Disorder and dynamics in bulk and nanostructured superionics

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We report simulation and theoretical work on superionic conductors with the fluorite crystal structure. Our aims are to clarify the relationship between microscopic disorder and macroscopic conductivity, and to test theoretical descriptions of superionicity, so that new materials with optimised properties may be developed. We examine nanostructured, doped and pure superionics. The decrease in the conductivity in a superionic as ions return to their perfect-crystal sites on cooling is similar to the structural arrest of a supercooled liquid as it is quenched into its glassy state. Part of our approach uses methods developed for supercooled liquids to analyse superionics [1]. We showed, for instance, that the Adam-Gibbs relation [2] holds well for certain superionics, while Tarneberg and Mellander applied the Vogel-Fulcher-Tamann equation to superionic lithium sulphate [3]. Most previous theories of superionicity were developed around the perfect crystal, and are ill suited to the disordered superionic, but methods constructed to deal with viscous liquids are forced to treat the collective behaviour of strongly interacting particles in highly disordered environments, and are ideal for superionics.

Figure 1 shows an inherent structure from a simulation of lead fluoride, a typical superionic. The term 'inherent structure' was coined nearly twenty years ago by Stillinger and Weber to describe a microscopic state of matter in mechanical equilibrium [4]. Just as a crystal vibrates around its state of high symmetry where forces on the atoms vanish, a viscous liquid vibrates around an amorphous state with vanishing forces, the inherent structure. The extra element in a liquid (or superionic) is that the system visits a series of inherent structures as mass, charge and momentum are transported in a manner forbidden for a perfect crystal. This elegant separation of vibration from transport has more recently been extensively used to analyse the structures and dynamics of glasses, and seemed a natural choice for application to superionics.

Defects in lead fluoride inherent structures have a strong tendency to cluster (see figure 1). The crystal expands across the transition, and the energy required to create a defect drops by an order of magnitude. The origin of the clustering is the minimisation of the energy of lattice distortion, so that there is an effective interaction between the defects. The inherent structures show that while the mean-field theories often used to describe variations in disorder fit the known data well, they are based on incorrect assumptions about disorder in the crystal [5, 6]. We have examined the change in the nature of the inherent structures as the crystal expands across the transition and related the various components of the energy and entropy to the number and arrangement of defects. We show how the inherent structures explain the temperature variation of the disorder and conductivity, including the position of the superionic transition.

An important recent development uses alternating layers of the fluorides of calcium and barium, about 16nm thick, deposited with Molecular Beam Epitaxy, which conduct parallel to the interface around a hundred times better than either pure material [7]. Disorder is increased near the interface, and the layer spacing maximises this disorder, but no theoretical study of influences on the disorder like that described above for bulk lead fluoride has been made.

We have performed molecular dynamics simulations of interfaces between the fluorides of calcium and barium, using a realistic model for the interactions between the ions that includes the effects of the ions' polarisability. The detailed information available from simulation allows us to separate out contributions to the conductivity increase from different aspects of the interface structures seen in electron microscopy experiments [8]. For instance, we compare the conductivities at interfaces with and without dislocations relieving the strain on the crystals. These simulations show an increase in the conductivity associated with stresses on the calcium fluoride phase, and show that there is virtually no transfer of charge from one phase to the other, a proposed explanation for the increase in disorder and conductivity. We discuss the role of screening by mobile ions and elastic deformations of the lattice of fixed ions.
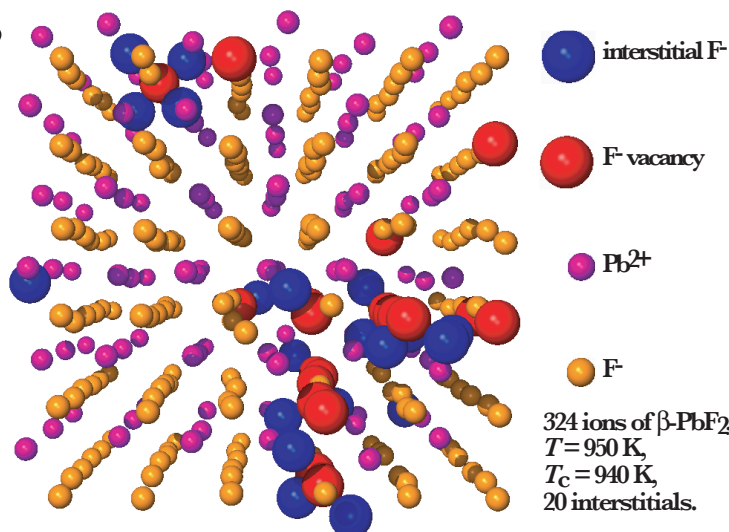
Figure 1: An inherent structure for lead fluoride calculated. In this configuration the forces on all ions vanish. Interstitials and vacancies cluster to minimise the strain on the lattice. By calculating these inherent structures for various temperatures and densities we can break thermodynamic properties into vibrational and configurational components and so relate the macroscopic properties to the defects and their interactions. We find the usual mean-field theories of defect interaction fail.
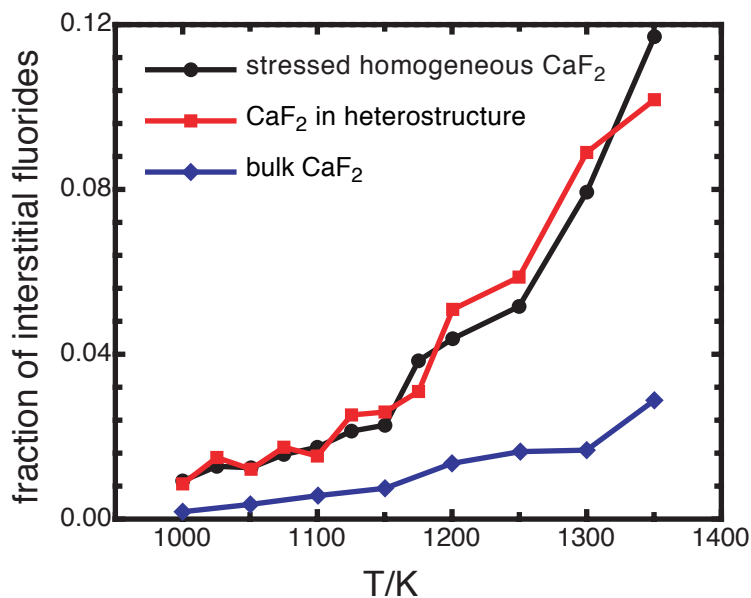
Figure 2: The fraction of fluoride ions in simulated CaF_2 that have moved off their perfect crystal sites to become interstitials. The blue diamonds are for the bulk crystal, the black circles are for the CaF_2 part of a CaF_2/BaF_2 layered structure, and the red squares are for a homogeneous CaF_2 simulation with the same (anisotropic) lattice parameters as are found in the layered structure. This shows that it is the strain induced by the interface that produces the extra disorder and conductivity, and not some transfer of charge across the interface.

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