Atomistic Simulations Of Ta, Mo & W And Their Binary Alloys Using Embedded Atom Method And Second Moment Approximation Of Tight Binding

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Abstract: One of the key issues limiting the ability for material scientists to design metallic materials from the atom up using atomistic simulation is the lack of interatomic potentials suitable for the desired alloy system. The embedded-atom method (EAM) has been used widely because of its low computational costs and ability to accurately model bulk properties and defects in metals. In this study, the embedded-atom method and the tight binding second moment approximation model of cohesion were employed to determine the models parameters (EAM and TB-SMA parameters) for Ta, Mo and W metals and their solid state electron densities were also determined. These model parameters and electron densities with and without adjustment were used to determine dilute-limit heats of solution (unrelaxed and relaxed) of the binary alloys of Ta, Mo and W. The result obtained shows how electron densities play a vital role in determining some of the properties associated with alloys and defects in metals. For all the possible alloys we considered, the heats of solution for both unrelaxed and relaxed are almost the same with the experimental values.

Keywords: Embedded atom method, second moment approximation of tight binding, function of alloys, electron densities and dilute-limit heats of solution (unrelaxed and relaxed)

I. INTRODUCTION

Atomistic computer simulations are an important tool to study complex phenomena in physics, chemistry, biology and materials science. With the widespread use of molecular mechanics simulations, multiple types of interatomic potentials have been developed, and they are: Pair-wise potentials of Lennard-Jones (1924) and Morse (1929) which are used in condensed matters of closed-shell atoms; Embedded Atom Method (EAM) potentials by Daw and Baskes (1983) and similar formulations which are for metals and alloys; Bond order potentials by Tersoff (1988) and Force fields by Mackerell (2004) for organic and oxide systems.

For metals and alloys, the EAM potential is the most widely used approach in the research literature. Three other formulations are effectively similar to the EAM potential and they are Finnis-Sinclair potential by Finnis and Sinclair (1984), the glue model by Ercolessi *et al* (1988) and the effective medium theory by Jacobsen *et al* (1996). Classical molecular mechanics simulations that are based on EAM potentials are prolific (producing result) for example, a recent review by Foiles and Baskes (2012) offers a glimpse of wide range applications. Johnson and Oh (1989) developed an analytical EAM for bcc metals where the electron density was taken as a decreasing function of distance, the model has been found to be suitable for bcc metals except Cr because of its negative Cauchy pressure. Guellil and Adams (1992) modified Johnson and Oh (1989) model by introducing a modification term and applied the model to study phonon dispersion, thermal and surface properties of metals and alloys. Oyang *et*

al (1996) developed EAM for bcc transition metals including Cr, an analytic modified term was also introduced in order to fit the negative Cauchy pressure. Large-scale molecular-dynamics (MD) and Monte-Carlo (MC) simulations of metals and alloys often make use of the embedded atom method EAM to calculate the interatomic energies and forces. In the standard EAM scheme, alloying effects are described in terms of the mixed pair interaction that has traditionally been adjusted to the heat of solution of a single impurity (dilute limit).

The TB-SMA method takes into account the essential band character of a metallic bond. The total energy of the system consists of a band-structure term, proportional to the effective width of the electronic band (and so to the square root of the second moment of the local density of states) and a repulsive pair-potential term, which incorporates the non-band-structure parts of the total energy, including electrostatic interactions. The expression for the total energy contains a small set of adjustable parameters, which can typically been determined by matching to experimental data of cohesive energy, lattice constant, bulk modulus, and elastic constants of the system. Cleri and Rosato (1993) found that the quality of the results is improved by including a sufficient number of interacting atoms (typically up to fifth neighbours). According to Ducastelle and Cyrot-Lackmann (1970) and Tomanek *et al* (1985), the potential can treat transition metals whose cohesive properties originate from the large *d*-band density of states and is based on small set of adjustable parameters and is suitable for extension to higher-order approximation by considering higher moment of the electron density of state.

The most widely used Ta-alloys are Ta-10W and Ta-2.5W. Ta-2.5W is often used in heat exchangers because these alloys can be formed easily. The ability of molybdenum to withstand extreme temperatures without significantly expanding or softening makes it useful in applications that involve intense heat including the manufacturer of armour, aircraft parts, electrical contacts, industrial motors and filaments. Both pure Mo and Mo-W alloy (70%/30%) are used for piping, stirrers and pump impellers. W-based alloys are used in variety of applications including light bulb filaments, in carbide cutting tools, as an alloying element in steels and superalloys in aerospace applications.

In the present study, due to more frequent use of EAM potentials than the other approaches, we took EAM to first identify issues and obtained the EAM potential parameters for Ta, Mo and W bcc metals. Because TB potentials generally outperform pair potentials in terms of their ability to state properties and have properties similar to those EAM potentials, we also used tight-binding second moment approximation TB–SMA method for these metals to determine the TB potentials parameters which were used to determine the electron densities and hence the dilute-limit heats of solution (unrelaxed and relaxed).

II. THEORY

A. EMBEDDED ATOM METHOD EAM

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 (Daw and Baskes, 1984), the total energy of a system of atoms consisting of two terms can be written as:

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

$$\rho_i = \sum_{i \neq j} f(r_{ij}) \tag{2}$$

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

$\phi(r_{ij})$ is the two-body (pair) potential interaction between atom i and atom j whose separation is given by r_{ij}

ρ_i is the background electron density at i due to all the other atoms.

$f(r)$ is the electron density of atom j as a function of distance from its centre.

To use the Embedded atom method in a lattice model calculation, the $f(r)$, $F(\rho)$ functions must be specified for each atomic species, and $\phi(r)$ for each possible combination of atomic species.

According to Johnson (1988),

The electron density can be taken as:

$$f(r) = f_e \exp\left[-\beta\left(\frac{r_1}{r_e} - 1\right)\right] \tag{3}$$

The two-body potential is taken as Born-Mayer repulsion. i.e, to have the same analytic form as $f(r)$

$$\phi(r) = \phi_e \exp\left[-\gamma\left(\frac{r_1}{r_e} - 1\right)\right] \tag{4}$$

The embedding function is given by Johnson (1988) as

$$F(\rho) = -E_c\left[1 - \frac{\alpha}{\beta}\ln\left(\frac{\rho}{\rho_e}\right)\right]\left(\frac{\rho}{\rho_e}\right)^{\frac{\alpha}{\beta}} - \Phi_e\left(\frac{\rho}{\rho_e}\right)^{\frac{\gamma}{\beta}} \tag{5}$$

$\rho_e = 12f_e$ *and* $\Phi_e = 6\phi_e$,   *for fcc metals*

$\rho_e = 8f_e$ *and* $\Phi_e = 4\phi_e$,   *for bcc metals*

$$f_e = \frac{SE_c}{\Omega} \tag{6}$$

$$\phi_e = \frac{E_c}{4} \tag{7}$$

$$\alpha = 3\sqrt{\frac{\Omega B}{E_c}}, \tag{8}$$

$\Omega = a_0^3$ *for sc*, $\Omega = \frac{a_0^3}{2}$ *for bcc*   *and* $\Omega = \frac{a_0^3}{4}$ *for fcc*

$$\beta = \sqrt{\frac{15E_c\Omega G}{E_v(E_v + E_c)}} \tag{9}$$

$$\gamma = \sqrt{\frac{15\Omega G(E_c + E_V)}{E_c E_V}} \tag{10}$$

B is the bulk modulus, G is the shear modulus and $E_v \& E_c$ are respectively mono-vacancy & cohesive energy of the metals used

Oni-Ojo *et al* (2005) found another version of the embedding energy function $F(\rho)$ on guess work and by forcing $F(\rho)$ to satisfy certain second order ordinary differential equation. Later, Matthew-Ojelabi *et al* (2012) formulated an embedding energy function $F(\rho)$ which incorporated the physics of the material in a way that considered the physical interaction of the slope of the embedding function at the equilibrium and even beyond. The numerical calculations performed with their version of $F(\rho)$ for fcc metals Matthew-Ojelabi *et al* (2013) and bcc metals Matthew-Ojelabi *et al* (2015) yielded good results at the early stage.

B. TIGHT – BINDING SECOND MOMENT APPROXIMATION, TB- SMA METHOD

The assumptions underlying the tight – binding model of metallic cohesion in the second moment approximation are reviewed by Cleri and Rosato (1989).

The total cohesive energy U_0 is given as:

$$U_0 = E_R + E_B \qquad (11)$$

In the potential, the band energy can be written for an atom i as:

$$E_B^i = F(\rho) = -\left[\sum_j \xi^2 \exp\left(-2q\left(\frac{r_{ij}}{r_0} - 1\right)\right)\right]^{1/2} \qquad (12)$$

The density function, $\rho(r)$ is

$$\rho(r) = \sum_j \exp\left[-2q\left(\frac{r_{ij}}{r_0} - 1\right)\right] \qquad (13)$$

$$f(r) = \frac{\rho(r)}{N} \qquad (14)$$

$$E_B^i = F(\rho) = \xi^2(\rho)^2 \qquad (15)$$

where, ξ is an effective hoping integral,

r_{ij} is the distance between atom i and j

r_0 is the first neighbour distance, $r_0 = \frac{a}{\sqrt{2}}$

The parameter q describes the distance dependence of the hoping integral.

In order to ensure stability of the system, a repulsive pairwise interaction of Born-Mayer type is added

$$E_R^i = 6\phi_{(r)} = A\sum_j \exp\left[-p\left(\frac{r_{ij}}{r_0} - 1\right)\right] \qquad (16)$$

C. FUNCTION OF ALLOY SYSTEM

For an alloy model, The embedding energy $F(\rho)$ of a guest atom (impurity) is determined by the electron density of the host system before the guest is added. This corollary can be understood as follows:
- ✓ The unperturbed host potential is determined by its electron density.
- ✓ When a guest (impurity) is introduced, the total potential is a sum of host and impurity potentials, so the energy of the host with guest is a functional of the host and impurity potentials.
- ✓ Since the host electron density and the guest potential are set by the position and charge of the guest nucleus, the energy of the host with guest is a functional of the unperturbed host electron density and a function of the impurity type and position.

For binary alloy model with a-type and b-type atoms, the embedding functions $F_a(\rho)$ and $F_b(\rho)$, the atomic electron-density functions $f_a(r)$ and $f_b(r)$ and the two-body potentials $\phi_{aa}(r)$, $\phi_{bb}(r)$ and $\phi_{ab}(r)$ must be specified.

For alloys, the only other functions needed are the pair cross potentials between species a and b. using the mixing rule as outlined by Johnson (1988), the pair cross potential between different species a and b can be constructed from their elemental potentials.

$$\phi_{ab}(r) = \frac{1}{2}\left[\frac{f_b(r)}{f_a(r)}\phi_{aa}(r) + \frac{f_a(r)}{f_b(r)}\phi_{bb}(r)\right] \qquad (17)$$

No mixing rule is needed for densities since the density at site i is simply the linear sum of density contributions of all the other atoms.

D. THE DILUTE – LIMIT OF THE UNRELAXED HEAT OF SOLUTION

Atom type – a is the host or solvent while atom type – b is the guest or solute and were calculated as summation of the following four terms:

(a) remove host:

$$\Delta H_1 = -F^a(\rho^a) - \sum_{i \neq 1}\phi^{aa}(r_e^a) \qquad (18)$$

(b) add guest:

$$\Delta H_2 = F^b(\rho^a) + \sum_{i \neq 1}\phi^{ab}(r_e^a) \qquad (19)$$

(c) adjust neighbours:

$$\Delta H_3 = -\sum_{i \neq 1}F_i^a(\rho^a) + \sum_{i \neq 1}F_i^a(\rho_e^a + \Delta\rho) \qquad (20)$$

$$\Delta\rho = -f^a(r_e^a) + f^b(r_e^a)$$

(d) Adjust cohesion energy

$$\Delta H_4 = -E_c^a + E_c^b \qquad (21)$$

Therefore, the heat of solution ΔH (unrelaxed) both in the EAM and in the TB-SMA is given as:

$$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 \qquad (22)$$

ρ_e^a is the equilibrium electron density at an atom site in a perfect crystal of a-type atom and

r_e^a is the equilibrium-nearest neighbour distance this perfect crystal of a-type

The input physical quantities lattice parameter a_0, (lattice volume Ω), cohesive energy E_c, vacancy-formation energy E_v, elastic constants (C_{11}, C_{12}, C_{44}), the bulk modulus B, the average shear modulus G, and the atomic electron density evaluated at the nearest-neighbour distance from quantum calculation of Ta, Mo and W are listed in Table I. The EAM model parameters, f_e, ϕ_e, α, β and γ were determined using equations (6-10) and these are listed in Table II. The tight binding model parameters A, ξ, p and q were determined by fitting the experimental values of cohesive energy, lattice parameter, bulk modulus, elastic constants (C_{11}, C_{12}, C_{44}) and vacancy formation energy using equations (11-16) and these are listed in Table III. The unrelaxed dilute-limit heats of solution for all the possible combinations (alloy) of three bcc metals Ta, Mo and W were obtained using equations (19-22) and are presented in Table IV together with the relaxed dilute-limit heats of solution and available experimental data.

III. RESULTS AND DISCUSSION

The dilute-limit heats of solution we firstly determined in this work were unrelaxed heats of solution (2nd column of table IV). In order to determine the relaxed heats of solutions, Foiles *et al* (1986) added another term and found that relaxation of the host atoms near the guest will give a decrease in the energy due to relaxation E$_r$ which strictly depends on the size mismatch and can be given by the relation $E_r = -\left[1.167\left(\dfrac{\Omega_G}{\Omega_H}-1\right)\right]^2$ with subscripts G and H respectively indicating the guest and host atoms.

We later determined the relaxed heats of solution for all the combinations of three bcc metals Ta, Mo and W (3rd column of table IV). For all the combinations of Ta & Mo [Ta(H)Mo(G) and Mo(H)Ta(G)] and Ta & W [Ta(H)W(G) and W(H)Ta(G)], the values for their relaxed heats of solution were less than their corresponding unrelaxed heats of solution as stated by Foiles *et al* (1986). But for the combination of Mo and W [Mo(H)W(G) and W(H)Mo(G)] systems, the values for both the relaxed and unrelaxed heats of solution remain the same. This could be as a result of their atomic size having almost the same value.

The most noticeable parameters are the lattice constant and the cohesive energy. Without considering other parameters, if the lattice constant and the cohesive energy are equal for both the guest and the host, the heat of solution will be equal to zero. For the alloys of Mo and W, the heat of solution is almost zero in this present work while their experimental value of Baskes (1992) is zero. Also, positive and negative heats of solution significantly depend on both the size and the cohesive energy of the guest and the host.

Positive heat of solution is as a result of large size of the guest while the cohesive energy is less than the corresponding quantities in the host or vice versa. This holds for Ta(H)W(G) alloy, here the heat of solution is positive because the size of W (guest atom) is less than that of Ta (host atom) and the cohesive energy of W is greater than that of Ta. However, negative heats of solution occur whenever the cohesive energy and the size of the guest are either both greater or less than the corresponding host quantities. This holds for W(H)Mo(G) and Ta(H)Mo(G) alloys, the heat of solution is negative because Mo (guest atom) has both its size and cohesive energy less than that of W(host) and Ta(H). But for W(H)Ta(G), though the size of Ta is greater than W(G) but the cohesive energy of W is slightly greater than Ta.

The variation of heat of solution as a function of pair cross potential is shown in figure 1. The result obtained in figure 1 revealed that there is agreement between the experimental values, unrelaxed and relaxed heats of solution for this present work. This seems to suggest that both EAM and TB-SMA are useful in the determination of heats of solution for alloys of bcc metals. The trend exhibited by different elemental alloys in figure 1 whose heats of solution were computed could be due to pair cross potentials, electron densities and potential parameters used in the computation.

Finally, as the bulk modulus of either the guest or the host increases, the heat of solution also increases. However, increasing the shear modulus of either the guest or the host decreases the heat of solution.

IV. CONCLUSION

We have developed and studied three bcc metals (Ta, Mo and W) and their alloys using EAM and TB-SMA models because the frequently used potential models for molecular dynamics simulations of transition metals include the EAM and TB-SMA. Though there is no fundamental distinction between the two models, mathematically, the TB-SMA potential is equivalent to an EAM potential having a square root embedding function and TB-SMA model is simpler in formulating. We have obtained the model parameters of these metals, the obtained parameters were used to determine their electron densities and the heats of solution of their alloys were determined. For all the possible alloys we considered, the heats of solution for both unrelaxed and relaxed are almost the same with the experimental values. This confirms that both EAM and TB-SMA are very useful potentials in describing properties of metals and alloys. We later observed how the size and the cohesive energy of either the host atoms or guest atoms significantly play an important role in determining whether the heat of solution will be zero, positive or negative. We have also seen how the heat of solution either increases or decreases with either the bulk modulus and shear modulus of both the host and guest. In our future studies, these models will be extended to study more thermodynamics properties of more metals and alloys.
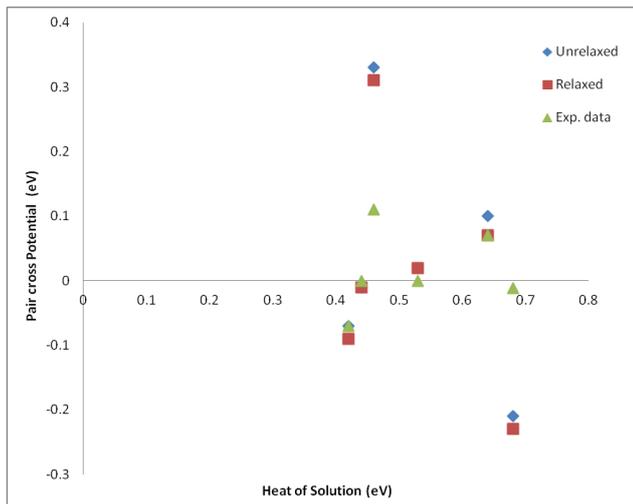
Figure 1: Variation of heat of solution with pair cross potential $\phi_{ab}(r)$ of possible alloys of Ta, Mo and W

Metals	a_0	Ec	E_{1f}	C_{11}	C_{12}	C_{14}	Ω	B	G
Ta	3.30	8.10	2.95	1.64	0.98	0.52	17.96	2.00	0.44
Mo	3.15	6.82	3.10	2.89	1.05	0.69	15.63	2.73	0.78
W	3.17	8.90	3.95	3.23	1.27	0.98	15.93	3.23	0.98

Table 1: The input physical quantities a_0, E_c & B are taken from Kittle (1979), E_v is taken from Zhang et al (1999) and C_{11}, C_{12}, C_{44} are taken form Brandes and Brooks (1992). a_0 is in Å, E_c & E_v are in eV, while C_{11}, C_{12}, C_{44}, B and G are in eV/Å³

Metals	f_e,	ϕ_e	α	B	γ
Ta	0.45	2.03	6.32	5.43	7.40
Mo	0.43	1.71	7.50	6.37	9.26
W	0.56	2.23	7.21	6.41	9.25

Table 2: The EAM model parameters, ϕ_e is in eV while f_e, α, β and γ are dimensionless

Metals	A	ξ	p	Q	r_o
Ta	0.3282	3.3010	8.2761	2.2369	2.8602
Mo	0.2040	2.5095	10.0151	2.0510	2.7253
W	0.2491	3.2057	10.3719	1.9920	2.7410

Table 3: Parameters of tight-binding potentials for Ta, Mo and W metals, the potentials are cut off beyond the third neighbour distance $\left(r > \sqrt{\frac{8}{3}r_0}\right)$. A and ξ are in eV while p and q are dimensionless. And r_o is in Å.

Possible alloys	Unrelaxed (present work)	relaxed (present work)	Exp. Data Baskes (1992)
Ta(H)Mo(G)	-0.07	-0.09	-0.07
Mo(H)Ta(G)	0.10	0.07	0.07
Ta(H)W(G)	0.33	0.31	0.11
W(H)Ta(G)	-0.21	-0.23	-0.11
Mo(H)W(G)	0.02	0.02	0.00
W(H)Mo(G)	-0.01	-0.01	0.00

Table 4: The unrelaxed and relaxed dilute-limit heats of solution for Ta, Mo and together with the available experimental data. H is the host atom (solvent) and G is the guest atom (solute). The heats of solution are all in eV

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