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

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Introduction

Classical hyperelastic constitutive models, from the fundamental Neo-Hookean formulation to sophisticated invariant-based frameworks, have proven highly successful in describing the mechanical response of rubber-like materials under the assumption of a static, affinely deforming polymer network with strict local incompressibility. However, recent experimental observations by Wang et al. [1] using advanced X-ray tomography have revealed striking anomalies that fundamentally challenge these assumptions. While elastomers maintain macroscopic incompressibility, they exhibit significant local compressibility. Most remarkably, the material shrinks locally under tension and swells under compression, a behaviour that appears to violate conventional thermodynamic principles and suggests apparent negative bulk moduli in regions of high strain gradients.

Thermodynamic Framework

This study aims to rationalize these observations by treating the elastomer as a multi-phase system where the mobile phase redistributes to reach thermodynamic equilibrium under mechanical loading. The macroscopic mechanical response emerges from the energetic competition between mobile phase and the fixed polymer network.
The free energy of the mobile phase comprises three physically distinct contributions that govern its kinetics and interaction with the fixed network. The first is an entropic term that captures the configurational entropy of the mobile species and their fundamental chemical interaction with the host network. The second contribution is a density-dependent osmotic pressure term that accounts for the physical volume occupied by the mobile phase and its resistance to local volumetric deformation. The third contribution is a deviatoric coupling term that links network distortion to the chemical potential of the mobile phase.
This interaction model provides the primary thermodynamic driving force for mass transport, promoting mobile phase migration toward regions of high shear strain. Such mechanism drives the formation of localized concentration gradients and the emergence of distinct high-density and low-density domains within the soft matrix.
Combined with osmotic interaction, this generates the observed anomalous behavior. Under compression, the mobile phase egresses from high-pressure regions, but the entropic contribution induces local volumetric relaxation as the concentration decreases. Conversely, under tension, mobile phase ingresses, and osmotic effects lead to local volumetric reduction despite tensile loading.

Crucially, while the model permits local Jacobian fluctuations reflecting the redistribution of the mobile phase, the global conservation of the mobile species ensures macroscopic incompressibility. This dual nature allows the framework to rigorously satisfy the constraints of rubber elasticity while providing a physical rationale for the anomalous volumetric inversions observed experimentally.

Numerical Implementation and Results

The coupled chemo-mechanical problem was implemented in a monolithic finite element framework. The governing equations comprise the mechanical equilibrium and the mass balance for the mobile phase, forming a system of coupled partial differential equations requiring simultaneous solution.

The framework successfully reproduces the striking experimental observations from Wang et al. [1] for four-point bending tests. Figure 1 presents simulation results showing (a) the spatial distribution of the Jacobian and (b) the mobile phase concentration field, n_m. The results capture the characteristic inversion of volumetric response, with the upper fibers subjected to tensile stress exhibiting negative volume change ($J < 1$) accompanied by elevated mobile fraction, while lower fibers under compression show volume swelling ($J > 1$) with mobile phase depletion. The magnitude of local volumetric strains reaches levels consistent with experimental measurements, while the global specimen volume remains essentially constant

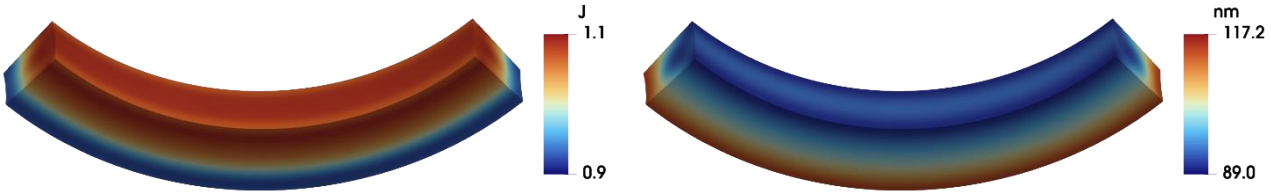

Figure 1 Simulation results for bending test showing (a) Jacobian of deformation and (b) mobile phase concentration, nm is the number of unbounded molecules per reference unit volume, initial uniform concentration is $n_m = 100$.

Conclusions

By treating mobile phase kinetics within a rigorous thermodynamic framework, we provide a physical and mathematical rationale for the anomalous elasticity observed in synthetic polymers. The proposed three-component free energy formulation captures the essential physics of mobile phase redistribution and its coupling to network deformation, enabling numerical capture of deformation inversion in three-dimensional continuum settings without requiring phenomenological modifications to classical hyperelasticity.

Future extensions may include rate-dependent formulations to capture viscous effects at extreme loading rates, investigation of the influence of cross-linking density on mobile phase content, and exploration of how this mechanism affects fatigue resistance and long-term mechanical performance in service conditions.

References

[1] Wang, X., et al. (2024). "Anomalous volumetric response in soft polymer networks." *PNAS, 121(25)*. https://www.pnas.org/doi/10.1073/pnas.2404205121