Stretching and polarizing a dielectric gel immersed in a solvent

Xuanhe Zhao, Wei Hong and Zhigang Suo[a]
School of Engineering and Applied Sciences, Harvard University, Cambridge, MA 02138

Abstract

This paper studies a gel formed by a network of cross-linked polymers and a species of mobile molecules. The gel is taken to be a dielectric, in which both the polymers and the mobile molecules are nonionic. We formulate a theory of the gel in contact with a solvent made of the mobile molecules, and subject to electromechanical loads. A free-energy function is constructed for an ideal dielectric gel, including contributions from stretching the network, mixing the polymers and the small molecules, and polarizing the gel. We show that the free-energy function is non-convex, leading to instabilities. We also show that mechanical constraint markedly affects the behavior of the gel.

a) suo@seas.harvard.edu

1. Introduction

When a species of long polymers are cross-linked into a three-dimensional network, the resulting material, known as an elastomer, is capable of large elastic deformation. Another species of molecules, of a low molecular weight, and capable of weak bonding with one another and with the polymers, can act as a solvent. When the elastomer is immersed in the solvent, the small molecules diffuse into the interstitial space of the network. The cross links in the network prevent the polymers from dissolving; rather, the network swells. The aggregate of the swollen network and the small molecules is known as a gel. As the small molecules diffuse in and out, the gel swells and shrinks reversibly.

This paper studies the behavior of a gel immersed in a solvent and subject to electromechanical loads. Attention is restricted to dielectric gels, in which both the network and the solvent are nonionic. When a battery in an external circuit applies a voltage between two electrodes attached to the gel, the molecules in the gel polarize, and a certain amount of electric charge flows through the external circuit from one electrode to the other. We assume that no charged species migrate inside the gel. Dielectric gels may be used as sensors and actuators (Filipcsei et al., 2000; Hirai, 2007; Hirai et al., 1994; Hirai et al., 2000; Popovic et al., 2001; Zheng et al., 2000; Zrinyi et al., 2000).

Scientific study of gels dates back to 1940s. Much of the literature has focused on the statistical mechanics of swelling; for reviews see Flory (1953) , Treloar (1975), Li and Tanaka (1992), and Horkay and McKenna (2007). As the small molecules mix with the polymers, the network is stretched. While the mixing increases the number of configurations of the mixture, stretching decreases the number of configurations of the individual polymer chains. Thus, swelling is mainly an outcome of the competition between the entropy of mixing and the entropy of stretching. Their compromise equilibrates the gel and the solvent, setting the equilibrium amount of swelling.

There has also been a large body of literature on the continuum theory of gels. Gibbs (1878) formulated a theory of finite deformation of an elastic solid that absorbs a fluid, assuming that the solid and the fluid have reached equilibrium. Biot (1941) accounted for the transient process of the fluid migrating in the solid using Darcy's law. Lai et al. (1991) extended the theory to include the effects of ions and electric fields. More recent work has been discussed by, among many others, Durning and Morman (1993); Dolbow et al. (2004), Ji et al. (2006), Korchagin et al. (2007); Tsai et al. (2004); and Li, et al. (2007a; 2007b).

We are unaware of any continuum theory of dielectric gels subject to electromechanical loads. Such a theory can be in principle reduced from the existing theories of ionic gels. We are, however, uncertain of the ways in which electrical effects are introduced in the existing theories. In particular, we do not believe that Maxwell stresses have any general theoretical significance in dielectrics, and the effect of electric field on stress should be considered as part of material laws. Furthermore, since ionic gels and dielectric gels can behave very differently, it is worthwhile to formulate a theory explicitly for dielectric gels.

This paper focuses on homogeneous deformation of dielectric gels and its stability. The treatment extends recent work of Suo et al. (2007), Zhao et al. (2007), and Zhao and Suo (2007) on dielectric elastomers. We construct a free-energy function of dielectric gels, including contributions from stretching, mixing, and polarizing. We show that the Maxwell stresses have no theoretical significance for dielectrics in general, but can emerge from special form of the free-energy function. We then apply the theory to analyze the behavior of a gel under representative loading conditions. We show that mechanical constraint can markedly affect electromechanical behavior.

2. A network of polymers immersed in a solvent and subject to electromechanical loads

Figure 1 illustrates the system to be studied. A species of long polymers are cross-linked into a three-dimensional network, while a species of small molecules form a liquid solvent. In a reference configuration (Fig. 1a), the network and the solvent are separated from each other, and the network is a solid block of dimensions $L_1 L_2 L_3$, sandwiched between two electrodes. In the current configuration (Fig. 1b), the network is immersed in the solvent. The small molecules in the solvent migrate into the interstitial space of the network. The paper will focus on homogenous fields in the gel, assuming that the polymers and the small molecules have reached thermodynamic equilibrium.

Let M be the number of the small molecules in the gel, and denote the nominal concentration of the small molecules in the gel by

$$C = M / \left(L_1 L_2 L_3 \right). \tag{1}$$

The gel swells to dimensions $l_1 l_2 l_3$. Denote the stretches of the gel by

$$\lambda_1 = \frac{l_1}{L_1}, \quad \lambda_2 = \frac{l_2}{L_2}, \quad \lambda_3 = \frac{l_3}{L_3}. \tag{2}$$

Three weights apply forces F_1, F_2 and F_3 to the gel in three directions. Define the nominal stresses s_1, s_2 and s_3 in the gel by

$$s_1 = \frac{F_1}{L_2 L_3}, \quad s_2 = \frac{F_2}{L_3 L_1}, \quad s_3 = \frac{F_3}{L_1 L_2}. \tag{3}$$

The weights may be applied via compliant and porous presses, allowing the gel to deform without constraint, and the small molecules to enter or leave the gel freely. Denote the true stresses by $\sigma_1 = F_1 / (l_2 l_3)$, $\sigma_2 = F_2 / (l_3 l_1)$ and $\sigma_3 = F_3 / (l_1 l_2)$, which relate to the nominal stresses by $s_1 = \sigma_1 \lambda_2 \lambda_3$, $s_2 = \sigma_2 \lambda_3 \lambda_1$ and $s_3 = \sigma_3 \lambda_1 \lambda_2$.

Through an external circuit a battery applies a voltage Φ between the two electrodes. Denote the nominal electric field in the gel by

$$\tilde{E} = \frac{\Phi}{L_3}. \tag{4}$$

By contrast, denote the true electric field by $E = \Phi / l_3$, which relates to the nominal electric field by $\tilde{E} = E \lambda_3$.

The gel is taken to be a dielectric, and let Q be the magnitude of the electric charge on either of the two electrodes. Denote the nominal electric displacement in the gel by

$$\tilde{D} = \frac{Q}{L_1 L_2}. \tag{5}$$

Denote the true electric displacement by $D = Q / (l_1 l_2)$, which relates to the nominal electric displacement by $\tilde{D} = D \lambda_1 \lambda_2$.

Molecular incompressibility

We assume that both the individual polymers and the individual small molecules are incompressible. Furthermore, the void space inside the gel is negligible. Let v be the volume per small molecule. When the gel gains M small molecules, the volume of the gel changes from $L_1L_2L_3$ to $l_1l_2l_3 = L_1L_2L_3 + vM$. Dividing this expression by $L_1L_2L_3$, we obtain that

$$\lambda_1\lambda_2\lambda_3 = 1 + vC . \tag{6}$$

This equation expresses the condition of molecular incompressibility.

Consider a gel and an external liquid solvent both subject to a state of uniform hydrostatic stress. Under the condition of molecular incompressibility, the hydrostatic stress does no work when a small molecule relocates from the external liquid to the gel. Consequently, a uniform hydrostatic stress applied on both the gel and the external liquid does not affect the thermodynamic state of the system. We should emphasize that this conclusion only applies when the external solvent is liquid. If the external solvent is gaseous, however, the hydrostatic stress does do work when a small molecule relocates from the gas to the gel. In this paper, we will only consider incompressible liquid solvents.

Free-energy function, equations of state, and generalized modulus

The gel, the liquid, the weights, and the battery together constitute a thermodynamic system. Let W be the free energy of the gel in the current state divided by the volume of the polymer in the reference state. To be specific, assume that the weights apply constant forces

F_1, F_2, F_3 to the gel, and that the battery applies a constant voltage Φ between the two electrodes. When the gel deforms from dimensions $L_1 L_2 L_3$ to $l_1 l_2 l_3$, the potential energy of weights decreases by $F_1(l_1 - L_1) + F_2(l_2 - L_2) + F_3(l_3 - L_3)$. When an amount of charge Q flows through the external circuit from one electrode to the other, the potential energy of the battery reduces by ΦQ. The free energy of the system, G, is the sum of that of the gel, the weights, and the battery, given by

$$G = W\left(\lambda_1, \lambda_2, \lambda_3, \tilde{D}\right) L_1 L_2 L_3 - F_1(l_1 - L_1) - F_2(l_2 - L_2) - F_3(l_3 - L_3) - \Phi Q . \tag{7}$$

In writing (7), we enforce the condition of molecular incompressibility, so that the free-energy of the gel is a function of four generalized coordinates, $\lambda_1, \lambda_2, \lambda_3, \tilde{D}$.

Thermodynamics dictates that a stable equilibrium state of the system should minimize G. Let $\left(\lambda_1, \lambda_2, \lambda_3, \tilde{D}\right)$ be an equilibrium state. When the state varies slightly, from $\left(\lambda_1, \lambda_2, \lambda_3, \tilde{D}\right)$ to $\left(\lambda_1 + \delta\lambda_1, \lambda_2 + \delta\lambda_2, \lambda_3 + \delta\lambda_3, \tilde{D} + \delta\tilde{D}\right)$, the free energy of the system varies by

$$\begin{aligned}
\frac{\delta G}{L_1 L_2 L_3} = & \left(\frac{\partial W}{\partial \lambda_1} - s_1\right)\delta\lambda_1 + \left(\frac{\partial W}{\partial \lambda_2} - s_2\right)\delta\lambda_2 + \left(\frac{\partial W}{\partial \lambda_3} - s_3\right)\delta\lambda_3 + \left(\frac{\partial W}{\partial \tilde{D}} - \tilde{E}\right)\delta\tilde{D} \\
& + \frac{\partial^2 W}{2\partial \lambda_1^2}\delta\lambda_1^2 + \frac{\partial^2 W}{\partial \lambda_1 \partial \lambda_2}\delta\lambda_1\delta\lambda_2 + \frac{\partial^2 W}{\partial \lambda_1 \partial \lambda_3}\delta\lambda_1\delta\lambda_3 + \frac{\partial^2 W}{\partial \lambda_1 \partial \tilde{D}}\delta\lambda_1\delta\tilde{D} \\
& + \frac{\partial^2 W}{2\partial \lambda_2^2}\delta\lambda_2^2 + \frac{\partial^2 W}{\partial \lambda_2 \partial \lambda_3}\delta\lambda_2\delta\lambda_3 + \frac{\partial^2 W}{\partial \lambda_2 \partial \tilde{D}}\delta\lambda_2\delta\tilde{D} \\
& + \frac{\partial^2 W}{2\partial \lambda_3^2}\delta\lambda_3^2 + \frac{\partial^2 W}{\partial \lambda_3 \partial \tilde{D}}\delta\lambda_3\delta\tilde{D} \\
& + \frac{\partial^2 W}{2\partial \tilde{D}^2}\delta\tilde{D}^2
\end{aligned} \tag{8}$$

We have included the variation up to the second power of the variations of the generalized coordinates.

To ensure $\left(\lambda_1, \lambda_2, \lambda_3, \tilde{D}\right)$ minimize *G*, the coefficients of the first variations vanish, leading to

$$s_1 = \frac{\partial W}{\partial \lambda_1}, \quad s_2 = \frac{\partial W}{\partial \lambda_2}, \quad s_3 = \frac{\partial W}{\partial \lambda_3}, \quad \tilde{E} = \frac{\partial W}{\partial \tilde{D}}. \tag{9}$$

In deriving (9), we have regarded $s_1, s_2, s_3, \tilde{E}$ as the loading parameters set by the weights and the battery. We may also regard $s_1, s_2, s_3, \tilde{E}$ as functions of the generalized coordinates $\left(\lambda_1, \lambda_2, \lambda_3, \tilde{D}\right)$. Thus, once the free-energy function of the gel, $W\left(\lambda_1, \lambda_2, \lambda_3, \tilde{D}\right)$, is prescribed, (9) gives the equations of state of the gel.

When the generalized coordinates vary by small amounts, $\delta\lambda_1, \delta\lambda_2, \delta\lambda_3, \delta\tilde{D}$, to maintain equilibrium, (9) dictates that the loading parameters vary by $\delta s_1, \delta s_2, \delta s_3, \delta\tilde{E}$, such that

$$\begin{bmatrix} \delta s_1 \\ \delta s_2 \\ \delta s_3 \\ \delta\tilde{E} \end{bmatrix} = \begin{bmatrix} \frac{\partial^2 W}{\partial \lambda_1^2} & \frac{\partial^2 W}{\partial \lambda_1 \partial \lambda_2} & \frac{\partial^2 W}{\partial \lambda_1 \partial \lambda_3} & \frac{\partial^2 W}{\partial \lambda_1 \partial \tilde{D}} \\ & \frac{\partial^2 W}{\partial \lambda_2^2} & \frac{\partial^2 W}{\partial \lambda_2 \partial \lambda_3} & \frac{\partial^2 W}{\partial \lambda_2 \partial \tilde{D}} \\ & & \frac{\partial^2 W}{\partial \lambda_3^2} & \frac{\partial^2 W}{\partial \lambda_3 \partial \tilde{D}} \\ sym & & & \frac{\partial^2 W}{\partial \tilde{D}^2} \end{bmatrix} \begin{bmatrix} \delta\lambda_1 \\ \delta\lambda_2 \\ \delta\lambda_3 \\ \delta\tilde{D} \end{bmatrix} \tag{10}$$

The matrix in (10), known as the Hessian, linearly maps the changes in the generalized coordinates to the changes in the loading parameters. That is, the Hessian is the generalized tangent modulus. At a given equilibrium state $\left(\lambda_1, \lambda_2, \lambda_3, \tilde{D}\right)$, the Hessian is a symmetric matrix, and has four real eigenvalues, $K_I, K_{II}, K_{III}, K_{IV}$, arranged from small to large. Each eigenvector represents a mode of change in state, and the associated eigenvalue is the modulus of this mode. The four eigenvectors are orthogonal to one another.

Stability

To ensure that a state $\left(\lambda_1, \lambda_2, \lambda_3, \tilde{D}\right)$ minimizes G, the sum of the second derivatives in (8) must be positive for arbitrary variation of the generalized coordinates. This condition is equivalent to that the Hessian is positive-definite at $\left(\lambda_1, \lambda_2, \lambda_3, \tilde{D}\right)$, or that all four eigenvalues of the Hessian are positive, or that the function $W\left(\lambda_1, \lambda_2, \lambda_3, \tilde{D}\right)$ is convex at $\left(\lambda_1, \lambda_2, \lambda_3, \tilde{D}\right)$.

The generalized coordinates $\left(\lambda_1, \lambda_2, \lambda_3, \tilde{D}\right)$ form a space, which we can divide into regions of two kinds. In one kind, the free-energy function is convex, and in the other, the free energy is non-convex. The boundary of the two kinds of the regions is given by the equation

$$K_I\left(\lambda_1, \lambda_2, \lambda_3, \tilde{D}\right) = 0 . \tag{11}$$

This boundary generalizes the inflexion point of a function of one variable.

A positive-definite Hessian only guarantees meta-stability. Under this meta-stable condition, the free energy is a local minimum against small variations of the generalized coordinates, but not necessarily a global minimum against finite variations of the generalized coordinates. This paper will be restricted to the meta-stable condition. See Zhao, Hong and Suo (2007) for an example of global minimum that leads to coexistent states in a dielectric elastomer.

3. Free-energy function of ideal dielectric gels

To carry out calculations, we need an explicit form of the free-energy function. Our intention is to illustrate the general procedure, and to describe approximate behavior of dielectric gels. As such, we will adopt a simplest form of the free-energy function. To describe accurate behavior of a specific gel would require adding terms and parameters to fit experimental data, a task that is beyond the scope of this paper.

The free energy of a dielectric gel comes from several molecular processes: stretching the network of polymers, mixing the polymers and the small molecules, and polarizing the gel. We assume that the free energy of the gel takes the form

$$W = W_s + W_m + W_p , \tag{12}$$

where W_s , W_m and W_p are, respectively, the contributions of stretching, mixing and polarizing.

The free energy of stretching a network of polymers is taken to be (Flory, 1953)

$$W_s\left(\lambda_1, \lambda_2, \lambda_3\right) = \frac{1}{2} NkT\left(\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3 - 2\log\lambda_1\lambda_2\lambda_3\right), \tag{13}$$

where N is the number of chains in the gel divided by the volume of the gel in the reference state, and kT is the temperature in the unit of energy.

When the polymers are not cross-linked, the polymers and the small molecules can form a solution. The free energy of mixing is taken to be (Flory, 1942; Huggins, 1941)

$$W_m\left(C\right) = -\frac{kT}{v}\left[vC\log\left(1 + \frac{1}{vC}\right) + \frac{\chi}{1 + vC}\right]. \tag{14}$$

Here vC is the volume of the small molecules in the gel divided by the volume of the polymers. The first term inside of the bracket of (14) comes from the entropy of mixing, and the second from the enthalpy of mixing, where χ is a dimensionless parameter. The enthalpy of mixing, motivates the small molecules to enter the solution if $\chi < 0$, but motivates the small molecules to come out of the gel if $\chi > 0$. The change in the free energy associated with relocating one small molecule from the liquid to the gel is

$$\frac{dW_m}{dC} = kT\left[\log\frac{vC}{1+vC} + \frac{1}{1+vC} + \frac{\chi}{(1+vC)^2}\right]. \tag{15}$$

We are interested in gels that contain mostly small molecules, namely, vC >> 1. As an approximation, we assume that the gel has a dielectric energy of the same form as a liquid, with a constant permittivity ε. Thus, the dielectric energy per unit current volume is $D^2/(2\varepsilon)$. Consequently, in terms of the nominal electric displacement $\tilde{D}$, the dielectric energy in the current state divided by the volume in the reference configuration is

$$W_p = \frac{\lambda_3\tilde{D}^2}{2\varepsilon\lambda_1\lambda_2}. \tag{16}$$

When the dielectric behavior of a gel is the same as that of a liquid, we refer to the gel as an ideal dielectric gel.

Partitioning the free energy of a gel into additive parts is itself an approximation. The approximation dates back at least to Flory and Rehner (1943a; 1943b) who, in a model of swelling, expressed the free energy of a gel as the sum of the free energy of stretching and the free energy of mixing. More recently, Zhao et al. (2007) modeled a dielectric elastomer by adding the free energy of stretching and the free energy of polarization. A justification of such a partition is as follows. The network of polymers has a low density of cross links, so that the processes of mixing and polarizing are nearly unaffected by stretching. Furthermore, we are mainly interested in a gel that contains a small volume fraction of polymers, but a large volume fraction of small molecules, so that the dielectric behavior of the gel is expected to be similar to that of the liquid solvent.

Substituting the above free-energy function into (9), we obtain the equations of the state of the model dielectric gel:

$$s_1 = NkT\left(\lambda_1 - \lambda_1^{-1}\right) + \frac{\lambda_2\lambda_3}{v}\frac{dW_m(C)}{dC} - \frac{\lambda_3\tilde{D}^2}{2\varepsilon\lambda_1^2\lambda_2} \tag{17a}$$

$$s_2 = NkT\left(\lambda_2 - \lambda_2^{-1}\right) + \frac{\lambda_3\lambda_1}{v}\frac{dW_m(C)}{dC} - \frac{\lambda_3\tilde{D}^2}{2\varepsilon\lambda_1\lambda_2^2} \tag{17b}$$

$$s_3 = NkT\left(\lambda_3 - \lambda_3^{-1}\right) + \frac{\lambda_1\lambda_2}{v}\frac{dW_m(C)}{dC} + \frac{\tilde{D}^2}{2\varepsilon\lambda_1\lambda_2} \tag{17c}$$

$$\tilde{E} = \frac{\lambda_3\tilde{D}}{\varepsilon\lambda_1\lambda_2} \tag{17d}$$

These equations can also be expressed in terms of the true quantities:

$$\sigma_1 = NkT\left(\lambda_1 - \lambda_1^{-1}\right)\lambda_2^{-1}\lambda_3^{-1} + \frac{1}{v}\frac{dW_m(C)}{dC} - \frac{1}{2}\varepsilon E^2 \tag{18a}$$

$$\sigma_2 = NkT\left(\lambda_2 - \lambda_2^{-1}\right)\lambda_3^{-1}\lambda_1^{-1} + \frac{1}{v}\frac{dW_m(C)}{dC} - \frac{1}{2}\varepsilon E^2 \tag{18b}$$

$$\sigma_3 = NkT\left(\lambda_3 - \lambda_3^{-1}\right)\lambda_1^{-1}\lambda_2^{-1} + \frac{1}{v}\frac{dW_m(C)}{dC} + \frac{1}{2}\varepsilon E^2 \tag{18c}$$

$$D = \varepsilon E \tag{18d}$$

In the expressions for the three stresses, the first terms are the elastic stresses caused by stretching the network of polymers, the second terms are the osmotic pressure due to the inability of the polymers to leave the gel, and the third terms are due to the electric field. The third terms coincide with the Maxwell stresses because we have assumed that the dielectric behavior of the gel is the same as that of a liquid. In general, however, the effect of the electric field on the stresses may take other forms. For example, if the permittivity ε is a function of the concentration *C*, more terms involving the electric displacement need be added to (17).

In following calculations, we will normalize the stresses by kT/v, the electric field by $\sqrt{kT/(v\varepsilon)}$ and the electric displacement by $\sqrt{\varepsilon kT/v}$. A representative value of the volume per molecule is $v = 10^{-28}\mathrm{m}^3$. At room temperature, $kT = 4\times 10^{-21}$J, and $kT/v = 4\times 10^{7}$ Pa. Taking $\varepsilon = 10^{-10}$ F/m, we find that $\sqrt{kT/(v\varepsilon)} = 6.3\times 10^{8}$ V/m, and $\sqrt{\varepsilon kT/v} = 6.3\times 10^{-2}$ C/m^2.

The model has two dimensionless material parameters: Nv and χ, which are readily changed in experiments. For example, χ may be varied by temperature, and the degree of cross-linking may be varied by enzymes. In the absence of small molecules, the cross-linked polymers has shear modulus *NkT* under the small-strain conditions, with the representative values $NkT = 10^4 - 10^7$ N/m^2, which gives the range $Nv = 10^{-4} - 10^{-1}$. The parameter χ is a dimensionless measure of the enthalpy of mixing, with representative values χ = $0.2 - 1.2$.

The free energy is a function of four variables, $W(\lambda_1, \lambda_2, \lambda_3, \tilde{D})$. We have not found a useful way to display this function in all its variables. Instead, we will discuss some representative cases.

4. Actuation under biaxial constraint

Consider a layer of a gel bonded to a rigid substrate, which constrains the in-plane stretches, $\lambda_1 = \lambda_2$, to a fixed value. A battery applies voltage Φ across the thickness of the layer. No weight is applied, and the gel is free to swell or shrink in the normal direction.

The system has two degrees of freedom, λ_3 and $\tilde{D}$, so that the Hessian reduces to a two-by-two matrix. The condition $K_I\left(\lambda_3, \tilde{D}\right) = 0$ is a curve that divides the plane $\left(\lambda_3, \tilde{D}\right)$ into two regions (Fig. 2). In the region above the curve, the free-energy function $W\left(\lambda_3, \tilde{D}\right)$ is non-convex; in the region below, the free-energy function is convex.

Because no weight is applied, $s_3 = 0$, so that (17c) becomes

$$Nv\left(\lambda_3 - \lambda_3^{-1}\right) + \lambda_1^2\left[\log\left(1 - \lambda_1^{-2}\lambda_3^{-1}\right) + \lambda_1^{-2}\lambda_3^{-1} + \chi\lambda_1^{-4}\lambda_3^{-2}\right] + \frac{\tilde{D}^2}{2\lambda_1^2\left(\varepsilon kT / v\right)} = 0 . \qquad (19)$$

This equation represents a loading path in the $\left(\lambda_3, \tilde{D}\right)$ plane, and is also plotted in Fig. 2. As the charge on the electrodes increases, the thickness of the gel decreases. The loading path lies in the region in which the free-energy function is convex. Consequently, the loading path consists of a sequence of stable states.

Figure 3 plots several quantities as functions of the nominal electric displacement, when the in-plane stretches are constrained at several values. Figure 3a is plotted by using (17d) and (19), regarding λ_3 as a parameter. The nominal electric field increases monotonically with the nominal electric displacement. When the in-plane stretches are constrained at a larger value, the same applied voltage can induce more charges on the electrodes. Figure 3b shows that the true electric field is linear in the nominal electric displacement, as expected from (17d). Figure 3c plots (19) for several fixed values of the in-plane stretches, indicating that the gel thins down as the charges on the electrodes increase. Recall the condition of molecular incompressibility, $1 + vC = \lambda_1^2\lambda_3$. Figure 3d plots vC as a function of the nominal electric displacement. The in-plane constraint markedly affects the amount of swelling: the larger the in-plane stretches are, the more the gel swells.

5. Unconstrained actuation

Consider a layer of a gel sandwiched between flexible electrodes. A battery applies a voltage, therefore $\tilde{E}$, across the thickness of the gel. No weight is applied, and the gel is free to swell in all three directions. The three stretches obey $\lambda_1 = \lambda_2 \neq \lambda_3$, and the system has three degrees of freedom, λ_1, λ_3 and $\tilde{D}$.

The Hessian reduces to a three-by-three matrix. The condition $K_I\left(\lambda_1, \lambda_3, \tilde{D}\right) = 0$ is a surface that divides the space $\left(\lambda_1, \lambda_3, \tilde{D}\right)$ into two regions (Fig. 4). In the region above the surface, the free-energy function $W\left(\lambda_1, \lambda_3, \tilde{D}\right)$ is non-convex; in the region below, the free-energy function is convex. Because no weights are applied, $s_1 = 0$ and $s_3 = 0$. These two conditions are two surfaces in the space $\left(\lambda_1, \lambda_3, \tilde{D}\right)$, and are also included in Fig. 4. The intersection of the two surfaces defines a loading path. As $\tilde{D}$ increases, the gel reduces its thickness and increases its lateral dimensions. When $\tilde{D}$ is small, the loading path falls in the region in which the free-energy function is convex. When $\tilde{D}$ is large, however, the loading path falls in the region in which the free energy function is non-convex. The loading path intersects with the surface $K_I\left(\lambda_1, \lambda_3, \tilde{D}\right) = 0$ at a point, which defines a critical condition $\left(\lambda_1^c, \lambda_3^c, \tilde{D}^c\right)$.

To understand the physical origin of the critical condition, Fig. 5 plots the electromechanical responses of the gel. In plotting these figures, we set $s_1 = s_3 = 0$ in (17a) and (17c), and solve the two nonlinear equations to obtain λ_1 and λ_3 for any given $\tilde{D}$. Figure 5a plots the nominal electric field as a function of the nominal electric displacement. By definition, $\tilde{E} = \Phi / L_3$ and $\tilde{D} = Q/(L_1 L_2)$. Because L_1, L_2, L_3 remain fixed during deformation, Fig. 5a is a normalized charge-voltage plot. When the voltage is small, the charge increases with the voltage. When the voltage is large enough, the gel thins down significantly, inducing a large true electric field in the gel. Consequently, to further increases the charge, the voltage needed reduces. The peak voltage corresponds to the critical condition. The critical condition is marked by crosses in all other plots in Fig. 5.

Figure 5d indicates that the lower the enthalpy of mixing is, the more the gel swells, as expected. Note that the amount of swelling remains nearly constant. That is, the electric voltage causes the gel to reduce the thickness and expand in the lateral directions, with the volume of the gel being nearly constant. Consequently, the actuation requires no long-range transport of small molecules, and is expected to be fast. In this case, once the gel is formed, the external liquid becomes superfluous, so that the actuator need not operate in the presence of the liquid.

6. Concluding remarks

This paper formulates a theory of a dielectric gel immersed in a solvent and subject to electromechanical loads. We find that the Maxwell stress has no general theoretical significance in dielectrics, but can emerge as part of special material laws. We show that the free-energy function of a dielectric gel is non-convex, leading to electromechanical instabilities.

We also show that mechanical constraint markedly affects the behavior of the gel. We expect that the theory can be used to analyze diverse phenomena found in dielectric gels.

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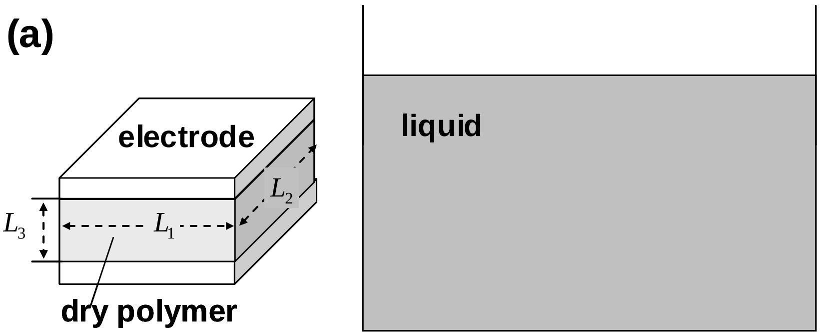
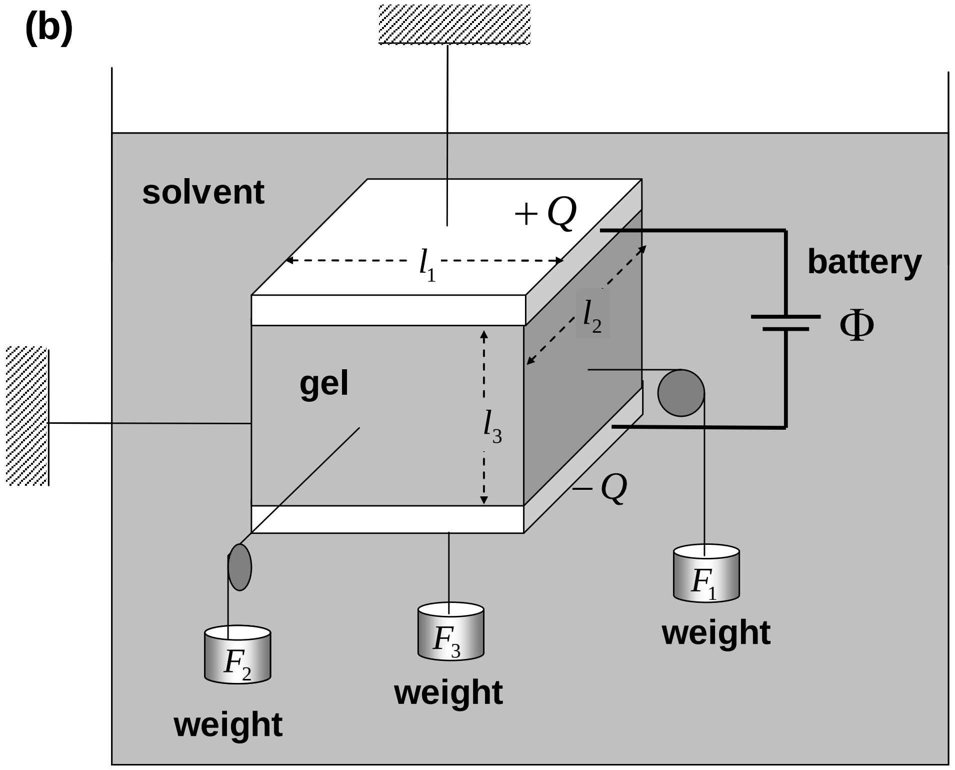


Reference Configuration



Current State

Figure 1 A species of polymers form a cross-linked network, which is then sandwiched between two electrodes. A species of small molecules form a liquid. (a) In the reference state, no weights or battery are applied on the elastomeric block, and no small molecules exist inside the block. The block is an elastomer with dimensions $L_1 L_2 L_3$. (b) In the current state, the elastomeric block is immersed in the liquid, which acts as a solvent. As the small molecules enter the interstitial space of the polymers, the combination forms a gel. Three weights apply forces F_1, F_2 and F_3 on the gel in three directions, while a battery applies a voltage Φ between the two electrodes. In equilibrium, M small molecules enter the block, the gel has dimensions $l_1 l_2 l_3$, and an amount of change Q flows from one electrode to the other through the external circuit.

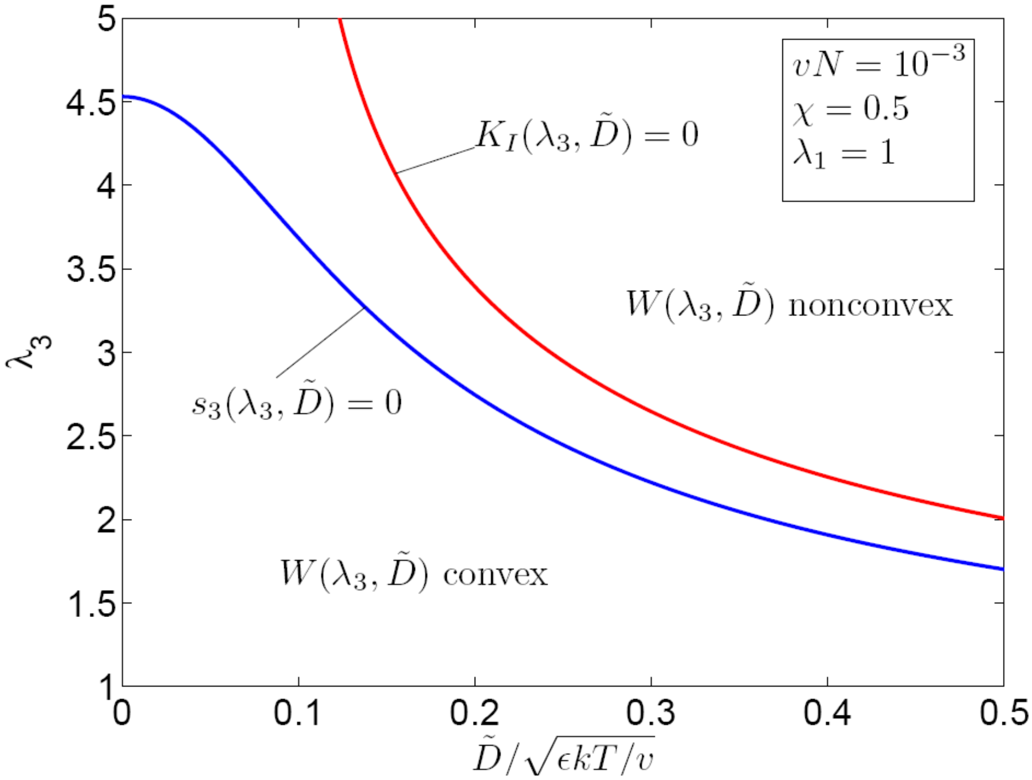


Figure 2. A gel ($\chi = 0.5$ and $Nv = 10^{-3}$) is subject to biaxial constraint $\lambda_1 = \lambda_2 = 1$, and to a voltage. The system has two degrees of freedom, λ_3 and $\tilde{D}$. The curve $K_I(\lambda_3, \tilde{D}) = 0$ divides the plane into two regions: $W(\lambda_3, \tilde{D})$ nonconvex and $W(\lambda_3, \tilde{D})$ convex. The loading path $s_3(\lambda_3, \tilde{D}) = 0$ lies in the region in which the free energy function is convex.

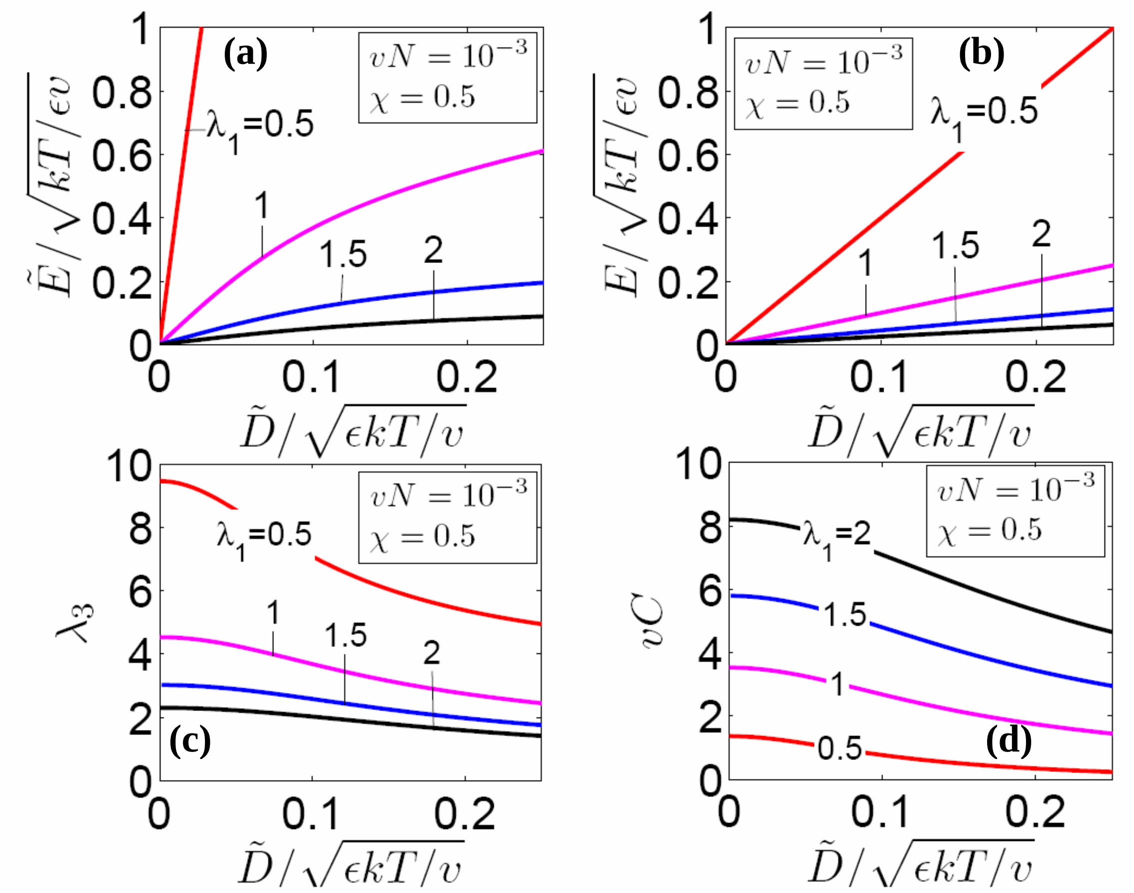


Figure 3. A gel ($\chi = 0.5$ and $Nv = 10^{-3}$) is subject to biaxial constraint and to a voltage. The variations of $\tilde{E}$, E, λ_3 and vC are plotted as functions of $\tilde{D}$. The biaxial constraint is set at several levels, λ_1 = 0.5, 1, 1.5, and 2.

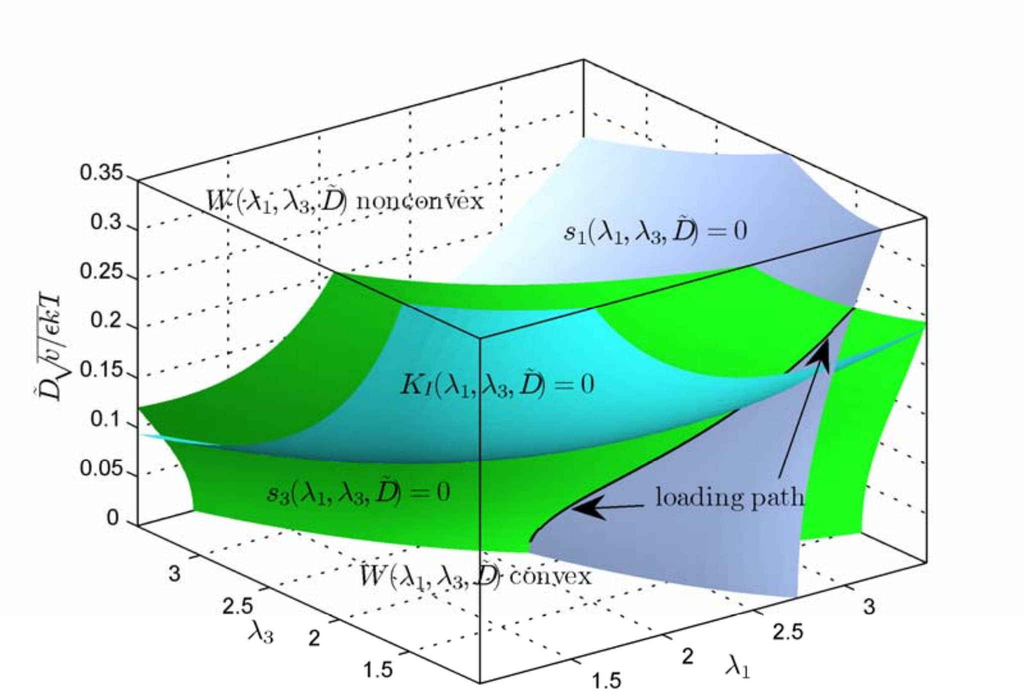


Figure 4. A gel ($\chi = 0.5$ and $Nv = 10^{-3}$) is subject to a voltage and can deform freely in three direction. The system has three degrees of freedom, λ_1, λ_3 and $\tilde{D}$. The surface of $K_I(\lambda_1, \lambda_3, \tilde{D}) = 0$ divides the space into two regions: $W(\lambda_1, \lambda_3, \tilde{D})$ nonconvex and $W(\lambda_1, \lambda_3, \tilde{D})$ convex. The conditions of $s_3 = 0$ and $s_1 = 0$ give another two surfaces, the intersection of which represents the loading path. It can be seen that only part of the loading path is in the convex $W(\lambda_1, \lambda_3, \tilde{D})$ region.

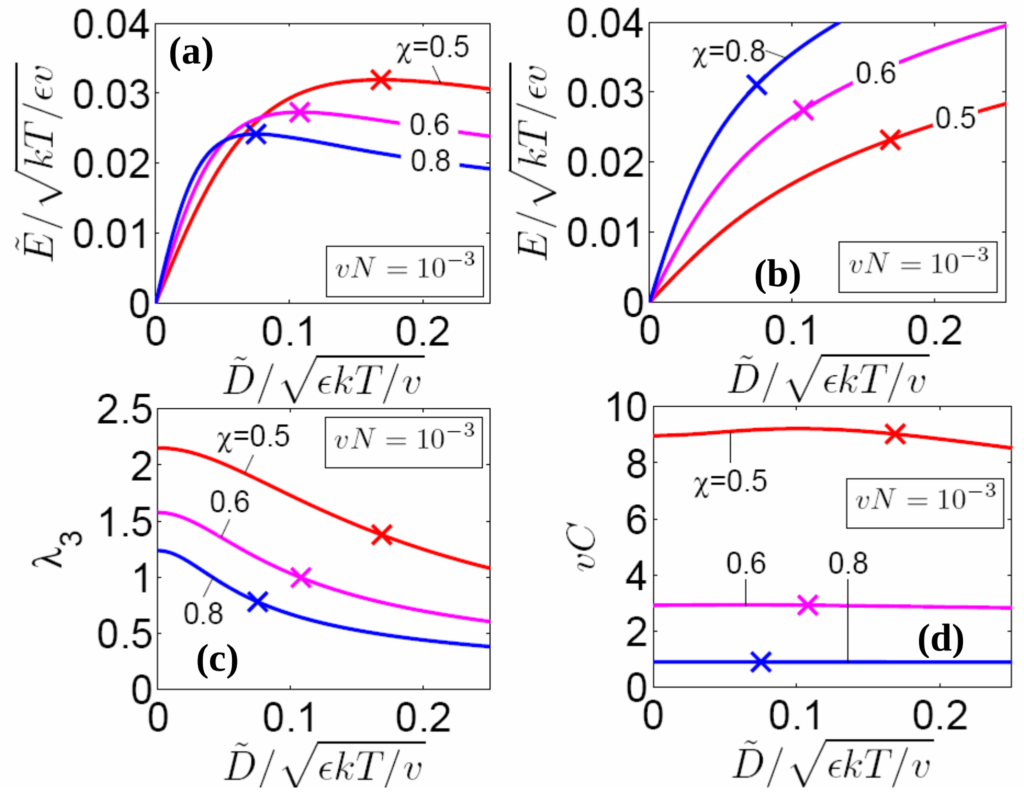


Figure 5. A gel is subject to a potential $\tilde{E}$ and no weights $s_1 = s_2 = s_3 = 0$. The variations of $\tilde{E}$, E, λ_3 and vC are plotted as functions of $\tilde{D}$ for $Nv = 10^{-3}$ and several values of χ. The critical points for noncovexity of $W(\lambda_1, \lambda_3, \tilde{D})$ are marked as crosses.