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Local volume changes in deformed elastomers with mobile chains

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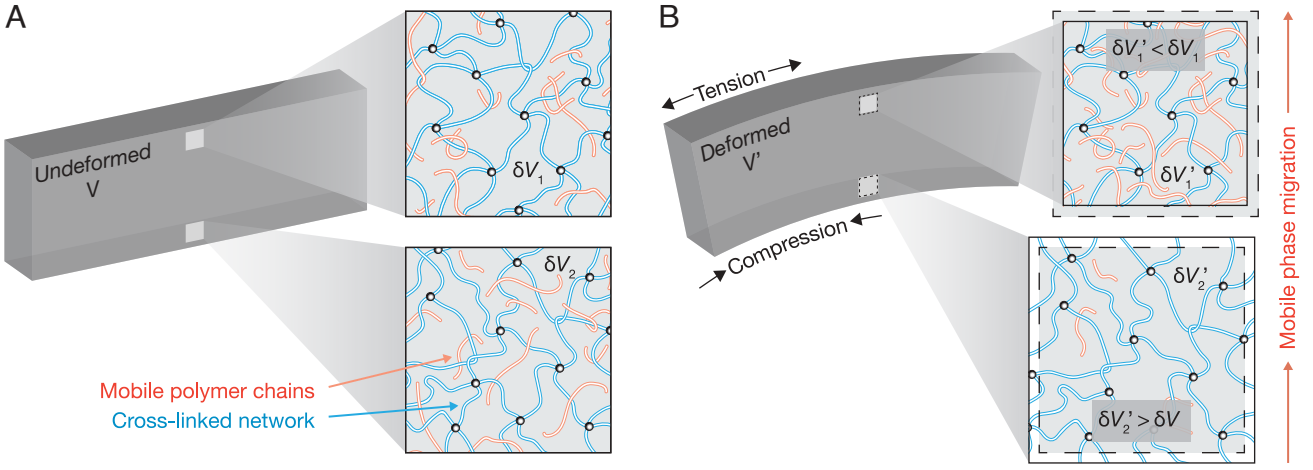

Fig. 1. Illustration of local volume changes during bending of an elastomeric specimen. (*A*) Common elastomers can contain mobile polymers (orange) scattered within a background cross-linked network (blue). Schematics depict a similar molecular picture within representative volumes δV_1 and δV_2 on the top and bottom of an undeformed sample. (*B*) Bending induces tension on top regions and compression on bottom regions in the deformed state. The deformation can drive the mobile phase from regions in compression toward those in tension. Surprisingly, the deformed local volume $\delta V'$ can increase in compression ($\delta V_2' > \delta V_2$) and decrease in tension ($\delta V_1' < \delta V_1$). The specimen conserves its global volume before and after the deformation such that $V' = V$.

Elastomers are abundant in daily commodities like car tires and clothing and advanced technologies like medical devices and spacecraft. Their distinctive mechanical response underscores their utility across such diverse applications. On the macroscopic scale, rubbers can reversibly undertake large deformations. On the molecular scale, long polymer chains can reversibly uncoil as governed by entropic elasticity within chemically cross-linked networks (1). Rubber elasticity bridges these length scales to explain the response of polymer networks to deformations (2). Many classical models in rubber elasticity describe network deformations by applying statistical mechanics to describe the collective contributions of individual polymer chains (3, 4). Experiments show that polymer networks conserve volume when deformed, motivating the incompressibility assumption used throughout rubber elasticity (5, 6). In PNAS, Wang et al. (7) report an interesting phenomenon in an elastomer system containing a cross-linked network and mobile polymer chains. They particularly leverage advances in X-ray computed tomography (XCT) and digital volume correlation (DVC) techniques to examine the details of bulk deformations in these elastomers, including local volume changes. Surprisingly, regions in compression increase their volume. Concurrently, regions in tension decrease their volume. Overall, the global sample volume is conserved.

The researchers find that advances in XCT and DVC enable detection of slight heterogeneities in relatively homogeneous materials to measure deformations of bulk solids. XCT is a common imaging modality that reconstructs the internal 3D structure of materials by capturing and resolving a series of 2D X-ray projections from different angles. While primarily employed in medical imaging, it has emerged as a central avenue for nondestructive structural visualization in materials science. Its utility in solid mechanics has been heightened since its pairing with DVC, a technique that traces markers or speckles in volumetric scans to measure displacements over time (8). Together, key physical parameters can be imaged and tracked while deforming a sample. Although XCT provides adequate images to perform DVC on most heterogenous materials (9), images of nominally homogeneous materials are usually unsuitable for DVC due to lack of a strong speckle. Flux enhanced tomography for correlation (FETC) offers a promising solution. A higher flux intensity supplied during XCT can capture minor heterogeneities in a nominally homogeneous solid; however, the increased supply of X-ray photons can also

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saturate the scan. Filters can diminish this effect if used to attenuate low-energy X-ray photons. FETC carefully balances a flux increase with filtering to produce suitably speckled images of relatively homogeneous materials to perform DVC. While the degree of microstructural heterogeneity required for its success has not been extensively studied, FETC provides sufficient detail to track material points in common polymers like silicone rubber, nylon, and high-density polyethylene.

To probe the large deformations typical of polymer networks, conventional DVC approaches must also be adapted to minimize the effects of large distortions. The displacement cannot be accurately calculated if voxels warp too much between scans. The authors resolve this by splitting the loading into short steps, effectively linearizing the deformation. Although this requires the node positions to be preset in space instead of within the material, the displacements can be recovered algorithmically in a process analogous to finite element remeshing. The incremented states can then be interpolated by computational methods to capture the entire loading procedure. In their paper, the researchers leverage both FETC and large deformation DVC to capture the displacements of local volumes while extending and bending incompressible silicone rubber specimens. These techniques enable the discovery of local volume changes within materials subject to large deformations.

In PNAS, Wang et al. report an interesting phenomenon in an elastomer system containing a cross-linked network and mobile polymer chains.

Wang et al. (7) further propose a hypothesis to explain these local volume changes. They suggest that the presence of un-cross-linked polymer chains within real elastomer systems could provide a vehicle for phase motion during loading. The process of cross-linking long polymer chains leads to two phases within silicone rubbers tested in their study: a network of cross-linked chains and a mobile phase of free chains. In an undeformed beam depicted in Fig. 1*A*, small representative volumes δV_1 and δV_2 in different parts of the sample contain similar relative densities of each phase. When bent, the deformation gradient can drive mobile chain migration. Un-cross-linked polymers can be forced from regions in compression to regions in tension. The regions in tension depicted in Fig. 1*B* undergo local volume reduction such that the deformed volume $\delta V_1' < \delta V_1$. In parallel, regions in compression undergo local volume enhancement to $\delta V_2' > \delta V_2$. The sample notably still conserves its global volume such that the total deformed volume V' is equivalent to the total undeformed volume V. The framework described by the authors suggests that deformations can facilitate chain egress from compressed regions and unexpectedly expand the local volume.

Novel tools and systems are a cornerstone for experimental progress. While existing modalities have refined structure-property relations, state-of-the-art imaging systems cannot yet fully capture interactions across length scales in materials under extreme loading conditions. Improving upon traditional XCT and DVC techniques, FETC now enables nondestructive local volume tracking in comparatively homogeneous materials under large deformations. This method for improving image correlation accuracy could serve as a valuable tool for exploring challenges in elasticity, fracture, materials science, and biomechanics. In common silicone rubbers, it led to unexpected measurements of local volume changes during large deformations. Advancements in other imaging modalities could also provide platforms for visually capturing interesting phenomena through experimental mechanics.

Further research is needed to fully explain each detail surrounding this phenomenon. For example, when water migrates out of one region in a hydrogel, the volume decreases (10). Unexpectedly, when the mobile phase migrates out of one region in the elastomer, the volume increases. While a plausible hypothesis is presented to justify this result, the underlying explanation could be reinforced through additional research. The timescales associated with each process must also be carefully considered. The authors observe sudden volume changes and no rate dependence of the kinetic response. This implies that the effective migration time of the mobile phase must be orders of magnitude faster than that of water in gels. While shear thinning effects could help to explain this gap, further studies could provide more insights into the details of mobile phase motion during large deformations.

This also raises questions about the extent to which this phenomenon occurs in polymers. Are local volume changes ubiquitous in elastomers with mobile chains? Do they occur broadly across polymers? Preliminary results studying Nylon and high-density polyethelene suggest local volume changes also occur in thermoplastics. The authors do not observe local volume changes in uncured natural rubbers. Whether mobile phases can migrate in broader classes of polymeric materials remains an open question.

The relevance of silicone rubber across commercial applications emphasizes the importance of these findings. This elastomer has been widely adapted throughout the biomedical, microfluidic, and aerospace industries. Manufacturers routinely use silicone rubber in products such as breast implants (11), catheters (12), microfluidic chips (13, 14), and sealants (15). In addition, technologies from emerging fields like stretchable electronics (16) and soft robotics (17) actively exploit the reversible large deformation behavior of elastomers to interface with the body and the environment. Understanding the relationship between external mechanical stimuli and internal elastic response is essential for designing elastomeric devices across disciplines that maintain reliable and predictable mechanical performance. The new observations, understandings, and tools reported by Wang et al. (7) could greatly impact many future applications.

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