Dynamics and thermodynamics of superionic materials: the case of α-AgI

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Superionics are materials that exhibit anomalously high ionic conductivities, with liquid-like diffusion of an ionic subspecies through a solid matrix. Despite their scientific and technological importance, particularly in view of their usefulness as solid-state electrolytes for fuel cell technology, the exact nature of their behavior remains poorly characterized at the atomistic level. Here, we perform extensive Car-Parrinello molecular dynamics simulations on the archetypical superionic conductor α-AgI in order to elucidate both the microscopic ion dynamics and the thermodynamic nature of this class of systems.

First-principles molecular dynamics are now easily able to access the timescales relevant to fast-ion conductors, and as such are ideal for identifying microscopic conduction mechanisms and pathways. In addition to tracing the most frequented lattice sites for the diffusing cationic sublattice, we were able to enumerate a set of phenomenological rules that govern its simultaneous ordering about the solid anionic lattice. Maximally-localized Wannier functions are used to characterize bonding in AgI, and we find evidence of well-defined chemical changes in the ionic bond as a function of the local environment.

Finally, we investigated the thermodynamics of the phase transitions in the AgI system, finding clear evidence of solid-to-liquid melting for the silver sublattice entering the superionic phase. Low-temperature metastable ordered phases have also been identified. Contributions to the phase behavior have been resolved by individual sublattices, providing a rich picture of the phenomenology of this material up to the melting point and consequent collapse of the superionic phase.