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

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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, the gel usually swells by a field of inhomogeneous and anisotropic deformation. We show that this field in the swollen gel is equivalent to that in a hyperelastic solid. We implement this theory 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.

Keywords: elastomer; gel; swelling; hyperelasicity; finite element method

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1. Introduction

Flexible, long polymeric molecules can chemically crosslink 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 solvent molecules and swells, resulting in an aggregate known as a gel. The swelling is also reversible: when the environment dries, the solvent molecules in the gel migrate out and evaporate. The gel has characteristics of both a solid and a liquid: elastic deformation results from strong chemical cross links between the long polymers, and viscous migration results from weak physical association between the long polymers and solvent molecules.

The unusual combination of properties of gels makes them ideal 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., 2008), 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.

This paper 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 and isotropic 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 (Hu et al., 1995; Klein et al., 2007; Ladet et al., 2008), or when the network is subject to a mechanical load or geometric constraint (Treloar, 1950; Kim et al., 2006; Zhao et al., 2008). Swelling can induce cavitation, debonding, creasing, and other forms of instability (Sidorenko et al., 2007; Hong et al.; 2007; Trujilo et al., 2008; Zhang et al., 2008).

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, 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 in general depends on the state of stress.

The theory of inhomogeneous deformation in a swelling solid was formulated by Gibbs (1878) and Biot (1941). See Sekimoto (1991), Durning and Morman (1993), Dolbow et al. (2005), Bassetti et al. (2005), Hui and Muralidharan (2005), Li et al. (2007), Westbook and Qi (2007), and Hong et al. (2008) for recent contributions with specific reference to polymeric gels.

This paper will continue our previous work (Hong et al., 2008), and show that the inhomogeneous field in a gel equilibrated with a solvent is equivalent to the field in a hyperelastic solid.   We implement this theory 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.

2. Equilibrium condition in variational forms

Fig. 1 illustrates a polymer network 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 network as the reference state, and name each small part of the network after its coordinate **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

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

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, the field $C(\mathbf{X})$ describes the distribution of the solvent molecules in the gel, and 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 mechanical force applied on the element of volume, and $T_i(\mathbf{X})dA(\mathbf{X})$ be the 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 molecule, and p_o as the vapor pressure. When the solvent is subject to a pressure p greater than the vapor pressure, $p > p_o$, the chemical potential of the solvent molecules is $\mu = v(p - p_o)$. When the solvent is subject to a pressure p less than the vapor pressure,

$p < p_o$, 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 $\mu = kT(p/p_o)$, 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 $WdV(\mathbf{X})$ be the Helmholtz free energy of the gel in the element of volume. We assume that the free-energy density of the gel is a function of the deformation gradient and the concentration, $W(\mathbf{F}, C)$. 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:

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

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

When the network equilibrates with the solvent and the mechanical load, the change in the free energy of the gel equals the sum of the work done by the mechanical force and by the solvent, namely,

$$\int \delta W dV = \int B_i \delta x_i dV + \int T_i \delta x_i dA + \mu \int \delta C dV. \tag{3}$$

The equilibrium condition is that this equation holds for arbitrary changes $\delta \mathbf{x}$ and δC.

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

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

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 $\hat{W}$ as a function of the deformation gradient of the network and the chemical potential of the solvent molecules, $\hat{W}(\mathbf{F}, \mu)$.

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

$$\int \delta \hat{W} dV = \int B_i \delta x_i dV + \int T_i \delta x_i dA .$$

(5)

As noted above, when the network equilibrates with the solvent and the mechanical load, 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 $\hat{W}(\mathbf{F}, \mu)$ 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.

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

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

(6)

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

we obtain that

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

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

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

in the volume of the gel, and

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

on the surface of the gel.

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

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

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

$$\delta W = s_{iK} \delta F_{iK} + \mu \delta C. \tag{11}$$

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

$$\delta \hat{W} = s_{iK} \delta F_{iK} - C \delta \mu, \tag{12}$$

so that

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

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

4. The condition of 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 by air. When solvent migrates out of a gel, however, the network 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., 2008)

$$1 + vC = \det \mathbf{F}.$$ (15)

In previous sections, we have assumed that the two fields, $C(\mathbf{X})$ and $x_i(\mathbf{X})$, vary independently. Equation (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 $\Pi(1 + vC - \det \mathbf{F})$, where Π is a Lagrange multiplier, a field to be determined. We then replace $W(\mathbf{F},C)$ by $W(\mathbf{F},C) + \Pi(1 + vC - \det \mathbf{F})$ 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. (2008).

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 $\hat{W}(\mathbf{F}, \mu)$. The behavior of a gel is mainly entropic. As the solvent molecules mix with the long 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 kinds of 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):

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

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 polymers.

We combine (4), (15) and (16), and obtain the desired free-energy function:

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

where $I = F_{iK} F_{iK}$ and $J = \det \mathbf{F}$ are invariants of the deformation gradient. Inserting (17) into (13), we obtain that

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

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/υ.

A representative value of the volume per molecule is $\upsilon = 10^{-28}\,\mathrm{m}^3$. At room temperature,

$kT = 4 \times 10^{-21}\,\mathrm{J}$ and $kT/\upsilon = 4 \times 10^7\,\mathrm{Pa}$.   The Flory-Rehner free-energy function introduces

two dimensionless material parameters: $N\upsilon$ and χ.   In the absence of solvent molecules,

the cross-linked polymers have a shear modulus NkT under the small-strain conditions, with the

representative values $NkT = 10^4 \sim 10^7\,\mathrm{N/m}^2$, which gives the range $N\upsilon = 10^{-4} \sim 10^{-1}$.   The

parameter χ is a dimensionless measure of the enthalpy of mixing, with representative values

$\chi = 0 \sim 1.2$.   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 $N\upsilon = 10^{-3}$ and

$\chi = 0.1$.

6. Notes on implementing the finite element method

The free energy (16) is singular when the network is solvent-free, $\upsilon C = 0$.   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 $vC > 0$. 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,

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

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

$$\mathbf{F}_0 = \begin{bmatrix} \lambda_0 & & \\ & \lambda_0 & \\ & & \lambda_0 \end{bmatrix}. \tag{20}$$

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

$$\mathbf{F} = \mathbf{F}'\mathbf{F}_0, \tag{21}$$

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

$$\hat{W}'(\mathbf{F}',\mu) = \lambda_o^{-3}\hat{W}(\mathbf{F},\mu). \tag{22}$$

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

$$\hat{W}'(\mathbf{F}',\mu) = \frac{\lambda_o^{-3}}{2}NkT\left(\lambda_o^2 I' - 3 - 2\log(\lambda_o^3 J')\right) - \frac{kT}{\upsilon}\left[\left(J' - \lambda_o^{-3}\right)\log\frac{\lambda_o^3 J'}{\lambda_o^3 J' - 1} + \frac{\chi}{\lambda_o^6 J'}\right] - \frac{\mu}{\upsilon}\left(J' - \lambda_o^{-3}\right), \tag{23}$$

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

$$s'_{iK} = s_{iK} / \lambda_o^2. \tag{24}$$

We have implemented the theory in the finite element package, ABAQUS, by coding (23) into a user-defined subroutine for a hyperelastic material (UHYPER). 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 $\bar{I}_1 = J^{-\frac{2}{3}}I$, rather than I.

7. Homogeneous state of deformation

Free swelling

A cubic block of a gel is immersed in a solvent. We represent the block with one or several 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).

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

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

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

$$\frac{\upsilon s_1}{kT} = N\upsilon\left(\lambda_1 - \frac{1}{\lambda_1}\right) + \left[\lambda_1\lambda_2^2 \log\left(1 - \frac{1}{\lambda_1\lambda_2^2}\right) + 1 + \frac{\chi}{\lambda_1\lambda_2^2} - \frac{\mu}{kT}\lambda_1\lambda_2^2\right]\frac{1}{\lambda_1} , \qquad (26)$$

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.

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. 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)

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gives

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

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

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

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

A spherical gel with a rigid core

Following Zhao 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 $\lambda_o=1.5$. 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 Zhao 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, υC, i.e., the ratio of the volume of solvent in the gel to the volume of the 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), υC 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.

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 inn 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 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.

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 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.

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

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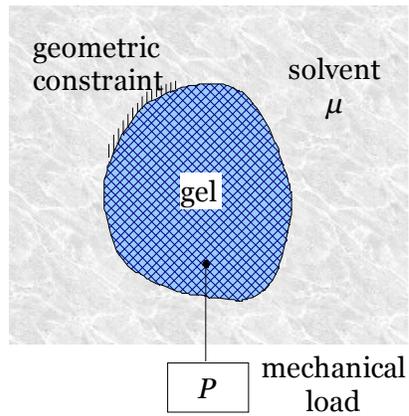
Fig. 1. A gel is in contact with a solvent of a fixed chemical potential, and subject to a mechanical load and geometric constraint.
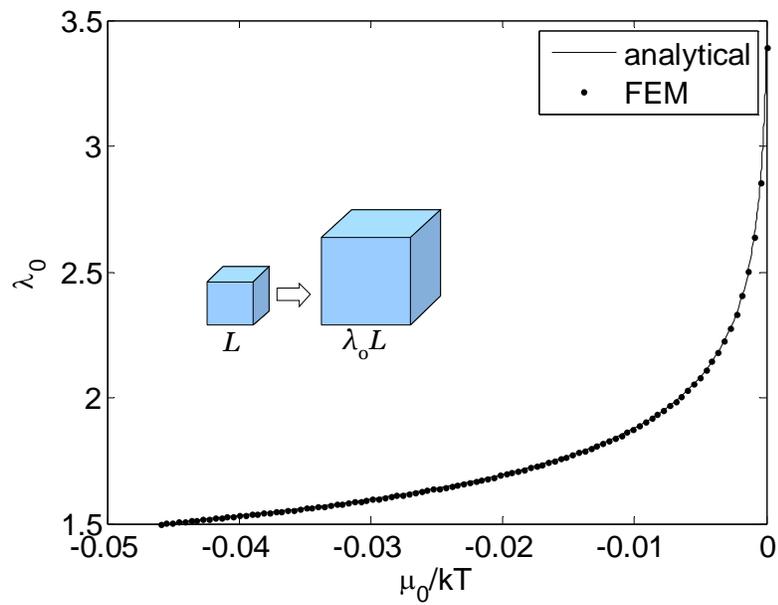

Fig. 2. The free-swelling stretch of a gel is plotted as a function of the chemical potential of the solvent molecules.
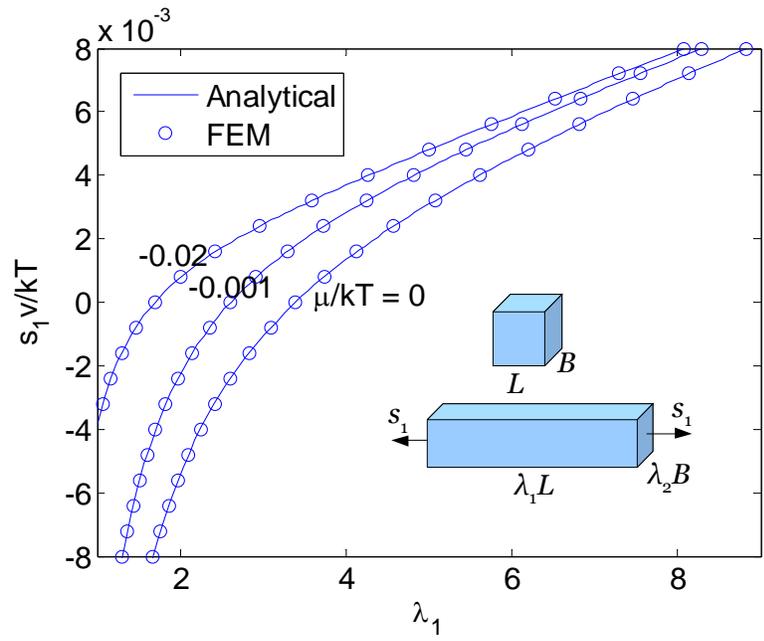
Fig. 3. A rod of a gel is subject to a uniaxial stress, and is in contact with a solvent of a given chemical potential. The applied stress is plotted as a function of the stretch, while the solvent is held at several levels of chemical potential.
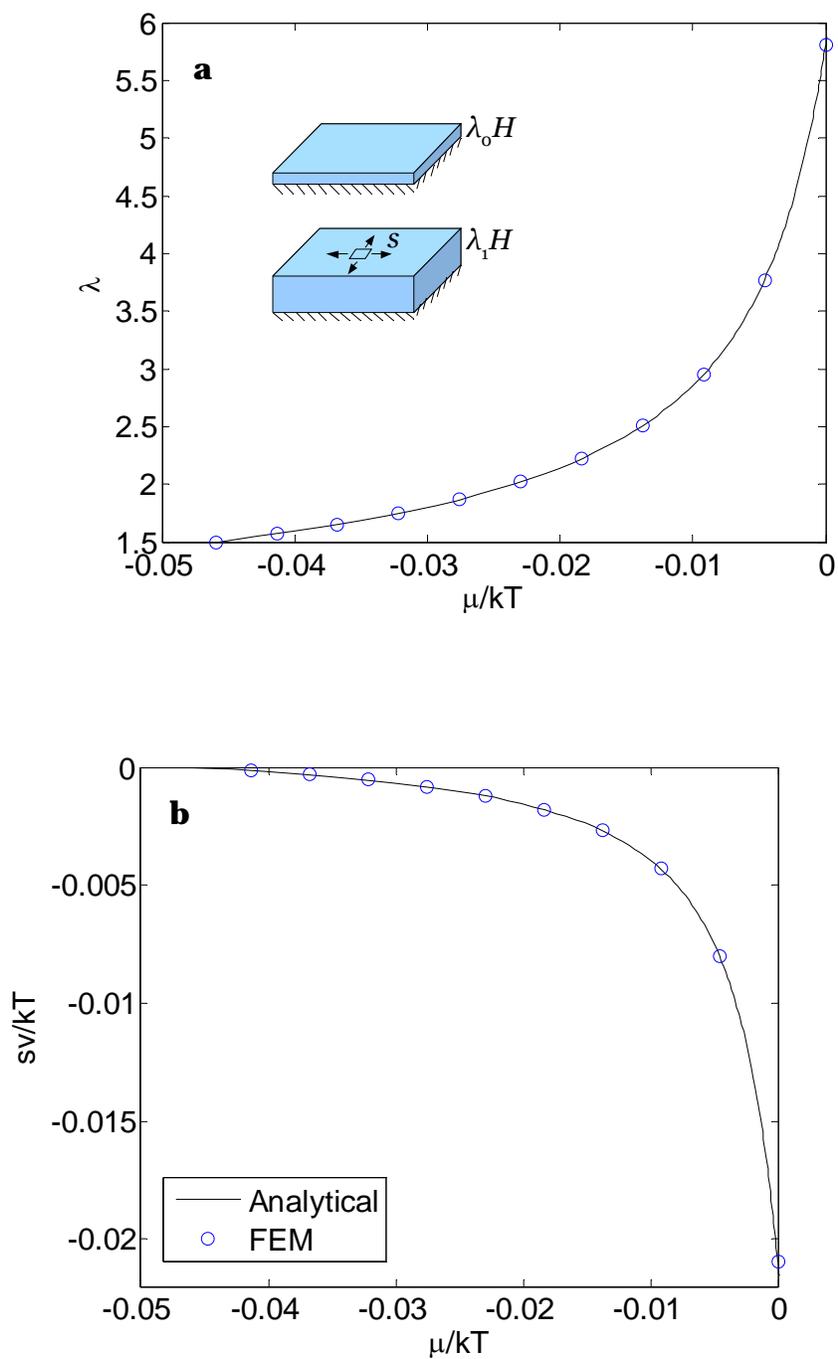
Fig. 4.   A blanket layer of a gel is bonded to a rigid substrate and is in contact with a solvent.

The gel swells in the normal direction (a), and develops an equal-biaxial compressive stress (b).
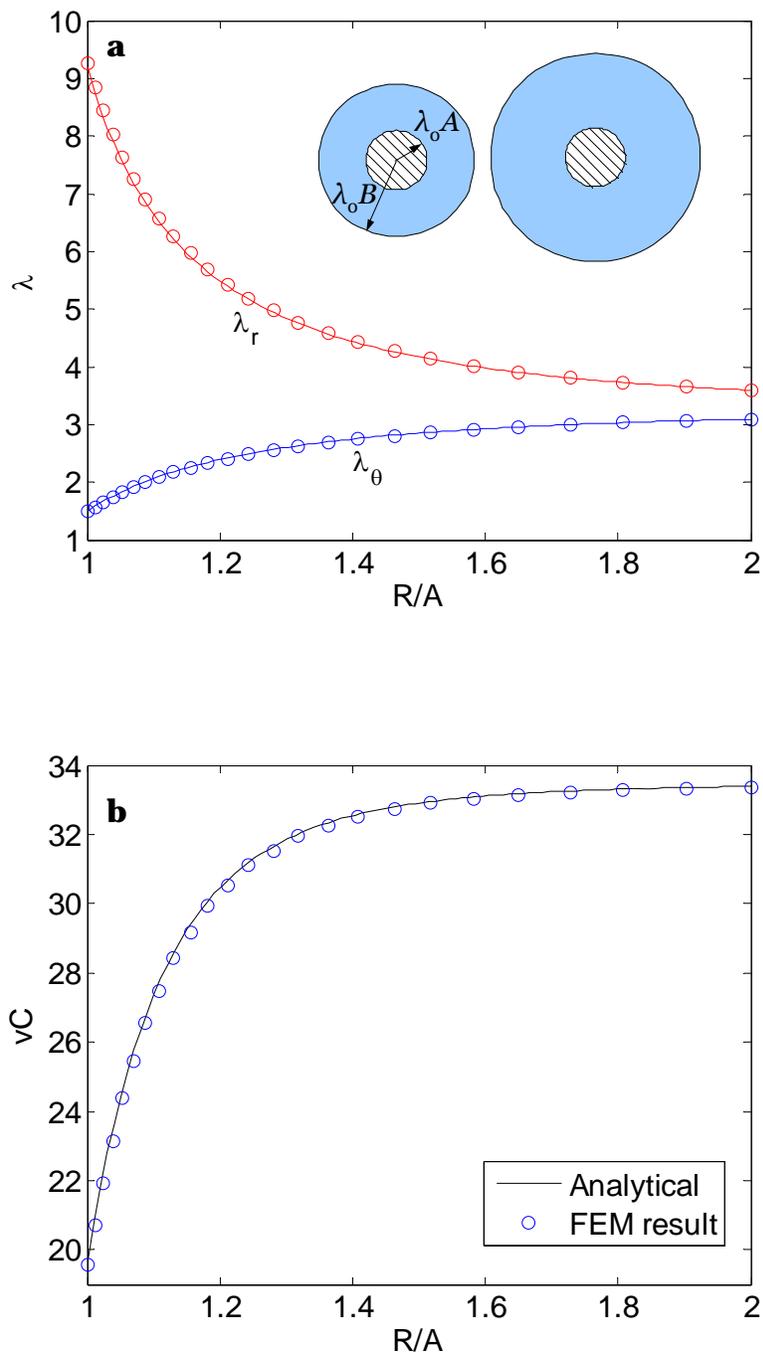
The initial swelling is set to be $\lambda_o = 1.5$.

Fig. 5. A spherical shell of a gel is grown 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 solvent in the
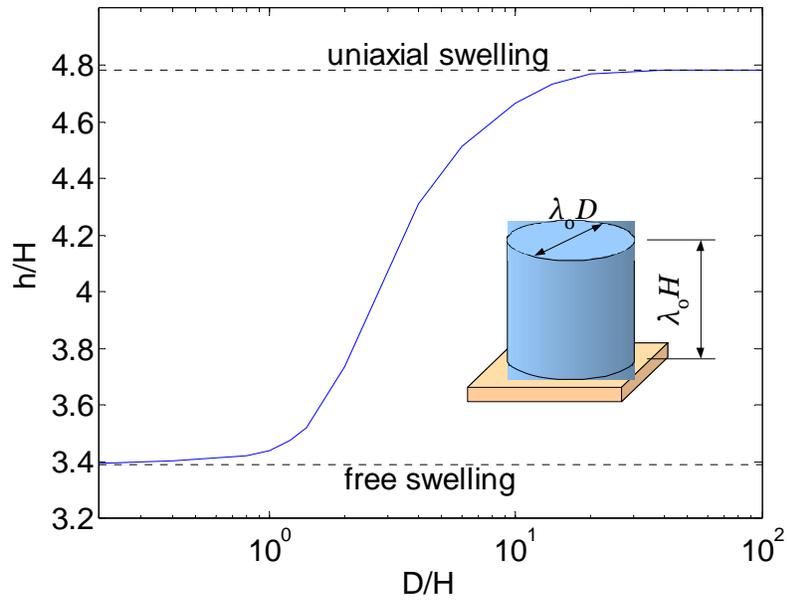
gel.

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.

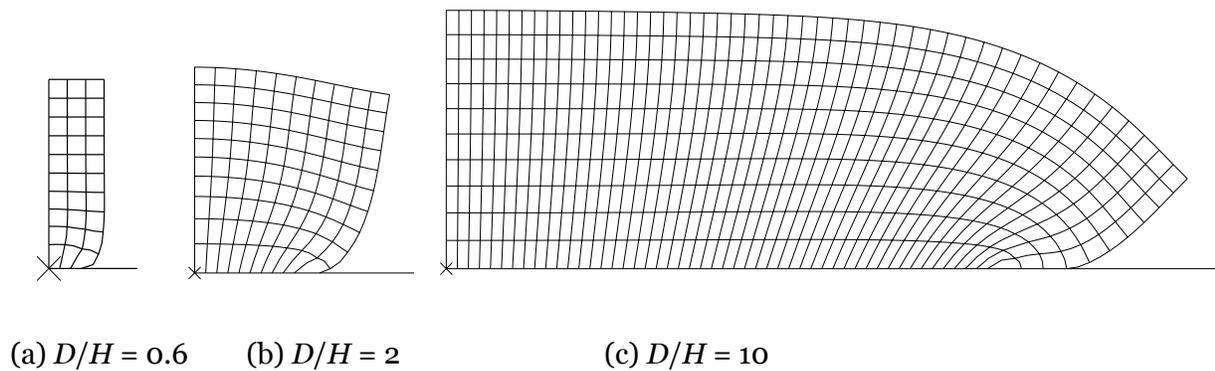(a) $D/H = 0.6$ (b) $D/H = 2$ (c) $D/H = 10$

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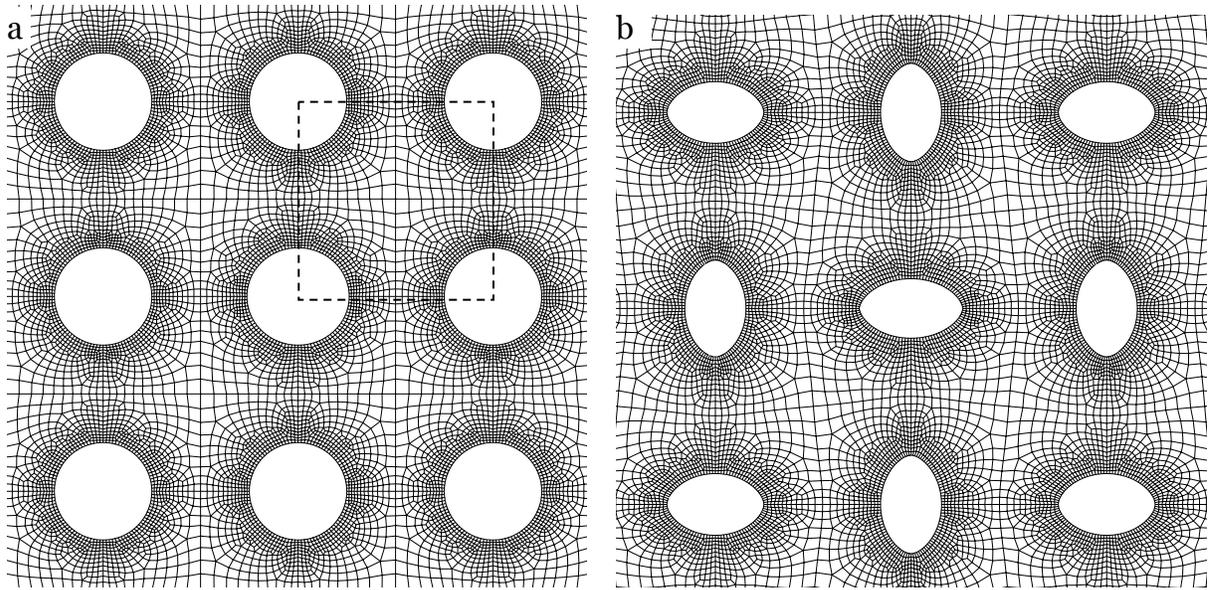
Fig. 8. A square lattice of cylindrical holes bifurcates into a periodic structure of ellipses with alternating directions. (a) The initial shape. (b) The deformed pattern.