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A binomial truncation function proposed for the second-moment approximation of tight-binding potential and application in the ternary Ni–Hf–Ti system

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Abstract

We propose a two-parameter binomial truncation function for the second-moment approximation of the tight-binding (TB-SMA) interatomic potential and illustrate in detail the procedure of constructing the potentials for binary and ternary transition metal systems. For the ternary Ni–Hf–Ti system, the lattice constants, cohesion energies, elastic constants and bulk moduli of six binary compounds, i.e. $L1_2$ Ni₃Hf, NiHf₃, Ni₃Ti, NiTi₃, Hf₃Ti and HfTi₃, are firstly acquired by *ab initio* calculations and then employed to derive the binomial-truncated TB-SMA Ni–Hf–Ti potential. Applying the *ab initio* derived Ni–Hf–Ti potential, the lattice constants, cohesive energy, elastic constants and bulk moduli of another six binary compounds, i.e. $D0_3$ NiHf₃, NiTi₃ HfTi₃, and $B2$ NiHf, NiTi, HfTi, and two ternary compounds, i.e. $C1_b$ NiHfTi, $L2_1$ Ni₂HfTi, are calculated, respectively. It is found that, for the eight binary compounds studied, the calculated lattice constants and cohesion energies are in excellent agreement with those directly acquired from *ab initio* calculations and that the elastic constants and bulk moduli calculated from the potential are also qualitatively consistent with the results from *ab initio* calculations.

1. Introduction

The physical properties of matter can be observed experimentally or determined, and they can also be theoretically calculated or predicted. Without any doubt, theoretical calculations based on quantum mechanics, i.e., first-principles calculations, give the most accurate results compared with other theoretical methods. Nonetheless, first-principles calculations are

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currently limited to studying matter systems consisting of only a few tens of atoms, because such calculations require a great computation effort to solve the Schrödinger equation. In comparison, calculations based on empirical interatomic potentials, which have less accuracy and no sound physical supporting arguments, can handle matter systems involving a great number of atoms and they allow us to study their static and dynamics properties. Great effort has therefore been made to develop relevant empirical potentials and, so far, several models have been proposed for systems of differing characteristics to study various issues [1, 2]. In particular, for metal systems, based on the concept of local electron density, significant progress was made during the 1980s by developing the many-body potential [3–5]. From then on, a number of many-body potentials have been proposed, such as the embedded-atom method (EAM) [3], modified embedded-atom method (MEAM) [6], Finnis–Sinclair (FS) potential [7], the second-moment approximation of tight binding potential (TB-SMA) [8], and so on. In addition to having different physical interpretations, these many-body potentials differ in the way that the functions are determined. In some cases, the researchers derive the functions and parameters by fitting the data to those acquired from *ab initio* calculations, while in many cases the researchers could make a guess of the functions and fit the parameters to available and reliable experiment data. For the details of the interaction potentials, one can refer for instance to the excellent review paper given by Vitek [9].

It is known that, for a currently used many-body potential, it can be divided into a repulsive component, i.e. a pair term, and an attractive component, i.e. a density or many-body term. The repulsive component dominates at short distance and models the repulsion between the atoms when they are brought very close to each other. The attractive component dominates at large distance and gives the cohesion to the system. Both repulsive and attractive components decrease quickly and eventually go nearly to zero. In practical application, a cutoff radius r_C is frequently established, and when the distance is greater than r_C , the interaction between atoms is disregarded, since the values of repulsive and attractive components as well as the potential at the cutoff radius r_C are very small. Such a treatment results in greatly simplifying the programming as well as saving computer resources. Unfortunately, the treatment creates a problem, i.e. whenever an atom pair ‘crosses’ the cutoff radius, the energy makes a little jump. A large number of these events can spoil the energy conservation or lead to non-physical behaviour in the simulations [10]. Accordingly, the truncation-shift method was developed, and in this method, the potential was truncated at the cutoff radius r_C and the whole potential was shifted such a value to let the potential equal zero at the cutoff radius [10]. In this case, there is no discontinuity of the interatomic potential. For the truncation-shift method, the interatomic forces are always finite, whereas the first derivative of the force is still discontinuous at the cutoff radius. In order to remove this discontinuity, a smooth transitional function, i.e. the truncation function, is conceived [11, 12]. By incorporating an appropriate truncation function, the energy, pressure, force and even the first derivatives of force can go continuously to zero at the cutoff radius. For instance, Stoddard and Ford constructed a quite complicated truncation function for the Lennard-Jones potential [11]. Concerning the truncation function of the EAM potential, Guellil and Adams have also proposed a polynomial equation consisting of four parameters [13]. Despite the TB-SMA potential having been used widely in computations and simulations, there is no corresponding applicable truncation function reported in the literature. We therefore attempt, in the present study, to develop a truncation function for the TB-SMA potential.

Furthermore, though there are many yet somewhat untidy reports concerning the method and procedure of the potential fitting, most of them involve pure elements. For example, Baskes has developed the EAM potentials for the fcc metals [14] and Adams has done so for the bcc metals [13]. Igarashi *et al* have parameterized the FS potentials for the hcp metals [15]. Mishin

and Farkas have employed a ‘two-step’ method to construct a reliable interatomic potential for the metals Al and Ni [16]. Youhong *et al* have derived an EAM potential for bcc Ta, by fitting the elastic constants, lattice constants, cohesion energy, unrelaxed vacancy formation energy, etc [17]. Nevertheless, in the present authors’ view, there are many technical details which should be clarified concerning the construction of an interatomic potential for binary or ternary metal systems, capable of describing the interaction between the different types of atom. We therefore intend, in the present study, to illustrate, taking the Ni–Hf–Ti system as a representative one, how to construct an interatomic potential for a ternary metal system.

In addition, since it is a frequently used shape memory alloy system, the structure and formation of the Ti–Hf–Ni alloy have been extensively studied in recent years [18, 19]. For example, by extended x-ray absorption fine structure measurements, Sadoc *et al* have investigated the local structure of the Ni–Hf–Ti amorphous alloys and found a new icosahedral ordering around the nickel atoms [20, 21]. Nevertheless, the detailed structural phase transition and microstructure of the Ni–Hf–Ti alloys are still in need of further studies, especially at an atomic scale. In order to perform an atomistic calculation and simulation, a realistic interatomic potential is required. To develop an interatomic potential of the Ni–Hf–Ti system, based on the TB-SMA scheme, is therefore the major objective of the present study.

2. Binomial-truncated TB-SMA interatomic potential

According to the TB-SMA scheme [8, 22], the energy of the d band is proportional to the square root of the second moment of the density of states. The latter is expressed in terms of a sum of the squares of the hopping/transfer integrals and accordingly the total potential energy of an atom i can be written as

$$E_i = \sum_{j \neq i} \phi(r_{ij}) - \sqrt{\sum_j f^2(r_{ij})} \quad (1)$$

where $\phi(r_{ij})$ is the repulsive interaction, i.e. pair terms, and the $f(r_{ij})$ are the hopping integrals between atoms i and j separated by the distance r_{ij} . In the original TB-SMA scheme proposed by Rosato, Guillope and Legrand, the $\phi(r_{ij})$ and $f(r_{ij})$ are taken to be exponential forms:

$$\begin{aligned} \phi(r_{ij}) &= A \exp\left[-p\left(\frac{r_{ij}}{r_0} - 1\right)\right] \\ f(r_{ij}) &= \xi^2 \exp\left[-2q\left(\frac{r_{ij}}{r_0} - 1\right)\right] \end{aligned} \quad (2)$$

where r_0 is the first-neighbour distance. p, q, A and ξ are four adjustable parameters i.e. potential parameters. From the physical point of view, ξ is an effective hopping integral and q describes the distance dependence of the hopping integral. The summations in equation (1) are restricted to the first neighbours in the study of Rosato [8], while the summations are calculated up to a cutoff radius r_C by Willaime [22]. Clearly, such treatment is too crude and therefore we propose a truncation function for the TB-SMA potential. Furthermore, for the sake of concise expression and convenient application, we also reformulate the SMA potential in an empirical way. The expression of the TB-SMA potential incorporating a truncation function can be written as follows:

$$E_i(x) = \sum_{j \neq i} \phi(r_{ij}x) + F(\rho_i) \quad (3)$$

with

$$F(\rho) = -\sqrt{\rho} \quad (4)$$

$$\rho_i(x) = \sum_j \psi(r_{ij}x) \quad (5)$$

and

$$\phi(r_{ij}x) = \begin{cases} A_1 \exp\left[-p\left(\frac{r_{ij}x}{r_0} - 1\right)\right], & r_{ij}x \leq r_{cm1} \\ A_2\left(\frac{r_{c1}}{r_0} - \frac{r_{ij}x}{r_0}\right)^3\left(1 - s\frac{r_{ij}x}{r_0}\right), & r_{cm1} < r_{ij}x \leq r_{c1} \\ 0, & r_{c1} < r_{ij}x \end{cases} \quad (6)$$

$$\psi(r_{ij}x) = \begin{cases} B_1 \exp\left[-p\left(\frac{r_{ij}x}{r_0} - 1\right)\right], & r_{ij}x \leq r_{cm2} \\ B_2\left(\frac{r_{c2}}{r_0} - \frac{r_{ij}x}{r_0}\right)^5\left(1 - t\frac{r_{ij}x}{r_0}\right), & r_{cm2} < r_{ij}x \leq r_{c2} \\ 0, & r_{c2} < r_{ij}x \end{cases} \quad (7)$$

where x is a scale variable. $x < 1$ and $x > 1$ indicate that the system is isotropically compressed and expanded, respectively, while $x = 1$ indicates that the system is in the equilibrium state. $E(x)$ is the total potential energy and r_{ij} is the distance between atoms i and j of the system at the equilibrium state. In the case of not being far away from the equilibrium state, i.e. no phase transition when the pressure varies, the scale variable x can be given as

$$x = \left(\frac{V}{V_0}\right)^{\frac{1}{3}} = \frac{R}{R_0} = \frac{a}{a_0}. \quad (8)$$

Here V , R and a stand for the system (also atomistic) volume, the nearest-neighbour distance and lattice constant, respectively. The subscripts 0 stand for the corresponding values of the system at equilibrium. For the sake of convenience and without considering the particular physical argument, ϕ and ψ are called here the pair term and density term, respectively. r_{cm1} and r_{cm2} are the knots of the pair and density terms, respectively. Since the pair term (dominating at a short distance) going to zero more quickly and earlier than the density term (dominating at a large distance), two different cutoff radii, i.e. r_{c1} and r_{c2} , are designed for the pair and density terms, respectively, leading to an improvement in the computation efficiency. The cutoff radii and transition points, r_{c1} , r_{cm1} for ϕ and r_{c2} , r_{cm2} for ψ , can be regarded as adjustable parameters in most cases. In contrast to the original TB-SMA, here r_0 is an ordinary potential parameter, often yet not necessarily equating to the nearest-neighbour distance. A_1 , p , A_2 , s and B_1 , q , B_2 , t are another eight potential parameters. The 13 parameters of the proposed potential, i.e. A_1 , p , A_2 , s , r_{cm1} , r_1 , B_1 , q , B_2 , t , r_{cm2} and r_{c2} , can be denoted, in terms of a set, as $\{A_1, \dots\}$. Considering the forms of truncation functions given above, we would like to call the realistic potential expressed by equations (3)–(7) the binomial-truncated TB-SMA interatomic potential.

In the following, we would like to give a detailed discussion of the truncation functions. From the form of the truncation functions expressed in equations (6) and (7), one can clearly see that pair and density terms as well as their high derivatives can continuously and smoothly go to zero at the cutoff radii r_1 and r_2 , respectively, thus removing the ‘jumps’ of total energy, pressure and force when an atom pair ‘crosses’ the cutoff radii. In order to totally avoid the discontinuity of energy, pressure and force in the whole calculated range, ϕ and ψ should be smooth, and their first derivative should be continuous at the transitional points. From these conditions, the parameters A_2 , s and B_2 , t can be determined. Figure 1 shows the curves of ϕ and ψ that are derived from the potential of Ni, which obviously shows that both ϕ and ψ are certainly continuous and smooth in whole calculated range. It should be noted that,

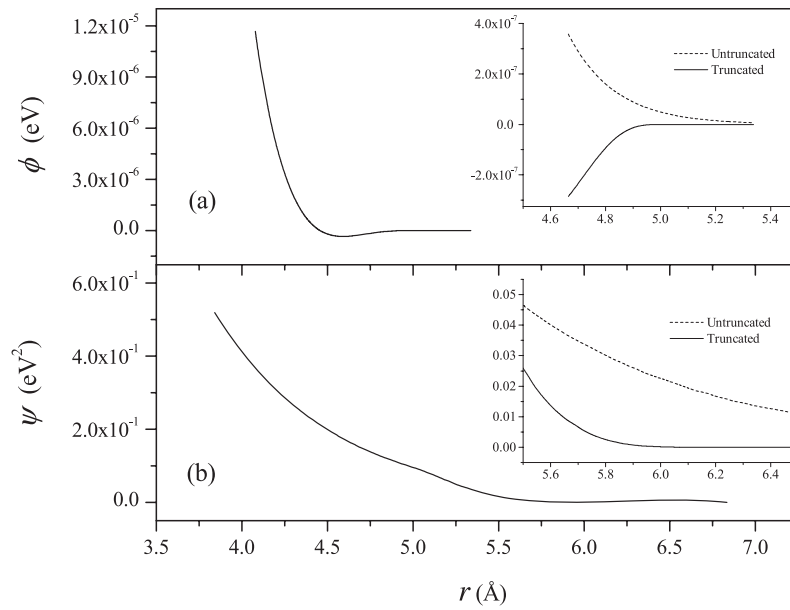


Figure 1. The curves of ϕ (a) and ψ (b) derived for the potential parameters of Ni.

for the proposed potential, ϕ is allowed to be negative in a particular range in some cases, as figure 1 shows, much differing from the original TB-SMA, in which ϕ and ψ are always positive. As a matter of fact, this situation does not cause any serious results in the simulation. Similarly, ψ may also be negative sometimes in a particular range, e.g. when x much larger than 1. This may lead to a catastrophic result in the case when the nearest interatomic distance is much larger than the equilibrium value. Fortunately, such a case can hardly take place in the condensed state, and therefore the binomial-truncated TB-SMA interatomic potential can be safely applied to computations and simulations in materials science as well as condensed matter physics. Of course, one can apply some complexity constraints in the fitting procedure so as to get positive ϕ and ψ in the whole calculated range. Nevertheless those constraints would be of not much significance except for deteriorating the performance of the potential. Besides, compared with other truncation functions, such as $f(x) = Ax^3 + Bx^2 + Cx + D$ proposed by Guellil and Adams for the EAM potential, one can find that there are only two parameters for the binomial truncation function, which can significantly simplify the fitting procedure and computation.

3. Construction the interatomic potential of the Ni–Hf–Ti system

In this section, we demonstrate in detail the method to construct the interatomic potential of the Ni–Hf–Ti system. In contrast to the case of a pure metal, e.g. Ni, in which there is only one set of parameters, i.e. $\{A_1, \dots\}_{\text{Ni}}$, for the binary Ni–Hf system, there are three sets of parameters needed, i.e. $\{A_1, \dots\}_{\text{Ni}}$, $\{A_1, \dots\}_{\text{Hf}}$ and $\{A_1, \dots\}_{\text{Ni–Hf}}$, to respectively describe the interaction between Ni–Ni, Hf–Hf and Ni–Hf atoms. Here $\{A_1, \dots\}_{\text{Ni–Hf}}$ is often called the cross potential, which describes the interaction between atoms of different type. Accordingly, for the ternary Ni–Hf–Ti system, there should be six sets of parameters, and three of them are cross potentials $\{A_1, \dots\}_{\text{Ni–Hf}}$, $\{A_1, \dots\}_{\text{Ni–Ti}}$ and $\{A_1, \dots\}_{\text{Hf–Ti}}$. Generally, when fitting the

cross potential, some properties of compounds such as the cohesion energy, lattice constants, bulk modulus and elastic constants are calculated from the potential, and then compared with the experimental results; thus the proper parameters are determined. In calculating, these properties of a compound can be obtained by averaging the corresponding quantities of all atoms in a unit cell.

First of all, it is necessary to give the formula to calculate the potential energy of a compound. Consider a unit cell consisting of N_{Ni} Ni atoms and N_{Hf} Hf atoms; the total potential energy $E_{\text{cell}}(x)$ can be calculated by

$$E_{\text{cell}}(x) = \sum_i^{N_{\text{Ni}}} E_{\text{Ni},i}(x) + \sum_k^{N_{\text{Hf}}} E_{\text{Hf},k}(x) \quad (9)$$

where $E_{\text{Ni},i}(x)$ and $E_{\text{Hf},k}(x)$ are the potential energy of a Ni atom and a Hf atom, respectively. x is the scale variable, which can be written as

$$x = \frac{R_{\text{Ni-Hf}}}{R_{\text{Ni-Hf},0}} = \frac{R_{\text{Ni}}}{R_{\text{Ni},0}} = \frac{R_{\text{Hf}}}{R_{\text{Hf},0}}. \quad (10)$$

The meanings of those symbols are equivalent to those of equation (8). In the same way, the potential energy of the Ni atom i can be calculated by

$$E_{\text{Ni},i}(x) = \sum_{j \neq i} \phi_{\text{Ni},i}(r_{ij}, x) + F(\rho_{\text{Ni},i}). \quad (11)$$

It is a reasonable approximation that both pair and density terms obey the rule of linear combination. Consequently, for the Ni atom i , the summations of the pair and density terms can be respectively calculated by

$$\sum_{j \neq i} \phi_{\text{Ni},i}(r_{ij}, x) = \sum_{j_1 \neq i} \phi_{\text{Ni-Ni},i}(r_{ij_1}, x) + \sum_{j_2 \neq i} \phi_{\text{Ni-Hf},i}(r_{ij_2}, x) \quad (12)$$

$$\rho_{\text{Ni},i}(x) = \sum_{j \neq i} \psi_{\text{Ni},i}(r_{ij}, x) = \sum_{j_1 \neq i} \psi_{\text{Ni-Ni},i}(r_{ij_1}, x) + \sum_{j_2 \neq i} \psi_{\text{Ni-Hf},i}(r_{ij_2}, x) \quad (13)$$

where $\phi_{\text{Ni-Ni},i}$, $\psi_{\text{Ni-Ni},i}$ denote the contributions from Ni atoms, which are determined by the parameters $\{A_1, \dots\}_{\text{Ni}}$, while $\phi_{\text{Ni-Hf},i}$, $\psi_{\text{Ni-Hf},i}$ denote the contributions from Hf atoms, which are determined by the cross potential $\{A_1, \dots\}_{\text{Ni-Hf}}$. Similarly, the corresponding formulae to calculate the potential energy of a Hf atom can be obtained by substituting the subscript Hf for Ni and Ni for Hf, respectively, in equations (11) and (12).

For a compound, no matter whether it is stable or metastable, when it is in equilibrium, its first derivative of potential energy should equate to zero, i.e.

$$\left. \frac{d}{dx} E_{\text{cell}}(x) \right|_{x=1} = 0. \quad (14)$$

Equation (14) is often called the equilibrium condition; from it the equilibrium point can be determined. Alternatively, the equilibrium point can also be determined from $\left. \frac{d}{dR_{\text{Ni-Hf}}} E_{\text{cell}}(x) \right|_{R_{\text{Ni-Hf}}=R_{\text{Ni-Hf},0}} = 0$, as is often done in the literature. However, considering that some treatments in the literature are vague, equivocal or even incorrect, it is necessary to explicitly point out that the four relations below always hold. One should bear in mind these relations, especially when calculating the derivatives of potential energy with respect to $R_{\text{Ni-Hf}}$ of a compound. As a matter of fact, these relations can be immediately obtained from

equation (10).

$$\begin{aligned}
\frac{d}{dR_{\text{Ni-Hf}}} \phi_{\text{Ni-Ni}}(r_{ij}, x) &= \frac{R_{\text{Ni},0}}{R_{\text{Ni-Hf},0}} \frac{d}{dR_{\text{Ni}}} \phi_{\text{Ni-Ni}}(r_{ij}, x) \\
\frac{d}{dR_{\text{Ni-Hf}}} \psi_{\text{Ni-Ni}}(r_{ij}, x) &= \frac{R_{\text{Ni},0}}{R_{\text{Ni-Hf},0}} \frac{d}{dR_{\text{Ni}}} \psi_{\text{Ni-Ni}}(r_{ij}, x) \\
\frac{d}{dR_{\text{Ni-Hf}}} \phi_{\text{Hf-Hf}}(r_{ij}, x) &= \frac{R_{\text{Hf},0}}{R_{\text{Ni-Hf},0}} \frac{d}{dR_{\text{Hf}}} \phi_{\text{Hf-Hf}}(r_{ij}, x) \\
\frac{d}{dR_{\text{Ni-Hf}}} \psi_{\text{Hf-Hf}}(r_{ij}, x) &= \frac{R_{\text{Hf},0}}{R_{\text{Ni-Hf},0}} \frac{d}{dR_{\text{Hf}}} \psi_{\text{Hf-Hf}}(r_{ij}, x).
\end{aligned} \tag{15}$$

Besides, when a compound is in equilibrium, the stress of each unit cell should equate to zero, i.e.

$$\sigma_{\text{cell},\alpha\beta}(x)|_{x=1} = 0. \tag{16}$$

Similarly, equation (16) is another equilibrium condition. The stress of the unit cell, $\sigma_{\text{cell},\alpha\beta}(x)$, can be calculated by

$$\sigma_{\text{cell},\alpha\beta}(x) = \frac{1}{\Omega(x)} \sum \Omega_i(x) \sigma_{i,\alpha\beta}(x) \tag{17}$$

where $\Omega(x)$ is the volume of the unit cell. $\Omega_i(x)$ and $\sigma_{i,\alpha\beta}(x)$ are the volume and stress of atom i , respectively. The stress of atom i can be calculated by

$$\sigma_{i,\alpha\beta}(x) = \frac{1}{\Omega_i(x)} \frac{\partial E_i(x)}{\partial \varepsilon_{\alpha\beta}} = \frac{1}{\Omega_i(x)} [A_{i,\alpha\beta}(x) + F'(\rho_i) V_{i,\alpha\beta}(x)]. \tag{18}$$

In equation (18), $F'(\rho_i) = \frac{dF(\rho_i)}{d\rho_i}$. $A_{i,\alpha\beta}(x)$ and $V_{i,\alpha\beta}(x)$ are given respectively by

$$\begin{aligned}
A_{i,\alpha\beta}(x) &= \sum \frac{d\phi(r_{ij}, x)}{d(r_{ij}x)} \frac{(r_{ij}^\alpha x)(r_{ij}^\beta x)}{r_{ij}x} \\
V_{i,\alpha\beta}(x) &= \sum \frac{d\psi(r_{ij}, x)}{d(r_{ij}x)} \frac{(r_{ij}^\alpha x)(r_{ij}^\beta x)}{r_{ij}x},
\end{aligned} \tag{19}$$

where r_{ij}^α and r_{ij}^β are Cartesian components of vector r_{ij} . The stress of the cell can thus be calculated from equation (17), once the stress of each atom is obtained from equations (18) and (19). Furthermore, from the equilibrium conditions, i.e. equations (14) and (16), the lattice constants of a compound can be determined.

In addition, the elastic constant plays an important role in fitting potential parameters, because it reflects more characteristics of the interaction than the cohesion energy and lattice constant do. It is necessary to deduct the calculating formulae so as to obtain the elastic constant from interatomic potential. In the same way as computing the stress, the elastic constants of a compound can be obtained by

$$C_{\text{cell},\alpha\beta uv}(x) = \frac{1}{\Omega(x)} \sum \Omega_i(x) C_{i,\alpha\beta uv}(x) \tag{20}$$

where $C_{i,\alpha\beta uv}(x)$ is the elastic constant of atom i , which can be calculated from

$$\begin{aligned}
C_{i,\alpha\beta uv}(x) &= \frac{1}{\Omega_i(x)} [B_{i,\alpha\beta uv}(x) + F'(\rho_i) W_{i,\alpha\beta uv}(x) + F''(\rho_i) V_{i,\alpha\beta}(x) V_{i,uv}(x)] \\
&\quad + \delta_{\alpha v} \sigma_{i,\beta v}(x) + \delta_{\beta v} \sigma_{i,\alpha v}(x).
\end{aligned} \tag{21}$$

Table 1. The parameters of binomial-truncated TB-SMA interatomic potential of the Ni–Hf–Ti ternary system. A_1 and A_2 are expressed in eV, B_1 and B_2 in eV², r_{c1m} , r_{c1} , r_{c2m} , and r_{c2} in Å.

	Ni	Hf	Ti	Ni–Hf	Ni–Ti	Hf–Ti
A_1	0.1095	0.1371	0.1666	0.0437	0.1299	0.2161
p	13.8078	14.7779	11.6459	14.3745	10.8702	14.0212
A_2	0.0110	0.0028	0.0234	0.0036	0.5086	0.0203
s	0.6145	0.5596	0.6070	0.6175	0.7781	0.6155
r_{c1m}	3.7412	5.2677	4.4861	4.2049	3.0550	4.6608
r_{c1}	4.9963	6.4453	6.3324	5.6065	5.1564	6.2144
B_1	1.3137	2.0818	1.9355	1.9812	2.3395	2.7308
q	2.3764	1.5169	3.1195	2.7735	3.8971	6.4792
B_2	2.0521	3.3629	0.4869	92.2265	38.9756	−0.1838
t	0.5783	0.6848	0.4540	0.6205	0.6305	0.5087
r_{c2m}	4.9883	5.6335	7.4768	4.9057	4.6751	6.9912
r_{c2}	7.0432	8.8622	9.7841	6.3074	6.0109	8.5448
r_0	2.4941	3.2226	2.9907	2.8033	2.6715	3.1072

In equation (21), $F''(\rho_i) = \frac{d^2 F(\rho_i)}{d\rho_i^2}$. $B_{i,\alpha\beta uv}(x)$ and $W_{i,\alpha\beta uv}(x)$ respectively stand for

$$B_{i,\alpha\beta uv}(x) = \sum \left[\frac{d^2 \phi(r_{ij}, x)}{d(r_{ij}x)^2} - \frac{1}{r_{ij}x} \frac{d\phi(r_{ij}, x)}{d(r_{ij}x)} \right] \frac{(r_{ij}^\alpha x)(r_{ij}^\beta x)(r_{ij}^u x)(r_{ij}^v x)}{(r_{ij}x)^2} \quad (22)$$

$$W_{i,\alpha\beta uv}(x) = \sum \left[\frac{d^2 \psi(r_{ij}, x)}{d(r_{ij}x)^2} - \frac{1}{r_{ij}x} \frac{d\psi(r_{ij}, x)}{d(r_{ij}x)} \right] \frac{(r_{ij}^\alpha x)(r_{ij}^\beta x)(r_{ij}^u x)(r_{ij}^v x)}{(r_{ij}x)^2}.$$

$V_{i,\alpha\beta}(x)$, $V_{i,uv}(x)$, $A_{i,\beta v}(x)$ and $A_{i,\alpha v}(x)$ can be computed by equation (19). The elastic constants of a compound can thus be calculated from equation (20), once the elastic constants of each atom are obtained from equations (21) and (22). One should note that the formulae deduced above can also be applied to a pure metal system. In contrast to the case of the cross potential, however, the formation energy of a vacancy is frequently considered in deriving the potential for pure metals. In addition, in order to evaluate the relevance of interatomic potentials, thermodynamic properties such as the melting point and phonon spectrum are frequently calculated from the derived potential and then compared with the experiments.

It should be pointed out that the scale variable x is incorporated into the potential equations (3)–(7) as well as the formulae deduced above, thus not only making it straightforward to compute the potential energy derivative, especially of a compound, but also giving an immediate way to calculate the properties of system at a non-equilibrium state. Moreover, the correlation between properties of a compound and volume (also pressure) can be obtained easily from these formulae. Since the physical properties used in fitting the potential parameters are the values of a system at the equilibrium state, one can set the scale variable x to be 1 in fitting process. In fact, once the potential parameters are figured out, one can also let the scale variable x always be 1 without regard to the actual value of V . The main reason for incorporating the scale variable x shown above is to simplify the deduction process.

4. Results and discussion

4.1. The binomial-truncated TB-SMA interatomic potential of pure Ni, Hf and Ti

Now we present the fitting result of the binomial-truncated TB-SMA interatomic potential of Ni–Hf–Ti system. For the sake of conciseness, table 1 displays the all parameters of the

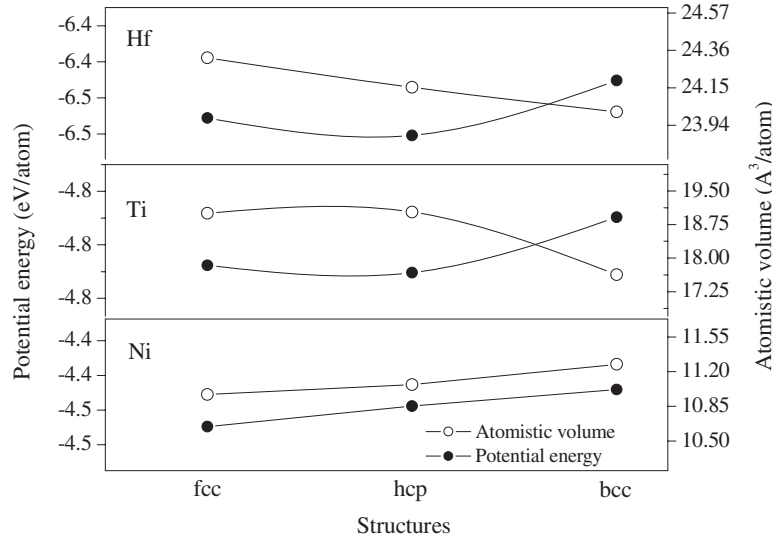


Figure 2. Potential energy and atomistic volume sequence of stable and metastable structures of Ni, Hf and Ti identified from the constructed potentials.

Table 2. The fitted and experimental properties [23, 24] of Ni, Hf and Ti. Lattice constants a and c are expressed in Å, the cohesion energies E_c in eV, and elastic constants C_{ij} in Mbar.

	fcc-Ni		hcp-Hf		hcp-Ti	
	Fitted	Exp.	Fitted	Exp.	Fitted	Exp.
a	3.527	3.523	3.267	3.190	3.003	2.950
c			5.226	5.050	4.874	4.680
E_c	4.5176	4.4564	6.4924	6.4400	4.8128	4.8496
C_{11}	2.296	2.480	1.903	1.881	1.689	1.624
C_{12}	1.550	1.550	0.712	0.772	0.703	0.920
C_{13}			0.602	0.660	0.585	0.690
C_{33}			2.264	1.969	1.942	1.807
C_{44}	1.291	1.240	0.475	0.557	0.375	0.467

ternary system that are fitted using the method described in section 4. Table 2 gives the fitted and experimental lattice constants, cohesion energies, elastic constants of fcc Ni, hcp Hf and Ti, from which one can clear see that the fitted properties match well with the experimental properties [23, 24]. It should be noted that the first derivative of energy and the remnant stress are all very small, less than 10^{-10} Mbar, indicating that the fitted structures of these metals are very close to the equilibrium points. One important approach to evaluate the relevance of interaction potential is to calculate the energies of metastable structures from the potential and then to check the energy sequence of stable and metastable structures. In contrast to the previous works, in which a constant-volume assumption is often employed, i.e. assuming the atomic volumes of hcp, fcc and bcc structures at equilibrium state equate to each other [25, 26], the hcp and bcc structures are first optimized using the constructed potential in the present study and then the potential energies and lattice constants of the metastable structures at equilibrium are calculated. Figure 2 shows the potential energy and atomistic volume sequence of stable and metastable structures of Ni, Hf and Ti identified from the constructed potentials (see

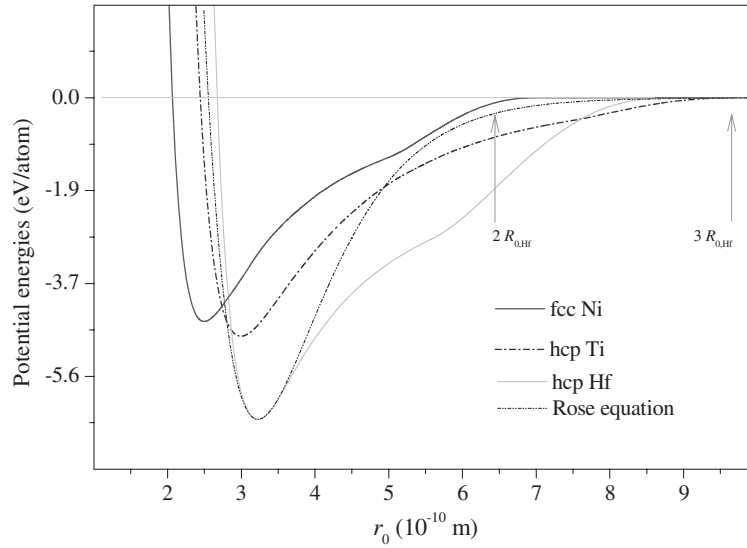


Figure 3. The EOSs of fcc-Ni, hcp-Hf and Ti derived from the binomial-truncated TB-SMA interatomic potential.

table 3). First, one can see from figure 2 that the stable order of stability and metastable structures identified by potential is consistent with the experimental observation. For instance, the potential energy of fcc Ni is -4.518 eV/atom, lower than -4.488 and -4.465 eV/atom, the potential energy of hcp and bcc Ni, indicating that fcc Ni is most stable among the three structures. Similarly, it can be seen that the hcp Hf and hcp Ti are most stable among the hcp, fcc and bcc structures. Table 2 shows the lattice constants and formation energies of Ni, Hf and Ti metastable structures that are determined by the interatomic potential and by *ab initio* calculations [27]. Clearly, the results obtained from the binomial-truncated TB-SMA interatomic potential qualitatively match with the *ab initio* calculations. Second, both the potential and *ab initio* calculations indicate that the atomistic volume may vary slightly from structure to structure. For example, the volumes of hcp, fcc and bcc Hf at equilibrium are determined by potential to be 24.153 , 24.318 and 24.015 \AA^3 /atom respectively. Clearly, the presumption that the atomistic volumes are constant in different structures is incorrect, since it brings some errors in determining the energy sequence of stable and metastable structures. This is why the lattice constants are allowed to vary in optimizing the metastable structures in present study.

Another approach to evaluate the relevance of the constructed potential is to check whether the potentials can describe the interatomic interaction of a system at non-equilibrium, i.e. to derive the equation of state (EOS) from the potential and then compare it with other EOSs that are obtained from theory or from experiment. The frequently used EOS in this field is the Rose equation [28] and its variant [29], which has been considered to be universal for all categories of solids. The EOSs, i.e. the potential energies as functions of the nearest-neighbour distance of fcc Ni, Hcp Hf and Ti, are therefore derived from the binomial-truncated TB-SMA interatomic potential and shown in figure 3 together with the Rose equation of hcp Hf. From figure 3, one sees that, for the potential energy, there is not any discontinuity in whole calculated range. In particular, at the cutoff radius, the potential energy and derivatives continuously go to zero as expected. Furthermore, one can find from figure 3 that, in the vicinity of the equilibrium point,

Table 3. The lattice constants and formation energies of Ni, Hf and Ti metastable structures that are determined by the interatomic potential (first line) and by *ab initio* calculations (second line) [27]. The lattice constants and formation energies are expressed in Å and Mbar, respectively.

	hcp-Ni	bcc-Ni	fcc-Hf	bcc-Hf	fcc-Ti	bcc-Ti
a	2.553	2.825	4.599	3.635	4.236	3.279
	2.483	2.799	4.471	3.538	4.099	3.241
c/a	1.536					
	1.647					
E_f	0.029	0.053	0.015	0.048	0.002	0.039
	0.022	0.094	0.071	0.176	0.057	0.107

Table 4. The properties of $L1_2$ Ni–Hf, Ni–Ti and Hf–Ti compounds that are fitted and those that are acquired from *ab initio* calculation. Lattice constants a are expressed in Å, the cohesion energies E_c in eV, and the elastic constants C_{ij} and bulk modulus B_0 in Mbar.

	a	E_c	C_{11}	C_{12}	C_{44}	B_0
$L1_2$ Ni ₃ Hf	3.788	5.473	2.637	1.406	0.953	1.320
	3.588	5.473	2.156	1.514	1.237	1.728
$L1_2$ NiHf ₃	4.274	5.933	1.310	0.996	0	1.101
	4.340	5.730	1.483	0.989	0.787	1.154
$L1_2$ Ni ₃ Ti	3.625	5.005	2.571	1.501	1.107	1.858
	3.553	5.004	2.340	1.513	1.155	1.788
$L1_2$ NiTi ₃	3.937	4.842	1.373	1.237	0	1.282
	4.003	4.757	1.646	1.097	0.791	1.280
$L1_2$ Hf ₃ Ti	4.410	5.965	0.873	1.322	0.722	1.173
	4.472	5.755	1.696	1.130	0.849	1.318
$L1_2$ HfTi ₃	4.216	5.172	0.801	1.210	0.574	1.074
	4.317	4.964	1.953	1.227	0.858	1.469

the EOS derived from the proposed potential is very close to the Rose equation, indicating that the interatomic potential constructed in the present study can be applied to describe the interatomic interaction of a system not very far away from the equilibrium state. Nevertheless, from the comparison between the derived EOS and the Rose equation, one can find that the cutoff distance is somewhat overlong. Figure 3 implies that the appropriate cutoff radii should be about $2R_0$, i.e. two times of distance of the nearest neighbour, instead of $3R_0$ in present study.

4.2. The cross potential of Ni–Hf, Ni–Ti and Hf–Ti

The lattice constants, cohesion energies, elastic constants and bulk moduli of $L1_2$ Ni₃Hf and NiHf₃ are used in fitting the cross potential of Ni–Hf. The properties of the two compounds are acquired by *ab initio* calculation using CASTEP [30]. In the *ab initio* calculation, the norm-conserving, non-local ultra-soft pseudo-potentials for Ni and Hf have been used, together with a kinetic energy cutoff of 350 eV on an $11 \times 11 \times 11$ k -point mesh in the first Brillouin zone and the PW91 GGA exchange–correlation functional [31]. Geometry optimizing is first performed to determine the lattice constants and total energies of the compounds at equilibrium, and then the elastic constants are calculated; meanwhile, the bulk moduli are obtained. The cohesion energies of compounds can be easily derived from the total energies obtained by the *ab initio* calculation. Similarly, the properties of $L1_2$ Ni₃Ti, NiTi₃ and $L1_2$ Hf₃Ti HfTi₃ are acquired and used in fitting the cross potential of Ni–Ti and Hf–Ti, respectively. Using the properties and the scheme described in section 4, the cross potential parameters of Ni–Hf, Ni–Ti and Hf–Ti can

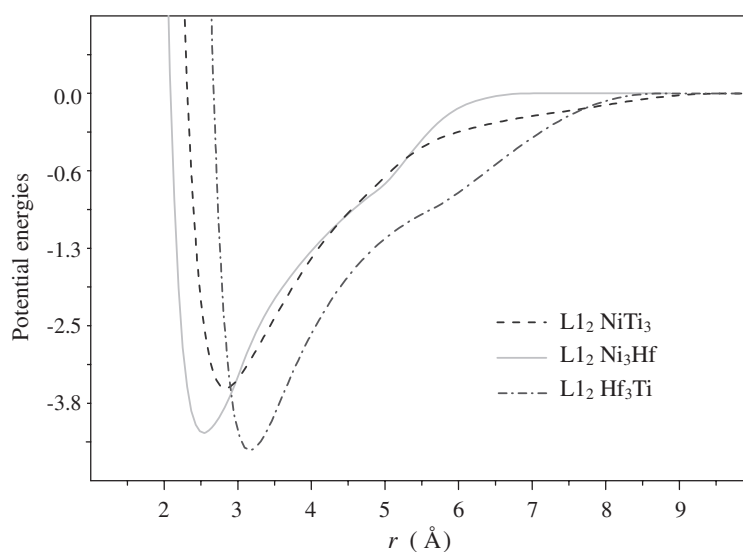


Figure 4. The EOSs of $L1_2$ Ni_3Hf , Ni_3Ti and Hf_3Ti compounds that are derived from the binomial-truncated TB-SMA interatomic potential. The potential energies are expressed by eV/atom.

be determined by fitting; these have been given in table 1. Table 4 lists the comparisons of the properties of $L1_2$ Ni–Hf, Ni–Ti and Hf–Ti compounds [32] that are fitted and acquired from *ab initio* calculation. It should be noted that the first derivative of energy and the remnant stress are all very small, less than 10^{-10} Mbar, indicating that the fitted structures of these metals are very close to the equilibrium points. One can see from table 4 that, except for the C_{11} of $L1_2$ Hf_3Ti and $HfTi_3$, the properties of the six compounds determined from potentials are fairly consistent with the *ab initio* calculation results. In particular, the lattice constants and cohesion energies obtained by both methods match each other quite well. Figure 4 plots the potential energies as functions of the nearest-neighbour distance; it shows that the potential energies of those compounds are also continuous and smooth in the whole range. Consequentially, for pure metals and their compounds, there are not any ‘jumps’ or discontinuities in energy as well as the pressure and force calculated from the binomial-truncated TB-SMA potential which avoid unphysical behaviour in simulations.

4.3. Properties of binary and ternary compounds calculated from interatomic potentials

It is interesting to derive, from the constructed potential, the properties of other compounds not involved in the fitting procedure, and to compare them with the results of *ab initio* calculations. A total of six binary compounds, i.e. $D0_3$ $NiHf_3$, $NiTi_3$, $HfTi_3$ and $B2$ $NiHf$, $NiTi$, $HfTi$, as well as two ternary compounds, i.e. $C1_b$ $NiHfTi$ and $L2_1$ Ni_2HfTi , are considered in present study. To determine the crystal structures of those compounds at equilibrium, geometry optimizations are conducted for the eight compounds using interatomic potential and *ab initio* calculations, respectively. And then their properties are calculated, also using the potential and *ab initio* calculations. Tables 4 and 5 displays the results of the two calculating methods. For the eight compounds, one can see from table 4 that there are remarkable discrepancies in the elastic constants acquired by the two methods, which may mainly result from three factors. The first one comes from the *ab initio* calculation. Our experiences show that the maximum errors of

Table 5. The properties of Ni–Hf, Ni–Ti and Hf–Ti compounds that are acquired from interatomic potential and *ab-initio* calculations. Lattice constants a are expressed in Å, the cohesion energies E_c in eV, and the elastic constants C_{ij} and bulk modulus B_0 in Mbar.

	a	E_c	C_{11}	C_{12}	C_{44}	B_0
D0 ₃ NiHf ₃	6.739	5.821	1.237	1.225	0.377	1.229
	7.015	5.685	1.030	1.085	0.949	1.067
D0 ₃ NiTi ₃	6.211	4.837	1.477	1.087	0.402	1.217
	6.739	4.358	1.328	1.571	1.125	1.490
D0 ₃ HfTi ₃	6.665	5.108	0.973	0.435	1.125	1.064
	6.970	4.709	1.500	1.790	1.267	1.694
B2 NiHf	3.207	5.841	2.495	1.355	0.523	1.735
	3.023	5.983	5.399	1.216	0.884	2.610
B2 NiTi	3.016	5.059	1.509	1.616	0.439	1.580
	2.976	4.951	3.780	1.137	0.575	2.018
B2 HfTi	3.407	5.515	0.845	1.196	0.430	1.082
	3.505	5.201	1.572	1.595	1.159	1.586
C1 _b NiHfTi	6.089	5.262	1.531	0.947	0.000	1.141
	6.590	4.223	0.642	0.969	0.732	0.860
L2 ₁ Ni ₂ HfTi	6.256	5.442	1.822	1.205	0.501	1.411
	5.973	5.419	4.753	1.414	0.943	2.527

elastic constants determined by *ab initio* calculation may be as large as ten per cent or even thirty per cent in some case. These errors may also bring some uncertainties in the fitting potential. The second one rests with the parameters of potential. If more time and effort are paid to the fitting procedure, the performance of the constructed potential may be improved. The third one is the intrinsic shortcoming of the interatomic potential, since it belongs to an empirical method. Therefore, no matter how we improve the quality of the potential, these discrepancies cannot be reduced to a considerably low level. However, it should be noted that the lattice constants as well as cohesion energies of the eight compounds acquired by interatomic potential are quite consistent with the results of *ab initio* calculations. The average error is less than 5% and maximum error less than 10%, except for the lattice constant of C1_b NiHfTi. It thus can be concluded that the interatomic potential can be reliably applied to issues related to the structure as well as energy, and that there exists considerable error in calculating the properties of compounds with interatomic potentials.

5. Summary

We propose, in this paper, a two-parameter binomial truncation function for the tight-binding interatomic potential and illustrate, in detail, the procedure of construction of the potentials for binary and ternary transition metal systems. For the Ni–Hf–Ti ternary system, the lattice constants, cohesion energies, elastic constants and bulk moduli of six binary compounds, i.e. L1₂Ni₃Hf, NiHf₃, Ni₃Ti, NiTi₃, Hf₃Ti and HfTi₃, are first acquired by *ab initio* calculations and then employed in fitting the binomial-truncated TB-SMA Ni–Hf–Ti potential. Applying the *ab initio* derived Ni–Hf–Ti potential, the lattice constants, cohesive energy, elastic constants and bulk moduli of another six binary compounds, i.e. D0₃ NiHf₃, NiTi₃ HfTi₃, and B₂ NiHf, NiTi, HfTi, and, moreover, two ternary compounds, i.e. C1_b NiHfTi and L2₁ Ni₂HfTi, are calculated, respectively. It is found that for the total of eight studied compounds, the calculated lattice constants and cohesion energies are in excellent agreement, and that the calculated elastic constants and bulk moduli are also qualitatively consistent with the results from *ab initio* calculations.

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