fixed charges. The counterions and the co-ions, as well as solvent molecules, are mobile and can cross the interface between the gel and the external solution.
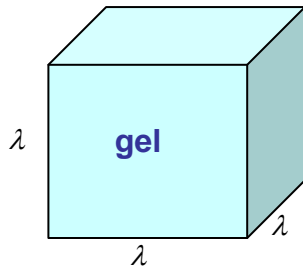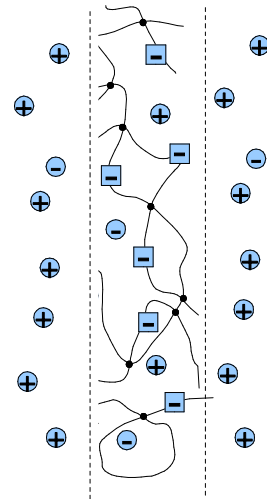
(a) Free swelling
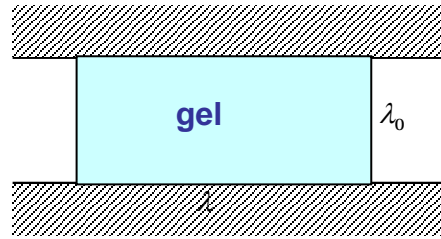
(b) Constrained swelling
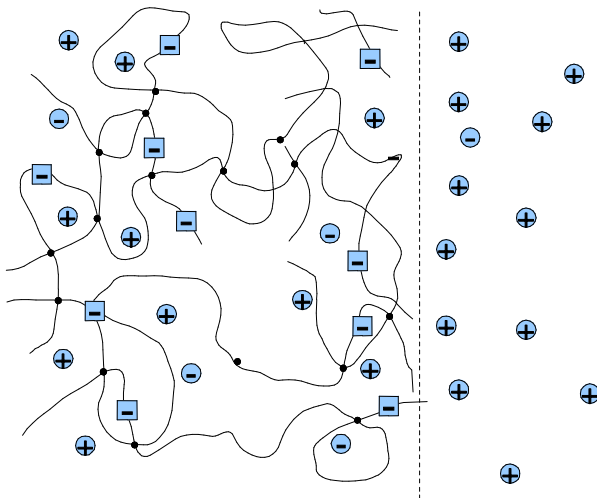
(c) Interface

(d) Thin layer of gel

Figure 2. Phenomena to be studied. (a) A gel swells freely in an ionic solution. (b) A disk of a gel swells freely in the radial direction, but is constrained in the thickness direction. (c) An electric double layer forms at the interface between a gel and an external solution. (d) A thin layer of a gel swells in an ionic soluti0n.

a) reference state

marker

$$\mathbf{X} = (X_1, X_2, X_3)$$

dry
polymer

b) current state

$\mathbf{x}(\mathbf{X}, t)$ pump

δM $\mu^1, \mu^2, \dots$

gel δQ

battery
Φ

P

weight $\delta \mathbf{x}$
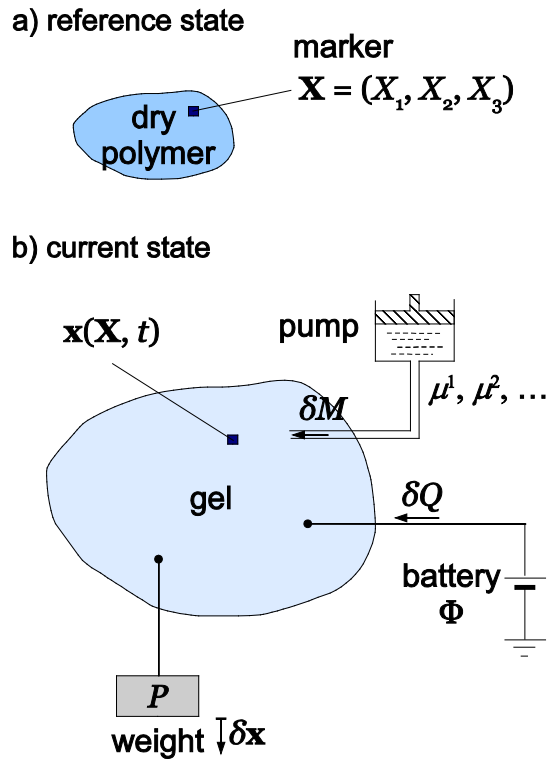
Figure 3. a) The reference state is a network of dry polymers. Each element of the network is identified by its coordinate $\mathbf{X}$ when the network is in the reference state. b) In the current state at time t, the element $\mathbf{X}$ occupies a place of coordinate $\mathbf{x}$, and external agents do work to the gel in three ways: mechanical work is done through the movements of a field of weights, electrical work is done as electrons flow from the ground into the gel through a field of batteries, and electrochemical work is done as solvent molecules and ions flow from external sources into the gel through a field of pumps.
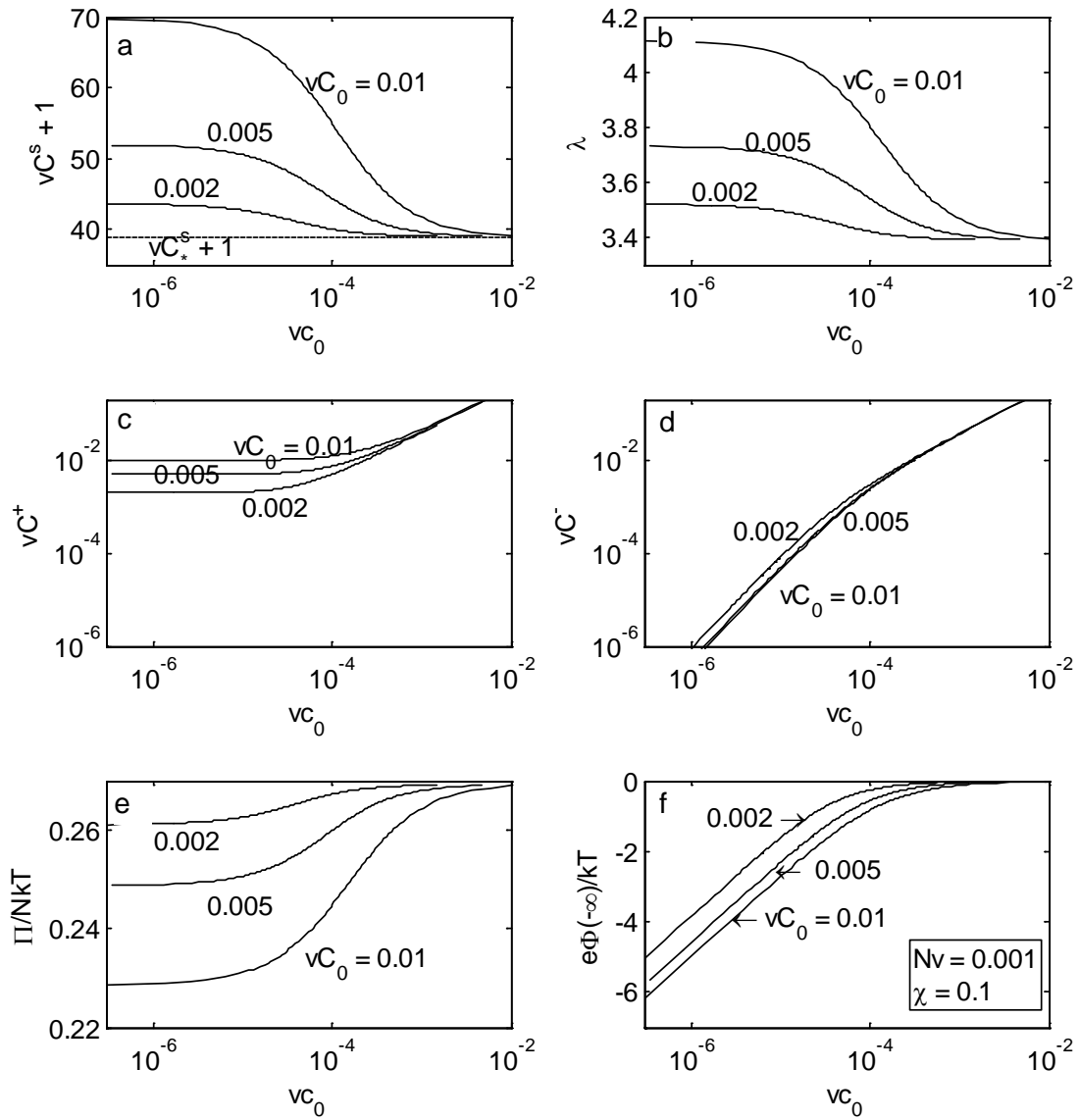
Figure 4. Numerical results for the free swelling of a polyelectrolyte gel immersed in an ionic solution. C_0 is the nominal concentration of the fixed charges on the network. c_0 is the true concentration of a species of ions in the external solution. (a) Swelling ratio. (b) Stretch in one direction. (c) Concentration of counterions in the gel. (d) Concentration of co-ions in the gel. (e) Osmotic pressure in the gel relative to the external solution. (f) Electric potential in the gel relative to the external solution.
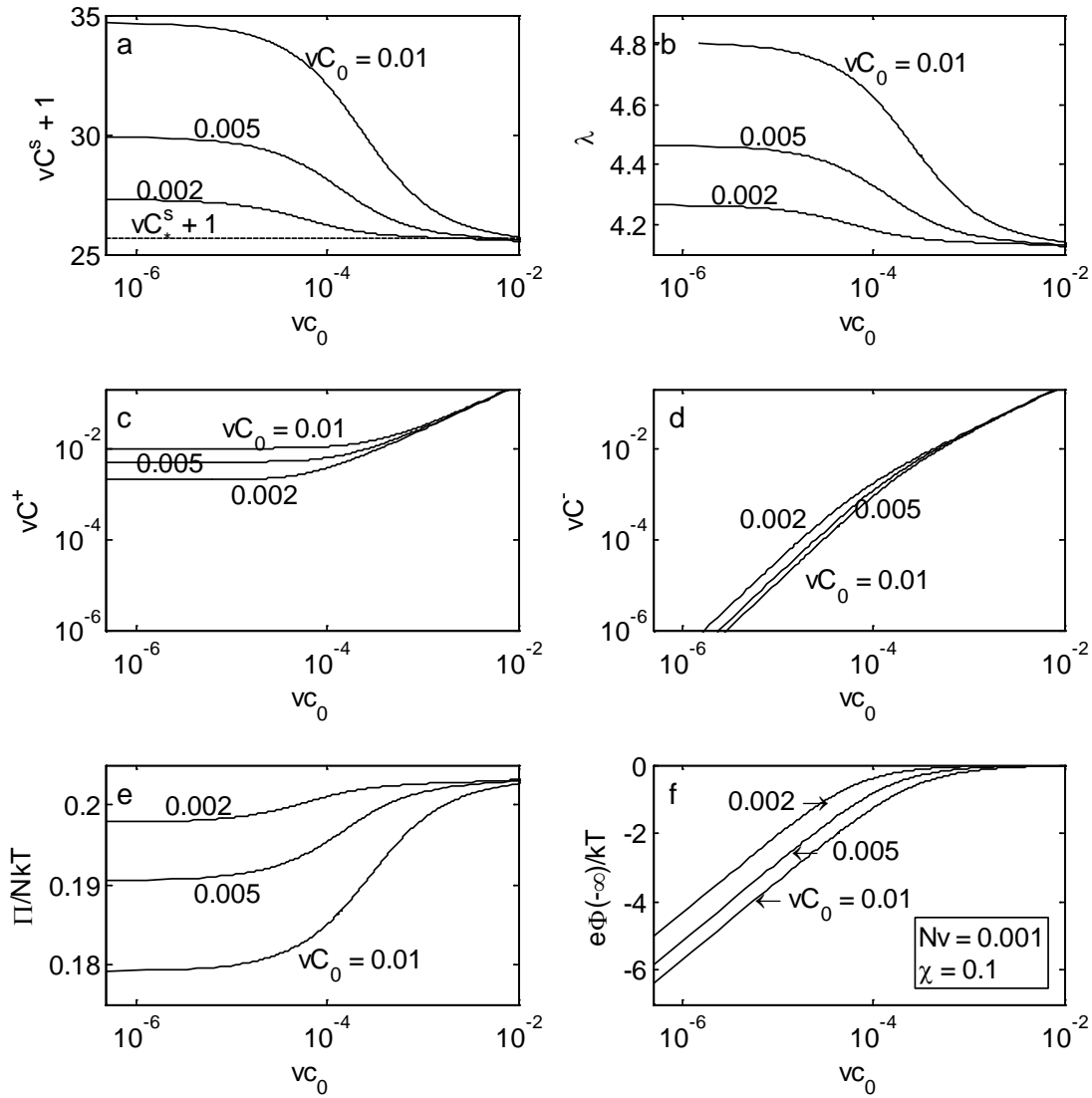
Figure 5. Numerical results for the constrained swelling of a disk of a gel immersed in an ionic solution. The height of the disk is fixed to a stretch $\lambda_0 = 1.5$, while the gel swells freely in the radial direction to a stretch λ. C_0 is the nominal concentration of the fixed charges on the network. c_0 is the true concentration of a species of ions in the external solution. (a) Swelling ratio. (b) Stretch in the radial direction. (c) Concentration of counterions in the gel. (d) Concentration of co-ions in the gel. (e) Osmotic pressure in the gel relative to the external solution. (f) Electric potential in the gel relative to the external solution.
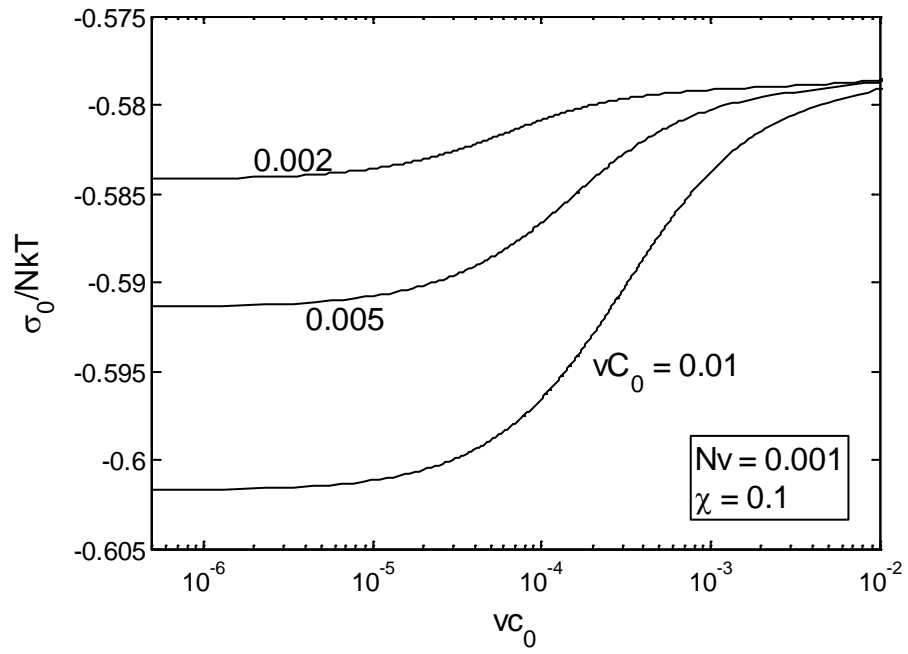
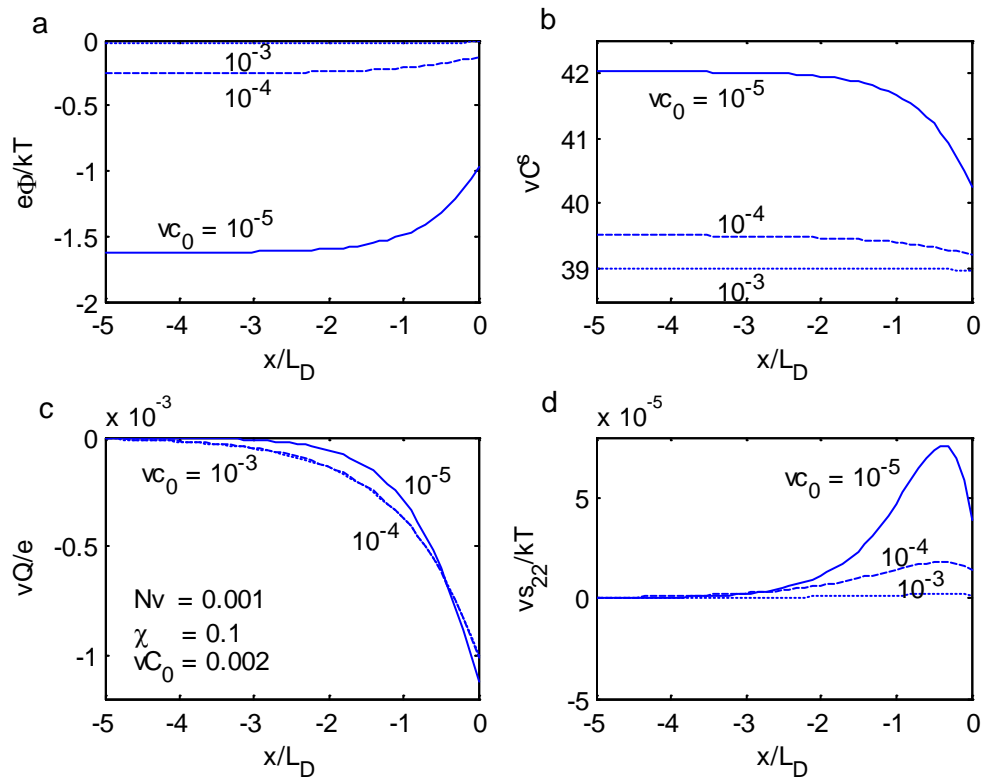Figure 6. A blocking stress develops in a gel swelling under a constraint.

Figure 7. The inhomogeneous fields in the gel near the interface. (a) Electric potential. (b) Swelling ratio. (c) Electric charge. (d) Stress in a direction parallel to the interface.
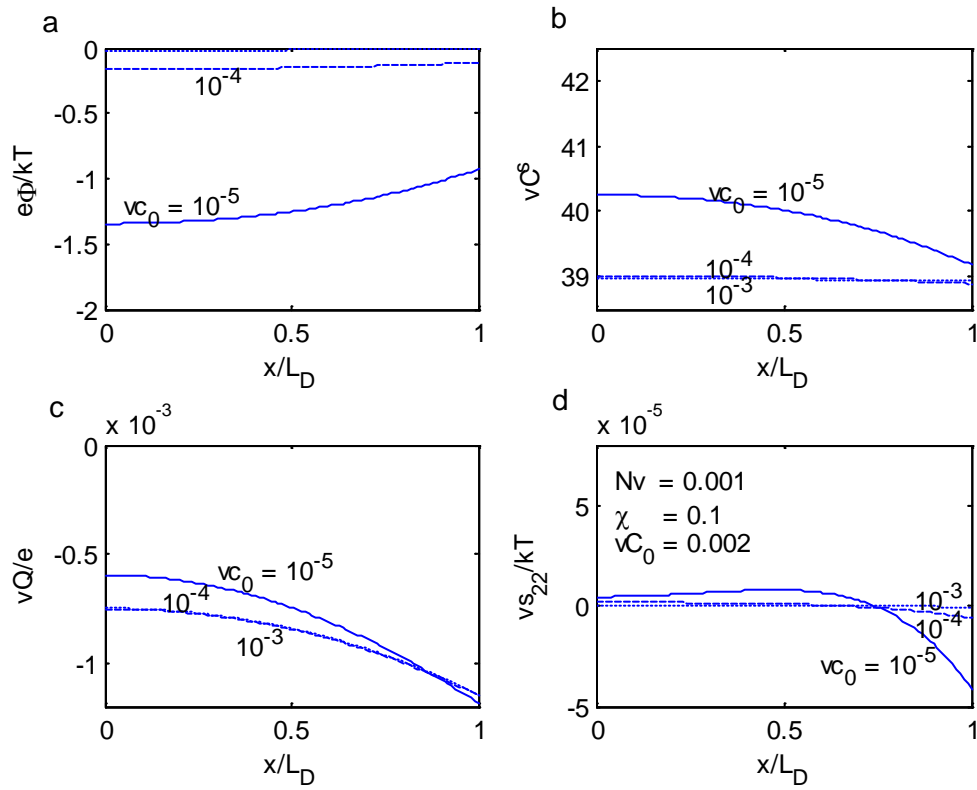
Figure 8 The inhomogeneous fields in a layer of a gel, of thickness twice the Debye length. (a) Electric potential. (b) Swelling ratio. (c) Electric charge. (d) Stress in a direction parallel to the interface.
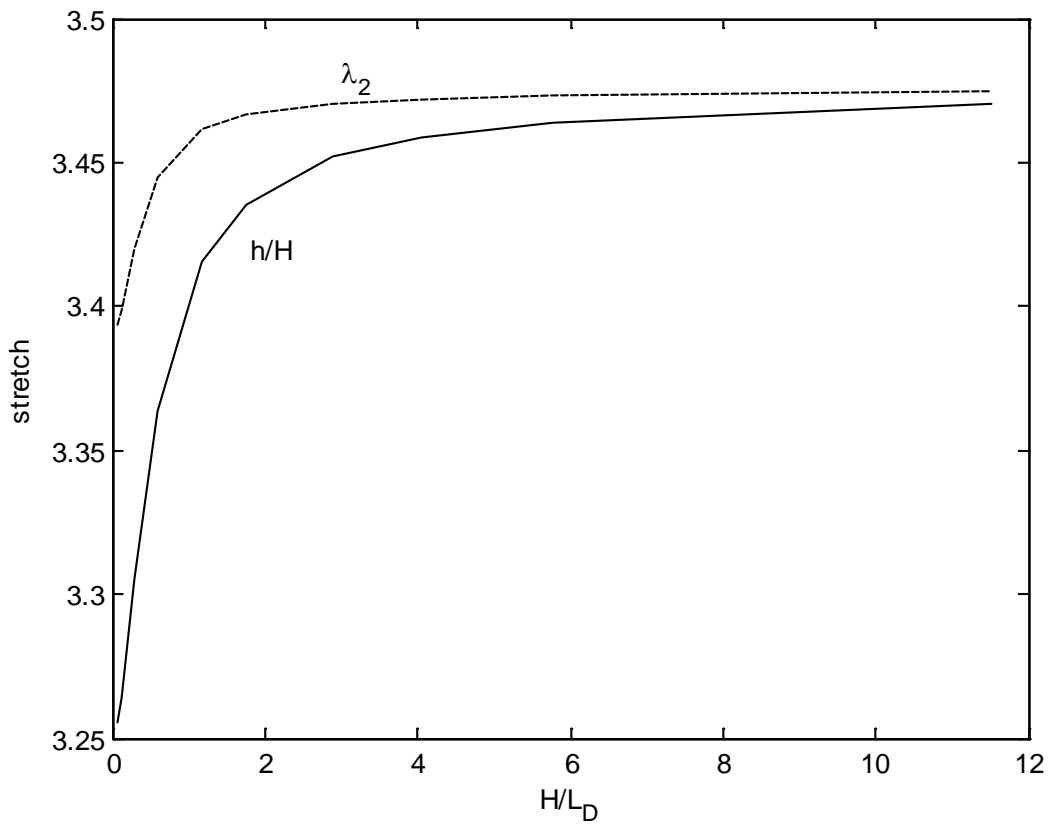
Figure 9. The amount of swelling as a function of the thickness of the gel. The concentration of the fixed charges is set to be $vC_0 = 0.002$, and the concentration of the ions in the external solution is set to be $vc_0 = 10^{-5}$.