



Inhomogeneous swelling of a gel in equilibrium with a solvent and mechanical load

Wei Hong^{a,1}, Zishun Liu^b, Zhigang Suo^{a,*}

^a School of Engineering and Applied Sciences, Harvard University, Cambridge, MA 02138, USA

^b Institute of High Performance Computing, 1 Fusionopolis Way, #16-16 Connexis, Singapore 138632, Singapore

ARTICLE INFO

Article history:

Received 7 May 2008

Received in revised form 17 November 2008

Available online 6 May 2009

Keywords:

Elastomer

Gel

Swelling

Hyperelasticity

Finite element method

ABSTRACT

A network of polymers can imbibe a large quantity of a solvent and swell, resulting in a gel. The swelling process can be markedly influenced by a mechanical load and geometric constraint. When the network, solvent, and mechanical load equilibrate, inside the gel the chemical potential of the solvent is homogeneous, but the concentration of the solvent and the deformation of the network can be inhomogeneous. We use the chemical potential of the solvent and the deformation gradient of the network as the independent variables of the free-energy function, and show that the boundary value problem of the swollen gel is equivalent to that of a hyperelastic solid. We implement this approach in the finite-element package, ABAQUS, and analyze examples of swelling-induced deformation, contact, and bifurcation. Because commercial software like ABAQUS is widely available, this work may provide a powerful tool to study complex phenomena in gels.

© 2009 Elsevier Ltd. All rights reserved.

1. Introduction

Flexible, long-chained polymers can crosslink by covalent bonds into a three-dimensional network. The resulting material, an elastomer, is capable of large and reversible deformation. When the elastomer is brought in contact with a solvent, the elastomer imbibes the solvent and swells, resulting in an aggregate known as a gel. The swelling is also reversible: when the environment dries, the solvent in the gel migrates out and evaporates. The gel has attributes of both a solid and a liquid: elastic deformation results from strong chemical crosslinks between the long-chained polymers, and viscous migration results from weak physical association between the long-chained polymers and the solvent molecules.

The unusual combination of the attributes makes gels the materials of choice for diverse applications, such as medical devices (Wichterle and Lim, 1960; Peppas et al., 2006), tissue engineering (Lee and Mooney, 2001; Wong et al., 2008), actuators responsive to physiological cues (Beebe et al., 2000; Dong et al., 2006; Cho et al., 2008), and packers in oil wells (Kleverlaan et al., 2005). Mixtures of macromolecular networks and solvents also constitute tissues in plants and animals, where the networks retain structural forms, while the solvents enable the transport of nutrients and wastes.

As noted in our previous paper (Hong et al., 2008a), a gel can undergo large deformation of two modes. The first mode results from the fast process of short-range rearrangement of molecules, allowing the gel to change shape but not volume. The second mode results from the slow process of long-range migration of the solvent molecules, allowing the gel to change both shape and volume. When a gel is subject to a sudden change in the environment, for example, a change in the mechanical load or in the chemical potential of the solvent, the gel adapts to the new environment by co-evolving the shape of the network and the distribution of the solvent molecules. Two limiting states can be identified. In the short-time limit, the solvent molecules inside the gel do not yet have time to redistribute, but the mechanical equilibrium has already been established. In the long-time limit, the gel has reached the equilibrium with both the mechanical load and the external solvent, so that the chemical potential of the solvent molecules is homogeneous throughout the gel, and is prescribed by the external solvent. The evolution from one limit to the other takes time, because the solvent molecules have to migrate in the gel. For example, the time to equilibrate a sphere of a gel to a solvent scales with the square of the diameter of the sphere.

We will focus on the long-time limit, namely, the state of equilibrium achieved when a network has been in contact with a solvent for a long time. In the absence of mechanical load or geometric constraint, a homogenous network equilibrates with a solvent by a homogenous and isotropic field of deformation. Such free swelling, however, rarely occurs in practice. Inhomogeneous or anisotropic state of equilibrium occurs, for example, when the network itself is in any way modulated (e.g., Hu et al., 1995; Klein et al., 2007; Ladet et al., 2008), or when the network is subject to a

* Corresponding author. Tel.: +1 617 4953789; fax: +1 617 4960601.

E-mail address: suo@seas.harvard.edu (Z. Suo).

¹ Present address: Department of Aerospace Engineering, Iowa State University, Ames, IA 50011, USA.

mechanical load or geometric constraint (e.g., Kim et al., 2006). Swelling can induce cavitation, debonding, creasing, and other forms of instability (e.g., Southern and Thomas, 1965; Sidorenko et al., 2007; Hong et al., 2008b; Trujillo et al., 2008; Zhang et al., 2008).

This paper describes a finite element method on the basis of a nonlinear field theory of swelling due to Gibbs (1878). We show that the inhomogeneous field in a gel equilibrated with a solvent is equivalent to the field in a compressible hyperelastic solid. We implement this theory as a user-supplied subroutine in the finite-element package, ABAQUS. This implementation enables us to use various two- and three-dimensional elements to analyze diverse phenomena, including large deformation, contact, and bifurcation. Because commercial software like ABAQUS is widely available, we hope that this work will enable other people to analyze complex phenomena in gels without spending much time on coding. The user-supplied subroutine is posted online, <<http://imechanica.org/node/3163>>.

It is sometimes proposed that swelling of a gel may be simulated by prescribing a volumetric strain. This practice is erroneous when swelling is anisotropic or inhomogeneous. As we will show, in general the volumetric strain cannot be prescribed, but should be solved as a part of a boundary value problem. Indeed, the volumetric strain can be inhomogeneous and can depend on the state of stress.

Our method builds upon the work of Gibbs (1878), who formulated a thermodynamic theory of nonlinear fields associated with mobile molecules in an elastic solid. Biot (1941) combined the thermodynamic theory and Darcy's law for mass transport in a porous medium. Both Gibbs and Biot used phenomenological free-energy functions, and their works were not specific for polymeric gels. Using statistical mechanics, Flory and Rehner (1943) developed a free-energy function for a polymeric gel, including the effects of the entropy of stretching the network, the entropy of mixing the network polymers and the solvent molecules, and the enthalpy of mixing. For reviews of subsequent theoretical contributions, see reviews by Treloar (1975), Sekimoto (1991), Durning and Morman (1993), Baek and Srinivasa (2004), Dolbow et al. (2005), Bassetti et al. (2005), Hui and Muralidharan (2005), Li et al. (2007), Westbrook and Qi (2008), and Hong et al. (2008a). An approach different from that of Gibbs (1878), known as the mixture theory, has been developed (e.g., Atkin and Craine, 1976; Rajagopal and Tao, 1995; Shi et al., 1981; Rajagopal et al., 1986; Gandhi and Usman, 1989a). It is beyond the scope of this paper to compare various theoretical approaches. Rather, this paper is focused on implementing a numerical method on the basis of the theory of Gibbs (1878).

A body of literature exists on analyzing gels swollen under various boundary conditions, using analytical or semi-analytical methods. For example, Treloar (1950) analyzed swelling in various homogenous but anisotropic states of strain. Sternstein (1972) and Zhao et al. (2008) analyzed swelling under spherical symmetry, such as swelling of a shell of a gel around a sphere of a rigid core. Treloar (1976), Gandhi and Usman (1989b), and Demirkoparan and Pence (2007) analyzed swelling under cylindrical symmetry. Gandhi et al. (1989) solved a swollen cylinder under combined extension and torsion. Gandhi et al. (1995) and Tsai et al. (2004) analyzed flexure of a rectangular block due to a bending moment or inhomogeneous swelling. Some of these analyses will be used to test our numerical method.

2. Equilibrium condition in variational forms

Fig. 1 illustrates a network of polymers in contact with a solvent, subject to a mechanical load and geometric constraint, and held at a constant temperature. We take the stress-free dry

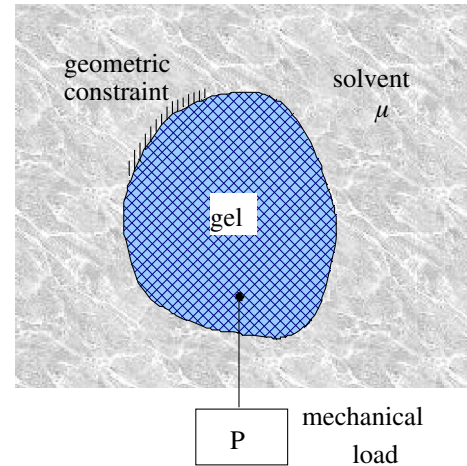


Fig. 1. A gel is in contact with a solvent of a fixed chemical potential, and is subject to a mechanical load and a geometric constraint.

network as the reference state, and name each small part of the network after its coordinate \mathbf{X} in the reference state. Let $dV(\mathbf{X})$ be an element of volume, $dA(\mathbf{X})$ be an element of area, and $N_K(\mathbf{X})$ be the unit vector normal to the element of area. In a deformed state, this part of the network moves to a place with the coordinate $x_i(\mathbf{X})$. The deformation gradient of the network is

$$F_{iK} = \frac{\partial x_i(\mathbf{X})}{\partial X_K}. \quad (1)$$

In the deformed state, let $C(\mathbf{X})dV(\mathbf{X})$ be the number of solvent molecules in the element of volume. The field $x_i(\mathbf{X})$ describes the deformation of the network, while the field $C(\mathbf{X})$ describes the distribution of the solvent molecules in the gel. The combination of the two fields describes the state of the gel.

In a deformed state, let $B_i(\mathbf{X})dV(\mathbf{X})$ be the external mechanical force applied on the element of volume, and $T_i(\mathbf{X})dA(\mathbf{X})$ be the external mechanical force applied on the element of area. When the network deforms by a small amount, $\delta x_i(\mathbf{X})$, the field of mechanical load does work $\int B_i \delta x_i dV + \int T_i \delta x_i dA$. The integrals extend over the volume and the surface of the network in the reference state.

The external solvent can be either a gas, or a pure liquid equilibrated with its own vapor. We take the latter to be the reference state of the solvent, where the chemical potential is set to be zero. We take the liquid solvent to be incompressible, and denote v as the volume per solvent molecule, and p_0 as the vapor pressure. When the solvent is subject to a pressure p greater than the vapor pressure, $p > p_0$, the solvent is in the liquid phase, and the chemical potential of the solvent molecules is $\mu = v(p - p_0)$. When the solvent is subject to a pressure p less than the vapor pressure, $p < p_0$, the solvent in equilibrium becomes a gas, which we assume to be an ideal gas, so that the chemical potential of the solvent molecules is $\mu = kT(p/p_0)$, where kT is the absolute temperature in the unit of energy. When the field of concentration in the gel changes by $\delta C(\mathbf{X})$, the external solvent does work $\mu \int \delta C dV$.

Let $W dV(\mathbf{X})$ be the Helmholtz free energy of the gel in the element of volume. We assume that the free-energy density of the gel, W , is a function of the deformation gradient of the network, \mathbf{F} , and the concentration of the solvent in the gel, C . Later we will adopt an explicit form of the free-energy function $W(\mathbf{F}, C)$, but for the time being this function is kept general. When the gel equilibrates with the solvent and the mechanical load, the chemical potential of the solvent molecules is homogeneous in the external solvent and in the gel:

$$\mu = \frac{\partial W(\mathbf{F}, C)}{\partial C}. \quad (2)$$

This thermodynamic equation will also be derived in the next section.

Now let the gel be in a state of equilibrium characterized by the two fields, $x_i(\mathbf{X})$ and $C(\mathbf{X})$. Thermodynamics dictates that the change in the free energy of the gel should equal the sum of the work done by the external mechanical force and by the external solvent, namely,

$$\int \delta W dV = \int B_i \delta x_i dV + \int T_i \delta x_i dA + \mu \int \delta C dV. \quad (3)$$

This equation holds for any small changes $\delta \mathbf{x}$ and δC from the state of equilibrium.

Introduce another free-energy function \widehat{W} by using a Legendre transformation:

$$\widehat{W} = W(\mathbf{F}, C) - \mu C. \quad (4)$$

Once the function $W(\mathbf{F}, C)$ is prescribed and the differential is taken, (2) is an algebraic equation, from which we can express C as a function of \mathbf{F} and μ . Consequently, (4) defines \widehat{W} as a function of the deformation gradient of the network and the chemical potential of the solvent molecules, $\widehat{W}(\mathbf{F}, \mu)$.

A combination of (3) and (4) gives that

$$\int \delta \widehat{W} dV = \int B_i \delta x_i dV + \int T_i \delta x_i dA. \quad (5)$$

As noted above, when the gel is in a state of equilibrium, the chemical potential of the solvent molecules inside the gel is homogenous and is equal to the chemical potential of the external solvent, μ . Indeed, the chemical potential plays a role analogous to that of the temperature. The equilibrium condition (5) takes the same form as that for a hyperelastic solid. Once the function $\widehat{W}(\mathbf{F}, \mu)$ is prescribed, we can implement a finite element method. Note that the theory has no intrinsic length scale, so that the field can only depend on lengths coming from the boundary conditions. Readers mainly interested in the implementation of this approach may wish to skip the following two sections and go directly to Section 5.

3. Equilibrium condition in differential forms

As a digression, following a tradition in continuum mechanics, we now reduce the equilibrium condition of the variational forms to that of differential forms. We have assumed that the free-energy density takes the functional form $W(\mathbf{F}, C)$. Associated with a small change in the deformation gradient of the network, δF_{iK} , and a small change in the concentration of the solvent molecules, δC , the free-energy density changes by

$$\delta W = \frac{\partial W(\mathbf{F}, C)}{\partial F_{iK}} \delta F_{iK} + \frac{\partial W(\mathbf{F}, C)}{\partial C} \delta C. \quad (6)$$

Substituting (6) into the equilibrium condition (3), and applying the divergence theorem, we obtain that

$$\int \left(\frac{\partial}{\partial X_K} \frac{\partial W}{\partial F_{iK}} + B_i \right) \delta x_i dV + \int \left(T_i - \frac{\partial W}{\partial F_{iK}} N_K \right) \delta x_i dA + \int \left(\mu - \frac{\partial W}{\partial C} \right) \delta C dV = 0. \quad (7)$$

In equilibrium, (7) holds for arbitrary changes δx_i and δC , so that the quantity in each pair of parentheses in (7) vanishes. Consequently, the equilibrium condition is equivalent to (2), along with

$$\frac{\partial}{\partial X_K} \frac{\partial W(\mathbf{F}, C)}{\partial F_{iK}} + B_i = 0 \quad (8)$$

in the volume of the gel, and

$$\frac{\partial W(\mathbf{F}, C)}{\partial F_{iK}} N_K = T_i \quad (9)$$

on the surface of the gel.

Define nominal stress as the work conjugate to the deformation gradient, so that

$$s_{iK} = \frac{\partial W(\mathbf{F}, C)}{\partial F_{iK}}. \quad (10)$$

This nominal stress gives (8) and (9) the familiar interpretation as the conditions for mechanical equilibrium. Using (2) and (10), we rewrite (6) as

$$\delta W = s_{iK} \delta F_{iK} + \mu \delta C. \quad (11)$$

A combination of (4) and (11) gives that

$$\delta \widehat{W} = s_{iK} \delta F_{iK} - C \delta \mu, \quad (12)$$

so that

$$s_{iK} = \frac{\partial \widehat{W}(\mathbf{F}, \mu)}{\partial F_{iK}}, \quad (13)$$

$$C = - \frac{\partial \widehat{W}(\mathbf{F}, \mu)}{\partial \mu}. \quad (14)$$

4. Molecular incompressibility

The often used analogy between a gel and a sponge is misleading in an important respect. When liquid drains from a sponge, pores remain inside the sponge and are filled with air. When solvent migrates out of a gel, however, the network of polymers contracts and leaves essentially no pores inside. Also, mechanical forces applied to gels are usually so small that chemical bonds in the gels are essentially undeformed. Furthermore, the volumetric change due to physical association of the molecules is small compared to the volumetric change due to imbibing molecules. These considerations together suggest an idealization: All molecules in a gel are incompressible, and the volume of the gel is the sum of the volume of the dry network and the volume of the pure liquid solvent. This idealization is written as (Hong et al., 2008a)

$$1 + \nu C = \det \mathbf{F}. \quad (15)$$

In Section 3, we have assumed that the two fields, $C(\mathbf{X})$ and $x_i(\mathbf{X})$, vary independently. Eq. (15), however, places a constraint between the two fields. To enforce this constraint, we add to the free-energy function $W(\mathbf{F}, C)$ a term $\Pi(1 + \nu C - \det \mathbf{F})$, where Π is a Lagrange multiplier, a field to be determined. We then replace $W(\mathbf{F}, C)$ by $W(\mathbf{F}, C) + \Pi(1 + \nu C - \det \mathbf{F})$ everywhere in the previous sections, and treat \mathbf{F} and C as independent fields. The resulting modifications of the equations can be found in Hong et al. (2008a).

The molecular incompressibility of a gel is not to be confused with the incompressibility of an elastomer. Unlike an elastomer, a gel can undergo an enormous change in volume by imbibing a solvent. The molecular incompressibility of a gel simply means that the volume of the gel equals the sum of the volumes of individual molecules of the network and the solvent.

5. Flory–Rehner free-energy function

This section resumes the main line of work of this paper, and prescribes a particular form of the free-energy function $\widehat{W}(\mathbf{F}, \mu)$. The behavior of a gel is mainly entropic. As the solvent molecules mix with the long-chained polymers, the network swells, so that the configurational entropy of the network decreases, but the configurational entropy of mixture increases. The compromise of the two contributions to entropy equilibrates the network and the

solvent. Free-energy functions for swelling elastomers have been reviewed by, among others, Horkay and McKenna (2007) and Boyce and Arruda (2001). The object of this paper is to demonstrate how to implement a finite element method for gels, rather than to study alternative forms of the free-energy function. Consequently, we will adopt the best known free-energy function due to Flory and Rehner (1943):

$$W = \frac{1}{2}NkT[F_{iK}F_{iK} - 3 - 2 \log(\det \mathbf{F})] - \frac{kT}{\nu} \left[\nu C \log \left(1 + \frac{1}{\nu C} \right) + \frac{\chi}{1 + \nu C} \right], \quad (16)$$

where N is the number of polymeric chains per reference volume, and χ is a dimensionless measure of the enthalpy of mixing. When $\chi > 0$, the solvent molecules like themselves better than they like the long-chained polymers.

A combination of (4), (15) and (16) gives the desired free-energy function:

$$\widehat{W}(\mathbf{F}, \mu) = \frac{1}{2}NkT(I - 3 - 2 \log J) - \frac{kT}{\nu} \left[(J - 1) \log \frac{J}{J - 1} + \frac{\chi}{J} \right] - \frac{\mu}{\nu}(J - 1), \quad (17)$$

where $I = F_{iK}F_{iK}$ and $J = \det \mathbf{F}$ are invariants of the deformation gradient. As mentioned in the previous section, when the deformation gradient of the network, \mathbf{F} , and the concentration of solvent, C , are used as the independent variables for the free-energy function, the Lagrange multiplier Π is needed to enforce the condition of molecular incompressibility (15). In the present paper, however, we use the deformation gradient of the network, \mathbf{F} , and the chemical potential of the solvent, μ , as the independent variables. Consequently, the condition of molecular incompressibility is enforced without using the Lagrange multiplier, but is instead enforced by substituting (15) into the Flory–Rehner free-energy function (16) to eliminate C . Indeed, a boundary value problem is fully specified by (1), (5) and (17), so that C will not appear in the process of solving the boundary value problem, but can be calculated from (15) once \mathbf{F} is solved.

Inserting (17) into (13), we obtain that

$$\frac{s_{iK}}{kT/\nu} = N\nu(F_{iK} - H_{iK}) + \left[J \log \left(1 - \frac{1}{J} \right) + 1 + \frac{\chi}{J} - \frac{\mu}{kT} \right] H_{iK}. \quad (18)$$

This equation of state relates the stress to the deformation gradient when a gel is held at a constant chemical potential by a reservoir of solvent molecules. When the field of stress in the gel is inhomogeneous and anisotropic, so is the field of the deformation gradient. In general, the volumetric strain J (and therefore the volume fraction of the solvent in the gel) will be inhomogeneous and anisotropic. One cannot prescribe a field of volumetric strain in a gel, but should solve it as a part of a boundary value problem.

We have normalized the chemical potential by kT , and normalize the stress by kT/ν . A representative value of the volume per molecule is $\nu = 10^{-28} \text{ m}^3$. At room temperature, $kT = 4 \times 10^{-21} \text{ J}$ and $kT/\nu = 4 \times 10^7 \text{ Pa}$. The Flory–Rehner free-energy function introduces two dimensionless material parameters: $N\nu$ and χ . In the absence of solvent molecules, the dry network have a shear modulus NkT under the small-strain conditions, with the representative values $NkT = 10^4 - 10^7 \text{ N/m}^2$, which gives the range $N\nu = 10^{-4} - 10^{-1}$. The parameter χ is a dimensionless measure of the enthalpy of mixing, with representative values $\chi = 0 - 1.2$. For applications that prefer gels with large swelling ratios, materials with low χ values are used. In the numerical examples below, we will take the values $N\nu = 10^{-3}$ and $\chi = 0.1$.

6. Notes on implementing the finite element method

The free energy (16) is singular when the network is solvent-free, $\nu C = 0$. This singularity comes from the entropy of mixing, and is harmless in practice because a gel contains a large number of solvent molecules. However, in the above we have chosen the dry network as the reference state. If a numerical calculation involves this state, the singularity does cause problems. To avoid this singularity, we can choose a reference state with $\nu C > 0$. In this paper, we choose a reference state such that the network, under no mechanical load, equilibrates with a solvent of chemical potential μ_0 . Relative to the dry network, the network in this state swells with isotropic stretches: $\lambda_1 = \lambda_2 = \lambda_3$. We denote this free-swelling stretch by λ_0 , which relates to the chemical potential μ_0 by setting stress (18) to be zero, namely,

$$N\nu \left(\frac{1}{\lambda_0} - \frac{1}{\lambda_0^3} \right) + \log \left(1 - \frac{1}{\lambda_0^3} \right) + \frac{1}{\lambda_0^3} + \frac{\chi}{\lambda_0^6} = \frac{\mu_0}{kT}. \quad (19)$$

Fig. 2 plots the free-swelling stretch as a function of the chemical potential of the solvent molecules.

Relative to the dry network, the state of free swelling is characterized by the deformation gradient

$$\mathbf{F}_0 = \begin{bmatrix} \lambda_0 & & \\ & \lambda_0 & \\ & & \lambda_0 \end{bmatrix}. \quad (20)$$

In numerical calculations, we wish to use this free-swelling state as a reference state. Write

$$\mathbf{F} = \mathbf{F}'\mathbf{F}_0, \quad (21)$$

where \mathbf{F} is the deformation gradient of the current state relative to the dry network, as in the previous sections, and \mathbf{F}' is the deformation gradient of the current state relative to the free-swelling state.

Using the free-swelling state as the reference state, we write the free-energy density as

$$\widehat{W}'(\mathbf{F}', \mu) = \lambda_0^{-3} \widehat{W}(\mathbf{F}, \mu). \quad (22)$$

Combining (17) and (22), we obtain that

$$\widehat{W}'(\mathbf{F}', \mu) = \frac{\lambda_0^{-3}}{2} NkT (\lambda_0^2 J' - 3 - 2 \log(\lambda_0^3 J')) - \frac{kT}{\nu} \left[(J' - \lambda_0^{-3}) \log \frac{J'}{\lambda_0^3 J' - 1} + \frac{\chi}{\lambda_0^6 J'} \right] - \frac{\mu}{\nu} (J' - \lambda_0^{-3}), \quad (23)$$

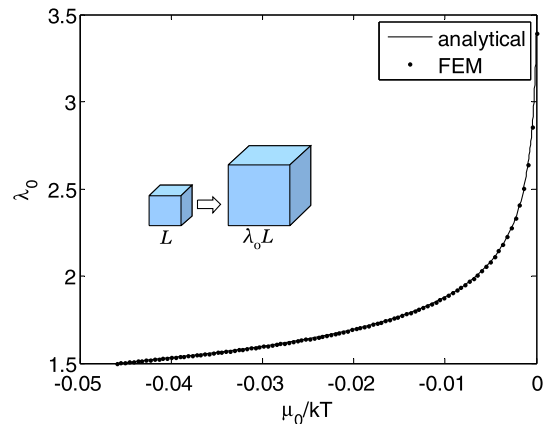


Fig. 2. The stretch of a free-swelling gel is plotted as a function of the chemical potential of the solvent.

where $I' = F'_{iK} F'_{iK}$ and $J' = \det \mathbf{F}'$. The nominal stress in the current state, with reference to the free-swelling state, relates to the nominal stress used in the previous sections by

$$s'_{iK} = s_{iK} / \lambda_0^2. \quad (24)$$

We have implemented the theory in the finite-element package, ABAQUS, by coding (23) into a user-defined subroutine for a hyperelastic material (UHYPER). Once again we emphasize that gels can undergo large changes in volume, so that we use elements that are compressible. The chemical potential is mimicked by a temperature-like variable, which is uniform in the gel, and is incremented as a loading parameter. The user-defined material behavior can be used together with any type of elements in two- or three-dimensional analysis. Note that ABAQUS uses $\bar{I}_1 = J^{-2/3} I$, rather than I .

7. Homogeneous state of equilibrium

This section describes several numerical examples of homogeneous deformation as benchmarks. Such states of homogenous swelling have been analyzed analytically by Southern and Thomas (1965). Due to the homogeneity, these examples can all be analyzed with a single element. Some of examples, however, are analyzed here with more than one element for the purpose of demonstration.

7.1. Free swelling

A cubic block of a gel is immersed in a solvent. We represent the block with eight 8-node brick elements. The block is constrained to prevent rigid-body motion, but is allowed to freely swell. The chemical potential of the solvent molecules is varied gradually. Fig. 2 compares the stretches obtained by using the finite element method with those plotted from (19).

7.2. A rod of a gel equilibrated with a solvent and subject to a uniaxial force

A rod of a gel is equilibrated in a solvent of chemical potential μ , and is subject to a uniaxial stress s_1 along the longitudinal direction. The state of deformation can be characterized by the longitudinal stretch λ_1 and two transverse stretches $\lambda_2 = \lambda_3$. The stresses in the transverse directions vanish, so that (18) gives

$$Nv \left(\lambda_2 - \frac{1}{\lambda_2} \right) + \left[\lambda_1 \lambda_2^2 \log \left(1 - \frac{1}{\lambda_1 \lambda_2^2} \right) + 1 + \frac{\chi}{\lambda_1 \lambda_2^2} - \frac{\mu}{kT} \lambda_1 \lambda_2^2 \right] \frac{1}{\lambda_2} = 0. \quad (25)$$

This equation determines the transverse stretch λ_2 for a given longitudinal stretch λ_1 . Eq. (18) also relates the longitudinal stress to the stretches:

$$\frac{vs_1}{kT} = Nv \left(\lambda_1 - \frac{1}{\lambda_1} \right) + \left[\lambda_1 \lambda_2^2 \log \left(1 - \frac{1}{\lambda_1 \lambda_2^2} \right) + 1 + \frac{\chi}{\lambda_1 \lambda_2^2} - \frac{\mu}{kT} \lambda_1 \lambda_2^2 \right] \frac{1}{\lambda_1}, \quad (26)$$

We use four 8-node brick elements to represent the block of the gel. Fig. 3 compares the finite element results and those plotted from (25) and (26). As expected, as the chemical potential of the solvent increases, the gel becomes more swollen and more compliant.

7.3. A blanket layer of a gel bonded to a rigid substrate

A layer of a gel is fabricated on a rigid substrate, with stress-free pre-swelling of isotropic stretch $\lambda_0 = 1.5$. Subsequently, the gel is brought into contact with a solvent with chemical potential μ .

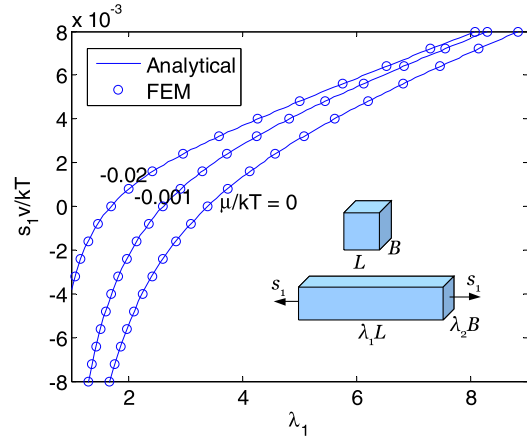


Fig. 3. A rod of a gel is subject to a uniaxial stress, and is in contact with a solvent of a given chemical potential. The applied stress is plotted as a function of the stretch, while the solvent is held at several levels of the chemical potential.

The gel swells further to a stretch λ in the direction normal to the layer, and develops a state of equal-biaxial stress s . The stress normal to the layer vanishes, so that (18) gives

$$\frac{Nv}{\lambda_0^2} \left(\lambda - \frac{1}{\lambda} \right) + \log \left(1 - \frac{1}{\lambda_0^2 \lambda} \right) + \frac{1}{\lambda_0^2 \lambda} + \frac{\chi}{(\lambda_0^2 \lambda)^2} = \frac{\mu}{kT}. \quad (27)$$

where the two in-plane stretches are constrained by rigid substrate to be the initial value λ_0 , but the out-of-plane stretch λ can vary with the chemical potential. The magnitude of the biaxial stress is given by

$$\frac{vs}{kT} = Nv \left(\lambda_0 - \frac{1}{\lambda_0} \right) + \left[\lambda \lambda_0^2 \log \left(1 - \frac{1}{\lambda \lambda_0^2} \right) + 1 + \frac{\chi}{\lambda \lambda_0^2} - \frac{\mu}{kT} \lambda \lambda_0^2 \right] \frac{1}{\lambda_0}. \quad (28)$$

We use 2×2 plane-strain elements to represent the layer. Fig. 4 shows the finite element results, along with those calculated from (27) and (28). Comparing with free swelling (Fig. 2), we note that the biaxial constraint can significantly increase the stretch in the direction normal to the layer.

8. Inhomogeneous state of equilibrium

8.1. A spherical gel with a rigid core

Following Sternstein (1972) and Zhang et al. (2008), we consider a spherical gel with a rigid core. The dry network takes the shape of a spherical shell, with inner radius A and outer radius B . In numerical calculations we set $B/A = 2$. When the gel forms on the rigid core, the gel has a stress-free pre-swelling of an isotropic stretch $\lambda_0 = 1.5$. Subsequently, the gel is immersed in a pure liquid solvent with the chemical potential $\mu = 0$, and is allowed to swell further. We model the gel as an axisymmetric system, using 8-node biquadratic axisymmetric quadrilateral hybrid elements (CAX8RH).

Our numerical results are compared with those in Zhang et al. (2008), who solved the problem by integrating ordinary differential equations. Fig. 5a plots the distribution of the stretches in the equilibrated gel. At the interface between the gel and the core, the hoop stretch is constrained to the pre-stretch $\lambda_0 = 1.5$, but the radial stretch is very large. At the outer surface, both stretches approach to the stretch of free swelling.

Fig. 4b plots the equilibrium concentration of solvent, vC , i.e., the ratio of the volume of solvent in the gel to the volume of the

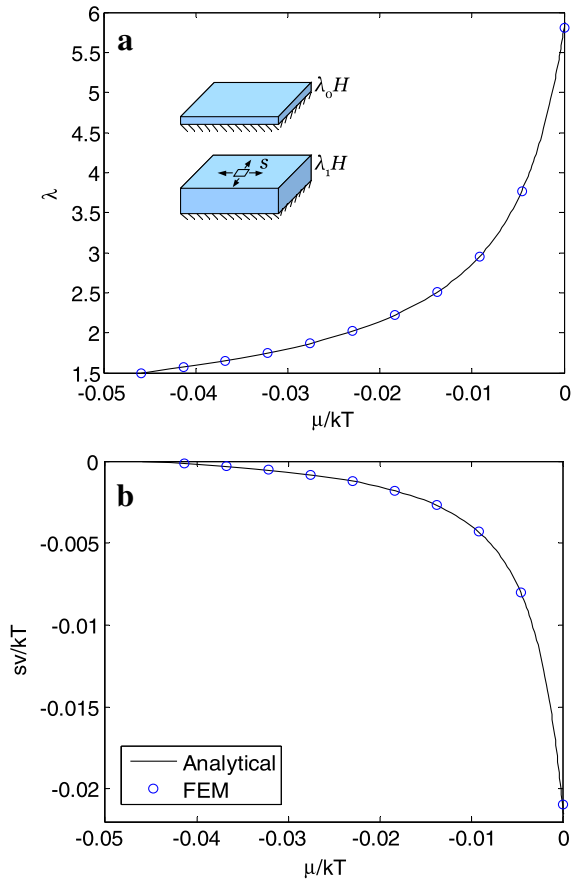


Fig. 4. A blanket layer of a gel is bonded to a rigid substrate and is in contact with a solvent. The gel swells in the normal direction (a), and develops an equal-biaxial compressive stress (b). The stretch of the initial swelling is set to be $\lambda_0 = 1.5$.

dry network. The equilibrium concentration of solvent in the gel is inhomogeneous. That is, to equilibrate with a solvent the gel homogenizes the chemical potential, rather than the concentration. This result casts serious doubt on part of the literature that assumes the migration of solvent molecules in a gel is driven by the gradient of the solvent concentration. Under the condition of molecular incompressibility, (15), vC is the volumetric strain. This example clearly shows that the volumetric strain cannot be prescribed, but should be solved as a part of the boundary value problem.

8.2. A gel of cylindrical shape fabricated on a rigid substrate

An elastomer of cylindrical shape, diameter D and height H in the dry state, swells freely by an isotropic stretch $\lambda_0 = 2$, and is then bonded to a rigid substrate. The gel is brought into contact with a pure liquid solvent with chemical potential $\mu = 0$, and is allowed to swell further to equilibrium. We represent the gel with the 8-node biquadratic axisymmetric quadrilateral hybrid elements (CAX8RH), and allow contact between the substrate and the sidewall of the cylinder.

Fig. 6 plots the height of the cylinder in equilibrium, h , as a function of the aspect ratio D/H . For a needle-like cylinder, $D/H \ll 1$, the substrate only constrains the bottom portion of the gel, and the main part of the gel swells freely, so that the overall higher of the cylinder is predicated by the stretch of free swelling. For a pancake-like cylinder, $D/H \gg 1$, the central part of the cylinder behaves just like that of a blanket layer bounded to a rigid substrate.

Fig. 7 shows the deformed meshes for cylinders of various aspect ratios. The undeformed elements are square, so that the shape

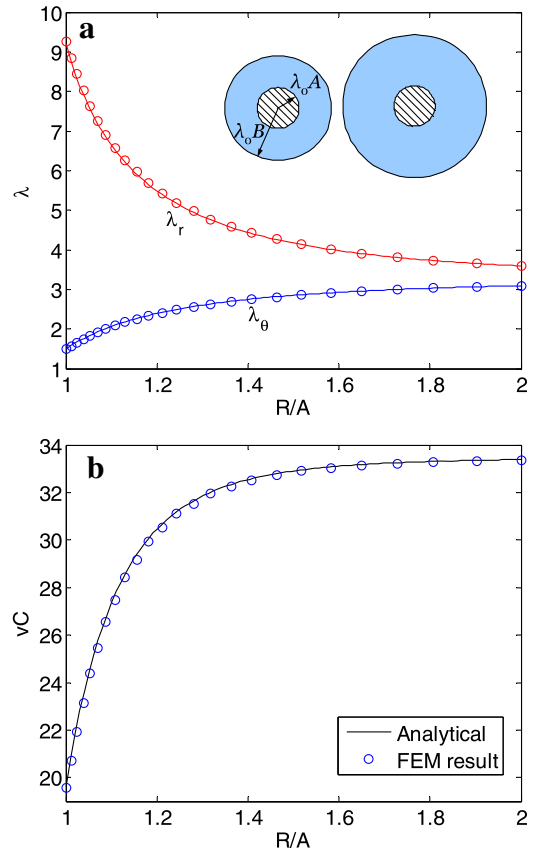


Fig. 5. A spherical shell of a gel is fabricated on a rigid core, and swells to equilibrate with a solvent. (a) The distribution of the radial and the hoop stretches. (b) The distribution of the concentration of the solvent in the gel.

of the elements shown in the figure indicates the deformation. Note the difference in the heights of the swollen gels in the three cases. In the case of $D/H = 10$, the edge of the cylinder deforms severely and makes contact with the substrate.

8.3. Swelling-induced bifurcation

We now turn to a swelling-induced bifurcation reported by Zhang et al. (2008). A square lattice of cylindrical holes is fabricated in a layer of an elastomer, which in turn is constrained on

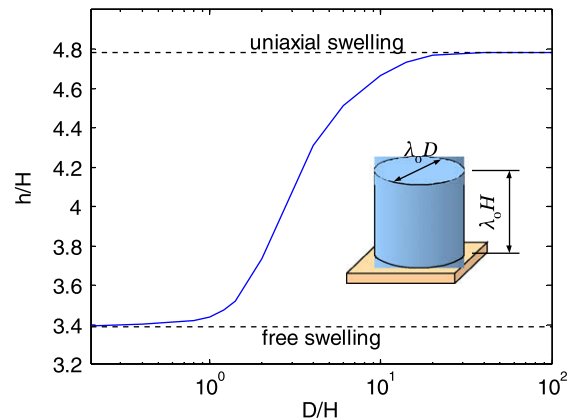


Fig. 6. A cylinder of a gel is bonded to a rigid substrate and is in contact with a solvent. The equilibrium height of the cylinder is plotted as a function of the aspect ratio of the dry polymer, D/H .

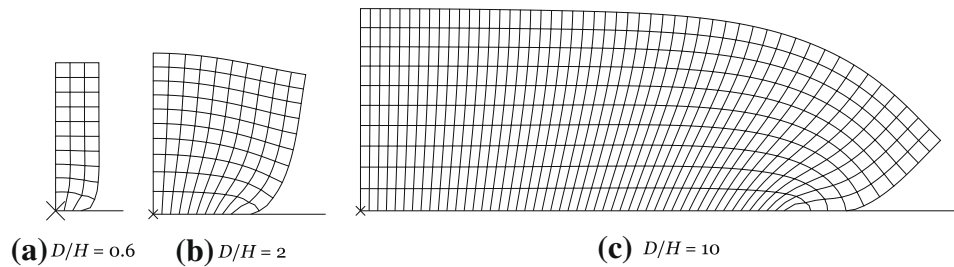


Fig. 7. The equilibrium configurations of the cylinders of several aspect ratios. In case (c) significant contact is observed between the side wall of the gel and the substrate.

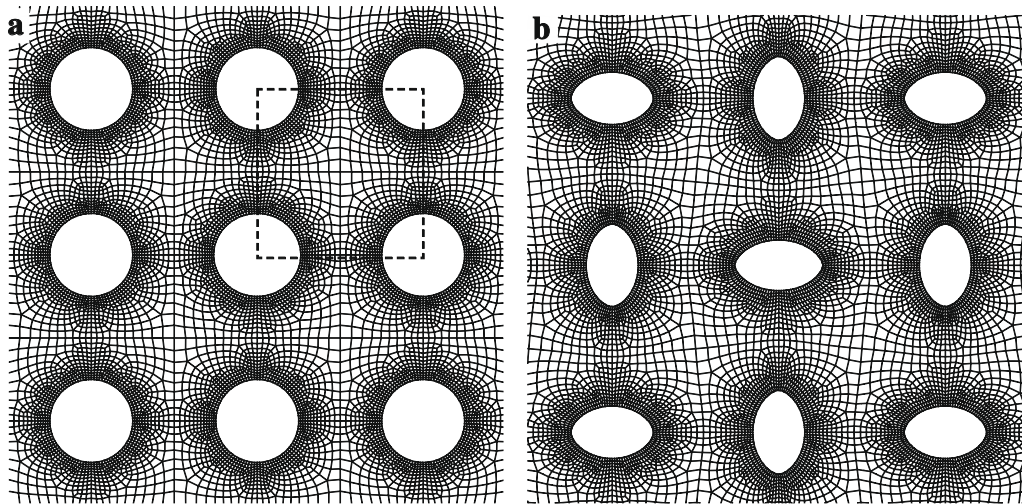


Fig. 8. A square lattice of cylindrical holes bifurcates into a periodic structure of ellipses with alternating directions. (a) The initial shape. (b) The deformed pattern.

a substrate. The layer then swells in a solvent. Each cylindrical hole collapses into a slit, and the square lattice breaks the symmetry and bifurcates into slits of alternating directions. Since the aspect ratio of the holes is large, we use generalized plane-strain elements. As shown in Fig. 8, we model a unit cell containing quarters of four neighboring holes. To help visualize the geometry, we duplicate the unit cell several times. From the deformed the mesh, it can be seen that besides the highly inhomogeneous deformation near the holes, there is also a rotation in the center part of the unit cell.

Further swelling will cause a snap-through instability and the elliptic hole will close down to a slit dynamically. ABAQUS Standard fails to calculate at the unstable point. The arc-length method (Riks, 1972) is expected to handle this type of instability and proceed with further calculation. However, in ABAQUS 6.7.1, the arc-length method has been implemented on the plane of generalized mechanical load and displacement, but we are unable to find a similar implementation on the plane of chemical potential and generalized displacement. Therefore, in the current stage, we are unable to calculate the whole deformation process from a cylindrical hole to a slit. Future work is needed to make the software more robust to simulate various forms of instability.

9. Concluding remarks

This paper focuses on inhomogeneous field in a swollen gel in equilibrium with a solvent and mechanical load. The chemical potential of the solvent molecules is homogeneous in the gel, and is set by the external solvent. Using a Legendre transformation, we show that the field in the equilibrated gel is analogous to the field in a compressible hyperelastic solid. We implement the theory in

the finite element package, ABAQUS, invoking a user-defined subroutine. This implementation enables us to use various two- and three-dimensional elements, and analyze diverse phenomena accompanying swelling, such as large deformation, contact, and bifurcation. It is hoped that this approach will help other workers to model phenomena of interest to themselves.

The user-supplied subroutine for ABAQUS is posted at <http://imechanica.org/node/3163>

Acknowledgement

This research was supported by the Army Research Office through contract W911NF-04-1-0170, and by the National Science Foundation through a project on Large Deformation and Instability in Soft Active Materials.

References

- Atkin, R.J., Craine, R.E., 1976. Continuum theories of mixtures: basic theory and historical development. *Q. J. Mech. Appl. Math.* 29, 209–244.
- Baek, S., Srinivasa, A.R., 2004. Diffusion of a fluid through an elastic solid undergoing large deformation. *Int. J. Non-linear Mech.* 39, 201–218.
- Beebe, D.J., Moore, J.S., Bauer, J.M., Yu, Q., Liu, R.H., Devadoss, C., Jo, B.H., 2000. Functional hydrogel structures for autonomous flow control inside microfluidic channels. *Nature* 404, 588–590.
- Bassetti, M.J., Chatterjee, A.N., Aluru, N.R., Beebe, D.J., 2005. Development and modeling of electrically triggered hydrogels for microfluidic applications. *J. Microelectromech. Syst.* 14, 1198–1207.
- Biot, M.A., 1941. General theory of three-dimensional consolidation. *J. Appl. Phys.* 12, 155–164.
- Boyce, M.C., Arruda, E.M., 2001. Swelling and mechanical stretching of elastomeric materials. *Math. Mech. Solids* 6, 641–659.
- Cho, E.C., Kim, J.W., Fernandez-Nieves, A., Weitz, D.A., 2008. Highly responsive hydrogel scaffolds formed by three-dimensional organization of microgel nanoparticles. *Nano Lett.* 8, 168–172.

- Demirkoparan, H., Pence, T.J., 2007. Swelling of an internally pressurized nonlinearly elastic tube with fiber reinforcing. *Int. J. Solids Struct.* 44, 4009–4029.
- Dong, L., Agarwal, A.K., Beebe, D.J., Jiang, H.R., 2006. Adaptive liquid microlenses activated by stimuli-responsive hydrogels. *Nature* 442, 551–554.
- Dolbow, J., Fried, E., Ji, H., 2005. A numerical strategy for investigating the kinetic response of stimulus-responsive hydrogels. *Comput. Meth. Appl. Mech. Eng.* 194, 4447–4480.
- Durning, C.J., Morman, K.N., 1993. Nonlinear swelling of polymer gels. *J. Chem. Phys.* 98, 4275–4293.
- Flory, P.J., Rehner, J., 1943. Statistical mechanics of cross-linked polymer networks II swelling. *J. Chem. Phys.* 11, 521–526.
- Gandhi, M.V., Usman, M., 1989a. Equilibrium characterization of fluid-saturated continua and an interpretation of the saturation boundary condition assumption for solid–fluid mixtures. *Int. J. Eng. Sci.* 27, 539–548.
- Gandhi, M.V., Usman, M., 1989b. On the non-homogenous finite swelling of a nonlinearly elastic cylinder with a rigid core. *Int. J. Nonlinear Mech.* 24, 251–261.
- Gandhi, M.V., Usman, M., Wineman, A.S., Rajagopal, K.R., 1989. Combined extension and torsion of a swollen cylinder within the context of mixture theory. *Acta Mech.* 19, 81–96.
- Gandhi, M.V., Kasiviswathan, S.R., Usman, M., 1995. Flexure of a fluid-saturated cuboid. *Acta Mech.* 111, 209–222.
- Gibbs, J.W., 1878. The scientific papers of J. Willard Gibbs, pp. 184, 201, 215. Digital copy of the book is freely available at <http://books.google.com/>.
- Hong, W., Zhao, X.H., Zhou, J.X., Suo, Z.G., 2008a. A theory of coupled diffusion and large deformation in polymeric gels. *J. Mech. Phys. Solids* 56, 1779–1793.
- Hong, W., Zhao, X.H., Suo, Z.G., 2008b. Drying-induced bifurcation in a hydrogel-actuated nanostructures. *J. Appl. Phys.* 104, 084905.
- Horkay, F., McKenna, G.B., 2007. Polymer networks and gels. In: Mark, J.E. (Ed.), *Physical Properties of Polymers Handbook*. Springer, New York, pp. 497–523.
- Hu, Z.B., Zhang, X.M., Li, Y., 1995. Synthesis and application of modulated polymer gels. *Science* 269, 525–527.
- Hui, C.Y., Muralidharan, V., 2005. Gel mechanics: a comparison of the theories of Biot and Tanaka, Hocker, and Benedek. *J. Chem. Phys.* 123, 154905.
- Kim, S.J., Spinks, G.M., Prosser, S., Whitten, P.G., Wallace, G.G., Kim, S.I., 2006. Surprising shrinkage of expanding gels under external load. *Nat. Mater.* 5, 48–51.
- Kleverlaan, M., van Noort, R.H., Jones, I., 2005. Deployment of swelling elastomer packers in Shell E&P, SPE/IADC Conference, 92346 Amsterdam, The Netherlands, 23–25 February 2005.
- Klein, Y., Efrati, E., Sharon, E., 2007. Shaping of elastic sheets by prescription of non-Euclidean metrics. *Science* 315, 1116–1120.
- Ladet, S., David, L., Domard, A., 2008. Multi-membrane hydrogels. *Nature* 452, 76–79.
- Lee, K.Y., Mooney, D.J., 2001. Hydrogels for tissue engineering. *Chem. Rev.* 101, 1869–1879.
- Li, H., Luo, R., Birgersson, E., Lam, K.Y., 2007. Modeling of multiphase smart hydrogels responding to pH and electric voltage coupled stimuli. *J. Appl. Phys.* 101, 114905.
- Peppas, N.A., Hilt, J.Z., Khademhosseini, A., Langer, R., 2006. Hydrogels in biology and medicine: from molecular principles to bionanotechnology. *Adv. Mater.* 18, 1345–1360.
- Rajagopal, K.R., Wineman, A.S., Gandhi, M., 1986. On boundary conditions for a certain class of problems in mixture theory. *Int. J. Eng. Sci.* 24, 1453–1463.
- Rajagopal, K.R., Tao, L., 1995. *Mechanics of Mixtures. Advances in Mathematics for the Applied Sciences*. World Scientific, Singapore.
- Riks, E., 1972. The application of Newton's method to the problem of elastic stability. *J. Appl. Mech.* 39, 1060–1066.
- Sekimoto, K., 1991. Thermodynamics and hydrodynamics of chemical gels. *J. Phys. II* 1, 19–36.
- Shi, J.J., Rajagopal, K.R., Wineman, A.S., 1981. Applications of the theory of interacting continua to the diffusion of a fluid through a nonlinearly elastic media. *Int. J. Eng. Sci.* 19, 871.
- Sidorenko, A., Krupenkin, T., Taylor, A., Fratzl, P., Aizenberg, J., 2007. Reversible switching of hydrogel-actuated nanostructures into complex micropatterns. *Science* 315, 487–490.
- Sternstein, S.S., 1972. Inhomogeneous swelling in filled elastomers. *J. Macromol. Sci. Phys. B6* (1), 243–262.
- Southern, E., Thomas, A.G., 1965. Effect of constraints on the equilibrium swelling of rubber vulcanizates. *J. Polym. Sci. A* 3, 641–646.
- Treloar, L.R.G., 1950. The swelling of cross-linked amorphous polymers under strain. *Trans. Faraday Soc.* 46, 783–789.
- Treloar, L.R.G., 1975. *The Physics of Rubber Elasticity*. Oxford University Press, Oxford.
- Treloar, L.R.G., 1976. Swelling of bonded-rubber cylinders. *Polymer* 17, 142–146.
- Trujillo, V., Kim, J., Hayward, R.C., 2008. Creasing instability of surface-attached hydrogels. *Soft Matter* 4, 564–569.
- Tsai, H., Pence, T.J., Kirkinis, E., 2004. Swelling induced finite strain flexure in a rectangular block of an isotropic elastic material. *J. Elasticity* 75, 69–89.
- Westbrook, K.K., Qi, H.J., 2008. Actuator designs using environmentally responsive hydrogels. *J. Intelligent Mater. Syst. Struct.* 19, 597–607.
- Wichterle, O., Lim, D., 1960. Hydrophilic gels for biological use. *Nature* 185, 117–118.
- Wong, A.P., Perez-Castillejos, R., Love, J.C., Whitesides, G.M., 2008. Partitioning microfluidics channels with hydrogel to construct tunable 3-D cellular microenvironments. *Biomaterials* 29, 1853–1861.
- Zhang, Y., Matsumoto, E.A., Peter, A., Lin, P.C., Kamien, R.D., Yang, S., 2008. One-step nanoscale assembly of complex structures via harnessing of an elastic instability. *Nano Lett.* 8, 1192–1196.
- Zhao, X.H., Hong, W., Suo, Z.G., 2008. Inhomogeneous and anisotropic equilibrium state of a swollen hydrogel containing a hard core. *Appl. Phys. Lett.* 92, 051904.