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Charge Optimized Many Body (COMB) potentials for simulation of nuclear fuel and clad ☆

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ABSTRACT

We briefly outline the Charge Optimized Many Body (COMB) potential formalism, which enables the molecular dynamics simulation of complex materials structures in which multiple types of bonding (metallic, covalent, ionic and secondary bonding) coexist. We illustrate its capabilities to address critical issues in the area of nuclear fuel. In particular, we look at U, UO_2 and the process of oxidation of U. Further, we characterize the mechanical behavior of Zr, representing LWR clad, and explore the effects of oxidation and hydridation on the mechanical response and briefly illustrate the capabilities of COMB simulations of corrosion. Finally, we briefly assess the materials fidelity of the COMB approach by examining the COMB description for the Zr-H system.

1. Introduction

Nuclear fuel is exposed to an aggressive physical, chemical and radiative environment both in operation and in post-use storage. The composition, atomic-level structure and microstructure of both the fuel pellet itself, UO_2 in commercial Light Water Reactors (LWRs), and the clad, usually a Zr alloy, continuously evolve at all length scales from the atomic to the macroscale. All of these changes have significant effects on fuel performance. Current fuel performance codes conflate all of the chemical, physical and microstructural phenomena into a single variable: the burn-up. While these codes, such as FRAPCON [1], have proven very successful in predicting the performance of the UO_2 fuel system, they do have significant limitations. First, their materials models are based on correlations in experimental data; they therefore work well within the domain of performance conditions to which they were fit. However, they are less successful in more extreme conditions. Second, the extensive experimental datasets acquired over decades for UO_2 are not available for other fuel systems. The development of such experimental databases for candidate fuel systems is a significant challenge. There is thus a considerable effort to deconvolute burn-up into its constitutive chemical, physical and microstructural processes, which can then be modeled at the appropriate length scales, thereby enabling the development of more flexible fuel-performance codes. In the United States, the MOOSE-BISON-MARMOT suite of codes are the focus of such development [2].

The atomic-level information for such multiscale fuel performance codes comes from electronic-structure level calculations, typically at the level of density functional theory (DFT), and atomistic methods, most importantly molecular-dynamics (MD) simulation. While DFT generally offers higher materials fidelity, it is limited to small system sizes, almost always less than 1000 atoms. MD is uniquely able to probe nuclear materials with atomic scale resolution and to determine their evolutions over (short) time, including the effects of temperature, stress and radiation. In MD, atoms are generally treated as indivisible, structureless objects, interacting with each other through empirical potentials which describe the interatomic forces between atoms. These potentials do not explicitly describe the electrons; rather, they attempt to incorporate all of the complex effects of the interacting electrons in the form of a functional form and/or numerical tables. Because they do not describe the electrons explicitly, simulations using empirical potentials are orders of magnitude faster than their DFT counterparts.

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There are well-known and very successful interatomic descriptions for the description of various classes of materials: embedded atom methods (EAM) and modified embedded atom method (MEAM) potentials for metals; bond order and many-body potentials for covalent materials; Coulomb potentials plus empirical short ranged potentials, such as Buckingham potentials, for ionic systems. However, it is only in the last few years that methods have been developed that allow the description of systems in which different types of bonding co-exist [3]. Such systems are endemic in nuclear materials. For example, oxide fuel can develop metallic fission product clusters; the oxide fuel and fission products can react chemically with the clad. Moreover, the clad is subject to oxidation and hydriding in the aggressive reactor environment.

In this paper, we discuss briefly the Charge Optimized Many Body (COMB) formalism, which is one particular type of interatomic potential capable of describing the different types of bonding in an integrated manner. We illustrate the capabilities of COMB for attacking various problems of interest in the area of nuclear fuels. The coverage of each area is perforce brief. The interested reader will be guided to the original papers throughout. While this review focuses on the COMB approach, it is important to note that there is a very extensive literature on the simulation of fuel systems, most particularly UO_2 using atomistic techniques.

The rest of this review is organized as follows. In Section 2, we briefly introduce the COMB formalism and identify the systems, both nuclear and non-nuclear, that have already been parameterized. In Section 3, we look at U, UO_2 and the process of oxidation of U. In Section 4, we look at the mechanical behavior of Zr, representing LWR clad, and explore the effects of oxidation and hydridation on the mechanical response. In Section 5, we describe the capabilities of COMB simulations of corrosion. Since there has been relatively little work done in this area, we also describe some work performed on non-nuclear materials, which illustrate the capabilities of COMB. Section 6 briefly describes some of the known limitations of the COMB approach. Section 7 contains our conclusions and identifies future research directions.

2. COMB formalism

Metallic bonding is characterized by the near uniform background of electrons shared among all of the atoms. By contrast, covalent bonding involves the sharing of electrons between two atoms, while ionic bonding involves the transfer of electrons from one atom to another. DFT methods show these differences clearly. While classical empirical potentials used in MD simulations do not explicitly describe the electrons, they do include surrogate quantities that account for the effects of electrons on bonding. For examples, the central concept of the EAM approach is a density function which, while determined from the positions of neighboring atoms, purports to describe the local density of the background electrons. Potentials typically capture covalency through a bond-order term, which modulates the strength of a bond between two atoms based on the number and nearness of their neighbors. Interestingly, it has been shown that there is a fundamental equivalence between the EAM approach and the bond-order approach [4]. Similarly, in descriptions of ionic materials, the effects of electron transfer between atoms are captured by the charges on the ions, which interact with each other through Coulombic interactions.

The COMB potential approach combines the ideas of bond order (aka electron density) and variable ionic charge to produce a flexible interatomic description of all three types of bonding [5–7]. Specifically, the charge on each atom is not fixed in COMB, but changes according to its local environment; for example, a Si atom in bulk silicon is charge neutral, while a Si atom in SiO_2 is positively charged. Moreover, the charge is not imposed on an atom but is determined autonomously on the fly during the simulation and changes as the local structural and chemical environment changes. While this paper focuses on the COMB potential, it shares many common features with the ReaxFF [8] approach [6,7].

COMB is straightforward in concept, in that it combines a bond-order approach with a charge equilibration methodology, which enables the charge on an atom to adjust autonomously, and in a self-consistent manner. In schematic form, the total energy function describing the COMB potential, E^{COMB}, can be written as

$$E^{COMB} = E^{self} + E^{Coul} + E^{polar} + E^{vdW} + E^{bond} + E^{other} \quad (1)$$

Here E^{self} is the energy associated with the ionization of an atom, E^{Coul} is the Coulombic interaction between ions, E^{polar} is the dipole and higher order electrostatic interactions, E^{vdW} is the van de Waals interactions, E^{bond} is the bond-order energy and E^{other} is used to describe very specific bond angle configurations. Each of these terms is written as a functional form depending on the charges $q = \{q_1, q_2, \ldots, q_N\}$ of the N atoms/ions in the system their positions $\mathbf{r} = \{\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N\}$. The full details of the COMB formalism are discussed in detail elsewhere [6]. Here we just highlight the key points that enable the description of all bonding types in a single formalism.

The key term involved in the self-consistent charge equilibration is the self-energy, which can be written as:

$$E^{self} = \sum_{i=1}^{N} \chi_i q_i + 1/2\, J_i q_i^2$$

Here χ_i is the electronegativity of species i and J_i is the chemical hardness; higher order terms can also be included. The self-energy term imposes a relative difference in energy cost for various charge states of a particular element. For example, we would expect oxygen to have zero charge in a covalent system and be negatively charged in an oxide, while a metallic atom such as Cu would be neutral in the metal and positively charged in an oxide. This is captured in the very different values of χ and J for O and Cu. The most important charge dependent terms are the Coulombic interactions and the bond order terms. The interested reader is referred to more detailed discussions [6].

The charge and position of each atom can be determined using a charge equilibration (Qeq) method [9] within an extended Lagrangian formalism:

$$L = \sum_{i=1}^{N} \frac{1}{2} m_i \dot{r}_i^2 + \sum_{i=1}^{N} \frac{1}{2} M_Q \dot{q}_i^2 - E^{COMB} - \lambda_L \sum_{i=1}^{N} q_i. \quad (2)$$

In Eq. (2), the first term is the kinetic energy associated with the physical movement of the ions, where m_i is the atomic mass of species i. The second term is the kinetic energy of the charges with a fictitious charge mass (M_Q), and λ_L is an undetermined multiplier that forces the charge in the system to be conserved. The incorporation of a fictitious charge mass is equivalent to the inclusion of a piston mass in the Andersen and Car-Parrinello barostats: it is an inertia and simply sets the timescale over which the charge of the system can adjust to equilibrium.

The Lagrangian can be analyzed in the usual manner to determine the equations of motion (EOMs) for the charge and the position of each atom. The EOM for the position is the standard Newtonian equation for the evolution of atomic positions. The EOM for the charge shows how the charge evolves in a coupled manner with the evolution of the atomic positions.

Although it is structurally quite simple, the current, third-generation COMB implementation, COMB3, has a large number of terms, required to describe various physical and chemical phenomena. As a result, it has a large number of parameters, many tens for