VOLUMETRIC PHASE TRANSITIONS AND CAVITATION IN POLYMER GELS

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Summary
We formulate a continuum theory for the interaction between deformation and solvent permeation in polymer gels. This theory is then applied to the study of volumetric phase transition and cavitation in spherical polymer gels.

INTRODUCTION

The concomitant action of deformation and solvent permeation arises in a variety of contexts involving solids. This special kind of interaction between mechanics and chemistry underlies the interesting phenomenon of volumetric phase transitions in gels. In this paper, we exploit recently developed approaches (see [1] and [2]) to investigate the possibility of cavitation in gels undergoing volumetric phase transition. This investigation is preceded by an analysis of the role played by the interaction of mechanics and solvent permeation on the occurrence multiphase equilibria.

More specifically, we consider an intact, i.e., not hollow, spherical gel undergoing a spherically-symmetric deformation and investigate swelling induced by the combined action of mechanical loads, defined in terms of the ambient pressure and a normal traction, and the absorption of a swelling agent. The gel is viewed as a two-component body composed of two incompressible constituents, the elastic solid and the swelling-agent. The state of the gel is, therefore, fully characterized by the distribution of the swelling agent and the radius of a central hole, which is zero if the swollen sphere remains intact. When the ambient chemical potential of the swelling agent is fixed and chemical equilibrium prevails at the interface between the solid and the environment, we describe two types of intact statesaccording to which the solvent concentration is either uniform or piecewise uniform. Whereas a state with uniform solvent concentration is shown to be an equilibrium state, as state with piewise uniform composition is assumed to be attained during the volumetric phase transition of the spherical gel. For these states, we also investigate the possibility of cavitation—i.e., the sudden appearance of a central traction-free cavity. Of importance in the analysis presented here is the notion of net-free-energy potential, the definition of which requires the specification of the chemical potential of the environment and the prescription for the constitutive equation for the free-energy density.

A detailed analysis is presented for the special case in which the environment is a pure and incompressible fluid bath and the free-energy density is chosen in consonance with the classical theory of swelling of rubbers ([3]). Accordingly, the free-energy density of the swollen sphere is given by the sum of an elastic contribution for a Gaussian network and a Flory–Huggins mixing contribution. In particular, we investigate the effects of the constitutive parameters entering the theory– namely the number c_S of polymer chains per unit reference volume, the volume υ occupied by a swelling-agent molecule, and the Flory–Huggins interaction parameter χ– on the characteristics of the two types of intact states.

SUMMARY OF THE GOVERNING EQUATIONS

Consider the absorption of a swelling agent, or, for brevity, solvent, by a solid body $\mathcal{B}$ identified with its placement in a fixed reference configuration. As a result, the solid undergoes two interdependent processes: a mechanical (macroscopic) processes due to deformation and a chemical (microscopic) process due to solvent absorption, transport, and accumulation. The state of $\mathcal{B}$ at time t is then defined in terms of its deformation $\mathbf{y}(\cdot,t)$ and solvent concentration $c(\cdot,t)$, which respectively assign to each material point $\mathbf{X}$ in $\mathcal{B}$ the corresponding spatial location and solvent content per unit reference volume at time t.

We now present equations that govern the uptake of a solvent by $\mathcal{B}$ under the action of mechanical loads. This set of equations, which is a particular version of the general equations of [1], is comprised by the constraint of incompressibility, which represents the classical assumption that the solid and solvent are both incompressible, and two field equations that describe the mechanical and chemical features of the problem. The equations are conveniently organized as follows:

- Incompressibility constraint:

$$\det \mathbf{F} = 1 + \upsilon c. \tag{1}$$

- Mechanics:

$$\operatorname{Div} \mathbf{S} = \mathbf{0}, \qquad \mathbf{S} = \frac{\partial \hat{\psi}(\mathbf{F}, c)}{\partial \mathbf{F}} - q\mathbf{F}^{-\top}. \tag{2}$$

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- Chemistry:

$$\frac{\partial c}{\partial t} = -\text{Div}\mathbf{J}, \qquad \mathbf{J} = -\hat{\mathbf{M}}(\mathbf{F}, c)\nabla\mu, \qquad \mu = \frac{\partial\hat{\psi}(\mathbf{F}, c)}{\partial c} + \frac{\upsilon q}{1 + \upsilon c}. \tag{3}$$

Here and henceforth, $\mathbf{F} = \nabla\mathbf{y}$ is the deformation gradient, υ is the volume occupied by a solvent molecule, $\mathbf{S}$ is the Piola stress tensor, $\hat{\psi}$ and $\hat{\mathbf{M}}$ are the constitutive response functions determining the free-energy density and the solvent mobility, q is a Lagrange multiplier field associated with the constraint (1), $\mathbf{J}$ is the solvent flux relative to the solid, and μ is the chemical potential of the solvent in the solid. Body force, inertial effects, and solvent supply are neglected here. Importantly, mechanics and chemistry are coupled via the incompressibility constraint. Additional couplings may also arise through the response functions $\hat{\psi}$ and $\hat{\mathbf{M}}$.

Along with the aforementioned governing equations, initial and boundary conditions must also be imposed. Whereas the former involves the prescription of the initial distribution of the solvent concentration c, the latter requires the prescription of conditions that describe interactions between the solid and the environment. Here, we suppose that $\mathcal{B}$ is immersed in an environment wherein the chemical potential of the solvent is constant and equal to μ_a and assume that at the interface $\partial\mathcal{B}$ between the solid and the environment a traction $\mathbf{s}$ is prescribed and chemical equilibrium prevails, that is, that

$$\mathbf{S}\mathbf{n} = \mathbf{s}, \qquad \mu = \mu_a, \tag{4}$$

where $\mathbf{n}$ is the unit normal to $\partial\mathcal{B}$.

Observe that (2) expresses mechanical equilibrium. Chemical equilibrium, on the other hand, requires that c be time-independent and that $\mathbf{J} = \mathbf{0}$. These imply that $(3)_1$ is trivially satisfied and that $(3)_2$ reduces to $\nabla\mu = \mathbf{0}$. For the environment under consideration, this condition and $(4)_2$ imply that

$$\mu = \mu_a \tag{5}$$

on $\mathcal{B}$. Mechanochemical equilibrium states are therefore governed by (1), (2), $(3)_3$, and (5), along with the boundary conditions $(4)_1$. That (5) holds on $\mathcal{B}$ ensures satisfaction of $(4)_2$. Further, if the mechanical loading is conservative, that is, if there exists a potential energy $\mathcal{L}[\mathbf{y}]$, mechanochemical equilibrium states correspond to critical points of the net potential-energy functional of $\mathcal{B}$

$$\mathcal{F}[\mathbf{y}, c] = \int_{\mathcal{B}} (\hat{\psi}(\mathbf{F}, c) - \mu_a c\,)\, dV + \mathcal{L}[\mathbf{y}], \tag{6}$$

subject to the constraint (1). On the basis of the energy criterion for stability, an equilibrium state is stable if it is a local minimum of $\mathcal{F}$ and otherwise is unstable.

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