



Adaptive cluster expansions and redox-dependent atomic ordering



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ABSTRACT

An adaptive cluster expansion (ACE) methodology is presented which enables exploration of atomic ordering interactions in solids as a function of the redox environment. A previously developed cluster expansion methodology is augmented via inclusion of explicit effective charge dependence within the topological cluster basis. This augmentation produces an enhanced fit precision across a wide composition range and the ability to directly control the model's redox state during Monte Carlo system equilibrations. The approach is validated in applications to yttria-stabilized zirconia (YSZ) and the perovskite (La_{0.8}, Sr_{0.2})(Cr_{0.8}, Ru_{0.2})O_{2.9} (LSCR), where significant variability in atomic ordering is seen across redox space. A locally adaptive lattice Monte Carlo sampling, utilizing the ACE methodology, is developed and validated in applications to determine the 0 K ground state configurations of YSZ and LSCR supercells with varying redox conditions. These equilibrations have direct relevance to solid-oxide fuel cell applications, whose components are subject to widely varying redox environments. The superior convergence of ACE results in a smaller number of numerically significant expansion terms, not only speeding the analysis but also permitting a physical interpretation of their meaning.

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1. Introduction

The starting point for many material models is to express the system internal or cohesive energy as a simple function (fit) of a cumulative set of local topological interactions, such as structurally distinct pairs, triplets, and quartets. The Cluster Expansion (CE) methodology is a highly successful example, in which structural features such as interatomic distances and angles are implicitly contained in the expansion coefficients. CE methods project libraries of first-principles and/or experimentally derived material properties (e.g. energy, magnetic moment, dielectric constants) onto an orthogonal set of topological clusters of sites, typically consisting mostly of short-range pair and triplet interactions [1]. What results from this projection is a semi-analytical equation (Eq. (1)) for the desired property using concentration and configuration space of a single crystallographic topological structure as component variables. While the summation in Eq. (1) is formally infinite and complete, the CE is necessarily truncated to achieve a desired precision [2].

$$E(\vec{\sigma}) = \sum_{\alpha} m_{\alpha} J_{\alpha} \langle \varphi_{\alpha}(\vec{\sigma}) \rangle \quad (1)$$

Here m_{α} is the multiplicity of cluster α , J_{α} are the variational coefficients of cluster α , and $\langle \varphi_{\alpha}(\vec{\sigma}) \rangle$ are the lattice averages of the cluster functions $\varphi_{\alpha}(\vec{\sigma})$ defining distinct site groupings. For

systems with only two possible lattice occupations, the calculation of the cluster function values is directly analogous to lattice spin models such as the Heisenberg, Ising, and Potts models. A graphic representation of clusters on a binary lattice is given in Fig. 1.

In the standard CE approach, the expansion coefficients are independent of component concentrations; considerable success has been obtained in representation of ordering and alloy effects in binary systems [2,3]. In a typical application CE and Monte Carlo (MC) sampling are combined to survey a wide concentration field, which would be inaccessible to purely first-principles calculations. Successful applications of the CE/MC methodology have been extended to ternary and quaternary systems [4–7]. However, application of expansions like Eq. (1) across a wide range of redox environments, phase spaces, and concentration spaces can lead to a lengthy series (for a specified level of precision, see below) with increasingly complex cluster topologies which are not susceptible to physical interpretation. For example, it would be naïve to assume that the interaction energy of two oxygen atoms within the yttria-stabilized zirconia (YSZ) electrolyte system is static across Y concentration space, within both highly reductive and oxidative environments; thus terms with as many as six or seven sites are required to capture the variation of local stoichiometry [5]. Fitting the multidimensional parameter space with more system-appropriate, flexible functions leads to more compact expansions with improved precision, as will be demonstrated.

A novel materials modeling scheme should be validated by application to nontrivial problems: in the present case, to materials for which redox variability plays a key role. Solid Oxide Fuel Cell

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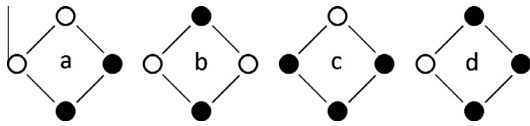


Fig. 1. Example of basic binary lattice with pair (a and b) and triplet (c and d) clusters where filled black symbols denote lattice points included in a cluster.

(SOFC) materials are chosen here precisely due to their particular critical responses to variable redox environments. SOFCs are under continual development as a technology to efficiently generate clean electricity from domestic fuel sources. Solid Oxide Electrolyser Cells (SOECs), essentially SOFCs operated in reverse, are also being evaluated as a means to produce fuel from excess electricity produced by renewable sources [8]. SOFC and SOEC performance is governed by the component materials' stability and conductivity (both electronic and ionic) at high temperatures and in various redox environments. In a previous work [5], an energy cluster expansion was developed for yttria stabilized zirconia (YSZ) to help clarify the relationship between dopants and defect structures. The atomic ordering properties of lanthanum perovskites ($\text{La}_{1-x}\text{Sr}_x$) ($\text{Cr}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$ (LSCF) and ($\text{La}_{1-x}\text{Sr}_x$)($\text{Cr}_{1-y}\text{Ru}_y$) $\text{O}_{3-\delta}$ (LSCR) were also previously explored [6] using energy CEs to elucidate connections between atomic ordering and composition. These SOFC/SOEC materials thus provide a significant and severe test of the extended modeling formalism which permits direct manipulation of a system's redox environment.

2. Methodology

2.1. Fitness criterion

Testing the degree of convergence and precision of an expansion requires definition of a fitness criterion. The fitness criterion used in this work is equal to the CE crossvalidation score (CV) [2] (Eq. (2)).

$$CV = \left(\frac{1}{N} \sum_{i=1}^N (E_i - E(\vec{\sigma}))^2 \right)^{1/2} \quad (2)$$

where E_i is the input database (typically *ab initio*) energy and i runs over the entire dataset. The associated predicted CE energy $E(\sigma)$ is found by a least-squares error minimization over $N-1$ structures (by deleting the i th element) of the training set. The CV score has proved to be a robust measure of 'goodness of fit' within the subspace spanned by the input data. It is clearly superior to a single test parameter such as overall mean square error.

CE cluster selection (*i.e.*, terms included in Eq. (1)) was here optimized using an efficient genetic algorithm (GA) developed in our previous work [6]. Genetic algorithms optimize an initial population of possible solutions, utilizing descent with modification to efficiently explore large variable spaces. Each successive child generation of solutions is derived from the characteristics of its parent generation; see Refs. [5,6] for further discussion of the specific application here. Use of the GA led to an observed order of magnitude reduction in computation time to generate an expansion of specified precision, compared to straightforward MC searches.

For complex materials such as YSZ and LSCR, convergence of the standard CE requires many higher order clusters (quadruplets, quintuplets, etc.) that obfuscate a simple chemical understanding of the underlying ECI. These higher order terms may be necessary for two reasons:

- (1) Particular multisite topologies are energetically significant.
- (2) Contributions of the included low-order clusters would 'prefer' to vary across concentration space.

Case (1) can be illustrated in LSCR [6] where angle-dependent triplet interactions between Ru and oxygen vacancies (Vac) are significant features. Here triplet terms distinguish a linear Vac–Ru–Vac cluster, from a 90° angle cluster with the same composition. The higher order terms, represented by YSZ, in Case (2) supplement the CE with more subtle information about concentration space and coordination variation that the low order terms cannot represent.

2.2. Adaptive cluster expansions

Valuable insights can often be gained by a physical interpretation of the effective cluster interactions (ECI, J_x of Eq. (1)), providing a chemically intuitive understanding of atomic interactions and their associated strengths. A CE constructed solely from pair clusters can be viewed as a model representing pairwise inter-atomic interaction energies; triplet interactions are also easily visualized. To this end, we find that one can frequently limit the usage of high order clusters while still maintaining an adequate CE convergence by utilizing an adaptive cluster expansion (ACE) [6], with more flexible ECI functions, as indicated in Eq. (3):

$$E(\vec{\sigma}) = \sum_x \left(\sum_{x=0}^n J_{x,x} \rho(\vec{\sigma})^x \right) m_x(\varphi_x(\vec{\sigma})) \quad (3)$$

Here ρ represents a system-dependent expansion parameter, such as the system's defect concentration or a measure of local stoichiometry, and n is the order of the polynomial expansion in powers of ρ .

2.3. Effective charge as expansion parameter

The ACE approach used in the present work was built upon libraries found in the Alloy Theoretic Automated Toolkit (ATAT) [2,9]. The effective charge ρ parameter will be defined here by the use of nominal ionic charge values (*e.g.* Zr^{4+} , Y^{3+} , O^{2-} , Vac^0 , La^{+3} , Sr^{+2} , Ru^{+3} , and Cr^{+3}) to assign an effective charge to a structure with a given stoichiometry. For instance, the structure ($\text{Zr}_{0.9}\text{Y}_{0.1}$) $\text{O}_{1.95}$ would be assigned an effective charge of $\rho=0$ (*i.e.*, $0.9 \times \text{Zr}^{4+} + 0.1 \times \text{Y}^{3+} + 1.95 \times \text{O}^{2-}$). This scheme was first applied [5] for the determination of low-energy (ground state) structures for given YSZ concentrations, and presented a significant improvement over standard CE methods. As we now show, a charge-expanded ACE opens the door to a more transparent modeling and interpretation of the evolution of atomic interactions as redox environments change.

The training library was built upon the Density Functional Theory (DFT) energies generated by the Vienna *Ab initio* Simulation Package (VASP) [10] with a charge-neutral periodic unit cell. Experiments with charged cells compensated by an artificial uniform background charge proved to be of little value in energetic estimates. Nevertheless, different redox environments can be modeled in a periodic system by varying the oxygen content of otherwise similar materials; *i.e.*, by deliberate deviation from stoichiometry. The depletion/addition of oxygen atoms induces a reductive/oxidative environment by changing the number of electrons associated with the remaining atoms in the cell. Formally, replacing one oxygen anion in a structure with a vacancy forces two excess electrons to 'return to' the remaining atoms. In the present approach this substitution would be described as a +2 effective cell charge. Thus, reduced systems are modeled within the ACE by increasing the expansion parameter ρ above that which the local stoichiometry requires and similarly, oxidized systems are modeled by decreasing the expansion parameter.

As the ACE is constructed from a DFT-derived structure library with a sizable range of effective charges, the polynomial ECI itself

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