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MODIFIED ANALYTICAL EMBEDDED ATOM METHOD (MAEAM) INTERATOMIC POTENTIALS FOR BODY CENTRED CUBIC (BCC) TRANSITION METALS AND VACANCY MECHANISM

Physics

KEYWORDS: Modified analytical embedded atom method (MAEAM), Finis and Sinclair (FS), negative Cauchy pressure, mono-vacancy formation energy E_{1f}, mono-vacancy migration energy E_{1m} and mono-vacancy activation energy Q_1,.

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ABSTRACT

In this work, modified analytical embedded atom method, MAEAM was extended to the study of interatomic potentials for body centred cubic (bcc) transition metals. In MAEAM, the modification term is a function of parameterization for all bcc transition metals considered in this work. The modified term is developed to model the effect of angular dependence of the electron density, which manifests itself in directional bonding and bond-bending forces in the bcc crystals. The results obtained in this work for mono-vacancy formation, migration and activation energies were in good agreement with the experimental data, this tells us that the modified analytical embedded atom method is useful in the determination of interatomic potentials for body centred cubic transition metals. The mono-vacancy formation energy neither increases nor decreases as the lattice constant increases. The computed value of mono-vacancy migration energy is lower than the result of ab initio calculation. These could be due to the discrepancy in the modification term, fitting parameter and the contribution to the energy from many-body effects in the embedding function. The computed value of mono-vacancy activation energy is lower at most point compare to some other result of ab initio calculation.

1.0 Introduction

A crystal is a solid composed of atoms and other microscopic particles arranged in an orderly repetitive array. Many important properties of materials depend on the structure of crystals and on the electron states within the crystals. Crystals possess different symmetry elements described by symmetry operation which leaves the crystal and its environment invariant during transformation (Pillai, 2010). Vacancy or interstitial in solid produce electrical charge deviations, the electron in a geometrically perfect lattice may themselves moves in such a way as to produce local fluctuations of charge (Kittel, 1976). Atoms of alkali metals are stacked in such a way as to form a body-centred cubic structure. Body-centred cubic (bcc) is a common metallic crystal structure which has a cubic unit cell with atoms located at all eight corners and a single atom at the cube centre (Kachhava, 1992). Molecular dynamics (MD) is a branch of science that models atomic interactions where known physical approximations provide a view of the motion of individual atoms. The large number of molecules which prevents the analytic solution of the system is solved using numerical methods (Plimpton, 1995). With the widespread use of molecular dynamics simulations, multiple types of interatomic potentials have been developed, this include (a) pair-wise potentials for condensed matters of closed-shell atoms (Jones, 1924) and (Morse, 1929), (b) embedded-atom-method (EAM) potentials (Daw and Baskes, 1983) (c) bond order potentials for covalent solids (Tersoff, 1988), and (d) force fields for organic and oxide systems (Mackerell, 2004). For metals and alloys, the EAM potential is probably the most widely used approach in the research literature. EAM potentials have two major advantages, relative to pair potentials, they are: the unphysical constraint on elastic constants and bond saturation at the bonding surface is better represented. At a special symposium of the World Materials Congress, the embedded-atom method (EAM) based on density-functional theory, is applied to the fcc or nearly filled *d*-band transition metals and the result obtained agree perfectly with available experimental values (Daw and Baskes, 1983). Embedded-atom method (EAM) is an approximation describing the energy between two atoms and is a popular method for computing many static and dynamical properties of metallic systems, the conceptual basis of the method rests on the notion that the energetic of an atom placed in the environment of a solid depends on the electron density of the host atoms alone. The success and popularity of EAM are a consequence of its sound theoretical foundation based on the density-functional theory DFT and its simple analytical expression. The embedded atom method measures the potential energy of an atom by summing the atom's embedding energy. The embedding energy is defined as the energy needed to move that particular atom's positive nucleus from infinity into the electron cloud created by all other atoms in the simulation. Consequently, a lot of efforts have been made to study the interatomic properties of different crystal structure and different group of metals based on embedded atom model, Jingzhou and Yongiie (2012) compute the theoretical strength and structural stability of BCC crystals for Fe, V, Nb and Ta under hydrostatic loading using the modified analytical embedded atom method. They obtain the values of the stable regions for lattice stretch, theoretical strength and tensile stresses and found that the calculated maximum tensile stress and the corresponding lattice stretch are consistent well with the results of Ab initio calculation. Matthew-Ojelabi et al (2015) obtained the surface energies of Body-Centre-Cubic Metals by extending the embedding energy function developed to the computation of the surface energies for low index facets of twelve bcc metals in the framework of the embedded atom method (EAM) and generate a consistent database for bcc metallic elements. This is fit to the experimental mono-vacancy formation energy. The calculated surface energy for each metal is reasonably good compared to existing theoretical data with similar background and experiments. Jingzhou and Yongiie (2012) study the static structure, thermodynamic and transport properties of liquid Iron using the modified analytic embedded atom method (MAEAM). And found that the calculated thermodynamic properties such as the internal energy, Helmholtz free energy and entropy are in good agreement with experimental values. The results for the computed self-diffusion coefficients are in reasonable agreement with experimental values and other ab initio calculation. Zhang and Quyang (ZQ) (1999) calculate the thermodynamic properties for binary alloys of bcc transition metals V, Nb, Ta, Mn, W. They proposed a cubic equation for the cut off potential and electron density

functions. The results obtained shows that there is an agreement between the calculations of heat and available experimental values. Baskes et al (1989) calculate the geometry and energetic of a thin metal over-layer on various interfaces substrates using Modified Embedded Atom Method (MEAM) by representing the energy of a given atom as one half the energy in two body bonds with its neighbouring atoms plus the energy to embed the atom in the electron density. The results of the calculated structure and energetic of a number of (111) Al layers on the (001) surface is in agreement with experimental values. Baskes (1991) extend the modified embedded atom method to a variety of cubic materials and impurities and developed basic equations which was applied to 2d elements. The materials modelled include metals, semi conductors, and diatomic gases all of which exhibit different types of bonding. The result obtained is in agreement with experimental value. Daw and Baskes, (1983) develop the embedded atom method based on density functional theory as a new means of calculating ground state properties of realistic metal systems. They also derive expression for the total energy of a metal using the embedding energy from which they obtained several ground state properties, such as the lattice constant, elastic constants, sublimation energy and vacancy formation energy. The result obtained is in agreement with experimental values. In this work, modified analytical embedded atom method (MAEAM) is extended to the study of inter-atomic potentials for body centred cubic (BCC) transition metals. The vacancy mechanism is also studied. The metals used in this study were chosen based on the availability of experimental data, their industrial and technological applications, and availability of some physical constants of metals that is required for computation.

2.0 Theory

The Embedded atom method EAM has been known to be one of the distinguished potentials which gains great success in describing the interaction of particles of metals and alloys. According to the scheme of embedded atom method, the energy of an atom in a system is obtained as

$$E_t = F(\rho_i) + \frac{1}{2}\sum_{i\neq j}\phi(r_{ij}) \quad (1)$$

Where, E_t is the total internal energy of the system, $F(\rho_i)$ is the energy to embed atom i into the background electron density (ρ_i) at site i, (r_{ij}) is the two-body (pair) potential interaction between atom i and atom j whose separation is given by r_{ij}, in equation (1), the negative Cauchy pressure cannot be fitted. This led to the development of new model known as modified analytical embedded atom method MAEAM. Here an analytical modified term M(P_i) is introduced.

In MAEAM, the total energy of a system E_{total} is expressed as

$$E_{(total)} = \sum E_i \quad (2)$$

where

$$E_i = F(\rho_i) + \frac{1}{2}\sum_{i\neq j}\phi(r_{ij}) + M(P_i) \quad (3)$$

therefore

$$E_{total} = \sum_i \left[F(\rho_i) + \frac{1}{2}\sum_{i\neq j}\phi(r_{ij}) + M(P_i)\right] \quad (4)$$

According to Johnson and Oh (1989), the background electron density ρ_i at i due to all other atoms and the non-spherical distribution of electron ρ_i is obtained as

$$\rho_i = \sum_{i\neq j} f(r_{ij}) \quad (5)$$

And

$$P_i = \sum_{i\neq j} f^2(r_{ij}) \quad (6)$$

Where, ρ_i is associated closely with the position of all other atoms around site i and the background electron density ρ_i may be regarded to as linear superposition of the spherical-symmetry contribution to ρ_i from all other atoms around site, i, $f(r_{ij})$ is the atomic electron density distribution function for an atom, r_{ij} is the separation distance between atom i and atom j.

The embedding function F (ρ_i) is obtained as

$$F(\rho_i) = -F_0\left[1 - n\ln\left(\frac{\rho_i}{\rho_e}\right)\right]\left(\frac{\rho_i}{\rho_e}\right)^n \quad (7)$$

where Fo is the value of embedding function at the equilibrium and is given as

$$F_o = E_e - E_{1f} \quad (8)$$

where, ρ_e is the background electron density at equilibrium reference structure, ρ_i is the background electron density at i due to all the other atom and n represents the parametrization, E_c is the cohesive energy and E_{1f} is mono-vacancy formation energy. The pair potential (r_{ij}) is of the form

$$\phi(r_{ij}) = K_0 + K_1\left(\frac{r_{ij}}{r_{1e}}\right)^2 + K_2\left(\frac{r_{ij}}{r_{1e}}\right)^4 + K_3\left(\frac{r_{ij}}{r_{1e}}\right)^{-12} \quad (for\ r_{ij} \le r_{2e}) \quad (9)$$

where, r_{1e} is the first-nearest neighbour distance at equilibrium and r_{2e} is the second-nearest neighbour distance at equilibrium. The modified term M (P_i) is obtained as

$$M(P_i) = \alpha\left(\frac{P_i}{P_e} - 1\right)^2 \ell x \rho_x\left[-\left(\frac{P_i}{P_e} - 1\right)^2\right] \quad (10)$$

The parametrization n in equation (7) is obtained as

$$n = \sqrt{\frac{\Omega(C_{11} + 2C_{12})(C_{11} - C_{12})}{216E_{1f}C_{44}}} \quad (11)$$

The atomic volume in bcc metals Ω is

$$\Omega = \frac{a_0^3}{2} \quad (12)$$

Where oa is the unstressed lattice constant and C_{11}, C_{12}, *and* C_{44} are the elastic constants of the metals considered. The model parameters K_o, K_1, K_2, K_3 and α used in this work is obtained as

$$K_0 = -\left[\frac{E_{1f}}{7} + \frac{\Omega(-57111C_{11} + 57111C_{12} + 51519C_{44})}{471800}\right] \quad (13)$$

$$K_1 = \Omega\left(\frac{-52563C_{11} + 52563C_{12} + 33327C_{44}}{269600}\right) \quad (14)$$

$$K_2 = \Omega\left(\frac{147456C_{11} - 147456C_{12} - 59049C_{44}}{1887200}\right) \quad (15)$$

$$K_3 = 1536\Omega\left(\frac{-C_{11} + C_{12} + 4C_{44}}{412825}\right) \quad (16)$$

$$\alpha = \frac{\Omega(C_{12} - C_{44}) - 4n^2 F_0}{32} \quad (17)$$

The atomic electron density used in this work is obtained as

$$f(r_{ij}) = f_e\left(\frac{r_{1e}}{r_{ij}}\right)^6 \quad (18)$$

where f_e is the atomic electron density at equilibrium and is given by

$$f_e = \left(\frac{E_c - E_{1f}}{\Omega}\right)^{3/5} \quad (19)$$

The separated distance between atoms ranges from r_{2e} to r_c is where, r_c is the cut-off radius and is obtained as

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$$r_c = r_{2e} + 0.75\,(r_{3e} - r_{2e}) \quad (20)$$

r_{2e} is the second neighbour distance at equilibrium, r_{3e} is the third neighbour distance at equilibrium.

The mono-vacancy formation energy is given as

$$E_{1f} = E_{total}(1,\Omega) - \frac{N-1}{N} E_{total}(0,\Omega) \quad (21)$$

$E_{total}(1,\Omega)$ is the cohesive energy with vacancy, $E_{total}(0,\Omega)$ is the total energy and the ratio in front of $E_{total}(0,\Omega)$ accounts for difference in the number of atoms between the initial bulk state and the final state containing a vacancy.

Equation (23) below, is used for the mono-vacancy migration energy.

$$D = D_o \exp\left[\frac{-E_{1m}}{k_B T}\right] \quad (22)$$

D is the diffusion coefficient, D_o is the pre-exponential factor, E_{1m} is the mono-vacancy migration energy, k_B is the Boltzman's constant and T is the temperature.

$$Q_{1v} = E_{1f} + E_{1m} \quad (23)$$

In this work, the mono-vacancy formation energy equation, mono-vacancy migration energy and the mono-vacancy activation energy of BCC transition metals were computed using equation (21), (22) and (23). The embedding energies $F(\rho_i)$ and the pair interactions ϕ *(rij)* are determined by fitting various physical quantities of the system such as cohesive energy E_c, Lattice constant a_0, mono-vacancy formation energy E_{1f} and elastic constants of the bcc transition metals. In MAEAM, a modification term $M(P_i)$ is introduced in the expression of total energy to resolve the negative Cauchy pressure in Johnson's model. The modification energy is a function of argument P, which is represented as the sum of second- order atomic electron density to correct the assumption of the linear superposition of atomic electron density in the original EAM.

FORTRAN programming Force 2.0 compiler was used in this computation to determine the model parameters.

3.0 Result and Discussion

The variation of mono-vacancy formation energy, mono-vacancy migration energy and mono-vacancy activation energy as a function of lattice constant are shown in figure 1- 3. The result obtained in figure 1-3 revealed that there is agreement between the experimental values, embedded atom model, Finis and Sinclair model and calculated value. This seems to suggest that the modified analytical embedded atom method is useful in the determination of inter-atomic potentials for body centred cubic transition metals. The trend exhibited by different elemental metals in figure 1-3 whose mono-vacancy formation energy, mono-vacancy migration energy and mono-vacancy activation energy were computed could be due to bond distance, local coordination and the modification of the fitting parameters that were used in the computation. Because in MAEAM, the modification term is a function of some parameters that the bcc transition metals depend upon. The modification term is positive for Fe, Mo, Nb, Ta, W and V but negative for Cr because Cr has a negative Cauchy pressure which is positive in ductile crystals and negative in brittle crystals.

From figure 1, it can be seen that for bcc crystal, the mono-vacancy formation energy neither increases nor decreases as the lattice constant increases. Such behaviour is due to background electron density which is the electron density at the reference atom due to the host and the symmetric local arrangements of the atoms. The result obtained in figure 1 is similar to that of ab initio calculations.

From figure 2, we can see that the result obtained for mono-vacancy migration energy is higher than the result of the ab initio while at some point, the computed value of mono-vacancy migration energy is lower than the result of ab initio calculation. These could be due to the discrepancy in the modification term, fitting parameter and the contribution to the energy from many-body effects in the embedding function. Also, it could be due to the difference between the energy for saddle point and the equilibrium site. The trend exhibited by metals in figure 2 revealed that there is agreement between the computed value and the result of Ab initio calculation.

From figure 3, we can see that the computed value of mono-vacancy activation energy is lower at most point compare to some other result of ab initio calculation. These could be due to the fact that there are some factors that the ab initio method takes into consideration that is not considered in this work, such as compressive and tensile theoretical strength of bcc crystals, saddle point and potential barrier

4.0 Conclusions

In this research work, a new procedure for building the EAM potential has been developed. A physically reliable universal method for determining the atomic electron density and pair potential functions has been presented; i.e., these can be obtained by MAEAM. This new version of the EAM eliminates all the prior arbiter choices in the determination of atomic electron density and potentials functions. The embedding function is taken as the parameterized universal form deduced by Brandes and Brooks (1992) based on density functional theory calculations

Modified analytical EAM interatomic potentials for seven bcc transition metals have been constructed. Calculations for activation energy of vacancy, migration and formation energies were obtained and compared with experimental data and theoretical work of other authors.

The graphs of monovacancy formation energy against the lattice constant, migration energy against the lattice constant and that of mono vacancy activation energy against the lattice constant are respectively presented in figure 1 -3.

Finally the work was motivated by the desire to understand the observed negative Cauchy pressure in Cr unlike other bcc transition metals. In the further study, the potential of this MAEAM can accurately predict the thermal expansion, phonon dispersion curves, mean-square displacements and surface relaxations of metals.

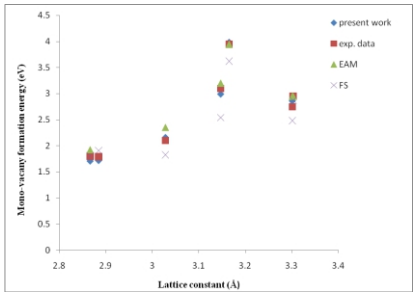

Figure 1: Variation of mono-vacancy formation energy with lattice constant

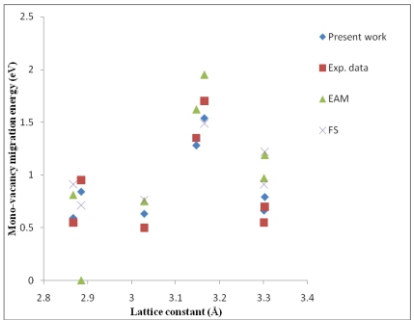

Figure 2: Variation of mono-vacancy migration energy with lattice constant

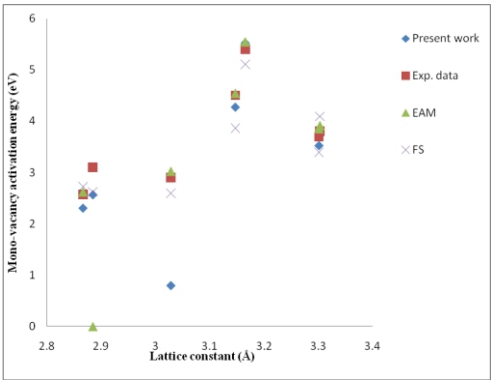

Figure 3: Variation of mono-vacancy activation energy with lattice constant

Table 1: The calculated mono-vacancy formation energy E_{1f} in comparison with the experimental data and other interatomic potentials calculation. Experimental value is obtained from Zhang et al. (1999), EAM value is taken from Guellil and Adams (1992) and FS value is from Harder and Bacon (1986).

Metals	a_0 (A^0)	Present work	Exp. Data	EAM	FS
Fe	2.8664	1.71	1.80	1.92	1.81
Cr	2.8846	1.72	1.79	-	1.91
Mo	3.1468	2.99	3.10	3.20	2.54
Nb	3.3008	2.86	2.75	2.95	2.48
Ta	3.3026	2.93	2.95	2.95	2.87
V	3.0282	2.16	2.10	2.35	1.83
W	3.1650	3.98	3.95	3.95	3.62

Table 2: The calculated mono-vacancy migration energy E_{1m} in comparison with the experimental data and other interatomic potentials calculation. Experimental data is from Shultz and Ullmaier (1991), EAM from Guellil and Adams (1992) and FS from Harder and Bacon (1986)

Metals	a_0 (A^0)	Present work	Exp. Data	EAM	FS
Fe	2.8664	0.59	0.55	0.81	0.91
Cr	2.8846	0.84	0.95	-	0.71
Mo	3.1468	1.28	1.35	1.62	1.32
Nb	3.3008	0.66	0.55	0.97	0.91
Ta	3.3026	0.79	0.70	1.19	1.22
V	3.0282	0.63	0.50	0.75	0.76
W	3.1650	1.54	1.70	1.95	1.49

Table 3: The calculated mono-vacancy activation energy Q_{1v} in comparison with the experimental data and other interatomic potentials calculation. Experimental data is from Askill and Tomlin (1965), Lubbehusen and Mehrer (1990), Marier et al. (1979) and Siegel et al. (1982). EAM is from Guellil and Adams (1992) and FS from Harders and Bacon (1986).

Metals	a_0 (A^0)	Present work	Exp. Data	EAM	FS
Fe	2.8664	2.30	2.57	2.62	2.72
Cr	2.8846	2.56	3.10	-	2.62
Mo	3.1468	4.27	4.50	4.54	3.86
Nb	3.3008	3.52	3.70	3.85	3.39
Ta	3.3026	3.72	3.80	3.91	4.09
V	3.0282	0.79	2.90	3.02	2.59
W	3.1650	5.52	5.40	5.54	5.11

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