SI^2: Automated Statistical Mechanics for the First-Principles Prediction of Finite Temperature Properties of Crystals

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Introduction

A major objective of materials science is to develop methods to predict the properties of new materials from first principles using quantum mechanics as a starting point. The properties of many materials, however, depend strongly on temperature, making it essential to use a statistical mechanics approach to connect quantum mechanical descriptions to macroscopic thermodynamic, mechanical and kinetic quantities.

An important tool in statistical mechanics approaches is the *effective Hamiltonian*, which is a mathematical function in a high dimensional space that can extrapolate expensive first-principles electronic structure calculations within Monte Carlo simulations. To date, effective Hamiltonians have been constructed on a case-by-case basis and are specially tailored for a particular degree of freedom.

The goal of this project is to extend the CASM software package to algorithmically construct effective Hamiltonians for arbitrarily complex crystal structures and for a wide variety of site degrees of freedom, including

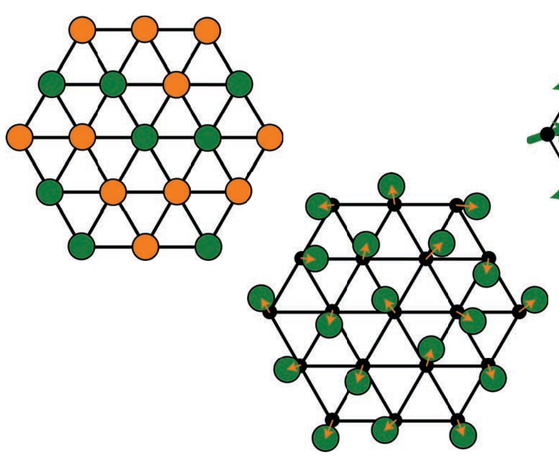
(i) chemical alloying degrees of freedom
(ii) vibrational excitations (harmonic and anharmonic)
(iii) magnetic degrees of freedom (including anisotropy and the Dzyaloshinskii-Moriya interaction)
(iv) molecular orientational degrees of freedom, of importance in molecular crystals

Effective Hamiltonians

Crystalline solids exhibit a multitude of atomic and electronic degrees of freedom that can be excited at finite temperature and thereby affect materials properties. Each site degree of freedom can be tracked with site variables. These include occupation variables, σ_i, for the chemical occupant of a site, displacement vectors for vibrational excitations, local magnetic moments in magnetic materials and orientational degrees of freedom in molecular crystals

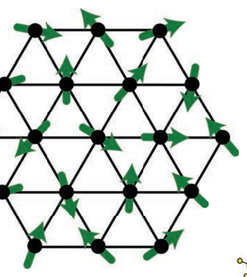
Alloy cluster expansion

$$E(\vec{\sigma}) = V_o + \sum_i V_i \sigma_i + \sum_{i,j} V_{i,j} \sigma_i \sigma_j + \sum_{i,j,k} V_{i,j,k} \sigma_i \sigma_j \sigma_k + \ldots$$



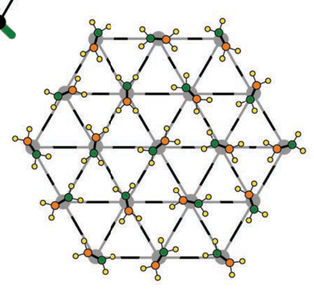
Spin cluster expansion

$$E(\vec{s}_1,..,\vec{s}_i,...,\vec{s}_N) = J_o + \frac{1}{2}\sum_{i,j}\sum_{\alpha,\beta} J^{i,j}_{\alpha,\beta} \cdot s^i_\alpha \cdot s^j_\beta$$



Phonon Hamiltonian

$$E(\vec{u}_1,..,\vec{u}_i,...,\vec{u}_N) = E_o + \frac{1}{2}\sum_{i,j}\sum_{\alpha,\beta} \Phi^{i,j}_{\alpha,\beta} \cdot u^i_\alpha \cdot u^j_\beta$$



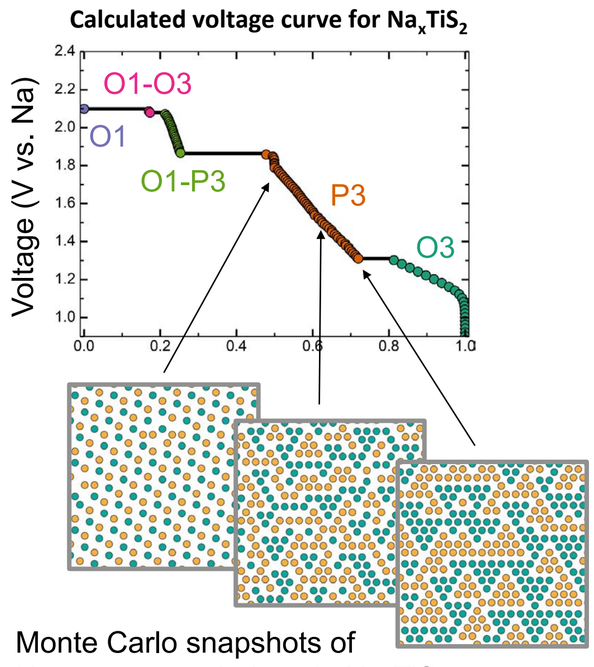
Rigid rotor cluster expansion

$$E(\vec{q}_1,..,\vec{q}_i,...,\vec{q}_N) = \Gamma_o + \frac{1}{2}\sum_{i,j}\sum_{\alpha,\beta} \Gamma^{i,j}_{\alpha,\beta} \cdot q^i_\alpha \cdot q^j_\beta + \ldots$$

The CASM software package algorithmically constructs effective Hamiltonians for arbitrarily complex crystal structures.

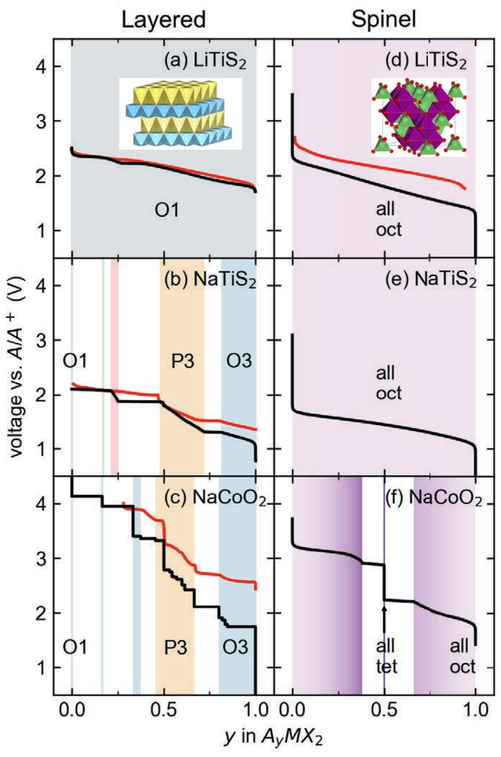
Battery materials

The voltage of a battery is related to the chemical potential of the shuttled ion



Monte Carlo snapshots of Na-vacancy orderings in Na_xTiS_2

Validation with experiment
(black = calculated, red = experiment)

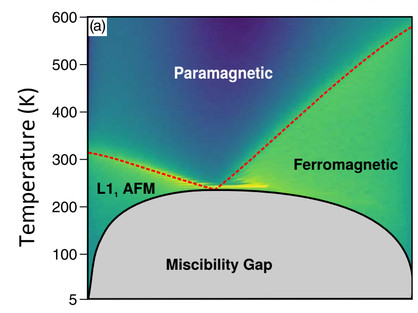


Alloys

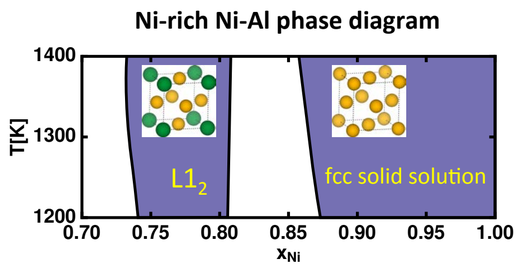
The CASM package can be used to calculate a variety Of important properties for alloy development, Including:

- phase diagrams
- diffusion coefficients

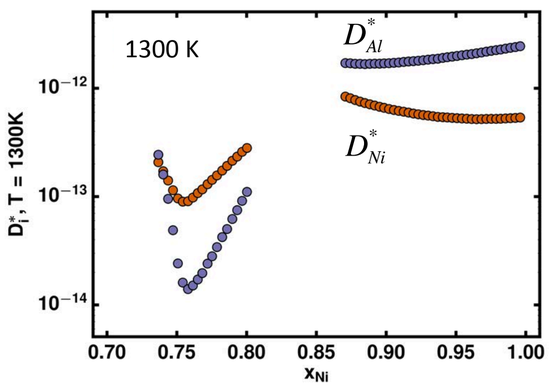
Magnetic Heusler $Mn_{1-x}Fe_xRu_2Sn$



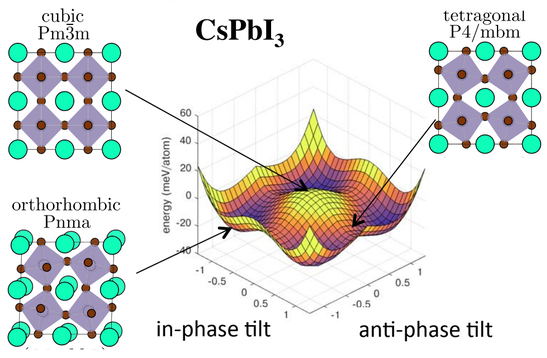
Ni-rich Ni-Al phase diagram



Tracer diffusion coefficients



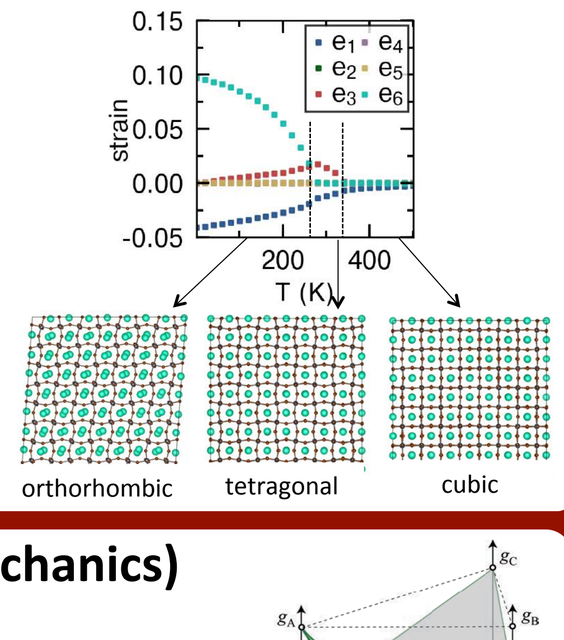
Halide perovskites



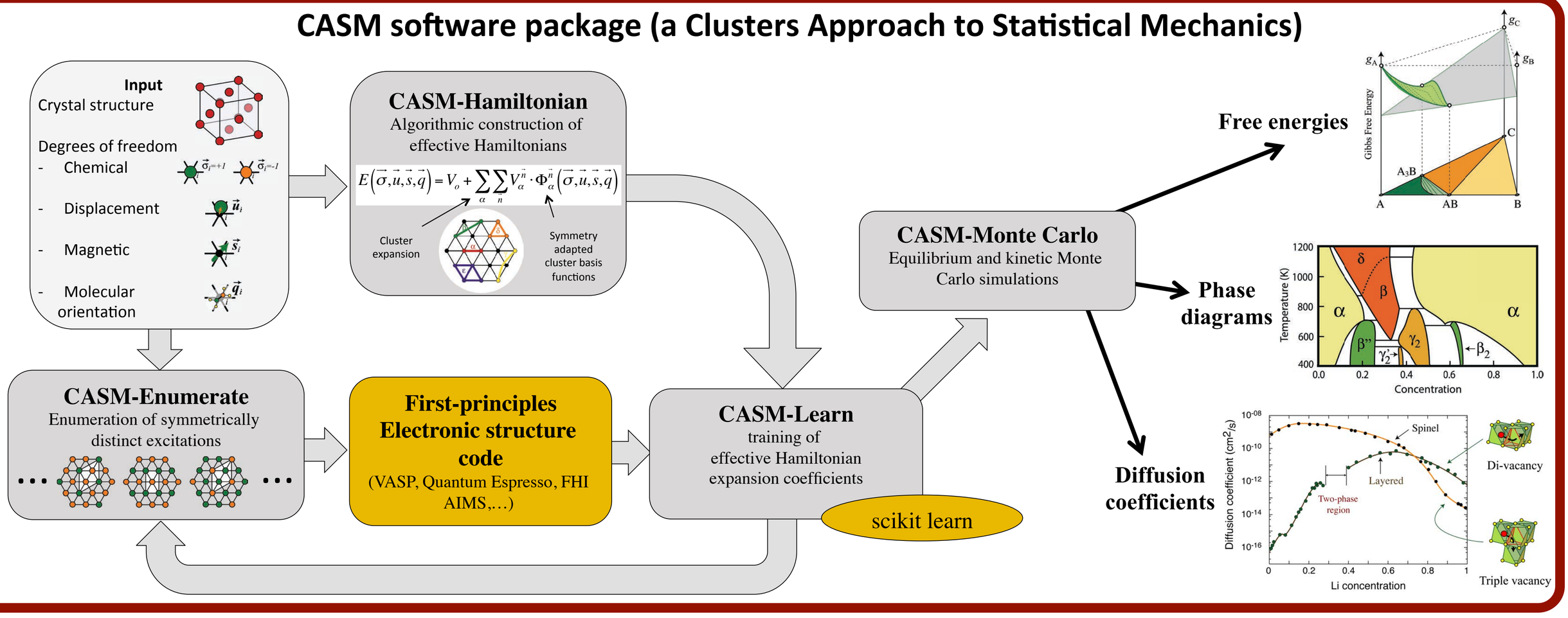
The complex energy surface of halide perovskites at zero Kelvin leads to a series of structural phase transitions upon heating.

Effective Hamiltonians combined with Monte Carlo simulations are able to predict experimentally observed structural phase transitions driven by anharmonic vibrational excitations

Dependence of strain as a function of temperature
(calculated with Monte Carlo simulations)



CASM software package (a Clusters Approach to Statistical Mechanics)



CASM code and documentation

https://github.com/prisms-center/CASMcode

https://prisms-center.github.io/CASMcode_docs/

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