Is gold really stiffer at the nanoscale?

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Abstract

The elastic properties of metallic nanostructures have been a subject of intense debate, often clouded by a lack of distinction between isolated nanoparticles and nanocrystalline solids. While the latter frequently exhibit size-dependent compressibility due to grain boundary effects and inter-crystallite constraints, the intrinsic elasticity of individual, ligand-protected nanoparticles remains an open question. Among these, gold stands out as a paradigmatic case where the literature remains divided; previous studies on Au nanoparticles report a chaotic landscape of bulk modulus K_0 values, with discrepancies of up to 70%—ranging from 133 to 290 GPa [1-3]—compared to the well-established bulk value of 167 GPa [4].

In this work, we demonstrate that these variations are largely experimental artifacts rather than intrinsic size effects. We present a systematic study using high-pressure synchrotron X-ray diffraction on a diverse library of Au nanostructures in colloidal dispersions: from single-crystalline spheres and rods [5] to penta-twinned decahedra and rods with tetragonal and orthorhombic symmetries [6]. By ensuring strictly hydrostatic conditions, we eliminate the deviatoric stresses that typically render diffraction data unreliable and lead to artificial overestimations of K_0. Our results reveal a remarkably consistent bulk modulus of $K_0 \sim 170$ GPa across all shapes, symmetries, and sizes (10–50 nm), echoing the behavior of bulk gold.

To push the limits of this invariance, we extended our research to the molecular regime by performing high-pressure single-crystal X-ray diffraction on the atomically precise $Au_{25}(PET)_{18}$ cluster. By successfully solving the complete crystal structure under pressure and tracking the individual inter-atomic Au-Au distances within the 13-atom gold core of the cluster, we provide direct evidence that, within our experimental accuracy, the Au-Au bond remains as compressible as in the macroscale. This work offers a consistent framework to reconcile previous discrepancies: once experimental artifacts and grain boundary effects are decoupled, gold's elasticity appears as an intrinsic property of the metallic bond, showing a remarkable size-independence from the macroscale down to the atomic cluster.

References

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