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A Coupled Chemo-Mechanical Framework for Anomalous Volumetric Response in Soft Polymers

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Extended Abstract

Abstract

The mechanical behavior of rubber-like materials is traditionally modeled using invariant-based hyperelastic potentials that assume a static polymer network and strict local incompressibility. Recent experimental evidence by Wang et al. [1] has challenged these assumptions, revealing striking anomalies. While elastomers remain macroscopically incompressible, they exhibit significant local compressibility, shrinking under tension and swelling under compression. These counter-intuitive phenomena suggest that the material possesses an internal degree of freedom typically neglected in standard continuum mechanics, the ability of its constituents to reorganize under stress. In this work, we develop a chemo-mechanical theoretical framework to rationalize these experimental findings. We treat the elastomer as a multi-phase continuum where a mobile phase, representing unbounded monomers or free chains, redistributes to reach thermodynamic equilibrium under mechanical loading. The macroscopic response emerges from the energetic competition between the fixed polymer network and this mobile species. We formulate a generalized free energy density comprising three essential contributions. First, an entropic term captures the statistical distribution of mobile species and their fundamental chemical interaction with the host network. Second, a density-dependent osmotic pressure term accounts for the physical volume occupied by the mobile phase and its resistance to local volumetric deformation. Third, a deviatoric coupling term links network distortion to the chemical potential, providing the primary thermodynamic driving force for mass transport by

promoting mobile phase migration toward regions of high shear strain. Unlike standard poroelasticity where fluid migrates to relax pressure, our model demonstrates that the mobile phase redistributes to minimize total free energy through shear-driven mechanisms. This shear-driven migration, combined with capillary-like interactions between the mobile phase and cross-linked network, generates the observed anomalous behavior. The resulting governing equations couple the balance of linear momentum with a conservation law for the mobile phase, governed by a chemical potential inherently linked to the mechanical stress state. Crucially, while local Jacobian fluctuations are permitted, global conservation of the mobile species ensures macroscopic incompressibility, rigorously satisfying rubber elasticity constraints while explaining anomalous volumetric inversions. We present a monolithic finite element implementation utilizing mixed formulations designed to ensure numerical stability and prevent volumetric locking. The framework successfully reproduces the experimental observations from Wang et al., including the spatial inversion of volumetric response, where regions under tension exhibit $J<1$ with elevated mobile phase concentration, while compressed regions show $J>1$ with mobile phase depletion. This study reveals that the interplay between mechanical deformation and internal mass transport represents a critical yet previously overlooked mechanism in polymer mechanics, offering new perspectives for understanding and designing soft materials.

Keywords:

Rubber elasticity Chemo-mechanical coupling Soft polymer mechanics Multi-phase polymers Mobile phase transport

References:

[1] Wang, Z., et al. (2024). 3D observations providestriking findings in rubber elasticity. PNAS, 121(24),e2404205121.