



Two-body potential model based on cosine series expansion for ionic materials



Takuji Oda ^{a,*}, William J. Weber ^{b,c}, Hisashi Tanigawa ^d

^a Department of Nuclear Engineering, Seoul National University, Republic of Korea

^b Department of Materials Science & Engineering, University of Tennessee, USA

^c Materials Science & Technology Division, Oak Ridge National Laboratory, USA

^d Fusion Research and Development Directorate, Japan Atomic Energy Agency, Japan

ARTICLE INFO

Article history:

Received 24 June 2015

Received in revised form 25 August 2015

Accepted 27 August 2015

Keywords:

Potential model

Fourier series

Ionic materials

ABSTRACT

A method to construct a two-body potential model for ionic materials with a Fourier series basis is examined. In this method, the coefficients of cosine basis functions are uniquely determined by solving simultaneous linear equations to minimize the sum of weighted mean square errors in energy, force and stress, where first-principles calculation results are used as the reference data. As a validation test of the method, potential models for magnesium oxide are constructed. The mean square errors appropriately converge with respect to the truncation of the cosine series. This result mathematically indicates that the constructed potential model is sufficiently close to the one that is achieved with the non-truncated Fourier series and demonstrates that this potential virtually provides minimum error from the reference data within the two-body representation. The constructed potential models work appropriately in both molecular statics and dynamics simulations, especially if a two-step correction to revise errors expected in the reference data is performed, and the models clearly outperform two existing Buckingham potential models that were tested. The good agreement over a broad range of energies and forces with first-principles calculations should enable the prediction of materials behavior away from equilibrium conditions, such as a system under irradiation.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Force-field methods such as classical molecular statics (MS) and molecular dynamics (MD) methods are important computational techniques in condensed matter physics. Since the interatomic interactions are approximately described by simplified equations, the so-called potential model, the computational cost for energy and force evaluations is largely reduced compared with first-principles calculations. Due to this approximation, however, the accuracy of simulation results is affected by the quality of the potential model. Hence, developing a potential model that appropriately describes a phenomenon of interest is a key step to obtain realistic results by a force-field method.

Constructing a potential model is generally composed of four steps, after determining a phenomenon and a system to be studied.

- (1) Gather reference data toward which a potential model is optimized.

- (2) Choose an interaction model frame: two-body representation, three-body representation, etc.
- (3) Define a function formula of the potential model: Lennard-Jones, Morse, Buckingham, etc., in the two-body representation, for example.
- (4) Determine a method to optimize the parameters in the model function, and then apply it.

At each step, some errors are incorporated into the potential model. Regarding step (1) for a solid material, early studies referenced experimental data on crystallographic, thermal, mechanical and vibrational properties of the target system. Since the number of model parameters must be sufficiently smaller than the number of reference data, a simple model function was required. This means that steps (2) and (3) were restricted by step (1). This situation was changed by the advancement of first-principles calculation. Nowadays, one can evaluate energies and forces of a system of interest with a high accuracy. Thus, a great number of reference data can be prepared to employ a complex model formula.

In the past few decades, several sophisticated model functions were suggested, such as the Tersoff [1] and Brenner [2] potentials

* Corresponding author. Tel.: +82 2 880 8988.

E-mail address: oda@snu.ac.kr (T. Oda).

for covalent materials, variable charge models [3,4] for ionic materials, and embedded-atom model (EAM) [5] and its modified version (MEAM) [6] for metallic materials. In addition, more complex potential models composed by multiple model functions, like the REAX-FF model [7] have been becoming popular to cover various chemical forms of substances at once. These sophisticated models were derived considering the physics and the chemistry of interatomic interactions.

Even for such sophisticated model functions, however, their numerical accuracy is still limited because available function space is restricted by prepared function formulas, namely errors in step (3). Hence, as another approach, mathematics-oriented methodologies using a more flexible representation of potential energy have been attracting increasing attention [8], such as potential energy fitting with interpolated moving least-squares methods (IMLS) [9,10], Gaussian approximation potentials (GAP) [11] based on Gaussian process regression [12], a method based on a linear regression using the least absolute shrinkage and selection operator (LASSO) [13], and generalized neural network representation [14]. These methods can construct a potential model which yields energies and forces close to first-principles calculations, such as a GAP model for tungsten [15]. However, the computational cost is largely increased [16].

For some applications that require long-time and/or large-system simulations, including simulation of irradiation damage processes in nuclear materials, a potential model that realizes reasonable accuracy with a low computational cost is practically vital. Regarding the computational cost, the two-body representation has the best advantage. Although the two-body representation is apparently insufficient for covalent and metallic systems, it is expected to provide reasonable accuracy for ionic materials, as many two-body potential models have been successfully developed. However, most two-body potential models for ionic materials are still composed by simple empirical functions such as the Buckingham and the Morse potential models, which can only use a small part of the function space available for the two-body representation. If the function space is fully utilized, the quality of two-body potential models may be largely improved.

In the present study, therefore, we examine a mathematics-oriented method to construct two-body potential models for ionic materials with a quasi-complete basis functions. For this purpose, a Fourier series is employed as the basis functions, instead of empirical model functions. The coefficients of the basis functions are uniquely and straightforwardly determined by solving linear simultaneous equations to minimize the sum of weighted mean square errors in energy, force and stress, where first-principles calculation results are used as the reference data. Since the Fourier series is reasonably regarded as a complete orthogonal system in the function space that two-body potential models belong to, if the fitting error from the reference data is appropriately converged with respect to the truncation of the Fourier series, this method provides a potential model adequately close to the one that has the minimum model error within the two-body representation. In short, the method constructs a virtually best two-body potential model. We may also expect that this method will uncover the limitation of two-body potential models without being interrupted by uncertainties caused by steps (3) and (4).

The remaining part of the paper is organized as follows. In Section 2, the potential model formula and its parameterization method is explained. In Section 3, first-principles calculation results that were not utilized in the parameterization step are used as the reference data to test validity of the methodology, and the convergence behaviors of the sum of weighted mean square errors in energy, force and stress are shown with respect to the truncation of both the number of reference data and the Fourier series. Magnesium oxide (MgO), which is one of the simplest metal oxides

and has a high ionicity, is selected as the test system. In Section 4, the quality of the potential model in MS and MD simulations is examined, including mechanical property, melting point, thermal expansion behavior, radial distribution functions and defect energies. In addition, we propose a two-step correction method for constructed potential models in order to revise errors, which are caused by the first-principles calculation, in the reference data. In Section 5, comparisons on the model quality with existing Buckingham potential models are briefly provided. Finally, the paper is closed with concluding remarks in Section 6.

2. Methodology

2.1. Potential model formula

We consider a periodic function between $-r_{\text{cut}}$ and $+r_{\text{cut}}$, where r_{cut} represents the cutoff distance of the short-range two-body interaction and is set to 10 Å in the present study. 10 Å is a typical cutoff distance in two-body potential models of ionic materials. Since the functional shape between $-r_{\text{cut}}$ and 0 does not need to have physical meanings, we arbitrarily define this periodic function as an even function so that its first derivative becomes 0 at r_{cut} . It is reasonable to assume that a realistic two-body model function is smooth in the range of possible interatomic distances in condensed matter, e.g. from around 1 Å to r_{cut} . Thus, we can expect that the non-truncated cosine series can compose a two-body potential model that holds the minimum error from the reference data, namely the best model within the two-body representation. With these considerations, the potential energy (E_{pot}) in an ionic system is described as follows:

$$E_{\text{pot}} = \sum_{ij}^{\text{Ewald}} \frac{q_i q_j}{r_{ij}} + \frac{1}{2} \sum_{i=1}^{N_A} \sum_{j=1}^{r_{ij} < r_{\text{cut}}} \left[\sum_{k=0}^{N-1} a_{\text{element}_i\text{-element}_j,k} \cos\left(\frac{k\pi r_{ij}}{r_{\text{cut}}}\right) \right] + E_{\text{ref}}, \quad \text{and} \quad (1)$$

$$E_{\text{ref}} = n_{\text{Mg}} e_{\text{Mg}} + n_{\text{O}} e_{\text{O}}, \quad (2)$$

where r_{ij} is an interatomic distance between two ions (i and j), q_i and q_j are their ionic charges, N_A the number of atoms in a unit simulation cell, N is the number of cosine functions to be utilized for the cosine series representation, and $a_{\text{element}_i\text{-element}_j,k}$ is the coefficient of k -th cosine function for combination of the elements of i -th and j -th ions (3 kinds of combinations: Mg–Mg, Mg–O and O–O). In the right-hand side of Eq. (1), the first term denotes the Coulomb interaction, which is evaluated using the Ewald summation method without truncation. In the present study, we simply set $q_{\text{Mg}} = +2e$ and $q_{\text{O}} = -2e$, which are typical values for MgO. The second term is of the short-range interaction term composed by a cosine series, where the first summation is taken over the number of atoms in the unit cell (N_A), the second summation is taken over all atoms that are located within the cutoff distance (r_{cut}) from i -th ion, including atoms in neighboring image cells, and the third summation is taken over the number of cosine basis functions (N). The multiplication by 1/2 is required to cancel the double counting of atomic combinations. The third term in Eq. (1) is the reference energy, which is needed to appropriately compare energies calculated by a potential model and energies determined by DFT calculation, because absolute energies given by pseudopotential DFT calculation have no clear physical meaning. E_{ref} is written as the sum of reference energies of atoms involved in a unit simulation cell, where n_{Mg} and n_{O} are, respectively, the numbers of Mg and O atoms involved in the unit simulation cell, and e_{Mg} and e_{O} are, respectively, the reference energies of the Mg and O atoms. e_{Mg} and e_{O} are independent of atomic configurations.

Download English Version:

<https://daneshyari.com/en/article/7959115>

Download Persian Version:

<https://daneshyari.com/article/7959115>

[Daneshyari.com](https://daneshyari.com)