

4at Simulations of Materials Systems with Multiple Coordination States Using a Reactive Force Field

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Using molecular dynamics (MD) simulations, we can elucidate phenomena that are inaccessible to experiments, such as geological processes in the Earth's interior, as well as address the long-standing problems in science, such as the origin of the anomalous thermo-mechanical properties and the nature of polyamorphic transitions in network glasses. Essential for the success of such simulations is the use of a new type of reactive interaction potential that realistically accounts for the charge redistribution associated with changes in bonding structure, and accommodates multiple coordination states during the MD simulations. Our model was initially designed for mixed ionic-covalent bonding systems. The directional character of the covalent bonding is modeled by angular constraints in terms of three-body interaction. The balance between the ionicity and covalency of a bond is controlled by a charge transfer function. It can easily be adopted to study reactive systems, especially with species undergoing different hybridization states.

Based on this model, we uncovered the nature of a particular high-pressure phase of silica, whose structure has remained elusive for over a decade following its initial experimental observation. Our simulations reveal a ubiquitous tendency for oxygen ordering in various crystalline phases of silica under high pressure, which seemingly represents the universal pathway for the densification of polyhedral network structures. We also uncovered the mechanisms of structural transitions in silica glass. Our studies show that thermo-mechanical anomalies, which are manifest at low pressures, are due to localized structural transitions that involve reversible atomic displacements similar to those of the alpha to beta transformation in cristobalite silica. Irreversible polyamorphic transitions occur at higher pressure and lead to permanent densification of silica and the creation of structures that are denser the higher the temperature.