

Los Alamos Unclassified Report LA-UR 93-3901

Author: Arthur F. Voter

Date: 1993

Cite as follows:

A.F. Voter, Los Alamos Unclassified Technical Report # LA-UR 93-3901 (1993).

Embedded Atom Method Potentials for Seven FCC metals: Ni, Pd, Pt, Cu, Ag, Au, and Al

Arthur F. Voter
Theoretical Division
Los Alamos National Laboratory
Los Alamos, New Mexico 87545

1. Introduction

Computer-driven atomistic simulation methods, such as molecular dynamics (MD) and Monte Carlo (MC), are playing an increasingly important role in materials science. Because the properties predicted by an atomistic simulation are only as good as the quality of the underlying interatomic potential, the development of accurate potentials is of considerable interest. The embedded atom method (EAM), proposed by Daw and Baskes[1], has revolutionized atomistic simulations for metallic systems due to its enhanced accuracy and capability for describing low density defects such as free surfaces. The EAM has been used with good effect in a large variety of studies, reviewed elsewhere[2,3]. The purpose of this report is to present parameters for EAM potentials developed at the Los Alamos National Laboratory for the seven fcc metals Ni, Pd, Pt, Cu, Ag, Au, and Al.

Although EAM is based on the physics embodied in density functional theory[4-6], it is important to realize that EAM is a semiempirical approach. This is both a strength and a weakness. If highly accurate, first principles results are desired, one can employ a quantum chemical or density functional method. However, these approaches are much more expensive, with computational work scaling as N^3 or worse, where N is the number of atoms. The virtue of the EAM is that it scales as N , requiring only 2-5 times the work of a pair potential model, yet includes some many-body effects that are important for the description of metallic systems. Although the development of more complex, more accurate potentials is an active area of research, there will always be a need for fast, N -scaling potentials such as the EAM form.

The EAM Form

In any N -scaling energy expression, the total energy (E_{tot}) of a system of N atoms can be written as a sum over atom energies,

$$E_{tot} = \sum_i^N E_i . \quad (1)$$

In the embedded atom method, E_i is given by

$$E_i = \frac{1}{2} \sum_j \phi(r_{ij}) + F(\bar{\rho}_i), \quad (2)$$

with

$$\bar{\rho}_i = \sum_j \rho(r_{ij}). \quad (3)$$

Here r_{ij} is the scalar distance between atom i and atom j , ϕ is the pairwise interaction between atoms, ρ is another pairwise interaction leading to the “density” term $\bar{\rho}_i$, and $F(\bar{\rho})$ is the “embedding function.” The sums over neighboring atoms (j) are limited by the range of the cutoff for ϕ and ρ , which is generally one to four neighbor shells in the perfect crystal.

The computational procedure for evaluating the EAM energy is similar to that for a pair potential. For atom i , both $\phi(r_{ij})$ and $\rho(r_{ij})$ are summed over neighbors j , and then a single evaluation of $F(\bar{\rho}_i)$ is performed. Evaluation of the energy derivatives necessary for MD is only slightly more complicated. As with a pair potential, it is the radial cutoff of $\phi(r)$ and $\rho(r)$ that causes the total computational work to scale as N .

The physical interpretation of EAM is discussed in detail elsewhere[3,7], but some observations are made here about the general form. It is reasonable to think of $\bar{\rho}_i$ as a measure of the atomic density in the neighborhood of atom i , which, in turn, requires that $\rho(r_{ij})$ be a monotonically decreasing function of r_{ij} . In this sense, EAM can be thought of as a generalization of the fixed-volume pair potentials[8], in which the “volume” is now defined for each atom rather than the whole system. This allows treatment of defects for which the volume is ill defined, such as free surfaces.

The key to EAM is the nonlinearity of the function $F(\bar{\rho})$. If F were purely linear, the two terms in Eq. (2) could be collapsed to give a simple pair potential. A nonlinear $F(\bar{\rho})$ thus provides a many-body contribution to the energy. Because $\bar{\rho}_i$ depends only on scalar distances to neighboring atoms, the many-body term has no angular dependence. Nonetheless, this spherically symmetric, many-body interaction is quite important. For example, with a simple pair potential, the vacancy formation energy is formally equivalent to the atomic cohesive energy, and the Cauchy pressure ($C_{12} - C_{44}$) is zero. Both of these conditions are nonphysical for transition metals, and are remedied in the EAM expression.

Functional Forms and Fitting Procedure

The approach used by most groups, and the one employed here, is to seek the best possible fit to experimental data, relying on the physical underpinnings of Eq. (2) to give a potential that is reasonable in other parts of configuration space. This empirical approach, while perhaps less satisfying than attempting to derive functional shapes from first principles, has worked quite well and has contributed to the widespread use of EAM for metal and alloy simulations. The particular procedure we follow is exactly the one reported for Ni and Al by Voter and Chen[9], although we report it in slightly more detail here. The Ag potential also has been reported previously[10].

The pairwise interaction is taken to be a Morse potential,

$$\phi(r) = D_M[1 - e^{\alpha_M(r-R_M)}]^2 - D_M, \quad (14)$$

where the three parameters, D_M , R_M , and α_M define the depth, position of the minimum, and a measure of the curvature at the minimum, respectively. The density function is taken as the density of a hydrogenic 4s orbital

$$\rho(r) = r^6[e^{-\beta r} + 2^9 e^{-2\beta r}], \quad (15)$$

where β is an adjustable parameter. Because $r^6 e^{-\beta r}$ turns over at short r , the second term has been added to maintain the monotonically decreasing character of $\rho(r)$ to shorter r (r values inside the maximum are forbidden in the simulations). This 4s orbital density, appropriate for Ni and Cu, also worked well for Al and the 5s and 6s transition metals. Allowing the exponent of r to vary resulted in only small deviations from 6.0, so r^6 was employed for simplicity.

To ensure that the interatomic potential and its first derivatives are continuous, both $\phi(r)$ and $\rho(r)$ are smoothly cut off at $r = r_{cut}$ by using

$$h_{smooth}(r) = h(r) - h(r_{cut}) + \left(\frac{r_{cut}}{m}\right) \left[1 - \left(\frac{r}{r_{cut}}\right)^m\right] \left(\frac{dh}{dr}\right)_{r=r_{cut}}, \quad (16)$$

where $h(r) = \phi(r)$ or $\rho(r)$ and $m = 20$. r_{cut} is used as a fitting parameter. Following Foiles[11], $F(\bar{\rho})$ is defined by requiring that the energy of the fcc crystal versus lattice constant is given by the universal energy form of Rose et al[12],

$$E_U(a^*) = -E_{coh} f(a^*), \quad (17)$$

where

$$f(a^*) = (1 + a^*)e^{-a^*}. \quad (18)$$

Here E_{coh} is the crystal cohesive energy (per atom) and a^* is a reduced lattice constant defined by

$$a^* = (a/a_0 - 1)/(E_{coh}/9B\Omega)^{\frac{1}{2}}, \quad (19)$$

where a is the lattice constant, a_0 is the equilibrium lattice constant, B is the bulk modulus, and Ω is the equilibrium atomic volume. Thus, knowing E_{coh} , a_0 , and B , the embedding function is defined by requiring that the crystal energy from Eq. (2) matches E_U from Eq. (17) for all values of a^* . The crystal energy needs to be zero when the crystal nearest-neighbor distance reaches r_{cut} (i.e., when $a^* = a_{cut}^*$). This is accomplished by modifying the universal function in a manner suggested by Foiles[13],

$$f_{mod}(a^*) = \frac{f[(1 - \epsilon)^{\frac{1}{2}} a^*] - \epsilon}{1 - \epsilon}, \quad (20)$$

where $\epsilon = f[a_{cut}^*]$. To make E_U go to zero at *exactly* a_{cut}^* requires shifting ϵ slightly. Defining q by

$$\epsilon = f(q), \quad (21)$$

we can solve iteratively for q using

$$q_{n+1} = \frac{1}{2} [q_n + [1 - f_{mod}(q_n)]^{\frac{1}{2}} a_{cut}^*], \quad (22)$$

with $q_1 = a_{cut}^*$ as a starting guess.

Having defined the functional forms, we now describe the fitting procedure. The five parameters defining $\phi(r)$ and $\rho(r)$ (D_M , R_M , α_M , β , and r_{cut}) are optimized by minimizing the root-mean-square (χ_{rms}) deviation between the calculated and reference properties of the material. Because $F(\bar{\rho})$ is redefined for each choice of the parameters, the potential always gives perfect agreement with the experimental values of a_0 , E_{coh} and B . The reference properties are the three cubic elastic constants (C_{11} , C_{12} and C_{44}), the unrelaxed vacancy formation energy (E_{vac}^f), and the bond length (R_e) and bond strength (D_e) of the diatomic molecule. In addition, the hcp and bcc crystal structures are required to be less stable than fcc. Because the function being minimized contains discontinuities (such as when the wrong crystal structure becomes more stable) and many local minima, the parameter space is searched using the very robust (albeit slow) simplex algorithm [14]. For each metal, multiple simplex searches were initiated with differing starting guesses for the parameters. As with any study of this type, no guarantee can be made that the lowest minimum found is the global minimum. The results for the seven fcc metals are shown in Table 1, and the resulting parameter sets are shown in Table 2. The quality of the fit is seen to best for Ni and Ag ($\chi_{rms} < 1\%$). Even the worst fits, for Pt and Au ($\chi_{rms} \sim 4\%$), give quite acceptable agreement with the experimental input.

Discussion and Comments

Relaxing the bulk vacancy structure lowers the predicted vacancy formation energy by ~ 0.05 eV, leaving it in the range of the experimental uncertainty. Al exhibits the greatest relaxation (0.10 eV). The experimental value chosen for Al (0.75 eV) is at the high end of the experimental range, so that the relaxed value is in good agreement with the best estimates.

Although it is outside the desired scope of this report to present applications of these potentials, we note that these fcc EAM potentials have been applied to surface diffusion of adatom clusters and vacancy clusters on Ag(100)[10], surface energies and adatom surface diffusion barriers[15], Pt dimer and trimer diffusion on Pt(100)[16], and surface reconstructions[17]. In addition, various studies of grain boundaries[3,18,19] and surfaces[20,21] in Ni-Al and Ni-Al-B alloys have been performed using potentials fit in the same way[9].

In general, for these potentials, surface energies tend to be too low[15] (this is a general characteristic of EAM potentials), surface diffusion barriers are within 0.3 eV or so (< 0.1 eV for Ni)[15], although some trends are predicted to much better accuracy[15,16]. Predicted surface layer relaxations are reasonable and sometimes quantitatively accurate[20]. The fcc(110) 1x2 missing row surface reconstruction is predicted to occur only for Au and Pt, in agreement with experiment[17]. The predicted melting points are found to be quite good or somewhat low (most notably for Al and Ni, which are roughly 300K too low)[22], and the thermal expansion coefficients are quite reasonable except for Al ($\sim 2\times$ too high)[22]. The interstitial structure is predicted to be a (100) dumbbell, in agreement with experiment.

These potentials, stored in numerical form as interpolation arrays, are available from the author upon request.

Acknowledgments

The author is grateful to S.P. Chen, D.J. Srolovitz, and P.J. Hay for discussions that helped in the work reported here. Thanks also go to F. Ercolessi for calculating melting points and thermal expansion coefficients for these potentials, and to J.B. Adams for providing information on improved vacancy formation data for Pd. This work was supported by the U.S. Department of Energy (DOE) contract number W-7405-36. Much of this work was supported by the Energy Conversion and Utilization Technologies (ECUT) Division of the DOE.

References

- [1] M.S. Daw and M.I. Baskes, Phys. Rev. Lett. **50**, 1285 (1983); Phys. Rev. B **29**, 6443 (1984).
- [2] M.S. Daw, S.M. Foiles, and M.I. Baskes, Mater. Sci. Reports **9**, 251 (1993).
- [3] A.F. Voter, in Intermetallic Compounds, Principles and Practice, edited by J.H. Westbrook and R.L. Fleischer (John Wiley and Sons, Ltd 1994), Vol. 1, p. 77.
- [4] P. Hohenberg and W. Kohn, Phys. Rev. B **136**, 864 (1964).
- [5] M.J. Stott and E. Zaremba, Phys. Rev. B **22**, 1564 (1980).
- [6] J.K. Norskov and N.D. Lang, Phys. Rev. B **21**, 2131 (1980); J.K. Norskov, Phys. Rev. B **26**, 2875 (1982).
- [7] M.S. Daw, Phys. Rev. B **39**, 7441 (1989).
- [8] W.A. Harrison, Pseudopotentials in the Theory of Metals, (Benjamin, New York, 1966).
- [9] A. F. Voter and S. P. Chen, Mat. Res. Soc. Symp. Proc. **82**, 175 (1987).
- [10] A.F. Voter, in Modeling of Optical Thin Films, M.R. Jacobson, Ed., Proc. SPIE **821**, 214 (1987).
- [11] S.M. Foiles, Phys. Rev. B **32**, 7685 (1985).
- [12] J.H. Rose, J.R. Smith, F. Guinea, and J. Ferrante, Phys. Rev. B **29**, 2963 (1984).
- [13] S.M. Foiles, private communication (1985).
- [14] J.A. Nelder and R. Mead, Comp. J. **7**, 308 (1965).
- [15] C.L. Liu, J.M. Cohen, J.B. Adams, and A.F. Voter, Surf. Sci., **253**, 334 (1991).
- [16] G.L. Kellogg and A.F. Voter, Phys. Rev. Lett., **67**, 622 (1991).
- [17] S.P. Chen and A.F. Voter, Surf. Sci. Lett., **244**, L107 (1991).
- [18] A.F. Voter, S.P. Chen, R.C. Albers, A.M. Boring, and P.J. Hay in Atomic Modeling of Materials: Beyond Pair Potentials,“ V. Vitek and D.J. Srolovitz, Eds., Plenum, (1989), p. 223.
- [19] S.P. Chen, A.F. Voter, R.C. Albers, A.M. Boring, and P. J. Hay, J. Mater. Res. **5**, 955 (1990), and refs therein.
- [20] S.P. Chen, A.F. Voter, and D. J. Srolovitz, Phys. Rev. Lett. **57**, 1308 (1986).
- [21] S.P. Chen, A.F. Voter and R.C. Albers, Phys. Rev. B **39**, 1395 (1989).
- [22] F. Ercolessi, private communication.

- [23] N.W. Ashcroft and N.D. Mermin, Solid State Physics (Holt, Rinehart, and Winston, New York, 1976).
- [24] Metal Reference Book 5th ed., edited by C.J. Smith (Butterworths, London, 1976), p. 186.
- [25] G. Simmons and H. Wang, Single Crystal Elastic Constants and Calculated Aggregate Properties (MIT Press, Cambridge, 1971).
- [26] K.P. Huber and G. Hertzberg, Constants of Diatomic Molecules (Van Nostrand Reinhold, New York, 1979).
- [27] R.W. Balluffi, J. Nucl. Mater. **69&70**, 240 (1978).
- [28] K. Kuribayashi, D. Eng. Thesis, University of Tokyo (1975), quoted by M. Doyama and J.S. Koehler, Acat Metall. **24**, 871 (1976).
- [29] W. Wycisk and M. Feller-Kniepmeier, J. Nucl. Mater. **69&70**, 616 (1978).
- [30] J.O. Noell, M.D. Newton, P.J. Hay, R.L. Martin, and F.W. Bobrowicz, J. Chem. Phys. **73**, 2360 (1980).
- [31] J.S. Koehler, in Vacancies and Interstitials in Metals, edited by A. Seeger, D. Schumacher, W. Schilling and J. Diehl (Horth Holland, Amsterdam, 1970), p 175.

TABLE 1. Metal properties used in fit. Where two numbers are given, the top is the calculated result and the bottom is the experimental value. Diatomic bond lengths in parentheses are interpolated from other species. Lattice constants are from Ref. 23, cohesive energies are from Ref. 24, elastic constants are from Ref. 25, vacancy energies are from Ref. 27 [except for Ni (Ref. 29), Pd (Ref. 28), and Al (Ref 31)]. The diatomic molecule data is from Ref. 26, except for Ni (Ref. 30) and Pt (Ref. xxx).

	Ni	Pd	Pt	Cu	Ag	Au	Al
a_0 (Å)	3.52	3.89	3.92	3.615	4.09	4.08	4.05
E_{coh} (eV)	4.45	3.91	5.77	3.54	2.85	3.93	3.36
B (10^{12} erg cm $^{-3}$)	1.81	1.95	2.83	1.42	1.04	1.67	0.79
C_{11} (10^{12} erg cm $^{-3}$)	2.44	2.35	3.21	1.79	1.24	1.88	1.08
	2.47	2.34	3.47	1.76	1.24	1.86	1.14
C_{12} (10^{12} erg cm $^{-3}$)	1.49	1.76	2.64	1.23	0.93	1.56	0.65
	1.47	1.76	2.51	1.25	0.934	1.57	0.619
C_{44} (10^{12} erg cm $^{-3}$)	1.26	0.72	0.78	0.81	0.46	0.42	0.32
	1.25	0.712	0.77	0.818	0.461	0.420	0.316
ΔE_{1v}^f (eV)	1.60	1.51	1.49	1.30	1.10	0.90	0.73
	1.6	1.54	1.5	1.3	1.1	0.9	0.75
D_e (eV)	1.94	0.70	3.15	2.07	1.66	2.29	1.54
	1.95	0.7	3.17	2.05	1.66	2.3	1.60
R_e (Å)	2.23	2.52	2.34	2.23	2.50	2.40	2.45
	2.2	(2.4)	2.45	2.2	(2.5)	2.47	2.47
χ (rms%)	0.75	1.87	3.68	1.22	0.15	1.26	3.85

TABLE 2. Optimized potential parameters.

	Ni	Pd	Pt	Cu	Ag	Au	Al
D_M (eV)	1.5335	1.6574	0.76551	0.7366	0.6721	0.6748	3.7760
R_M (Å)	2.2053	2.3520	2.5446	2.3250	2.5700	2.5686	2.1176
α_M (Å ⁻¹)	1.7728	1.5450	2.0035	1.9190	1.8260	1.8964	1.4859
β_M (Å ⁻¹)	3.6408	3.3470	3.84120	4.0430	3.9060	3.6967	3.3232
r_{cut} (Å)	4.7895	5.4120	5.5758	4.9610	5.5420	5.5155	5.5550