A new embedded-atom method approach based on the $p$th moment approximation

Kun Wang$^{1,2,4}$, Wenjun Zhu$^2$, Shifang Xiao$^1$, Jun Chen$^4$ and Wangyu Hu$^1$

1 College of Materials Science and Engineering, Hunan University, Changsha 410082, People’s Republic of China
2 Laboratory for Shock Wave and Detonation Physics, Institute of Fluid Physics, Mianyang 621900, People’s Republic of China
3 Department of Applied Physics, Hunan University, Changsha 410082, People’s Republic of China
4 Laboratory of Computational Physics, Institute of Applied Physics and Computational Mathematics, Beijing 100088, People’s Republic of China

E-mail: wyuhu@hnu.edu.cn (Wangyu Hu) and wjzhu@caep.cn (Wenjun Zhu)

Received 14 April 2016, revised 28 August 2016
Accepted for publication 31 August 2016
Published 19 October 2016

Abstract
Large scale atomistic simulations with suitable interatomic potentials are widely employed by scientists or engineers of different areas. The quick generation of high-quality interatomic potentials is urgently needed. This largely relies on the developments of potential construction methods and algorithms in this area. Quantities of interatomic potential models have been proposed and parameterized with various methods, such as the analytic method, the force-matching approach and multi-object optimization method, in order to make the potentials more transferable. Without apparently lowering the precision for describing the target system, potentials of fewer fitting parameters (FPs) are somewhat more physically reasonable. Thus, studying methods to reduce the FP number is helpful in understanding the underlying physics of simulated systems and improving the precision of potential models. In this work, we propose an embedded-atom method (EAM) potential model consisting of a new many-body term based on the $p$th moment approximation to the tight binding theory and the general transformation invariance of EAM potentials, and an energy modification term represented by pairwise interactions. The pairwise interactions are evaluated by an analytic-numerical scheme without the need to know their functional forms a priori. By constructing three potentials of aluminum and comparing them with a commonly used EAM potential model, several wonderful results are obtained. First, without losing the precision of potentials, our potential of aluminum has fewer potential parameters and a smaller cutoff distance when compared with some constantly-used potentials of aluminum. This is because several physical quantities, usually serving as target quantities to match in other potentials, seem to be uniquely dependent on quantities contained in our basic reference database within the new potential model. Second, a key empirical parameter in the embedding term of the commonly used EAM model is found to be related to the effective order of moments of local density of states. This may provide a way to improve the precision of EAM potentials further through more precise approximations to tight binding theory. In addition, some critical details about construction procedures are discussed.

Keywords: atomistic simulations, EAM potential, aluminum, mechanical behaviors, equation of states, melting

(Some figures may appear in colour only in the online journal)
1. Introduction

With the increasing computation capabilities of modern computers and their broadening applications in scientific and engineering fields, ultra-large atomic simulations have been proven to be an effective tool for research on a wide range of fields due to their high calculation efficiency and reasonable precision, such as nano-thermodynamics [1], biology [2], geophysics [3], material physics [4–6] and compression science [7–13]. Upon application to solve a certain problem, the atomistic simulations should be combined with proper interatomic potentials. Rapid development of material research fields requires an effective way to construct accurate and transferable interatomic potentials with high efficiencies. The embedded-atom method (EAM) potential proposed by Daw and Baskes [14, 15] is one of the most widely used semi-empirical interatomic potentials, which is based on density functional theory. While another important EAM potential proposed by Finnis and Sinclair [16] is derived from the second moment approximation to tight binding, which is usually named the FS potential. Despite the different theoretical backgrounds, they share a similar form of energy expression. Different parameterization schemes have been designed to construct the EAM potentials for target applications. Because of complex relationships between EAM potential parameters and the resultant behavior of the potential, the traditional construction procedure involves a two-step iterative process [17, 18]. First, EAM parameters are determined based on a handful of critical material properties in a selected reference structure. Second, the new potential is applied to circumstances not included in the construction phase in order to test its validation and transferability. If the validation is not satisfactory, one needs to repeat the two steps from the beginning with construction processes which are very tedious and time-consuming. To overcome this drawback, Ercolessi and Adams [19] developed a force-matching method that fits a cubic-spline based potential to \textit{ab initio} atomic forces of various atomic configurations at finite temperature. Recently, Kim and his coworkers [17] have extended the force-matching method to develop a multi-objective optimization (MOO) procedure for the construction of the modified embedded-atom method (MEAM) potentials. The MOO procedure, represented by the weighted sum method, could optimally reproduce multiple target values that consist of material properties, and enable one to construct MEAM potentials with minimal manual fittings. The weighted sum method is also employed by other researchers for the construction of different EAM potentials [20–23]. In principle, the method allows one to incorporate an arbitrary number of physical properties, whose collection is referred to as the reference database set, in the construction procedure of a certain EAM potential. To make EAM functions flexible enough to reproduce experimental results, more potential parameters are often required for the bigger reference database set, which is usually achieved by introducing cubic spline functions instead of the ones based on certain theoretical analysis [19–22]. This method has been proven to be a very powerful approach to EAM potentials of various elements under complex circumstances, for example simulating properties of the iron–phosphorus system [20], phase transformations in zirconium [24] and the mechanical behaviors of magnesium [17, 25]. However, with the growing complexities of application circumstances (characterized by a large target reference database), the fitting parameter (FP) number of the cubic-spline style potentials may be too large to find an optimal potential which match best with the reference database. It should be noted that the transferability of a potential is reflected by the number of unconsidered physical quantities which could be reproduced, rather than the number of properties incorporated in the construction phase. To control the increment of FPs, it may be helpful to find out the smallest reference database (SRD) for a target application. Theoretically, any physical quantities in the SRD cannot be uniquely determined by other quantities in the SRD within a certain potential model. If the SRD is a complete set, all extrapolated results of the potential could be uniquely determined by the quantities in the SRD. Obviously, sensitivities of extrapolated results to uncertainties of the SRD are main obstacles to obtain a transferable potential. Recently, studies [26, 27] on the sensitivities of the modified EAM potential of aluminum to the input uncertainties show that all modified EAM parameters interdependently influence the model outputs to varying degrees. That is to say, extrapolated results are insensitive to some FPs which may be not necessary for the potential. Unfortunately, the methods of reducing the redundant number of FPs are not specially discussed. Here, we find that the knowledge of SRD and its influence on the extrapolated results could be employed to reduce the redundant number of FPs. Besides, the FP number required for describing a certain system is largely determined by reliabilities of potential models or the functional forms adopted by the model. Because the precise functional forms of the EAM potential are unknown and approximations of the functional forms may change from case to case [18], several potential parameters are introduced by today’s potential models through various methods. Still, some analytic style EAM potentials, represented by the works of Johnson [28, 29], are proposed and successfully applied to model complex metallic systems [30]. Unlike many existing EAM models [17, 19, 31, 32] where the universal equation of states (EOS) [33] (or Rose equation) serves as a basic equation, the EOS is an extrapolated result of the analytic EAM potential of Johnson. Their embedding term is a universal function which is widely adopted in the constructions of EAM potentials. Though the extrapolated EOS at high pressure is not always satisfactory, the analytic scheme could effectively reduce the FP number and promote efficiencies of constructions. A drawback of the analytic EAM, as well as its variations (such as modified analyses EAM potential [12]), is that it may not have sufficient flexibilities to satisfy all the quantities of interest, and eventually affect its precisions when applied to complex cases which involve a large target database set needing to be reproduced. Hence, a suitable analytic-numerical approach may be expected to have both the advantages of the cubic-spline style potentials and the analytic potentials, and thus to reduce the FP number of potentials without affecting the precisions.
To do this, we propose a new EAM model based on approximations of the \( p \)th moment to tight binding theory. To compensate the discrepancy of energy, as well as other physical quantities predicted by the \( p \)th moment approximations, a pairwise style interaction is employed in this model which could be thus determined in a direct manner from physical quantities in aid of numerical interpolation schemes. Details of the new model are described in section 2. Then in section 3, the new EAM model is validated by constructing and testing three potentials of aluminum. It is known that aluminum has a relatively accurate database due to its absence of \( d \) electrons, and can be accurately simulated without angular force. These features could help us avoid the possible difficulties brought by uncertainties of the reference database and spherically averaged approximations adopted in the EAM framework. Our results show that the new potential has a lower FP number and a smaller cutoff distance than some commonly used potentials of aluminum. Additionally, the equivalence between our new manybody term and the universal function in the vicinities of equilibrium states are addressed, which may be helpful for understanding the physical bases of EAM models constructed via the universal function.

2. Theoretical method

2.1. EAM potential

According to the formulism of the EAM potential [14], the total energy of any configuration of nuclei can be expressed as a summation of atomic energy, that is

\[
E = \sum_i \sum_j \phi(r_{ij}) + \sum_i F(\rho_i),
\]

(1)

where \( \phi(r_{ij}) \) represents the pairwise interaction potential between atom \( i \) and neighbor atom \( j \) at a radial distance \( r_{ij} \), and \( F(\rho) \) is the so-called embedding energy which is a nonlinear function of total electron density \( \rho_i \) at site \( i \). The embedding energy-electron density curves, for H through Ar, have been calculated within a density-functional scheme [34, 35]. Banerjea et al [36] further express the scaled embedding energy-electron density curves as a universal function which could be parameterized as

\[
F(\rho_i) = -F_0 \left[ 1 - n \ln \left( \frac{\rho_i}{\rho_c} \right) \right] \left( \frac{\rho_i}{\rho_c} \right)^p,
\]

(2)

where \( F_0 \) and \( n \) are parameters, \( \rho_c \) is the electron density at equilibrium state (where the total energy of the lattice reaches a minimum with respect to the change of lattice parameter). If not specified, we will use subscript \( e \) to discriminate the quantities of the equilibrium state from others and neglect the subscript of the central atom index. Although expression (2) is physically reasonable at large \( \rho_c \), it approaches zero at \( \rho_e = 0 \) with infinite slope and yields poor values for the pressure derivative of the bulk modulus [28]. Wadley avoided the problem via using expression (2) only at large \( \rho_e \) while the remaining segments of the embedding function are replaced by simple cubic polynomials [28, 37]. Below, we will interpret the embedding energy (i.e. manybody term) in a different way, which gives a new EAM approach to interatomic potentials.

Inspired by the work of Finnis and Sinclair [16], the total energy of a system of interest could be evaluated through the \( p \)th moment approximation of tight binding theory [38–40] which is essentially a manybody interaction. The \( p \)th moment \( \mu_p \) of the density of states connects to band energy, whose center has been shifted to zero, and Hamiltonian matrix \( H \) by

\[
\mu_p = \int E^n n(E) dE = \text{Tr}[H^p] = \sum_i [H^p]_{ii}.
\]

(3)

where \( n(E) \) is the local density of states. In tight binding theory, the diagonal and off-diagonal terms of the \( N \)-dimension matrix \( H \) corresponds to onsite and hopping integrals for an \( N \)-atom cluster, respectively. Because \( [H^p]_{ii} \) involves \( p \)-hop chains (that is \( H_{ij}H_{ik}H_{kl} \ldots H_{mn} \)) and could be calculated from local topology, the \( p \)th moment reflects \( p \)-body interactions. For simple metals where atom \( i \) and its surrounding atoms are equivalent, \( \sum_i [H^p]_{ii} \) could be represented by \( \mu_p \) where \( \mu_p \equiv \langle n_p \rangle \) is proportional to \( \sum_j b(r_{ij})^p \) and \( b(r_{ij}) \) is a two-center hopping integral, which therefore stands for the contribution of atom \( j \) to \( \rho_i \). In the above derivations, we have assumed that the \( p \)-hop chain of \( [H^p]_{ii} \) could be expressed by exponentiation of the two-center hopping integral. Except for interaction models of the first nearest neighbors, the exponent is not necessarily equal to \( p \) for the models whose interaction range is beyond the first nearest neighbors, which has been denoted by \( \theta \) instead. In addition, from the first equation of (3), the energy \( E \) relates to \( \mu_p \), thus \( \rho_c \) by \( E \propto \sqrt{\mu_p} \) for a rectangular band. Assuming that the pairwise interaction potential in expression (1) serves as a correction to energetic, structural and elastic properties of a certain material, the energy \( E \) corresponds to the embedding energy in equation (1). This idea is equivalent to the tight binding theory [41] if \( E \) corresponds to the valence bond and promotion energies, and the pairwise interaction corresponds to the total electrostatic and exchange-correlation energies. Further, by considering the transformation invariance relations of the EAM potential and setting the first derivative of the embedding energy at \( \rho_e \) to be zero like Banerjea [36] does, we have

\[
F(\rho_i) = F_0 (p\rho_i^p/\rho_c^p - \rho_i/\rho_c),
\]

(4)

where \( p = 1/n^2 \), \( F'_0 = F_0 (1 - p) \). In our construction procedures, \( p \) is allowed to be a fractional number for convenience. Thus, \( p \) stands for an ‘effective’ order of the moments. It is worth noting that the meaning of \( \rho_i \) in the above expression is different from the one in expression (2), which will be described further below. From the above derivation, expression (1) is still valid within the new framework except for the physical meanings of the embedding term and the pairwise interaction. That is to say, the ideas of the new approach have no relations with the original EAM model, which is termed ‘EAM’ simply because of its similar functional form of the total energy. We will use expression (2) at \( \rho_i > \rho_c \) and expression (4) at \( \rho_i < \rho_c \) for the construction of the first EAM potential (EAM-I) of aluminum, and only use expression (4) for the construction of the second one (EAM-II). The results of these
two potentials, corresponding to two different EAM models, will be discussed in section 3. In the original EAM model, the total electron density of site \( i \) is assumed to be a linear superposition of electron density per atom surrounding the site. A spherical atomic electron density (\( f(r_{ij}) \)) is found to be good enough for many metallic systems [12, 42], but poorly satisfied for covalently bonded systems where angular dependency cannot be neglected [43, 44]. In the present work, the former is our major consideration while the latter will be left for further works. Then, \( \rho_i \) is given by

\[
\rho_i = \sum_{j \neq i} f(r_{ij}),
\]

where the summation of the atomic electron density is over all neighbors defined by a cutoff distance \( r_{oc} \). The spherical atomic electron density is assumed to be several kinds of analytic forms semi-/empirically [12, 20, 22, 30]. According to the derivation of expression (4), the definition of expression (5) is still valid for \( \rho_i \) in the expression (4) when \( f(r_{ij}) \propto b(r_{ij})^\theta \). The expression of \( f(r_{ij}) \) in our previous work [12] is found to meet these requirements, that is

\[
f(r_{ij}) = f_0 \left( \frac{r_{ij}}{r_{oc}} \right)^\theta \left( \frac{r_{oc} - r_{ij}}{r_{oc} - r_{ce}} \right)^2,
\]

where \( \theta \) is a potential parameter. This means that \( b(r_{ij}) \) takes the form of \( r_{ij}/r_{oc} \). The value of \( f_0 \) has no effect on the calculations of elemental qualities; it is retained for the construction of alloy potentials in the future. Then, parameterization procedures can begin if an expression of the pairwise interactions is given. However, rather than adopting this routine, we take an analytic scheme, which is combined with the weighted sum method, to determine the pairwise interaction dynamically. In the next section, the analytic scheme is introduced to find pairwise interactions dynamically, which could effectively avoid the theoretical difficulties from the lack of sufficient knowledge of pairwise interactions.

### 2.2. An analytic scheme of pairwise-interaction construction

The precise solution of pairwise interactions associates with an extremely complex ion-electron system governed by quantum mechanics, which is usually unknown except for some simple case (such as hydrogen). Alternatively, the pairwise interactions could be inferred from physical quantities of elements. One typical example is the applications of the lattice inversion method [45–47] to calculate interatomic potentials from the EOS. Here, we calculate the pairwise interactions from some basic physical quantities of elements, which include lattice parameter, cohesive energy, single vacancy formation energy and elastic constants. The calculation procedure is different from the traditional analytic construction scheme because of decoupling between many body effects, denoted by the embedding term, and pairwise interactions.

Before we introduce the analytic scheme, we recall some basic properties of a crystal. The first one is cohesive energy which could be expressed by

\[
E_{\text{coh}} = \frac{1}{2} \sum_{i \neq j} \phi(r_{ij}) + F(\rho_i) = \frac{1}{2} \sum_i n_i \phi(ba_0) + F(\rho_i),
\]

where \( a_0 \) is the lattice parameter at equilibrium states. \( n_i \) denotes the atom number of the \( I \)th nearest neighbors and \( b_l \) is the corresponding separation distance reduced by \( a_0 \), which could be evaluated by minimizing the total energy of different lattice parameters. That is to say, the derivative of the total energy with respect to the lattice parameter is zero at \( a_0 \). Then we have

\[
E'(a_0) = \frac{1}{2} \sum_i n_i b_l \phi'(b a_0) + F'(\rho_i) \sum_i n_i b_l f'(b a_0) = 0.
\]

The formation energy of the single vacancy is usually considered in atomic simulations because it is the simplest point defect whose un-relaxed formation energy is about the order of \( \sim 0.1 \text{eV} \) larger than the relaxed one. Supposing that a vacancy is introduced into an ideal crystal, originally consisting of \( N \) atoms with a cohesive energy of \( E_{\text{coh}} \) per atom (i.e. its total energy \( E_N = N E_{\text{coh}} \)), the total energy of the resulting system, containing one vacancy, is \( E_{N-1} \). Then, the un-relaxed vacancy formation energy is given by

\[
E_{1v} = E_{N-1} - (N-1)E_{\text{coh}} = (E_{N-1} - E_N) + E_{\text{coh}} = \Delta F - E_{\text{coh}} + F(\rho_i),
\]

where

\[
\Delta F = \sum_i n_i [F(\rho_i) - f(b a_0)] - F(\rho_i).
\]

To involve the second derivatives of the EAM potentials, the elastic properties of a crystal are considered. From lattice dynamics theory, elastic constants of a pure element could be expressed as

\[
C_{\alpha\beta\mu\nu} = -\frac{1}{2\Omega_0} \sum_{k,k'} \Phi_{\alpha\beta}(k,k')r_{kk'}^\alpha r_{kk'}^\beta,
\]

where \( \Omega_0 \) is the volume per atom of the crystal at equilibrium states, and \( \alpha, \beta, \mu, \) and \( \nu \) denote the Cartesian index. The summation, with respect to atom \( k \) and \( k' \), runs over all atoms in the system of interest. Force constant \( \Phi_{\alpha\beta}(k,k') \) could be evaluated by

\[
\Phi_{\alpha\beta}(k,k') = \left[ -\phi''(r_{kk'}) + \frac{\phi'(r_{kk'})}{r_{kk'}} \right] r_{kk'}^\alpha r_{kk'}^\beta - \delta(\alpha - \beta) (F_k + F_{k'}) \left\{ F''(r_{kk'}) + f'(r_{kk'}) \right\} r_{kk'}^\alpha r_{kk'}^\beta + f'(r_{kk'}) \delta(\alpha - \beta)
\]

\[
+ F_k f'(r_{kk'}) r_{kk'}^\alpha r_{kk'}^\beta \sum_{i=k'} f'(r_{ki}) r_{ki}^\alpha r_{ki}^\beta - F_k' f'(r_{kk'}) r_{kk'}^\alpha r_{kk'}^\beta \sum_{i=k} f'(r_{ki}) r_{ki}^\alpha r_{ki}^\beta + F_k f'(r_{kk'}) f'(r_{kk'}) r_{kk'}^\alpha r_{kk'}^\beta.
\]
From formula (2) or (4), we have
\[
F(\rho_i) = F_0, \quad F'(\rho_i) = 0, \quad F''(\rho_i) = F_0 \rho_i^2 \rho_i^2.
\]
Then, formula (8) and (11) could be rewritten as
\[
E'(a_0) = \frac{1}{2} \sum_i n_i b_i \phi'(b_i a_0) = 0 \tag{14}
\]
and
\[
\Omega_0 C_{\alpha\beta\mu\nu} = B_{\alpha\beta\mu\nu} + F''(\rho_k)V_{\alpha\beta}V_{\mu\nu}.
\]
where
\[
B_{\alpha\beta\mu\nu} = \frac{1}{2} \sum_i \left[ -\phi''(r_{ie}) + \frac{\phi'(r_{ie})}{r_{ie}} \right] \rho_i^\alpha \rho_i^\beta \rho_i^\mu \rho_i^\nu r_{ie}^2 \tag{16}
\]
\[
V_{\alpha\beta} = \sum_i \rho_i^\alpha \rho_i^\beta r_{ie} r_{ie}. \tag{17}
\]
For a cubic lattice, three independent elastic constants in the Voigt notation are
\[
C_{11} = [B_{11} + F''(\rho_k)V_{11}^2] / \Omega_0, \tag{18}
\]
\[
C_{12} = [B_{12} + F''(\rho_k)V_{11}^2] / \Omega_0, \tag{19}
\]
and
\[
C_{44} = B_{12}/\Omega_0. \tag{20}
\]
The effects of pairwise interaction and the manybody term on the elastic properties could be seen more clearly by rewriting formula (18) and (19) in the below formula:
\[
C' = \frac{1}{2} (C_{11} - C_{12}) = \frac{1}{2} (B_{11} - B_{12})/\Omega_0, \tag{21}
\]
\[
C_d = C_{12} - C_{44} = F''(\rho_k)V_{11}^2/\Omega_0. \tag{22}
\]
That is to say, $C'$ and $C_{44}$, as importance indicators of lattice stabilities, are completely determined by pairwise interactions, while $C_d$ is uniquely determined by the embedding term. From the discussions above, we find that equations (14), (19) and (20) only depend on $\phi(r_{ij})$ and its derivatives, while equation (7) and (9) rely on both pairwise interaction and embedding terms. Namely, the coupling effects between the manybody term and pairwise interactions are only reflective in cohesive energy and single vacancy formation energy in the present situation. Therefore, $\phi(r_{ij})$ could be evaluated at certain points via equations (7), (9), (14), (19) and (20) if all parameters of the embedding term, that are $F_0, n_i, n$ are known. To this end, the MOO procedure [17, 22] is employed to find the embedding parameters as well as other underdetermined parameters of pairwise interactions, where the remaining parameters of $\phi(r_{ij})$ could be calculated in every attempt of the search. To incorporate the information between each equilibrium separation and obtain a reliable potential via this scheme, a robust numerical scheme for solving the equations of $\phi(r_{ij})$ is needed, which will be described in the next section.

### 2.3. Numerical scheme and parameterization of the EAM potential

From the analyses above, the basic qualities at equilibrium states could be guaranteed if equations (7), (9), (14) and (20)–(22) are all satisfied. Among these relations, only equations (7), (14), (20) and (21) are employed for solving the value of $\phi(r_{ij})$ as well as its derivatives at each equilibrium separations $r_{ij}$, while equations (9) and (22), associated with single vacancy formation energy and Chauvy pressure, are served as target qualities involved in the MOO procedure. It should be noted that the four equations cannot determine all values of $\phi(r_{ij}), \phi'(r_{ij})$ and $\phi''(r_{ij})$, where $I = 1, 2, \ldots, N$ if we take the cutoff distance $r_c$ of $\phi(r)$ to be
\[
r_c = r_N + k_c(r_{N+1} - r_N), \tag{23}
\]
where $k_c$ is a potential parameter ranging from 0.1–0.9. That is to say, to completely determine the values of $\phi(r_{ij})$ and its derivatives, we still lack $3N - 4$ equations. Besides, values of $\phi(r_{ij})$ between two adjacent equilibrium separations cannot be reflected by the qualities at equilibrium states. In order to solve these two problems, we firstly find an approximate numerical solution of $\phi(r_{ij})$ at equilibrium states, and then correct it with other qualities of both equilibrium and non-equilibrium states. In the present work, we start by assuming $\phi''(r_{ij})$ to be nearly linearly changed between adjacent $r_{ij}$ and thus linear interpolation could be used between adjacent values of $\phi''(r_{ij})$, which will result in a cubic spline interpolation between adjacent values of $\phi(r_{ij})$. If we select $\phi(r_{ij})$ and $\phi''(r_{ij})$ as parameters to be determined, that is
\[
\phi(r_{ij}) = y_I, \quad \phi''(r_{ij}) = M_I, \quad (I = 1, 2, \ldots, N + 1), \tag{24}
\]
where we have used the notation $r_{N+1}, y_{N+1}$ and $M_{N+1}$ to denote $r_c, \phi(r_c)$ and $\phi''(r_c)$, respectively. If not specified, these notations will be used in the rest of this section. Then the expression of $\phi(r_{ij})$ could be obtained by integrating $\phi''(r_{ij})$ twice, that is
\[
\phi(r_{ij}) = \frac{(r_{ij+1} - r_{ij})^3}{6h_I} M_I + \frac{(r_{ij} - r_{ij-1})^3}{6h_I} M_{ij-1} + \left( y_I - \frac{h_I^2}{6} M_I \right) r_{ij+1} - r_{ij} + \left( y_{ij-1} - \frac{h_I^2}{6} M_{ij-1} \right) r_{ij} - r_{ij-1}, \quad (r_{ij} \leq r < r_{ij+1}, \quad I = 1, 2, \ldots, N), \tag{25}
\]
where
\[
h_I = r_{ij+1} - r_{ij}. \tag{26}
\]
The derivation of equation (25) has already considered the continuity conditions of $\phi(r_{ij})$ and $\phi''(r_{ij})$ at $r_{ij}$ ($I = 2, \ldots, N$), while the continuity conditions of $\phi'(r_{ij})$ should be considered separately, which could be written as
\[
\phi'(r_{ij}) = \phi'(r_{ij-1}), \quad (I = 2, \ldots, N), \tag{27}
\]
Considering equations (24) and (25), equations (9) and (14) could be expressed as
\[
\sum_{I=1}^N n_I y_I = 2(E_{coh} - F_0), \tag{28}
\]
\[ n b_1 h y_1 + \sum_{i=2}^{N} \left( \frac{1}{2} n_{i-1} b_{i-1} h_{i-1} + n b_1 h_1 \right) M_i + 3 \left[ n b_1 h_1 y_1 + \sum_{i=2}^{N} \left( n b_1 h_i - n_{i-1} b_{i-1} h_{i-1} \right) y_i \right] = 0, \]

where \( b_i \) relates to \( r_i \) by

\[ b_1 a_0 = r_1. \]

Similarly, equations (20) and (21) could be rewritten as

\[ a_1 y_1 - \sum_{i=2}^{N} (a_{i-1} - a_i) y_i + A_1 1 + \frac{1}{3} h_i^2 \] \[ + \sum_{i=2}^{N} \left[ \frac{1}{6} A_{i-1} h_{i-1} - A_i \left( 1 + \frac{1}{3} h_i^2 \right) \right] M_i = D, \]

where

\[ A_i = \sum_{\{i\}} r_i^2, r_i^2, r_i^2, \]

\[ D = 4 \Omega_0 C_{dd}, \]

for equation (20) and

\[ A_i = \sum_{\{i\}} (r_i^2 - r_i^2, r_i^2, r_i^2), \]

\[ D = 4 \Omega_0 C_{d}, \]

for equation (21), respectively. \( h_i^2 \) and \( a_i \) are defined as

\[ h_i^2 = h_i/r_i, \]

and

\[ a_i = A_i r_i h_i. \]

This numerical scheme contains totally \( N + 3 \) equations of \( 2(N + 1) \) parameters, that is \( \{ y_i, M_i \} \) (\( i = 1, 2, \ldots, N, N + 1 \)). Below, we will use \( \{ y_i, M_i \} \) to denote the unknown parameters of pairwise interactions. In comparison with the \( 2(N + 1) \) unknown parameters, \( N - 1 \) more equations are required to form complete equations. Here, the third neighbor model (3NM) will be developed in detail, whose idea could be easily generalized to the \( N \text{th} \) neighbor model by introducing \((N - 3)\) additional parameters. For 3NM, two more equations are required. It is naturally thought that equation (9) could serve as one equation for 3NM. However, we find that equations (7) and (9) cannot be included in the equation sets simultaneously, otherwise the numerical solution of \( \{ y_i, M_i \} \) may turn out to be infinite. To avoid this problem, we set \( y_{N+1} \) and \( M_{N+1} \) to be zero instead of utilizing equation (7) to solve \( \{ y_i, M_i \} \). Because expression (25) does not guarantee that the first order derivative of \( \phi(r) \) at \( r_0 \) is zero, \( \phi(r) \) is redefined at the range of \( [r_N, r_{N+1}] \) or \( [r_{N+1}, r_N] \) below:

\[
\phi(r) = \begin{cases} 
\left( \frac{(r_{N+1} - r)^3}{6 h_N} + \frac{(r - r_N)^3}{6 h_N} \right) M_{N+1} + \left( y_N - \frac{h_N^2}{6} M_N \right) r_{N+1} - \frac{r}{h_N}, & 0 \leq r \leq r_0, \\
\left( \frac{y_{N+1} - \frac{h_N^2}{6} M_N}{h_N} \right) + \left( \frac{r}{h_N} h(r), \right), & r_0 < r \leq r_0. 
\end{cases}
\]

where the Taylor function \( h(r) \) is

\[ h(r) = \sum_{i=0}^{5} \lambda_i \left( 1 - \frac{r - r_i}{r_c - r_N} \right)^i, \]

where \( \lambda_i \) takes values which make \( h(r) \) satisfy

\[
\begin{cases} 
h(r_N) = 1, & h(r_N) = 0, \\
h(r_c) = 0, & h'(r_c) = 0, \quad h''(r_c) = 0. 
\end{cases}
\]

Therefore, the pairwise interaction could be uniquely determined via values of cohesive energy, lattice parameter and elastic constants measured at equilibrium states if \( F_0 \), as a coupling parameter, is known. Here, we have used the term ‘coupling parameters’ to represent undetermined parameters (or potential parameters) of our potential in order to emphasize its coupling nature between the pairwise interaction and the embedding energy. In other words, any changes of the coupling parameters will affect energy partitions between pairwise interaction and embedding energy, which could be determined by an optimization procedure. Unfortunately, the resulting potential of this scheme fails to reproduce dispersion relations and single vacancy formation energy simultaneously, no matter how complex an atomic electron density function is used. The main reason is that the interpolation scheme is not precise enough to calculate \( \phi(r) \) despite the accuracy of \( \phi_i(r_i) \) and \( \phi_d(r_i) \). To improve the calculation precision of \( \phi(r_i) \), \( Z \) additional nodes are inserted into the original nodes defined at equilibrium separations. Still, continuity conditions are obeyed at all nodes, which contributes to the \( Z \) additional equations while introducing \( 2Z \) unknown parameters \( \{ y_i, M_i \} \) \((i = 1, 2, \ldots, Z)\). Again, the remaining \( Z \) parameters \( \{ M_i \} \) are taken to be coupling parameters which will be optimized by fitting them to other physical quantities through the MOO method. Thus, there are \( Z + 4 \) potential parameters to be optimized, which are \( n, F_0, \theta, k_c, \{ M_i \} \) \((i = 1, 2, \ldots, Z)\). The additional nodes make the potential more flexible and enable the potential to adapt to various application circumstances.

Additionally, qualities at extreme conditions may be involved in the fitting procedures which require a complete definition of \( \phi(r) \). We use the Morse function, consisting of a repulsive and an attractive term, as short range pairwise interactions, that is

\[ \phi(r) = D_a e^{-2(\alpha(r_r - \chi)} - 2e^{-\alpha(r_r - r_0)}, \quad (r < r_0) \]

where \( r_0 = r_0 \chi, 0 \leq \chi \leq 1 \). The value of \( \chi \) ranges from 0.8–1.0 depending on the elements. Other commonly used two-body functions, like the LJ (Lennard-Jones) function, could also be applied here. Though it may affect the EOS at compressed states, the quality of the potential is unchanged for applications near equilibrium states based on our testing. The remaining parameters \( (D_a, \alpha, r_0) \) in expression (39) could be determined by smooth connection conditions at \( \phi(r_0) \). The cutoff distance of atomic electron density is \( r_c = r_{N+1} + 0.5(r_{N+2} - r_{N+1}) \) where \( r_{N+1} \) and \( r_{N+2} \) are the \((N + 1)\)th and \((N + 2)\)th nearest neighbor separation of the reference lattice at equilibrium states, respectively.

In summary, this potential model contains only five FPs which are \( n, F_0, \theta, k_c \) and \( \chi \). Several additional FPs could be involved in the model through additional nodes inserted
between equilibrium separations depending on application circumstances. The additional FP number is equal to the number of additional nodes for 3NM. To make the total FPs as small as possible, we need to choose the smallest number of additional nodes to reproduce the SRD of a target application. However, the final FP number relies on the reliabilities of a potential model for a certain system. In the next part, we will test this model in aluminum.

3. Results and discussions

3.1. Fitting parameters of interatomic potentials of aluminum

The method mentioned in section 2 has been implemented in a software tool we have called ‘constraint multi-object fitting procedure’ (CMOFP). CMOFP utilizes the MOO method combined with some optimization algorithms (the simplex algorithm of Nelder and Mead is employed here) to find the optimal potential parameters which achieve the best match between the predicted results of the new potential and reference database. In the present work, we intend to construct a 3NM potential of aluminum with a smaller FP number than some reported potentials [22, 30, 48], while still being as accurate as them. Our reference database consists of a lattice parameter, cohesive energy, single vacancy formation energy, elastic constants, phonon dispersion spectra and EOS at stretched states. An extended reference database is used to construct the 3NM potential EAM-I and EAM-II, which include two additional quantities, i.e. stacking faults energy (SFE) and unstable stacking fault energy (USFE). To find the SRD, the basic reference database is also used to construct the 3NM potential EAM-II’ as a comparison with EAM-II. EAM-I and EAM-II are different in their functional form of embedding energy as mentioned above, while the embedding function of EAM-II’ is the same as EAM-II. Two additional nodes are inserted between the first and the second nearest neighbor separation, and one additional node is inserted between the second and the third nearest neighbor separation. After several trials, the resulting potentials are insensitive to the detailed positions of these three additional nodes, which are simply fixed at

Table 1. Potential parameters of aluminum, as well as Morse function parameters ($D_e$, $\alpha$, $r_e$), in the present work.

| Parameter   | EAM-I       | EAM-II      | EAM-II’     |
|-------------|-------------|-------------|-------------|
| $F_0$       | 2.699 978 11 | 2.699 977 35 | 2.699 950 08 |
| $n$         | 0.712 105 60 | 0.724 999 39 | 0.745 083 59 |
| $\theta$    | 2.009 549 60 | 1.886 118 85 | 1.693 915 00 |
| $k_c$       | 0.635 610 00 | 0.692 050 00 | 0.362 560 00 |
| $\chi$      | 0.900 000 00 | 0.820 000 00 | 0.880 000 00 |
| $M_1^a$     | 0.838 465 64 | 0.687 681 14 | 0.717 746 11 |
| $M_2^a$     | -0.846 529 56 | -0.714 718 45 | -0.751 249 98 |
| $M_3^a$     | 0.061 826 87 | 0.070 601 33 | 0.026 767 01 |
| $M_4^a$     | 0.367 063 06 | 0.299 186 46 | 0.236 576 17 |
| $D_e$       | 0.107 910 28 | 0.165 040 66 | 0.131 979 48 |
| $\alpha$    | 1.113 131 35 | 0.874 169 42 | 1.074 277 11 |
| $r_e$       | 3.264 046 99 | 3.426 499 93 | 3.232 024 76 |

Note: The Morse parameters are the intermediate variables which can be determined by the potential parameters.

Figure 1. Pairwise interactions of EAM potentials of aluminum.

Figure 2. Embedding energy as a function of $\rho/\rho_e$.

Figure 3. Atomic electron density function of EAM potentials of aluminum.
unfitted qualities, that is, the cohesive energy of the BCC (body centered cubic) and HCP (hexagonal close-packed) structures and surface energies, also reasonably agree with experimental measurements or \textit{ab initio} calculations when the best fitting to the reference database is achieved. The best fitting means that the value of the multiple-objective function reaches its minima, which could be achieved by repeating the fitting procedure three or four times. The good agreements between the prediction results (in table 2 and figure 4) and the reference data indicate that we have achieved the best fitting with the potential parameters. Although the cohesive energies of the BCC and HCP structures are bigger than that of the FCC (face centered cubic) structure as expected, the cohesive energy of the BCC structure changes from \(-3.10\) eV to \(-3.34\) eV depending on the position of additional nodes, while the cohesive energy of the HCP structure will always be close to the correct value (\(-3.33\) eV) when the best fitting is achieved.

3.2. Testing the potentials of aluminum

The critical properties of aluminum are predicted by the three potentials as well as two commonly used potentials developed by Zhou \textit{et al} [30] and Mishin \textit{et al} [22] (see table 2). Our results show that the intrinsic stacking fault energy \(\gamma_{\text{SF}}(1\ 1\ 2)\) cannot be correctly predicted without incorporating it into the reference database, which is an important property for descriptions of mechanical behaviors of aluminum. Other
The EOS is of fundamental importance for describing the mechanical response to shock compressions [50, 51]. As shown in figure 5, the EOS of aluminum at compressed states has been predicted at 0 K with the three potentials. The results of Zhou et al and Mishin et al are also provided in the figure. From the results, we find that the EOS predicted by us agrees quite well with experiment measurements [52, 53] up to more than 150 GPa, as per the results of Mishin et al. In spite of the similar results, the difference between ours and Mishin’s lies at the construction procedures. Mishin et al [22] have utilized the EOS, in terms of the universal Rose equation, as one of the functions to construct their potential of aluminum, which will surely result in the correct EOS. The EOS at compressed states is not incorporated in our reference database, which is merely a result of extrapolations from equilibrium and stretched states to the compressed states. We find that more FPs are needed to match the reference database if the universal Rose equation instead of equation (4) is present in our EAM potentials. Furthermore, the predicted EOS at compressed states is sensitive to the uncertainties of the reference database, which cannot be studied by potentials containing the universal Rose equation. We will discuss the roles of the sensitivity played on the improvements of transferability without adding additional FPs in the next section.

Besides, as shown in figure 2, the embedding function defined by (4) could generate similar behaviors at vicinities of \( \rho_e \) as the one defined by expression (2), and the precisions of EAM-I and EAM-II, corresponding to that of (4) and (2) at \( \rho > \rho_e \), are also comparable (see table 2 and figures 4 and 5). Then expression (4) may provide another explanation for (2), whose empirical parameter \( n \) could relate to the effective order of moments of the local density of states by \( p = 1/n^2 \). If the order of moments is much larger than two, our approximations in the derivations of expression (4) should be improved in order to make a satisfactory prediction. Considering the similar behaviors between expression (4) and (2), this condition may also be applied for (2). Fortunately, the effective orders of moments for the cases of aluminum under consideration are within ranges of (1.8, 1.98), which meet the condition. This may be a reason that the new EAM model could correctly simulate the bulk properties of aluminum and exhibit a good compatibility between the SRD and the extrapolated results (see section 3.3).

The melting point is a critical property for crystal materials at elevated temperatures, which will be predicted by molecular dynamics (MD) simulations using the three new potentials of aluminum. To observe the melting of aluminum, a \( 30a_0 \times 30a_0 \times 30a_0 \) single crystalline aluminum sample is equilibrated over the range from 600 K to 1500 K at 1 atm via constant temperature and pressure simulations for 80 ps, respectively. Each simulation is performed with a large-scale atomic/molecular massively parallel simulator [54]. The Nosé–Hoover thermostat and barostat are employed to fix the temperature and pressure during the simulations. Bond order parameters [55] are employed to distinguish isentropic liquids from crystalline solids, which are calculated and averaged over the last 1000 steps for each MD simulation. Parameter \( Q_6 \) as a function of temperature (T) is shown in figure 6, where the sudden drop in the value of \( Q_6 \) indicates the occurrence of melting. Thus, the predicted melting point is about 1200 K, 1100 K and 1100 K for EAM-I, EAM-II and EAM-II', respectively, which is larger than the experimental value 933 K [56]. This is because the aluminum sample employed here is an ideal single crystal whose melting point will decrease in the presence of lattice defects, for example, dislocations and grain boundaries. Besides, this prediction method of the melting point is the so-called gradual heating method, whose results are usually larger than its real ones because of an extraordinarily high heating rate [57]. More reliable prediction could be made through the free energy approach, which will be conducted in the next paragraph. The melting transition could also be observed through adaptive common neighbor analyses.
Additionally, there is a sudden rising in the $Q_6-T$ curve near the melting point for EAM-II', while the behaviors of aluminum do not have this abnormality for EAM-I and EAM-II. This result suggests that the extended reference database employed here does not affect the prediction of the melting point, but does have an influence on the detailed material behaviors near the melting point. By comparing the melting point predicted by EAM-I and EAM-II, we find that the embedding function defined by expression (4) gives a more accurate melting point than that of expression (2).

Alternatively, the melting point could be predicted by equating the free energy of the solid phase with that of the liquid phase. To complement the predictions of the melting points with the gradual heating method, the free energy approach is employed to calculate the melting point of aluminum with EAM-II. Here, free energies of the solid and liquid phase are calculated by the reversible scaling (RS) technique [59, 60] and the adiabatic switch (AS) approach [60–62]. Supposing that the system of interest contains $N$ atoms of equal mass $m$, its Hamiltonian could be expressed as

![Figure 5. Equation of states of aluminum predicted by different EAM potentials (a[30]; b[22]; c[52]; d[53]).](image)

![Figure 6. Bond parameters ($Q_6$) as a function of temperature, where the sudden drop indicates the occurrence of a melting transition.](image)
where \( r_i \) and \( p_i \) are the position and momentum vectors of atom \( i \), \( U_0 \) denotes the potential energy. If the system is in thermal equilibrium under constant temperature \( T_0 \) and constant volume \( V \), the Helmholtz free energy is given by

\[
\int = - \frac{F_T k T}{N k T} \ln \exp \left( \frac{U_0}{k T} \right), \tag{41}
\]

where \( k_B \) is Boltzmann’s constant and \( \Lambda(T_0) \) denotes the thermal de Broglie wavelength \( \hbar / \sqrt{2 \pi m k_B T_0} \). The AS technique rescales the system of interest by a factor \( \lambda (\lambda > 0) \) to create a new system whose Hamiltonian and Helmholtz free energy are written as

\[
H_0(\lambda) = \sum_{i=1}^{N} \frac{p_i^2}{2m} + U_0(r_i, \ldots, r_N), \tag{40}
\]

\[
F_0(T_0) = -k_B T_0 \ln \left[ \int d^{3N} r \exp \left( -\frac{U_0}{k_B T_0} \right) \right] + 3Nk_B T_0 \ln \lambda(T_0), \tag{41}
\]

\[
F_0(T_0, \lambda) = -k_B T_0 \ln \left[ \int d^{3N} r \exp \left( -\frac{U_0}{k_B T_0} + \lambda T_0 \right) \right] + 3Nk_B T_0 \ln \lambda(T_0), \tag{42}
\]

\[
F_0(T_0, \lambda) = -k_B T_0 \ln \left[ \int d^{3N} r \exp \left( -\frac{U_0}{k_B T_0(\lambda)} \right) \right] + 3Nk_B T_0 \ln \lambda(T_0), \tag{43}
\]



Figure 7. Snapshots of adaptive common neighbor analyses of simulated aluminum sample after relaxing for 80 ps at different temperatures covering its melting point. The potential of aluminum employed for the simulations is EAM-II. Similar results are observed by other potentials constructed in the present work.

Figure 8. \( W/N \) as a function of time for FCC aluminum and its liquid phase.

Figure 9. Comparison of \( \langle U_1 - U_2 \rangle \), calculated by RS technique and AS approach at different \( \lambda \), which suggests that either of the two methods could be employed for the evaluations of reversible work during adiabatic phase switch.
If \( \lambda \) slowly changes its value from \( \lambda(0) \) to \( \lambda(t) \) with time \( \tau \) under constant \( T_0 \) and constant \( V \) so that a reversible thermodynamic path is created between \( \lambda(0) \) and \( \lambda(t) \), then the AS approach could be used to connect \( F_1(T_0, \lambda(t)) \) and \( F_1(T_0, \lambda(0)) \) via a cumulative reversible work \( W(t) \),

\[
\Delta F_1(\lambda(t), \lambda(0)) \equiv F_1(T_0, \lambda(t)) - F_1(T_0, \lambda(0)) = \int_0^\tau \frac{d\lambda}{dt} U_0(\mathbf{n}(\tau), \ldots, \mathbf{n}(\tau)) \, d\tau = W(t). \tag{45}
\]

Substituting equation (45) back to (44), the Helmholtz free energy at \( T \) could be expressed as

\[
F_0(T(t)) = F_0(T(0)) + W(t) = \frac{F_0(T(0))}{T(0)} + \frac{W(t)}{T_0} - \frac{3}{2} N k_B \ln \frac{T(t)}{T_0}, \tag{46}
\]

where \( T(t) = T(0)/\lambda(t), \lambda(0) = T(0)/\lambda(0) \). Thus, the temperature dependence of \( F_0(T) \) could be determined by a time-dependence function \( W(t) \) and its initial value \( F_0(T(t)) \) (or \( F_0(T_0) \)). Practically, the time \( \tau \) dependence of \( \lambda \) adopts the below form

\[
\lambda(\tau) = \frac{\lambda_0}{1 + \frac{\lambda_0}{\lambda(\tau)} - 1}, \tag{47}
\]

where \( \lambda_0 = \lambda(0), \lambda_1 = \lambda(t) \). To obtain \( W(t) \), we perform MD simulations under constant \( T_0 \) and constant \( V \) ensemble at zero pressure for FCC aluminum and its liquid phase, respectively. The corresponding settings are: \( T_0 = 245 \) K, \( \lambda(0) = 1 \) and \( \lambda(t) = 0.204167 \) (i.e. \( T(t) = 1200 \) K) for the solid phase, and \( T_0 = 1400 \) K, \( \lambda(0) = 1 \) and \( \lambda(t) = 1.55556 \) (that is \( T(t) = 900 \) K) for the liquid phase. Setting the switch time to 40 ps would meet the requirements of the RS technique in this work. As shown in figure 8, \( W(t) \) per atom are calculated by the AS approach for the solid and liquid phases of aluminum, respectively.

The potential energy of an Einstein solid is known to be

\[
U = \frac{1}{2} m \omega_0^2 \sum_i (\mathbf{r}_i - \mathbf{r}_0)^2. \tag{51}
\]
Then the free energy is

\[ f_N = kT \ln \frac{T}{T_0} - B_0 E \lambda \]

where Einstein temperature \( T_E \) is

\[ T_E = \frac{1}{\omega_E} \]

Our simulation box consists of \( 10 \times 10 \times 10 \) primitive cells of FCC aluminum, totaling 4000 atoms. MD simulations, where \( \lambda \) ranges from 1–0 with an interval of 0.1, are run at 245 K for 40 ps at isobaric–isothermal conditions with zero extra pressure. Einstein frequency \( \omega_E \) is taken to be the value which makes the average root-mean-squared displacement equal to that of the original system, that is

\[ m \omega_E^2 = 3.219 \text{ eV \ Å}^{-2} \] (\( m = 26.9815386 \text{ a.u.} \)). Then the free energy of the Einstein solid is

\[ f(\lambda = 0) = 3.555 \times 10^{-3} \text{ eV} \]

Our simulation box consists of \( 10 \times 10 \times 10 \) primitive cells of FCC aluminum, totaling 4000 atoms. MD simulations, where \( \lambda \) ranges from 1–0 with an interval of 0.1, are run at 245 K for 40 ps at isobaric–isothermal conditions with zero extra pressure. Einstein frequency \( \omega_E \) is taken to be the value which makes the average root-mean-squared displacement equal to that of the original system, that is

\[ m \omega_E^2 = 3.219 \text{ eV \ Å}^{-2} \] (\( m = 26.9815386 \text{ a.u.} \)). Then the free energy of the Einstein solid is

\[ f(\lambda = 0) = 3.555 \times 10^{-3} \text{ eV} \]

Thus the free energy of FCC aluminum at 245 K is

\[ f(T(0)) = f(\lambda = 0) + \Delta f = -3.347105 \text{ eV} \]
\[ U_l = 4\varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right], \quad (r < r_c) \] (54)

where \( \varepsilon = 0.01 \text{eV} \), \( \sigma = 2.474873734 \text{Å} \), \( r_c = \sqrt{2}\sigma = 3.5 \text{Å} \). According to the AS approach, the difference between these two systems is

\[ \Delta f_i = \frac{1}{N} \int_0^{\lambda_i} (U - U_l) d\lambda. \] (55)

In the second step, the LJ liquid is expanded isothermally to the ideal gas limit. During this process, the change of the free energy is

\[ \Delta f_2 = \frac{1}{N} \int_{V_0}^{\infty} (P - P_i) dV, \] (56)

where \( P_i \) is the ideal gas pressure, \( \langle U - U_l \rangle_\lambda \) as a function of \( \lambda \) and \( P - P_i \) as a function of \( V \) have been shown in figure 10. As shown in figure 10(b), \( P - P_i \) quickly approaches to zero by increasing \( V \). That is to say, the integration in the right hand side of equation (56) could be well evaluated by choosing a large final volume. In this work, we uniformly expand the volume of the LJ liquid to 3.375 times its initial value (\( V_0 \)) within 15 ps. According to equations (55) and (56), the free energy of the liquid phase at \( T_0 \) could be calculated by

\[ f_i = \Delta f_1 + \Delta f_2 + f_{id}(T_0, V_0). \] (57)

where \( f_{id} \) is the free energy of ideal gas. The values of each term in the above equation have been listed in table 3. Finally, the free energy of FCC aluminum and its liquid phase as a function of temperature at zero extra pressure are obtained, as shown in figure 11. This approach predicts a bulk melting point of 982 K, comparable to the experimental result of 933 K [56]. The good consistency in the bulk melting point between our result and the experimental data may result from the correction database of EAM-II from 0.5 to 1.1 eV and reconstruct the energies database of EAM-II

3.3. Sensitivity of extrapolated results of potentials to the reference data

According to our construction procedures, the qualities of the constructed potentials are mainly influenced by the accuracies of the reference database. In this work, we could construct a transferable potential of aluminum partly because it has a basic reference database with small uncertainties. Among the basic reference database, the uncertainty of single vacancy formation energy is the largest, which can be as large as 10.96% [26]. Thus, it is necessary to discuss the sensitivity of the extrapolated qualities of constructed potentials to the uncertainties of single vacancy formation energy. Here, we change the value of the single vacancy formation energy in the reference database of EAM-II from 0.5 to 1.1 eV and reconstruct the potential EAM-II. Figure 12 has shown the influence of the single vacancy formation energy on the predicted EOS at compressed states, where we find that the predicted EOS would achieve a good match with experimental data when the value of single vacancy formation energy is within the range of (0.67, 0.80) eV. The value of the single vacancy formation energy by density functional theory is 0.72 eV, which is well within this range. Moreover, the range of surface energies at (001), (110) and (111) with respect to the uncertainties of single vacancy formation energy are predicted to be (0.76, 0.87), (0.98, 1.12) and (0.68, 0.78) J m\(^{-2}\), respectively (see figure 13). Values of the three surface energies calculated by density functional theory [48, 63] are 0.84, 0.91 and 0.75 J m\(^{-2}\), respectively, while the experimental value is 0.98 J m\(^{-2}\) averaged over different surfaces [64]. This indicates that our predicted ranges of the surface energies agree well with the results of density functional theory and also experimental values. However, the cohesive energy of the HCP structure, as well as the corresponding lattice parameter, does not change with the increase of the single vacancy formation energy, while the cohesive energy and lattice parameter of the BCC structure changes irregularly around −3.29 eV and 3.18 Å, respectively. This is due to the large differences between the surroundings of atoms in the BCC and FCC structures so that the pairwise interactions at equilibrium separations of the BCC structure cannot be evaluated with sufficient precision through values at the equilibrium separations of the FCC structure, which results in the uncertainty of the predicted cohesive energy of the BCC structure. This could be improved by constraining the lattice parameter and cohesive energy of the BCC structure. Similarly, due to the equilibrium atomic separations of the HCP structure being close to that of the FCC structure, the pairwise interactions could be correctly evaluated at its equilibrium states and thus, we could obtain a correct cohesive energy of the HCP structure. From the discussion above, we find that quantities of high precision could be used to evaluate quantities of low precision by utilizing the sensitivities of extrapolated results to the uncertainties of the SRD. The sensitivities also provide an approach to match quantities of interest with reference data rather than adding additional FPs, which will eventually improve the precision of the potential. It should be pointed out that the correct extrapolations greatly rely on the reliabilities of the potential model,

![Figure 13. Surface energy as a function of single vacancy formation energy (E\(_v\)).](image-url)
which, in turn, proves the accuracies of our EAM model for describing properties of bulk aluminum.

4. Summary and conclusions

In conclusion, we have discussed the methods of reducing the FP number of EAM potentials from two aspects. Firstly, the FP number is controlled from the EAM model without affecting its flexibility and scalability. To do this, a new EAM framework is established, which is a generalization of the results of Finnis and Sinclair to the $p$th moment approximations of tight binding theory. Under the present EAM framework, a pairwise interaction potential is employed to compensate the discrepancy of energy, as well as other physical quantities, predicted by the $p$th moment approximations, which could be thereby evaluated through an analytic–numerical scheme. The analytic–numerical scheme, designed in this work, enables us to construct a potential without the need to know the functional forms of the pairwise interactions in advance, and it could utilize several physical quantities (lattice parameter, cohesive energy, single vacancy formation energy, elastic constants, phonon dispersion frequencies and EOS) at equilibrium states and stacking fault energy, as well as the energy difference between the stacking fault and unstacked stacking fault, to achieve a correct extrapolation to the compressed segments of pairwise interactions. Our connection function at the compressed segments adopts the Morse function. Other commonly used two-body functions, such as the LJ function and Rose-style function, are also tested in this work. Different connection functions could generate a similar EOS up to 100 GPa without affecting the physical quantities of elements at equilibrium states. The detailed numerical scheme for parameterizations of potentials of aluminum is a linear approximation of the second order derivatives of pairwise interactions, which results in a cubic spline function of the pairwise interactions. Due to the simple approximation, a few additional nodes are inserted between equilibrium neighbor separations to improve the precision of the pairwise interactions at equilibrium neighbor separations, which is realized by the cooperation between the analytic scheme and the MOO procedure. Other numerical schemes of high precisions for calculating the pairwise interactions could also be implemented within the present framework. Validations of the potential model are demonstrated by the construction and testing of three aluminum potentials. Secondly, the fewest additional FPs (or additional nodes for cubic spline) is used by utilizing the conception of SRD. Firstly, the smallest FP number of the potential is selected to reproduce the SRD. Then the precisions of the potential are guaranteed by using the sensitivities of the extrapolated results to the uncertainties of quantities in SRD. That is to say, the extrapolated results could be matched with the reference data by adjusting the values of quantities in SRD within the ranges of their uncertainties, but the effectiveness of this method is dependent on the reliabilities of the potential models adopted.

Besides, our results indicate that the new manybody term shows similar behaviors with a commonly used embedding function at the vicinity of equilibrium states, and the effective order ($p$) of moments of the local density of states in our model relates to the empirical parameter $n$ in the latter one by $p = 1/n^2$. According to the derivations of the new manybody terms, we find that the new model could well reproduce bulk properties of simple metals if $p$ is not much larger than two. This condition may also be applied for EAM models using the latter embedding function.

Acknowledgments

The present work is supported by the National Natural Science Foundation of China (NSFC-NSAF U1530151 and NSFC 11102194, 11402243), National Key Laboratory Project of Shock Wave and Detonation Physics (No. 077120), the Science and Technology Foundation of National Key Laboratory of Shock Wave and Detonation Physics (Nos. 9140C670201110C6704 and 9140C6702011103) and Chinese National Fusion Project for ITER with Grant No. 2013GB114001.

References

[1] Sankaranarayanan S K R S, Bhethanabotla V R and Joseph B 2005 Phys. Rev. B 71 195145
[2] Wertabuzynski J and McCammon J A 2012 Q. Rev. Biophys. 45 1–25
[3] Belonoshko A B, Skorodumova N V, Rosengren A and Johansson B 2008 Science 319 797–800
[4] Vo N Q, Averback R S, Bellon P, Odunuga S and Caro A 2008 Phys. Rev. B 77 154108
[5] Trautt Z T and Mishin Y 2012 Acta Mater. 60 2407–24
[6] Schäfer J and Albe K 2012 Acta Mater. 60 6076–85
[7] Shao J-L, Wang P, He A-M, Duan S-Q and Qin C-S 2013 J. Appl. Phys. 113 163507
[8] Liao Y, Xiang M, Zeng X and Chen J 2015 Mech. Mater. 84 12–27
[9] Ma W, Zhu W J and Hou Y 2013 J. Appl. Phys. 114 163504
[10] Zimmerman J A, Winey J M and Gupta Y M 2011 Phys. Rev. B 83 184113
[11] Ma W, Zhu W and Jing F 2010 Appl. Phys. Lett. 97 121903
[12] Wang K, Xiao S, Deng H, Zhu W and Hu W 2014 Int. J. Plast. 59 180–98
[13] Kadau K, Germann T C, Lomdahl P S and Holian B L 2002 Science 296 1681–4
[14] Daw M S and Baskes M I 1984 Phys. Rev. B 29 6443
[15] Daw M S and Baskes M I 1983 Phys. Rev. Lett. 50 1285
[16] Finnis M and Sinclair J 1984 Phil. Mag. A 45 55–55
[17] Kim S-G, Horstemeyer M, Baskes M, Rais-Rohani M, Kim S, Jelinek B, Houze J, Moitra A and Liyanage L 2009 J. Eng. Mater. Technol. 131 041210
[18] Daw M S, Foiles S M and Baskes M I 1993 Mater. Sci. Rep. 9 251–310
[19] Ercole F and Adams J B 1994 Europhys. Lett. 26 583
[20] Ackland G J, Mendelev M I, Srolovitz D J, Han S and Barashev A V 2004 J. Phys.: Condens. Matter 16 52629–42
[21] Mendelev M I, Han S, Srolovitz D J, Ackland G J, Sun D Y and Asta M 2003 Phil. Mag. 83 3977–94
[22] Mishin Y, Parkas D, Miel M J and Papakonstantopoulos D A 1999 Phys. Rev. B 59 3393–407
[23] Mishin Y and Lozovoi A Y 2006 Acta Mater. 54 5013–26
[24] Mendelev M I and Ackland G J 2007 Phil. Mag. Lett. 87 349–59
[25] Wu Z, Francis M and Curtin W 2015 *Modelling Simul. Mater. Sci. Eng.* 23 015004

[26] Hughes J, Horstemeyer M, Carino R, Sukhija N, Lawrimore W II, Kim S and Baskes M 2015 *JOM* 67 148–53

[27] Horstemeyer M, Hughes J, Sukhija N, Lawrimore W II, Kim S, Carino R and Baskes M 2015 *JOM* 67 143–7

[28] Wadley H N G, Zhou X, Johnson R A and Neurock M 2001 *Prog. Mater. Sci.* 46 329–77

[29] Johnson R A 1989 *Phys. Rev.* B 39 12554–9

[30] Zhou X et al 2001 *Acta Mater.* 49 4005–15

[31] Ravelo R, Germann T C, Guerrero O, An Q and Holian B L 2013 *Phys. Rev.* B 88 134101–17

[32] Mishin Y, Mehl M J, Papaconstantopoulos D A, Voter A F and Kress J D 2001 *Phys. Rev.* B 63 224106

[33] Rose J H, Smith J R, Guinea F and Ferrante J 1984 *Phys. Rev.* B 29 2963–9

[34] Puska M J, Nieminen R M and Manninen M 1981 *Phys. Rev.* B 24 3037–47

[35] Stott M and Zaremba E 1982 *Can. J. Phys.* 60 1145–51

[36] Banerjea A and Smith J R 1988 *Phys. Rev.* B 37 6632–45

[37] Wadley H N G, Zhou X, Johnson R A and Neurock M 2001 *Prog. Mater. Sci.* 46 555

[38] Wass T and Konings R 2012 *Comprehensive Nuclear Materials* (Oxford: Elsevier) pp 465–80

[39] Masuda K and Sato A 1981 *Phil. Mag. A* 44 799–814

[40] Masuda K, Kobayashi K, Sato A and Mori T 1981 *Phil. Mag. B* 43 19–28

[41] Sutton A P, Finnis M W, Pettifor D G and Ohta Y 1988 *J. Phys. C: Solid State Phys.* 21 35

[42] Wenhua L, Wangyu H, Shifang X, Huqiu D and Fei G 2010 *Int. J. Mater. Res.* 101 1361–8

[43] Avinash M D, Bruce L, Douglas L I, Arunachalam M R, Mohammed A Z and Donald W B 2012 *Modelling Simul. Mater. Sci. Eng.* 20 035007

[44] Dongare A M, Neurock M and Zhigilei L V 2009 *Phys. Rev.* B 80 184106

[45] Nan-xian C, Xi-jin G, Wen-qing Z and Feng-wu Z 1998 *Phys. Rev.* B 57 14203–8

[46] Nan-xian C, Zhao-dou C and Yu-chuan W 1997 *Phys. Rev.* E 55 85–8

[47] Xiao-Jian Y, Nan-Xian C, Jiang S and Wangyu H 2010 *J. Phys.: Condens. Matter* 22 375503

[48] Choudhary K, Liang T, Chernatynskiy A, Lu Z, Goyal A, Phillipot S R and Sinnott S B 2015 *J. Phys.: Condens. Matter* 27 015003

[49] Jelinek B, Groh S, Horstemeyer M, Houze J, Kim S, Wagner G, Moitra A and Baskes M 2012 *Phys. Rev.* B 85 245102

[50] Lukyanov A A and Segletes S B 2012 *Appl. Mech. Rev.* 64 040802

[51] Lukyanov A A 2008 *Int. J. Plast.* 24 140–67

[52] Dewaele A, Loubye P and Mezouar M 2004 *Phys. Rev.* B 70 094112

[53] Nellis W J, Moriarty J A, Mitchell A C, Ross M, Dandrea R G, Ashcroft N W, Holmes N C and Gathers G R 1988 *Phys. Rev. Lett.* 60 1414–7

[54] Steve P 1995 *Comput. Mater. Sci.* 4 361–4

[55] Steinhardt P J, Nelson D R and Ronchetti M 1983 *Phys. Rev.* B 28 784–905

[56] Woan G 2003 *The Cambridge Handbook of Physics Formulas* (Cambridge: Cambridge University Press)

[57] Eike D M, Brennecke J F and Maginn E J 2005 *J. Chem. Phys.* 122 014115

[58] Stukowski A 2012 *Modelling Simul. Mater. Sci. Eng.* 20 045021

[59] de Koning M, Antonelli A and Yip S 1999 *Phys. Rev. Lett.* 83 3973–7

[60] de Koning M and Antonelli A 1996 *Phys. Rev.* E 53 465–74

[61] Mei J and Davenport J W 1992 *Phys. Rev.* B 46 21–5

[62] Frenkel D and Smit B 2001 *Understanding Molecular Simulation: From Algorithms to Applications* (New York: Academic)

[63] Tang F L, Cheng X G, Lu W J and Yu W Y 2010 *Phys. B: Condens. Matter* 405 1248–52

[64] Murr L E 1975 *Interfacial Phenomena in Metals and Alloys* (Reading, MA: Addison-Wesley)

[65] Stedman R and Nilsson G 1966 *Phys. Rev.* 145 492–500

[66] Animalu A, Bonsignori F and Bortolani V 1966 *Il Nuovo Cimento B* 10 159–71

[67] Winey J M, Kubota A and Gupta Y M 2010 *Modelling Simul. Mater. Sci. Eng.* 18 029801

[68] Rautioaho R H 1982 *Phys. Status Solidi b* 112 83

[69] Westmacott K H and Peck R L 1971 *Phil. Mag.* 23 611