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Ab initio lattice dynamics for materials design and characterisation

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First-principles modelling is a well-established tool in the materials sciences, regularly providing explanatory support to experimental characterisation. Recent advancements in computing power and the continuing development of practical, high-level simulation tools such as density-functional theory have made large-scale computational screening a viable prospect, as typified by undertakings such as the Materials Project.

Despite many successes, a key element that is often omitted from contemporary modelling studies is the lattice dynamics. Routine solid-state calculations tend to probe the "athermal" structure with the atoms frozen in their equilibrium positions, whereas in reality, atoms show zero-point fluctuations about their equilibrium positions even at absolute zero, and the structural dynamics at finite temperature are intimately connected to the physical properties.

Simulation of the phonon modes (lattice vibrations) of a periodic solid allows the dynamical stability of a hypothetical material to be checked through the presence or absence of imaginary frequencies, and readily provides access to a range of simulated spectra (e.g. IR/Raman) to aid experimental characterisation. The phonon frequencies also enable temperature-dependent thermodynamic free energies to be calculated, which is crucial for capturing more subtle effects such as the thermodynamic equilibria between energetically-similar phases or polymorphs. Using more sophisticated calculations, other temperature-dependent properties can be calculated from first principles, including thermal expansion (and its effect on "static" properties such as the electronic structure), mechanical stiffness, and lattice thermal conductivity.

Although the theoretical infrastructure has existed for more than a decade, it is only very recently that the codes and computing power needed to apply it routinely in conjunction with high-level simulation techniques have become available. Over the past three years, we have been benchmarking lattice-dynamics techniques across a diverse range of systems and problems, with the overall aim of establishing their utility as a core component of the modelling "toolbox". Our studies have ranged from photovoltaic absorbers[1] and thermoelectric materials[2] to molecular pharmaceuticals, with systems including lead and tin chalcogenides, hybrid halide perovskites[3] and molecular crystals.

This talk will cover the basic theory of lattice dynamics and illustrate its application to various challenges in contemporary materials design, including: (1) assessing material stability, (2) simulating vibrational spectra, (3) modelling structure and properties at finite temperature, and (4) studying phase transitions.

Figure | Applications of lattice dynamics. (a) Calculated thermal expansion of PbTe from 0-500 K compared to experimental data. (b) Simulated terahertz spectrum of the hybrid perovskite (CH3NH3)PbI3 in the low-temperature orthorhombic phase. (c) Calculated free energy of decomposition of Sn2S3 from 0-1000 K, showing the reaction to be thermodynamically unfavourable.

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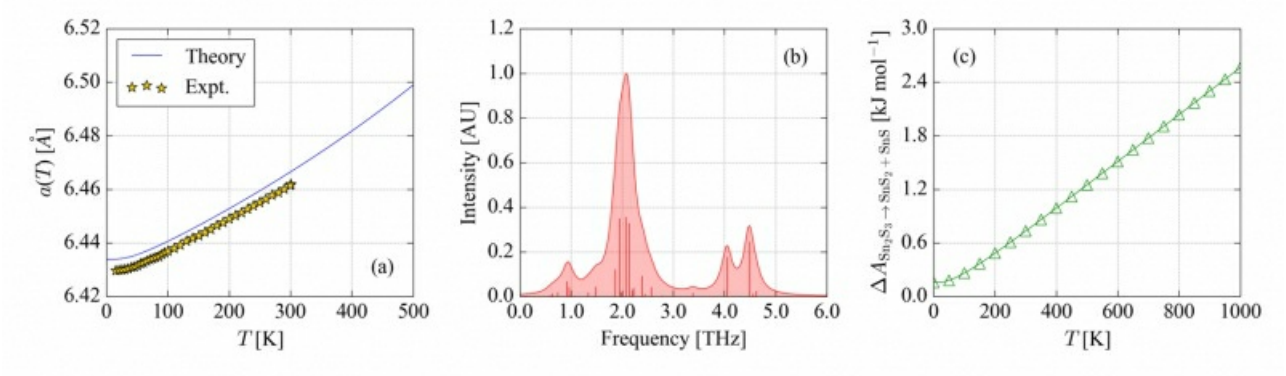

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