Extreme Thermodynamics: Coupling thermodynamic instabilities to mechanics in macroscopic polymer gels

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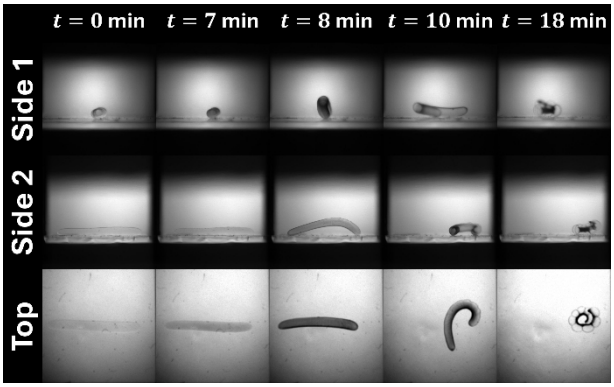
Among thermoresponsive hydrogels, poly(N-isopropylacrylamide) (pNIPAM) gels are well known for their sharp volume-phase transition near T ≈ 32ºC, at which they expel most of their solvent. Under slow, quasistatic heating, the gel shrinks affinely. The successive equilibrium states are defined by the condition that the chemical potential of the solvent inside the gel equals that in the surrounding bath. In contrast, a rapid temperature quench produces an effectively impermeable outer skin that fixes the total volume, preventing the solvent from equilibrating in and outside the gel. Instead, under this state of constrained equilibrium, phase separation between solvent-rich and solvent-poor regions occurs. For cylindrical gels, the simpler phase separation is axisymmetric: the outer region collapses while the interior remains swollen. Introducing a polarization vector to describe the solvent distribution reveals that axisymmetry is spontaneously broken, as this lowers the system's free energy. If the gel's centerline is initially curved, this polarization couples to the local curvature and tends to point opposite to the normal vector, thereby biasing the phase separation process and dictating how the gel bends. This coupling generates a feedback loop: curvature influences polarization, and polarization in turn drives further shape change. In S-shaped gels, where the curvature reverses sign, the discontinuity in the polarization vector is reconciled by a twist along the central section. Finally, we show that cylindrical gels of different diameters quenched above T exhibit distinct size- and temperature-dependent instabilities.

Keywords:
Hydrogels, Phase separation, Geometric evolution, Pattern formation



Evolution of a cylindrical hydrogel inside a bath under a rapid heating, imaged from three orthogonal directions. The hydrogel darkens as an impermeable skin forms, fixing its volume. Its geometry evolves, along with the solvent distribution, in a feedback loop. Finally, a 'bubble' pattern appears.

References:

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