Multiphysics Modeling of Swelling Gels

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Abstract: Polymer gels belong to the realm of soft active materials as they are capable of responding to a non-mechanical stimulus – the permeation of a solvent – with a mechanical action – a volume change, thanks to the coupling between different physics. This mechanism of coupling can be exploited in a wide range of applications, including biomedical devices, making crucial the understanding of the dynamics of these systems. To this aim, we develop a nonlinear multiphysics theory and solve numerically the resulting model using the finite element method.

Keywords: gel, swelling, diffusion, polymer

1. Introduction

Polymer gels are soft elastic materials consisting of an elastic network of cross-linked polymers and a fluid, generally a liquid solvent, which permeates the elastic medium, inducing large volume deformations (swelling/shrinking). Some species of gels are also able to respond to non-mechanical stimuli as temperature or pH changes, or light activation, and vary accordingly their swelling degree.

The growing interest in soft materials is strongly related to their analogies with living tissues, making them suitable for biomedical applications. Specifically, gels are commonly employed as drug release devices and in tissue engineering. A part from the biomedical applications, gels can be found in the food industry, in coating and printing processes, in microfluidic devices and in cosmetics [1].

Mathematical models of gels involve at least two coupled physics: the mechanics of the polymer network and the migration of the solvent. In the following sections, we describe a nonlinear multiphysics theory coupling diffusion and large deformations [2]. In particular, the solvent-polymer mixture is seen as a single homogenized continuum allowing for the mass transport of the solvent. The theoretical model is then implemented in COMSOL Multiphysics and benchmarked on two representative problems.

2. Governing Equations

To establish the notation, we denote with $\mathcal{B}$, a region of the three-dimensional Euclidean space $\mathcal{E}$, the *reference* configuration of the material body and with $\partial\mathcal{B}$ its boundary; $\boldsymbol{m}$ is the unit normal to $\partial\mathcal{B}$. Let us also introduce the motion f, a smooth map that assigns to each material point $X \in \mathcal{B}$ and time $\tau \in \mathcal{I}$ a place $x = f(X, \tau) \in \mathcal{E}$; we denote with $\boldsymbol{F}$ its gradient, with $J = \det \boldsymbol{F}$ the Jacobian determinant and with $\boldsymbol{F}^* = J\boldsymbol{F}^{-T}$ the cofactor of $\boldsymbol{F}$. The displacement $\boldsymbol{u}$ of X is defined as $\boldsymbol{u}(X, \tau) = f(X, \tau) - X$; its gradient is related to the deformation gradient by $\boldsymbol{F} = \boldsymbol{I} + \nabla\boldsymbol{u}$. We call *actual* configuration the region of space $\mathcal{B}_\tau = f(\mathcal{B}, \tau)$ occupied by the body at time τ.

We can think of the actual swelling process from the dry state, that we denote with $\mathcal{B}_d$, to the current configuration as made of two subsequent processes: a free swelling from $\mathcal{B}_d$ to $\mathcal{B}$ and a further swelling from $\mathcal{B}$ to $\mathcal{B}_\tau$. This way, that is by choosing as reference configuration a swollen state distinct from $\mathcal{B}_d$, we circumvent the numerical problems due to the fact that the Flory-Rehner free energy [1] that is commonly employed to model swelling phenomena in polymer gels is singular at the dry state, *i.e.* when the solvent concentration is zero. In particular, since $\mathcal{B}$ is reached from $\mathcal{B}_d$ through a free swelling process, *i.e.* the system is allowed to swell without forces or mechanical constraints and attain chemical equilibrium, it has the same shape as $\mathcal{B}_d$ but is scaled by a uniform stretch λ_o, so that the volume ratio between the swollen and the dry configuration is $J_o = \lambda_o^3$. This quantity depends on the amount of solvent c_o present within the gel, measured per unit volume in $\mathcal{B}$: indeed, it is usually assumed that both the polymer and the solvent are incompressible, so that a local volume change is directly related to a change in solvent content. We can express this fact in the form of a volume constraint connecting J_o and c_o: $J_o = 1 + \Omega c_{do}$, being Ω is the solvent molar volume and $c_{do} = J_o c_o$ the solvent concentration measured per unit dry volume (in $\mathcal{B}_d$). Thus, $c_o = (J_o - 1)/\Omega J_o$.

An analogous constraint holds for the volume ratio between the actual and the dry configuration: $J_d = 1 + \Omega c_d$, with $c_d = Jc$ and c the concentration per unit dry and reference volume, respectively, associated with the swelling process from $\mathcal{B}_d$ to $\mathcal{B}_\tau$. Since the two processes from $\mathcal{B}_d$ to $\mathcal{B}$ and from $\mathcal{B}$ to $\mathcal{B}_\tau$ contribute multiplicatively to the swelling ratio $J_d = J_o J$, solving for J gives

$$J = \frac{1}{J_o} + \Omega c. \tag{1}$$

In addition to the volume constraint (1), the set of governing equations includes the balance of forces, the balance of solvent and the constitutive equations. The balance equations are naturally formulated in integral form and then localized into the following relations, holding in the reference configuration $\mathcal{B}$:

$$\text{div } \mathbf{S} + \mathbf{b} = \mathbf{0}, \tag{2}$$
$$\dot{c} = -\text{div } \mathbf{h}, \tag{3}$$

where $\mathbf{S}$ is the (Piola-Kirchhoff) stress, $\mathbf{b}$ is the bulk load per unit reference volume, and $\mathbf{h}$ is the solvent mass flux.

As concerns the constitutive equations, these are the outcome of the application of the thermodynamic principles, once a representation form of the free energy of the system has been given. Here, we choose the Flory-Rehner free energy, which is well established in the analysis of swelling gels. The volume constraint (1) is enforced, in the present formulation, by adding the term $p(J - 1/J_o - \Omega c)$ to the free energy of the system, where p is a Lagrange multiplier having the role of a pressure field. Leaving the details of the derivation to [2], we have

$$\mathbf{S} = \frac{G}{\lambda_o} \mathbf{F} - p\mathbf{F}^*, \tag{4}$$

$$\mu = \mathcal{R}T \left(\log\left(\frac{\Omega J_o c}{1 + \Omega J_o c}\right) + \frac{1}{1 + \Omega J_o c} \right. $$
$$\left. + \frac{\chi}{(1 + \Omega J_o c)^2} \right) + \Omega p, \tag{5}$$

$$\mathbf{h} = -\frac{cD}{\mathcal{R}T} \nabla \mu, \tag{6}$$

being G the shear modulus of the dry polymer, μ the chemical potential of the solvent inside the gel, $\mathcal{R}$ the universal gas constant, T the temperature, χ the dimensionless measure of the enthalpy of mixing and D the diffusivity of the solvent.

To complete the formulation of the model, Eqs. (2) and (3) must be supplemented by the appropriate boundary and initial conditions:

$$\begin{aligned} \mathbf{Sm} &= \mathbf{t} \text{ on } \partial_t \mathcal{B} \times \mathcal{I}, \\ \mathbf{u} &= \bar{\mathbf{u}} \text{ on } \partial_u \mathcal{B} \times \mathcal{I}, \end{aligned} \tag{7}$$

$$\begin{aligned} -\mathbf{h} \cdot \mathbf{m} &= q \text{ on } \partial_q \mathcal{B} \times \mathcal{I}, \\ \mu &= \mu_{ext} \text{ on } \partial_c \mathcal{B} \times \mathcal{I}, \end{aligned} \tag{8}$$

$$\begin{aligned} \mathbf{u}(X, 0) &= \mathbf{0}, \\ p(X, 0) &= p_o, \\ c(X, 0) &= c_o. \end{aligned} \tag{9}$$

$\partial_t \mathcal{B}$ and $\partial_u \mathcal{B}$ the parts of the boundary where a traction $\mathbf{t}$ and a displacement $\bar{\mathbf{u}}$ are assigned, respectively; $\partial_q \mathcal{B}$ and $\partial_c \mathcal{B}$ are the portions where the boundary source q is prescribed and the solvent concentration c is controlled through the chemical potential μ_{ext} of the external solvent, respectively. The constant pressure field $p_o = G/\lambda_o$ ensures that the initial state, which coincides with the reference swollen state, is stress-free.

The Dirichlet boundary condition $(8)_2$ for the diffusion problem corresponds to assuming the chemical equilibrium between the boundary surface of the gel and the external solvent. It is important to note that such condition is implicit in the concentration field (see Eq. 5): this fact has consequences in the numerical approach, as will be discussed in Section 3.

To summarize, in the framework of the model outlined here, solving an initial-boundary value problem consists in finding a displacement $\mathbf{u}$, a pressure p and a solvent concentration c such that the balance equations (2)-(3), the constitutive equations (4)-(6), the volume constraint (1) and the corresponding boundary and initial conditions (7)-(9) are satisfied.

3. Use of COMSOL Multiphysics

In order to implement the theoretical model described in the previous section in COMSOL Multiphysics v4.2a using the Weak Form PDE mode, the governing equations have to be recast in weak form:

$$-\int_{\mathcal{B}} (\boldsymbol{S} \cdot \nabla \widetilde{\boldsymbol{u}})\, \mathrm{d}V + \int_{\partial_t \mathcal{B}} (\boldsymbol{t} \cdot \widetilde{\boldsymbol{u}})\, \mathrm{d}A = 0, \quad (10)$$

$$\int_{\mathcal{B}} (\dot{c}\tilde{c})\, \mathrm{d}V = \int_{\mathcal{B}} (\boldsymbol{h} \cdot \nabla \tilde{c})\, \mathrm{d}V + \int_{\partial_q \mathcal{B}} (q\, \tilde{c})\, \mathrm{d}A, \quad (11)$$

$$\int_{\mathcal{B}} \left(J - \frac{1}{J_o} - \Omega c \right) \tilde{p}\, \mathrm{d}V = 0, \quad (12)$$

$$\int_{\partial_c \mathcal{B}} (\mu - \mu_{ext})\, \tilde{c}_b = 0. \quad (13)$$

Note that also the boundary condition on the chemical potential has been written in weak form. Indeed, as remarked in Section 2, the boundary condition on the assigned chemical potential $\mu = \mu_{ext}$ on $\partial_c \mathcal{B}$ takes the form of an implicit Dirichlet condition for the concentration c, being the balance of solvent written in terms of this state variable. So we cannot assign the concentration on $\partial_c \mathcal{B}$ directly. We treat the boundary concentration c_b as an additional state variable defined on the boundary where the chemical potential is assigned and employ a separate Physics Interface (Weak Form PDE – Boundary) for c_b, which is then computed by solving the algebraic equation (13). Hence, the continuity condition $c = c_b$ becomes a Dirichlet condition for the bulk concentration c.

A special treatment also deserves the volume constraint. In dealing with it, we adopt a mixed approach: the pressure field p is considered as an unknown of the problem (instead of introducing the constraint directly in the governing equations to eliminate p) and the constraint is imposed in weak form (Eq. (12)). To avoid volumetric locking, we use linear shape functions for the pressure field and quadratic Lagrange elements for the displacement and the other fields.

Other possible numerical issues are related to the presence of concentration boundary layers appearing, for example, in the early stages of transient free swelling processes. To resolve the sharp gradients without resorting to an excessive mesh refinement in the regions where boundary layers are present, we implement a change of variable, as suggested in [3]. We set $c = \exp(C)$ and solve for C within the computational model.

4. Results and Discussion

The finite element model was employed in two numerical experiments: the free swelling of a cubic gel and the squeezing of a thin gel layer.

In the first experiment, an almost dry cube ($\lambda_o = 1.001$) is brought into contact with a solvent bath at constant chemical potential $\mu_{ext} = 0$. Symmetry arguments allow to model only one-eighth of the cube and apply the appropriate symmetry boundary conditions. We used a structured mesh made of brick elements. The values of the parameters of the model were chosen as follows: $G = 40$ kPa, $\chi = 0.2$, $D = 8 \times 10^{-10}$ m^2/s, $\Omega = 6.023 \times 10^{-5}$ m^3/mol, $T = 293$ K. Denoted with L the length of the edge, the dimensionless time is defined as the ratio $\tau/(\frac{L^2}{D})$.

As can be observed from Figure 1, the swelling process is not homogeneous: the corners and the edges swell first, as they have a larger contact surface with the solvent in comparison with the other parts of the gel. This causes the faces of the cube to show a bowl-like shape, during the transient. This behavior has been observed experimentally, as reported in [4].

At steady state, the chemical potential μ of the solvent inside the gel equals the one μ_{ext} of the solvent outside, the concentration c is homogeneous and the deformation $\boldsymbol{F}$ is homogeneous and isotropic, that is the sample recovers its original cubic shape. The steady state can be determined analytically [2] in order to check the validity of the results obtained through the numerical simulation.
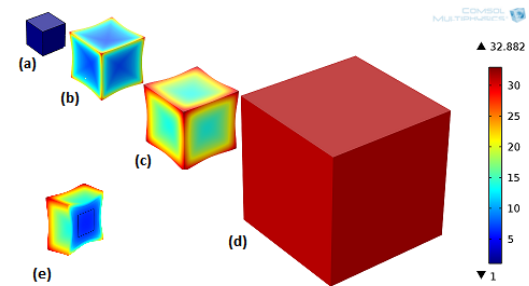

Figure 1. Several frames of the free swelling of a cubic gel immersed in a solvent bath. Color map shows the volume ratio $\boldsymbol{J}$ at different dimensionless times: (a) 0, (b) 1, (c) 10, (d) ∞. The cut view (e) is taken at the dimensionless time 10.
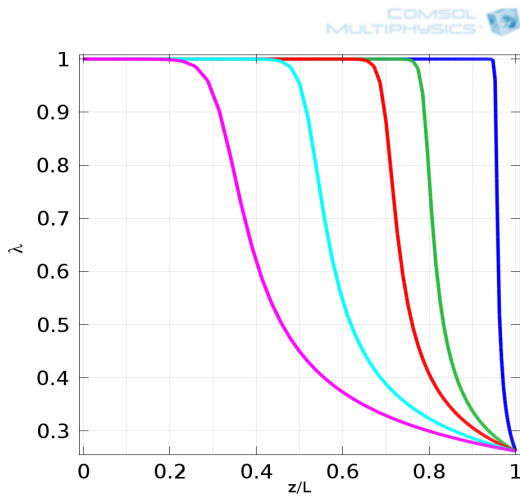
Figure 2. Stretch along the dimensionless coordinate z/L of a squeezed thin gel layer at several dimensionless times: (from right to left) 1, 10, 20, 50, 100.

In the second experiment a thin gel layer is pre-swollen ($\lambda_o \cong 3.51$) through immersion in a solvent bath at zero chemical potential and then is bonded to a rigid and impermeable substrate. To have a one-dimensional swelling, the gel is laterally confined by impermeable surfaces. We denote with L the swollen thickness of the layer and with z the coordinate along the thickness such that $z/L = 0$ is the bottom surface bonded to the substrate, while $z/L = 1$ is the top surface exposed to the solvent. The dimensionless time has the same definition as for the experiment of the cube.

After the initial swelling and bonding to the substrate, the chemical potential of the external bath is held fixed and a homogeneous compressive force $t = -sm$ is applied on top surface, squeezing the gel. The force causes the chemical potential of the solvent inside the gel to rise to a value greater than zero: this difference in chemical potential drives the solvent outside the gel. As shown in Figure 2, this does not happen immediately: the stretch λ along the thickness with respect to the reference (swollen) configuration is different from 1 (initial condition) only in the vicinity of the top surface, which is in contact with the solvent and the force. Then the system tends towards a new equilibrium steady state characterized by $\lambda < 1$.

The parameters of the model were chosen as: $G = 40$ kPa, $\quad \chi = 0.2, \quad D = 1\times10^{-9}$ m^2/s, $\Omega = 6.023\times10^{-5}$ m^3/mol, $\quad s\lambda_o^2\Omega/\mathcal{R}T = 0.05$, $T = 293$ K.

To resolve the steep stretch profile in the early transient the finite element mesh was locally refined. The numerical solution reported here was validated by comparison with the solution of a one-dimensional problem defined along the thickness [5].

5. Conclusions

We have described a nonlinear multiphysics field theory that allows to analyze the swelling phenomena that take place in polymer gels. We have implemented the theory in COMSOL Multiphysics v4.2a using the Weak Form PDE mode and successfully assessed the validity of the model through several benchmarks.

This model represents a valuable tool to have insight into the physical processes occurring in gels and to aid the design of gel-based devices.

6. References

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