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Interatomic potential that describes martensitic phase transformations in pure lithium

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ABSTRACT

An interatomic potential for the pure lithium system is developed on the basis of the second nearest-neighbor modified embedded-atom method formalism, utilizing the force-matching method with a DFT database of various atomic configurations. The developed potential accurately reproduces fundamental physical properties including an unusual order of surface energies of the bcc lithium, $(100) < (110) < (111)$. Subsequent molecular dynamics simulations verify that the present potential can be successfully applied to study martensitic phase transformations of pure lithium at low temperatures. The present results provide detailed insights into the formation of a disordered polytype structure consisting of short-ranged fcc- and hcp-type stacking sequences supporting the experimental observation of this structure in high-purity lithium.

1. Introduction

The materials systems with lithium (Li) have received a great attention nowadays owing to their technical importance to many applications. In the electrochemical industry, Li and its alloy, e.g. pure Li, Li–Si, Li–Sn and Li–Sb, are notable materials due to their application in electrodes [1]. For the aerospace and automotive applications, Li is a promising alloying element to improve mechanical properties of aluminum [2,3] and magnesium [4–8] alloys. Moreover, Li and its alloy has been a promising candidate for a liquid phase plasma-facing component in fusion power reactors because of their reactivity with hydrogen and its light weight [9,10].

For the aforementioned applications, a detailed understanding of material phenomena in Li and its alloy is important. However, many of these phenomena are often difficult to investigate only by experiments if they are originated from atomic-scale mechanisms. Therefore, a theoretical study by means of atomistic simulations such as molecular dynamics (MD) and Monte Carlo (MC) is highly required to complement experiments by providing a detailed understanding of the atomic-scale mechanisms. To enable large-scale atomistic simulations with high predictive accuracy, the availability of a reliable interatomic potential to describe the atomic interactions is of crucial importance. Especially, an accurate description of the pure Li system should take precedence since it is a basis of interatomic potentials for concerned multi-component systems.

So far, several interatomic potentials are available in literature for the pure Li system. There were earlier works based on pair potential models [11–14], but the practical utilization of these potentials is greatly limited because the many-body nature of metallic bonding in pure Li is not properly considered. Instead, there were available many-body interatomic potentials based on the embedded-atom method (EAM) [15], the modified embedded-atom method (MEAM) [16], and the second nearest-neighbor modified embedded-atom method (2NN MEAM) [17–19] models. The EAM potentials for pure Li were developed by Johnson and Oh [20], by Chantasiriwan and Milstein [21], by Derlet et al. [22], by Hu and Masahiro [23], by Wilson and Riffe [24], and by Belashchenko [25]. The MEAM potential for pure Li were developed by Baskes [16], and by Yuan et al. [26]. For the 2NN MEAM model, several potentials are available by Cui et al. [27], by Kim et al. [28], and by Alam and Groh [29].

In the pure Li system, however, there have been challenging issues which were not properly dealt by previous potentials. The first issue is an extraordinary order of surface energies of the body-centered cubic (bcc) Li which is expected by the DFT calculation [30,31]. According to the typical broken-bond model, the energy of a surface with the highest atomic density is expected to be the lowest. The order of surface energies of usual bcc metals, $(110) < (100) < (111)$, well corresponds to this model, but that of bcc Li was reported as an exception, $(100) < (110) < (111)$ [30,31].

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The accurate description of the surface energy is often important for applications of the Li potential, e.g., the dendrite formation on the anode surface of Li-O_2 and Li-S batteries [32], but this have not been reproduced by previous potentials [29]. The second issue is an occurrence of martensitic phase transformation at low temperatures. It has been reported that several alkali metals such as Li and Na show the martensitic phase transformation from the bcc (austenite) to 9R or disordered polytypes (martensite) phases [33–41]. Despite the theoretical importance of the martensitic phase transformation, presently available interatomic potentials were not faced with this issue because they were developed by mostly focusing on physical properties of the bcc phase which is stable at ambient temperature.

In the present study, we have tackled these issues with a newly developed interatomic potentials based on the 2NN MEAM model. The 2NN MEAM parameterization was selected following information from a recent study [42] which compares the performance of several EAM [25], MEAM [16,26], and 2NN MEAM [27,28] potentials. The study [42] revealed that while there is still room for improvement, the 2NN MEAM [27,28] potentials show generally reliable performance to reproduce properties at finite temperatures ensuring an adequate computational efficiency. The 2NN MEAM model was also successfully applied for simulations of the martensitic phase transformations in Ni-Ti shape-memory alloys [43].

In addition to the selection of a potential model, the selection of a proper optimization method of potential parameters is required. In previous works for 2NN MEAM potentials [27–29], potential parameters were optimized to a database which contains both experimental and density-functional theory (DFT) information focusing on specific physical properties. In the present study, on the contrary, the parameters were optimized to a database which contains only DFT information because the consideration of both experimental and DFT information for the fitting inevitably results in the presence of unintended noises in the database. The experimental information was only utilized for the purpose of evaluating the transferability of a developed potential after the fitting. The present optimization was performed utilizing the force-matching method proposed by Ercolessi and Adams [44]. This method considers not a physical property itself but forces and energies related to various atomic configurations expected from only DFT calculation. This method can greatly improve the accuracy of the potential at finite temperatures by including atomic configurations at finite temperatures in the DFT database [43,45,46].

The remainder of this article is organized as follows. Section 2 describes details of DFT calculations for the construction of a database and the optimization process of potential parameters. In Section 3, the accuracy and transferability of the developed potential is presented. In Section 4, the developed potential is applied to study the martensitic phase transformation of pure Li. Finally, conclusion is drawn in Section 5.

2. Optimization of an interatomic potential

We developed an interatomic potential to accurately describe the physical properties of pure Li based on the 2NN MEAM formalism and the force-matching method. The development of the potential was performed in a systematic manner. First, DFT calculations were performed to provide a database of atomic forces and energies related to various atomic configurations. To assure the sufficient transferability of the potential to diverse possible applications, configurations resulting from various conditions were included in the DFT database. Then, the optimization of potential parameters was performed by minimizing errors between the DFT database and the expectation by potential parameters. The general procedure follows a previous work [43] in which 2NN MEAM potentials for pure Ni and Ti were determined based on the force-matching method.

2.1. Construction of a DFT database

A database for the fitting was constructed by performing a series of DFT calculations using VASP code [47–49] based on the projector augmented wave (PAW) method [50]. For the exchange-correlation functional, the Perdew-Burke-Ernzerhof generalized gradient approximation (GGA) [51] was used. A plane-wave kinetic energy cutoff of 350 eV and the Methfessel-Paxton smearing method with a width of 0.1 eV were used. A k-point mesh of $19 \times 19 \times 19$ was selected for the bcc and face-centered cubic (fcc) primitive unit cells, and the corresponding k-point density was employed for the hexagonal-close-packed (hcp) primitive unit cell and supercells. The supercell geometries containing 128 atoms, 108 atoms and 96 atoms were used for bcc, fcc and hcp structures, respectively. For the calculation of the cohesive energy, magnetism was included by considering spin-polarized calculations for a state with a single atom.

The lattice constants and bulk modulus were calculated by employing the Birch-Murnaghan equation of state [52,53]. For the calculation of properties involved with point defects, positions of each atom were relaxed at a constant volume and cell shape. The vacancy migration energy was calculated with a suitable saddle-point configuration utilizing the nudged elastic band (NEB) method [54,55]. For the calculation of the surface energy, rectangular cells with a stacking of 20–25 Å thick slab and a vacuum region of 10 Å were employed. The convergence criteria for energy and forces of all defect calculations were 10^{-6} eV and 10^{-2} eV/Å, respectively. Phonon calculations were performed using the "Phonopy" code [56] based on the direct force constant approach [57]. A bcc supercell of 250 atoms was used for the phonon calculation with the convergence criteria for energy and forces of 10^{-8} eV and 10^{-4} eV/Å, respectively.

Atomic configurations at finite temperatures were obtained by conducting two-step DFT calculations. First, *ab initio* MD simulations [47] were performed based on relatively low convergence parameters such as a single k-point and a default value of the cutoff energy in the PAW potential. The *ab initio* MD simulations were performed for a total of 2000 steps with a timestep of 1.5 fs. Then, well-converged calculations with a higher cutoff energy (350 eV) and denser k-point mesh were performed using obtained snapshots from *ab initio* MD simulations to determine accurate energies and forces of each configuration.

2.2. Optimization of potential parameters

In the 2NN MEAM potential formalism, a pure substance can be described with 14 independent potential parameters. Four parameters [the cohesive energy (E_c), the equilibrium nearest-neighbor distance (r_e), the bulk modulus (B) of the reference structure and the adjustable parameter d] are involved with to the universal equation of state. Seven parameters [the decay lengths ($\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$, $\beta^{(3)}$) and the weighting factors ($t^{(1)}$, $t^{(2)}$, $t^{(3)}$)]] are involved with the electron density. The parameter A is required for the embedding function and two parameters ($C_{\min}$ and $C_{\max}$) are required for the many-body screening. Detailed explanations on these potential parameters are fully available in literature [17–19].

The optimization of potential parameters was started by dividing DFT calculation results into two groups. The first group of DFT results comprises structural energies and forces between atoms in perfect and defected (with vacancies) configurations of bcc, fcc and hcp phases which is directly used in the parameter optimization. Especially, the results from *ab initio* MD simulations