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INTERATOMIC INTERACTION IN FCC METALS

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The parameters of interatomic potential for 10 fcc metals are presented in this paper. The potential is based on the embedded atom method [6]. Parameters are determined empirically by fitting to the equilibrium lattice constant, cohesion energy, vacancy formation energy, bulk modulus and three elastic constants. The proposed potentials are suitable for atomistic computer simulations of practical applications in areas of material science and engineering.

Keywords: interatomic potential, embedded atom method.

Notation

a	— equilibrium lattice constant,
E_c, E_{vf}	— cohesion energy per atom and unrelaxed vacancy formation energy,
B	— bulk modulus,
c_{11}, c_{12}, c_{44}	— crystal elastic constants,
$c_{11}^{(a)}$, $c_{12}^{(a)}$, $c_{44}^{(a)}$, $B^{(a)}$	— calculated values of elastic constants.

1. Introduction

Computer simulations have become an increasingly powerful tool for studying material properties. While first principle quantum methods generally give the most accurate results, they can rarely be applied to complex systems, which require a large number of atoms or longer calculations. However, empirical potentials have proven to be efficient for investigating the structure and properties of materials in many fields, though these results are less accurate than first principle quantum calculations. The embedded-atom method (EAM) is widely used to represent the interaction between metal atoms. A general description of the method was done by Daw and Baskes [1, 2]. In the framework of EAM, the total energy of a system can be written as

$$E_{tot} = \sum_{n=1}^{N} E_n \ , \ E_n = F\left(\rho_n\right) + \frac{1}{2} \sum_{\substack{m=1 \\ m \neq n}}^{N} \varphi\left(r_{nm}\right) \ , \ \rho_n = \sum_{\substack{m=1 \\ m \neq n}}^{N} \rho\left(r_{nm}\right),$$

where E_{tot} — total energy of the system of N atoms, E_n — the internal energy associated with atom n, ρ_n — the electron density at atom n due to all other atoms, $\rho(r_{nm})$ — the contribution to the electron density at atom n due to atom m at the distance r_{nm} from atom n, $F(\rho_n)$ — the embedding energy of the atom into the electron density ρ_n, $\varphi(r_{nm})$ — the two body central potential between atoms n and m separated by r_{nm}. Interpretation and functional form of $\varphi(r)$, $\rho(r)$, and $F(\rho)$ depend on a particular method.

The popularity of the EAM model results from its quantum mechanical justification, as well as its mathematical simplicity, which makes this model conducive to large-scale computer modeling.

In recent years, a number of EAM potential models for fcc metals have been proposed. For example, Sheng *et al.* [3] have developed EAM potentials for fourteen fcc metals. The potentials were developed by fitting the potential-energy surface of each element derived from high-precision first-principles calculations. The three determining functions were expressed with quintic spline functions for each element. Typically, 15 equidistant spline knots were used for both the density and the pair functions, and 6 spline knots were used for the embedding function. This results in a great quantity of fitting parameters. Hijazi and Park [4] have proposed potential for seven fcc metals: Ag, Al, Au, Cu, Ni, Pd and Pt. They have used the following potential functions:

$$\rho(r) = \rho_0 \exp\left(-\alpha\left(r - r_e\right)\right),$$

$$\varphi\left(r\right) = -\varphi_0\left(1 + \gamma\left(\frac{r}{r_e} - 1\right)\right)\exp\left(-\beta\left(\frac{r}{r_e} - 1\right)\right),$$

$$F\left(\rho\right) = F\left(\rho_e\right)\left(1 - a \cdot \ln\left(\frac{\rho}{\rho_e}\right)\right)\left(\frac{\rho}{\rho_e}\right)^a,$$

where r_e is the equilibrium nearest distance. This potential has six adjustable parameters, α, β, γ, a and ρ_e. Dai *et al.* [5] have proposed an extended Finnis-Sinclair potential for six fcc metals: Ag, Au, Cu, Ni, Pd and Pt. The following potential functions have been employed

$$\rho(r) = \begin{cases} \left(r - r_1\right)^2 + a^2\left(r - r_1\right)^4 & , \; r \leqslant r_1 \\ 0 & , \; r > r_1 \end{cases},$$

$$\varphi\left(r\right) = \begin{cases} \left(r - r_2\right)^2\left(c_0 + c_1 r + c_2 r^2 + c_3 r^3 + c_4 r^4\right) & , \; r \leqslant r_2 \\ 0 & , \; r > r_2 \end{cases},$$

$$F\left(\rho\right) = F_0\sqrt{\rho},$$

where r_1 and r_2 are cut-off parameters assumed to lie between the second and third neighbor atoms. By this means, one needs to fit nine parameters.

The above mentioned potential models do not provide an equally accurate description of basic properties for all fcc metals to which those potentials have been applied to. The purpose of this paper is to present potential parameters for a consistent and practicable EAM model [6], which can be applied to widely used fcc metals.

2. Embedded atom potential

Zalizniak and Zolotov [6] have assumed that the atomic electron density has the following functional form:

$$\rho(r) = \rho_0(1 + \beta r)^2 \exp\left(-\alpha r\right), \tag{1}$$

where α and β are parameters of the atomic electron density distribution. Pair potential follows from the electrostatic interaction of two atoms that have positively charged nuclei and the electron densities defined by expression (1). The resulting expression is rather cumbersome and it can be written in a concise form as follows [6]:

$$\varphi\left(r\right) = \varepsilon \cdot \exp\left(-\alpha r\right)\sum_{n=-1}^{6} a_n\left(\alpha r\right)^n, \tag{2}$$

where parameters a_n depend on α and β. The embedding function $F(\rho)$ is taken in the polynomial form

$$F(\rho) = \sum_{n=0}^{4} c_n \left(\frac{\rho}{\rho_e} - 1 \right)^n, \tag{3}$$

where ρ_e — equilibrium electron density.

3. Results of potential fitting

In order to define the potential of interaction between the same metal atoms one need to fit only two parameters: α and β. The experimental data used in the fitting procedure consist of the equilibrium lattice constant, the cohesive energy, the vacancy formation energy, the bulk modulus and three elastic constants, given in Table 1.

Table 1. Pure metal properties used in fitting

	a, A	E_c, eV	E_{vf}, eV	B, eV/A^3	c_{11}, eV/A^3	c_{12}, eV/A^3	c_{44}, eV/A^3
Al	4.05 [7]	3.34 [7]	0.64 [8]	0.474 [12]	0.666 [12]	0.377 [12]	0.177 [12]
Ca	5.58 [7]	1.84 [7]	0.70 [9]	0.133 [13]	0.173 [13]	0.114 [13]	0.102 [13]
Ni	3.52 [7]	4.44 [7]	1.79 [10]	1.161 [12]	1.548 [12]	0.967 [12]	0.775 [12]
Cu	3.61 [7]	3.49 [7]	1.28 [10]	0.863 [14]	1.042 [14]	0.754 [14]	0.466 [14]
Pd	3.89 [7]	3.89 [7]	1.85 [11]	1.205 [12]	1.417 [12]	1.099 [12]	0.447 [12]
Ag	4.09 [7]	2.95 [7]	1.10 [10]	0.632 [12]	0.763 [12]	0.566 [12]	0.283 [12]
Ir	3.84 [7]	6.94 [7]	1.97 [8]	2.216 [15]	3.683 [15]	1.554 [15]	1.635 [15]
Pt	3.92 [7]	5.84 [7]	1.35 [10]	1.765 [12]	2.164 [12]	1.565 [12]	0.478 [12]
Au	4.08 [7]	3.81 [7]	0.90 [10]	1.083 [12]	1.204 [12]	1.022 [12]	0.259 [12]
Pb	4.95 [7]	2.03 [7]	0.58 [10]	0.279 [12]	0.310 [12]	0.264 [12]	0.094 [12]

Table 2. Parameters of the atomic electron density distribution (1)

	α, 1/A	β, 1/A	ρ_0, e/A^3
Al	1.8008	-2.5380	0.1844
Ca	1.0958	-6.0630	0.0031
Ni	1.5900	14.6900	0.0041
Cu	1.6300	-28.0390	0.0014
Pd	1.5239	-18.3850	0.0039
Ag	1.5568	-5.0950	0.0642
Ir	2.6116	-1.4845	37.2065
Pt	2.2320	-1.7440	9.4854
Au	2.0585	-1.7950	5.6041
Pb	1.2000	-13.2940	0.0040

As the fitting procedure [6] suggests, the equilibrium lattice constant, cohesive energy, vacancy formation energy and bulk modulus are reproduced exactly. The fitting procedure is performed using a cutoff distance of $2a$, so that long-range interactions are included.

The results of fitting for ten fcc metals are presented below. Table 2 lists the parameters of the atomic electron density distribution. Parameters of pair potential are

Table 3. Parameters of pair potential (2)

	Al	Ca	Ni	Cu	Pd
ε, eV	4.4736	4.2963	9.1686	7.2840	10.3465
a_{-1}	1	1	1	1	1
a_0	0.7236	0.6932	0.6747	0.6854	0.6867
a_1	0.8981	0.5757	0.4606	0.5229	0.5331
a_2	5.6170E-02	2.2931E-02	1.0457E-02	1.7243E-02	1.8342E-02
a_3	-1.4951E-02	-1.3498E-02	-1.2742E-02	-1.3173E-02	-1.3238E-02
a_4	-1.9584E-03	-1.6589E-03	-1.5067E-03	-1.5930E-03	-1.6062E-03
a_5	-1.9226E-04	-1.4436E-04	-1.2237E-04	-1.3462E-04	-1.3654E-04
a_6	-1.3088E-05	-7.4251E-06	-5.5519E-06	-6.5523E-06	-6.7185E-06

Table 4. Parameters of pair potential (2)

	Ag	Ir	Pt	Au	Pb
ε, eV	7.2321	28.0893	10.4249	6.4193	2.6628
a_{-1}	1	1	1	1	1
a_0	0.7010	0.6979	0.7351	0.7360	0.6874
a_1	0.6366	2.4252	1.5272	1.3442	0.5361
a_2	2.9404E-02	0.19029	0.1149	9.8534E-02	1.8674E-02
a_3	-1.3835E-02	-1.8071E-02	-1.6559E-02	-1.6179E-02	-1.3258E-02
a_4	-1.7277E-03	-2.4684E-03	-2.2677E-03	-2.2009E-03	-1.6101E-03
a_5	-1.5489E-04	-2.2692E-04	-2.3969E-04	-2.3129E-04	-1.3711E-04
a_6	-8.4546E-06	-4.3189E-05	-2.5063E-05	-2.1497E-05	-6.7690E-06

Table 5. Parameters of embedding function (3)

	Al	Ca	Ni	Cu	Pd
ρ_e, e/A^3	0.6726	0.4105	2.3029	2.2059	2.7952
c_0, eV	-3.3376	-1.8389	-4.4357	-3.4868	-3.8874
c_1, eV	-0.5328	-0.6987	-1.7850	-1.2768	-1.7893
c_2, eV	1.0845	0.0032	0.0098	0.0006	0.8255
c_3, eV	-0.6668	0.1761	0.5071	0.2571	1.8814
c_4, eV	1.0536	1.3131	3.1479	2.4665	3.1539

Table 6. Parameters of embedding function (3)

	Ag	Ir	Pt	Au	Pb
ρ_e, e/A^3	2.4369	3.8042	4.0881	3.7648	2.4181
c_0, eV	-2.9485	-6.9379	-5.8390	-3.8094	-2.029765
c_1, eV	-1.0896	-1.9624	-0.9382	-0.6167	-0.4593
c_2, eV	0.1118	0.0404	3.4135	2.4495	1.7075
c_3, eV	0.4725	-1.8474	-0.0709	0.3350	0.6488
c_4, eV	2.2196	3.0877	1.4164	1.0778	0.5118

Table 7. Calculated and experimental properties of pure metals, the proposed potential (1)—(3). The first lines present the experimental values of the three elastic constants (they are used in fitting procedure) and the commonly accepted values of vacancy formation energies. The second lines present the values predicted by the potential

	c_{11}, eV/A^3	c_{12}, eV/A^3	c_{44}, eV/A^3	B, eV/A^3	E_{vf}, eV	d, %
Al	0.666	0.377	0.177	0.474	0.62-0.66 [8]	0.14
	0.666	0.377	0.176	0.474	0.64	
Ca	0.173	0.114	0.102	0.133	0.7 [9]	10
	0.177	0.111	0.066	0.133	0.70	
Ni	1.548	0.967	0.775	1.161	1.6, 1.79 [16, 10]	7.1
	1.583	0.950	0.586	1.161	1.79	
Cu	1.042	0.754	0.466	0.863	1.28, 1.3 [10, 17]	5.3
	1.130	0.729	0.422	0.863	1.28	
Pd	1.417	1.099	0.447	1.205	1.7, 1.85 [10, 11]	1.9
	1.422	1.096	0.478	1.205	1.85	
Ag	0.763	0.566	0.283	0.632	1.1 [10, 17]	0.25
	0.762	0.567	0.281	0.632	1.1	
Ir	3.683	1.554	1.635	2.216	1.79, 2.27*[10, 18]	5.5
	3.823	1.412	1.484	2.216	1.97	
Pt	2.164	1.565	0.478	1.765	1.35, 1.5 [10, 17]	0.05
	2.165	1.565	0.479	1.765	1.35	
Au	1.204	1.022	0.259	1.083	0.89, 0.93 [11, 10]	0.6
	1.217	1.016	0.257	1.083	0.9	
Pb	0.310	0.264	0.094	0.279	0.58 [10]	9
	0.304	0.266	0.060	0.279	0.58	

* — result of *ab initio* calculations

listed in Tables 3 and 4, while coefficients of the embedding function $F(\rho)$ are given in Tables 5 and 6.

The calculated properties of pure metals from the proposed potential were compared with the experimental values, to which they were fitted in Table 7. The first lines contain the experimental values, while the second lines contain the values predicted by the potential. The last column presents the average discrepancy

$$d = \frac{1}{4}\left(\frac{\left|c_{11}^{(a)} - c_{11}\right|}{c_{11}} + \frac{\left|c_{12}^{(a)} - c_{12}\right|}{c_{12}} + \frac{\left|c_{44}^{(a)} - c_{44}\right|}{c_{44}} + \frac{\left|B^{(a)} - B\right|}{B}\right)$$

computed for every metal. For softer materials, such as Ca, Pb and Ni, the average discrepancies between the calculated and experimental results were found to be relatively large, but for other metals, the match between experiment and the proposed EAM model was good.

For comparative purposes, pure metal properties derived for ten fcc metals using the optimized EAM potential [3] and analytic EAM potential [4] are shown in Tables 8 and 9. The equilibrium lattice constant and the cohesive energy were reproduced exactly by all potentials. Generally, the proposed potential and the optimized EAM potential [3]

Table 8. Calculated and experimental properties of pure metals, optimized EAM potential [3]. The first lines present the experimental values of the three elastic constants (they are used in fitting procedure) and the commonly accepted values of vacancy formation energies. The second lines present the values predicted by the potential

	c_{11}, GPa	c_{12}, GPa	c_{44}, GPa	B, GPa	E_{vf}, eV	d, %
Al	114	61.9	31.6	76	0.62-0.66 [8]	1
	113	61.6	32	77	0.67	
Ca	28	18.2	16.3	14.1–19.3	0.7 [9]	7.8
	28	18	17	21	0.95	
Ni	261	151	132	180	1.6, 1.79 [16, 10]	2.5
	263	154	127	186	1.12	
Cu	176	125	82	140	1.28, 1.3 [10, 17]	1.4
	175	124	79	141	0.99	
Pd	234	176	71.2	180	1.7, 1.85 [10, 11]	5.7
	235	180	82	188	1.44	
Ag	132	97	51	100	1.1 [10, 17]	0.7
	131	97	51	98	1.17	
Ir	582	241	262	320	1.79, 2.27*[10, 18]	4.3
	578	241	243	350	1.67	
Pt	347	251	77	228–275	1.35, 1.5 [10, 17]	3
	347	253	78	282	1.50	
Au	193	163	42	180.3	0.89, 0.93 [11, 10]	2.9
	197	165	45	178	0.98	
Pb	49.4	42.1	14.9	46	0.58 [10]	1.5
	50.1	42	15.2	45	0.45	

* — result of *ab initio* calculations

provide similar descriptions of the elastic properties for ten fcc metals (see Tables 7 and 8). The values of vacancy formation energy estimated by the EAM potential [3] were not in satisfactory agreement with the data measured for most metals. Analytic EAM potential [4] provided a better description of elastic properties for Cu and Ni in comparison with the proposed potential, but for the other metals, the proposed potential gave a better fit to the experimental data (see Tables 7 and 9).

4. Conclusion

This paper presents parameters of a new EAM potential model to describe pure fcc metals. The potential model has a simple function form with two adjustable parameters and is easy to use in computer simulations. The potential parameters were determined by fitting the pure metal bulk properties: equilibrium lattice constant, cohesive energy, bulk modulus, three elastic constants and vacancy formation energy. The fitting procedure was applied to ten fcc metals: Al, Ca, Ni, Cu, Pd, Ag, Ir, Pt, Au, and Pb. The equilibrium lattice constant, cohesive energy, bulk modulus and vacancy formation energy were reproduced exactly. The agreement between the calculated elastic constants and the

Table 9. Calculated and experimental properties of pure metals, analytic EAM potential [4]. The first lines present the experimental values of the three elastic constants (they are used in fitting procedure) and the commonly accepted values of vacancy formation energies. The second lines present the values predicted by the potential

	c_{11}, GPa	c_{12}, GPa	c_{44}, GPa	B, GPa	E_{vf}, eV	d, %
Al	114	61.9	31.6	79	0.62-0.66 [8]	17.1
	98	69.9	44.7	79	0.866	
Ni	246.5	147.3	124.7	180.4	1.6, 1.79 [16, 10]	3.3
	232.4	154.8	127.6	180.2	1.7	
Cu	170	122.5	75.8	138	1.28, 1.3 [10, 17]	1.1
	167	124.3	77.3	138	1.3	
Pd	234.1	176	71.2	195	1.7, 1.85 [10, 11]	3.8
	225.5	180	77.7	195	1.54	
Ag	124	93.4	46.1	104	1.1 [10, 17]	1.4
	122	94.2	47.5	103	1.1	
Pt	347	251	76.5	283	1.35, 1.5 [10, 17]	8.9
	324	262	95.4	283	1.6	
Au	186	157	42	167	0.89, 0.93 [11, 10]	0.9
	184	157	43	167	0.9	

experimental data was good. The proposed EAM potentials are believed to find applications in diverse areas of materials science and engineering.

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