A theory of amorphous viscoelastic solids undergoing finite deformations with application to hydrogels

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Abstract

We consider a hydrogel in the framework of a continuum theory for the viscoelastic deformation of amorphous solids developed by Anand and Gurtin [Anand, L., Gurtin, M., 2003. A theory of amorphous solids undergoing large deformations, with application to polymeric glasses. International Journal of Solids and Structures, 40, 1465–1487.] and based on (i) a system of microforces consistent with a microforce balance, (ii) a mechanical version of the second law of thermodynamics and (iii) a constitutive theory that allows the free energy to depend on inelastic strain and the microstress to depend on inelastic strain rate. We adopt a particular (neo-Hookean) form for the free energy and restrict kinematics to one dimension, yielding a classical problem of expansion of a thick-walled cylinder. Considering both Dirichlet and Neumann boundary conditions, we arrive at stress relaxation and creep problems, respectively, which we consider, in turn, locally, at a point, and globally, over the interval. We implement the resulting equations in a finite element code, show analytical and/ or numerical solutions to some representative problems, and obtain viscoelastic response, in qualitative agreement with experiment.
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1. Introduction

It is widely known that many solids appear in a disordered form; such solids are commonly referred to as *amorphous*. The purpose of this paper is to formulate a macroscopic theory for the finite viscoelastic deformation of an amorphous solid under isothermal conditions, and subsequently apply it to modeling of stimulus-responsive hydrogels.

Hydrogels are crosslinked, macromolecular polymer networks whose composition can be tuned to exhibit large volumetric swelling in response to a variety of environmental stimuli, including small changes in temperature, pH, and electrical current. In order to model the response of hydrogels, there is a clear need for a

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satisfactory model of hydrogel behavior in the bulk. A large number of investigations into the bulk mechanical properties of hydrogels have been conducted; a review of many of these was provided in Anseth et al. (1996). Hydrogels exhibit rubber-like response to mechanical loading in the sense that they are capable of sustaining large strains before the onset of permanent damage. The interaction between the crosslinked macromolecular polymer network and the underlying solvent also gives rise to nonlinear viscoelastic behavior.

However, methods traditionally employed in viscoelasticity in general (see, e.g., Lakes, 1999) and in gel modeling in particular do not reflect advancements in continuum mechanics and thermodynamics of materials with microstructure.[1] On the contrary, our modeling approach is based on the viewpoint that to each independent kinematic process there should correspond a system of power conjugate forces. Such an approach has been taken by Ericksen (1961) in his works on liquid crystals, by Goodman and Cowin (1972) on granular and porous materials, and by a number of authors (Capriz and Podio-Guidugli, 1983; Capriz, 1989; Fried and Gurtin, 1993; Fried, 1996; Gurtin, 1996) for a variety of other problems. In this framework, the basic underlying mechanical quantity is power as opposed to force, and it is postulated that the power expended by each independent rate-like kinematical descriptor be expressible in terms of an associated force system consistent with its own balance. This requirement, together with the strong principle of virtual power, gives rise to a set of laws consisting of standard macroscopic force and moment balances and nonstandard microforce balance. Next, we adopt a set of constitutive functions properly restricted by the requirements of frame-indifference, material isotropy, and thermodynamics. Those restrictions, combined with the basic balances, give us a set of governing equations for the medium. Kinematic restrictions then give rise to a classical one-dimensional problem involving the expansion of thick-walled, infinitely long radially-loaded cylinder.

This problem serves as an elementary application of the derived viscous gel bulk theory. In particular, we consider in turn the inner boundary of the specimen to be fixed while the outer boundary is hard-loaded, leading to a Dirichlet problem, and the inner boundary to be pressure loaded while the outer boundary is traction free, leading to a Neumann problem. Each case leads to a nonlinear boundary-value problem which we first study analytically and then discretize using the finite element method.

This paper is organized as follows. To keep the paper reasonably self-contained, in Sections 2 and 3 we summarize the pre-existing theoretical framework, based for the most part on Anand and Gurtin (2003); namely, in Section 2, we give the basic equations associated with microforce theory and in Section 3 we impose the general restrictions on the constitutive functions associated with amorphous hydrogels. The original contribution starts with Section 4 as we choose a particular free energy density and derive the associated force fields, while in Section 5 we adopt kinematics associated with radially symmetric solutions and scale the resulting governing equations. Further, in Section 6, we consider the Dirichlet problem and the stress-relaxation behavior, both locally and globally. In Section 7 we do the same for the Neumann problem and creep, considering pure shear kinematics for localization. We conclude with a summary of our results and discussion of future work in Section 8.

2. Basic laws

To account for the roles of elastic mechanisms such as stretching and rotation of the intermolecular structure, as well as inelastic mechanisms, such as relative slippage of the molecular chains, we adapt the inelastic microforce theory of Anand and Gurtin (2003), originally applied to modeling of viscoplastic behavior of polycarbonate.

We consider a hydrogel that, in a given *reference state*, occupies a region $\mathcal{B}_*$, and denote by X an arbitrary point of $\mathcal{B}_*$. A motion of $\mathcal{B}_*$ is a smooth one-to-one mapping $x = y(X,t)$ with *deformation gradient, velocity* and *velocity gradient* (in the deformed configuration) given by[2]

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[1] For a *material with microstructure* we recognize a material, that, for a complete mechanical description, necessitates the introduction of additional, with respect to standard strain, kinematical fields, e.g. plastic strain, internal state-variables etc. A classic example of such material is liquid crystal with the associated director field.

[2] Grad and div denote the gradient and divergence operators in the deformed configuration, whereas Grad and Div denote these operators in the reference configuration.