Computational Materials Science 126 (2017) 308–320

Contents lists available at ScienceDirect

Computational Materials Science

journal homepage: www.elsevier.com/locate/commatsci

Editor's Choice

Understanding the uncertainty of interatomic potentials' parameters and formalism

A.P. Moore [a,b,*], C. Deo [a], M.I. Baskes [c,d,e], M.A. Okuniewski [f,g], D.L. McDowell [h]

[a] Nuclear and Radiological Engineering Program, George W Woodruff School of Mechanical Engineering, Georgia Institute of Technology, 770 State Street, Atlanta, GA 30332, USA
[b] Sandia National Laboratories, P.O. Box 5800, Albuquerque, NM 87185, USA
[c] Mississippi State University, 105 Lee Boulevard, MS 39762, USA
[d] University of California, San Diego, 9500 Gilman Drive, La Jolla, CA 92093, USA
[e] Los Alamos National Laboratory, PO Box 1663, Los Alamos, NM 87545, USA
[f] Purdue University, 610 Purdue Mall, West Lafayette, IN 47907, USA
[g] Idaho National Laboratory, PO Box 1625, Idaho Falls, ID 83415, USA
[h] Mechanical Engineering Program, George W Woodruff School of Mechanical Engineering, Georgia Institute of Technology, 770 State Street, Atlanta, GA 30332, USA

ARTICLE INFO

Article history:
Received 27 July 2016
Received in revised form 18 September 2016
Accepted 19 September 2016

Keywords:
Uncertainty
Sensitivity analyses
Atomistic modeling
bcc metals
MEAM potential

ABSTRACT

A sensitivity analysis of the modified embedded atom method (MEAM) potential for body-centered-cubic uranium and zirconium was performed in order to examine and understand the uncertainty in the parameters and formalism of the interatomic potential. The sensitivity analysis was conducted using one-at-a-time (OAT) sampling of the parameters and how they affected the ground state, thermal, and alloy structural and thermodynamic properties. The performed analysis was able to uncover the properties that can be easily varied or adjusted like the lattice constant, and the properties that had little variance like the heat capacity. The observed analysis on the ground state properties was found to correspond well with previously published results, after which the thermal and alloy properties were examined. A new method of categorizing changes in the alloy properties was developed that allows for the discrimination of bonding behaviors, determining if the strength of the bonding between atoms changed or if the manner in which they were bonded together changed.

1. Introduction

Analytical Interatomic Potentials (AIPs) are mathematical formulae that provide a means to compute the potential energy of an ensemble of atoms with known spatial co-ordinates [1–4] and are widely used as the physical basis of molecular dynamics and Monte Carlo simulations in materials science.

While several standard potential functions have emerged for particular classes of systems [5], at present there is no definitive functional form that adequately describes all types of multi-atom bonding. Instead, potentials are often developed for specific applications with functions and parameters determined on an ad hoc basis. In the past, practitioners [2] have often referred to the procedure of developing interatomic potentials as being as much as an art as a science. Recently, several quantitative procedures have been developed that aim to automate the process of developing interatomic potentials and that ensure fidelity of the analytics potential with respect to more accurate quantum mechanical calculations [6–10]. Even so, there exists considerable and justified uncertainty with regard to the reliability of quantitative results produced by molecular dynamics simulations of materials based on analytic potentials. Such uncertainty is rarely explored, qualitatively or quantitatively.

Uncertainties in such simulations may be investigated by sensitivity analysis (SA), which investigates the connection between inputs and outputs of a (computational) model. The objective of SA is to identify how the variability in an output quantity of interest is connected to an input in the model. SA allows the practitioner to build a ranking of the input sources, which might dominate the response of the system. Note that strong large sensitivities derivatives do not necessarily translate in critical uncertainties because the input variability might be very small in a specific device of interest. Sensitivity analysis is thus usually considered to be a subset of uncertainty quantification methods [11–13].

In the case of AIPs, inputs for SA are parameters that have been chosen by the practitioner to represent the materials system of

* Corresponding author at: Nuclear and Radiological Engineering Program, George W Woodruff School of Mechanical Engineering, Georgia Institute of Technology, 770 State Street, Atlanta, GA 30332, USA.
E-mail address: amoore31@gatech.edu (A.P. Moore).

http://dx.doi.org/10.1016/j.commatsci.2016.09.041
0927-0256/

interest while outputs are specific material properties that are of interest. Usually, these properties are ground state quantities used in the fitting procedure that describe the material of interest such as the lattice parameter, cohesive energy, and vacancy formation energy at 0 K. However, an intriguing feature of an interatomic potential is its transferability [14] – the ability to predict properties that have not been used in the fitting procedure. These may be thermodynamic and or mechanical properties of the material at ambient and high temperature where atomic motion introduces some variability in the computation of properties. Further the material system may be composed of multiple elements (e.g. alloys) that exhibit ordering or disordering tendencies. A comprehensive procedure to perform sensitivity analysis of interatomic potentials in such situations is lacking and is addressed in this work.

We choose, as an example on which to test our SA procedure, a recently developed interatomic potential of uranium zirconium alloys [15,16]. This potential is based on the Modified Embedded Atom Method (MEAM) [17], which is an extension of the Embedded Atom Method (EAM) [18]. The basis of both EAM and MEAM formalisms is that the cohesive energy can be expressed in terms of embedding energies. In this view, each atom in the metal is embedded into the electron gas created by the other atoms. In addition, the MEAM formalism includes the ability to model atomic systems that exhibit directional bonding that is often found in metals and alloys that have complex non-cubic crystal structures.

Neither U or Zr, nor their alloys lend themselves easily to atomistic analysis. Uranium is an actinide that has three distinct stable solid phases. The transition between these phases can be attributed to the behavior of the de-localized f orbital-electrons. The ground state uranium phase is the α (orthorhombic) phase. As temperature increases, uranium will first transition to the β (tetragonal) and then to the γ (body-centered-cubic) phases with transition temperatures 940.85 K ± 1.3 K (α to β), 1047.95 K ± 1.6 K (β to γ), and 1405.95 K ± 0.8 K (γ to liquid) [19]. Zirconium is a transition metal with two distinct solid phases: the ground state α hexagonally closed packed (hcp) phase, and the β high temperature body centered cubic (bcc) phase (above 1139 K). The U-Zr alloy transitions from a δ (partially ordered C32 crystal structure) to γ (bcc) phase around 65–75% Zr and 890 K. Using atomistic simulations we have previously analyzed small configurations of U-Zr alloys and looking for thermodynamic driving forces and unit mechanisms of ordering and phase separation [16].

In this work, the sensitivity of the MEAM potential on the ground state and thermal properties are thoroughly examined. The sensitivity analysis is conducted using the uranium, zirconium, and uranium-zirconium MEAM potentials. Sensitivity of ground state as well as thermal properties is conducted. Previous 0 K sensitivity analyses have been performed using MEAM potentials [20–22]. In addition, there have also been attempts to quantify MEAM uncertainty using confidence intervals around specific values to obtain an uncertainty interval for various ground state properties [23,24]. To our knowledge, this is the first sensitivity analysis for elemental thermal properties and alloys, for which a new method of analyzing the effects that parameters have on the alloy properties has been developed. Such sensitivity analyses are helpful in potential development and the understanding of these interatomic potentials.

The atomistic simulations were conducted using molecular statics and molecular dynamic simulations on the MEAM U-Zr system. The molecular statics/dynamics (MS/MD) code DYNAMO [25] was used to perform all the atomistic simulations. The MD simulations performed in this research, unless otherwise specified, were conducted with a supercell consisting of $10 \times 10 \times 10$ unit cells held in an isothermal-isobaric (NPT) ensemble. The thermal MD simulations were performed for 100 ps with a time step of 2 fs with time averaged properties obtained over the last 35 ps. Alloy samples were constructed in random atomic configurations.

The second nearest neighbor 2NN MEAM potential theory is described in Appendix A, and is the formalism used during this sensitivity analysis. First, the elemental MEAM parameters are examined on how they change the ground state properties of the bcc phase and relative phase stability, and are compared to previous sensitivity analyses. In these sensitivity analyses, the MEAM parameters are varied one at a time, after which the effect that the change has on the properties is examined. This is followed by the elementary MEAM parameter thermal property sensitivity analyses, in which the heat capacity, lattice constant, thermal expansion and melting point are examined. In particular, some of the more complex analysis concerns how the interatomic potentials behave with thermal properties. Then the elementary and alloy MEAM parameters' effects on the alloy properties like Vegard's law for lattice constants and the enthalpy of mixing is examined. Since this is the first reported sensitivity analysis for thermal and alloy properties, a new method of quantifying how a change in a parameter affects the thermal and alloy response/properties was developed.

2. Results and discussion

2.1. Sensitivity analysis methodology

A sensitivity analysis was performed on the degree to which the MEAM parameters affect the ground state and thermal properties of the elemental and alloy systems. In the past, there have been a few sensitivity analyses of the MEAM potential performed on ground state properties [20,22,26], but this is the first reported sensitivity analysis of the MEAM potential performed on the thermal properties, which tend to be more complex and somewhat chaotic due to their nonindependent spatial parameters causing fluctuations. The thermal motion combined with the complexity of the angular partial electron densities and the screening parameters does not allow for a directly quantitative sensitivity analysis. Therefore, a semi-quantitative approach was used to describe the potential significance of how a change in the MEAM parameters could affect the ground state and thermal properties of the system. The sensitivity analysis performed uses one-at-a-time (OAT) sampling [13] where one parameter changes values between consecutive simulations, after which the results are analyzed. However, the input parameters are non-independent input factors creating seemingly random fluctuations or jumps over ranges of input parameters. In addition, the range of acceptable inputs for the parameters in this case is unknown, since changes in the parameters may lead to a destabilization of the phase of interest. Therefore, the maximum parameter change examined is set to be a percentage of the initial parameter value, and after each simulation the phase stability is examined ensuring the input change did not cause phase changes.

The OAT sampling is computationally expensive, therefore, the sensitivity analysis was conducted fully on the uranium potential, after which a more detailed analysis was conducted on the parameters determined to be significant with both the U and Zr potential.

2.2. Effects of elemental MEAM parameters on ground state properties

We begin by examining the ground state sensitivity analysis and comparing it to those previously published. The bcc phase elastic constants and bulk modulus are calculated, as well as the relative phase stability in terms of change in energy. Molecular