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Embedded atom method for materials with a negative Cauchy discrepancy

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Abstract

An earlier suggested generalized embedding function by Oni-Ojo et al [J. Nig. Ass. Math. Phys. Vol. 9, 507 (2005) [2]] is here utilized to set up an embedded –atom method (EAM) for materials with a negative Cauchy discrepancy. To be able to do this it was found necessary to drop the usual assumptions that the curvature of the embedding function must be positive definite, while its slope must be negative. Concrete results are provided for the material strontium (S_r).

1.0 Introduction

Semi empirical atomistic simulations have become an important tool in the study of the structure and properties of materials. And in the past several years the methods for empirical and semi empirical calculations of metals and covalent materials have evolved rapidly [1-7]. One of the most popular of such methods is the embedded-atom method of Daw and Baskes [6,7], which is based on density-functional theory. The EAM has been successfully applied to study several properties of diverse materials.

However, it is well known [1,8] that

1. the EAM predicts single crystal surface energies as much as 50% below the polycrystalline experimental values [1], and
2. the EAM appears incapable of handling materials, like Strontium (Sr), and Iridium (Ir), etc, that possess a negative Cauchy discrepancy [8].

While several efforts to address the first problem, mentioned above, abound in the literature [1,9,10], we are not aware that the second problem has enjoyed any attention, Tackling this second problem is then the motivation for this study.

The organization of this paper is as follows. A brief review of the EAM basic equations is given in the next section. The review will allow us to indicate very clearly the problem being studied. In section 3, EAM parameters are determined for strontium (Sr) and the results of typical surface energies obtained are analyzed and discussed in section 4. Concluding remarks are then given in section 5.

2.0 The basic equations of the EAM for an FCC metal

We refer the interested reader to the several published papers on the EAM for more details than contained here, and we confine ourselves here strictly to the aspects required for this study.

If U_o denotes the total energy per atom, ie the negative of the cohesive energy, and if F(ρ) denotes the embedding function, and $\phi_1(r)$ denotes the nearest neighbour pair potential,

and ρ(r) is the electron density function at position r, then within a nearest neighbour model it can be shown that for a monoatomic FCC solid [7,9,10,]

$$U_o = 6\,\phi_1(r_o) + F(\rho_o) \tag{2.1}$$

$$O = \phi'_1(r_o) + 3F(\rho_o)V_{11}/r_o \tag{2.2}$$

$$3a\,B_o/4 = \phi''_1(r_o) + \frac{a}{4\Omega_o}\left[F(\rho_o)(2W_{11} - 8W_{12} - 5V_{11})\right] - \frac{a}{4\Omega_o}\left[2F''(\rho_o)V_{11}^2\right] \tag{2.3}$$

$$C_{11} = G_{11} + \frac{1}{\Omega_o}F'(\rho_o)W_{12} + \frac{1}{\Omega_o}F''(\rho_o)V_{11}^2 \tag{2.4}$$

$$C_{12} = G_{11} + \frac{1}{\Omega_o} = F'(\rho_o)W_{12} + \frac{1}{\Omega_o}F''(\rho_o)V_{11}^2 \tag{2.5}$$

$$C_{44} = G_{12} + \frac{1}{\Omega_o}F'(\rho_o)W_{12} \tag{2.6}$$

where
$$G_{11} = \phi'_1(r_o)/(2r_o) + \phi''_1(r_o)/2 \tag{2.7}$$

and
$$G_{12} = -5\phi'_1(r_o)/(4r_o) + \phi''_1(r_o)/4 \tag{2.8}$$

B_o and C_{ij} are, respectively, the bulk modulus and the elastic constants written in the Voigt notation. The equilibrium nearest neighbour distance is r_o $\left(=\left[\frac{a}{\sqrt{2}}\right]\right)$, while a is the lattice constant and ρ_o [=ρ(r_o)] is the value of the electron density function at $r = r_o$, the volume per atom is Ω_o $(= a^3/4)$, while V_{11}, W_{11} and W_{12} are three basic parameters of the EAM.

Equations (2.1 - 2.6) constitute the six basic equations of the EAM. Essentailly, these equations depend on the fundamental functions $F(\rho)$, ρ(r), and $\phi_1(r)$, and their first and second derivatives with respect to r. On the whole the equations contain the nine unknown parameters $\phi_1(r_o), \phi'_1(r_o), \phi''_1(r_o), F(\rho_o), F'(\rho_o), F''(\rho_o), V_{11}, W_{11}, W_{12}$ and the standard physical inputs required to determine these unknowns are the lattice constant a, the cohesive energy E_o (= - U_o), the bulk modulus B_o, and the three elastic constants C_{11}, $C_{12,}$ and C_{44}.

An expression for the monovacancy formation energy E_{1v}^f in the form;

$$E_{1v}^f = 12F(\rho_o) - 11F(\rho_o) - U_o \tag{2.9}$$

is often consired as an additional equation that would aid in the determination of the unknown quantities, if we take E_{1v}^f to be a known physical input.

Subtracting equation (2.6) from equation (2.5) we get the result

$$V_{11} = \sqrt{\frac{\Omega_o(C_{12} - C_{44})}{F''(\rho_o)}} \tag{2.10}$$

For many materials, $C_{12} > C_{44}$ and it is then sensible to require that $F''(\rho_o)$ be positive definite. But for materials with a negative cauchy discrepoancy (i.e. $C_{12} < C_{44}$), then $F''(\rho_o)$ must be negative, if the EAM is to make sense.

However, Foiles et al [11] in an early study on the EAM has furnished us with the following characterization of the embedding function: The embedding energy $F(\rho)$, defined relative to the free-atom energy, must go to zero for zero electron density and should have a negative slope [$F'(\rho_o) < 0$] and positive curvature [$F''(\rho_o) > 0$] for the background electron densities found in metals. Clearly, if this characterization is allowed to stand then the EAM cannot be applied to materials with a negative cauchy discrepancy where $C_{12} < C_{44}$, in view of equation (10)

Idiodi and Obodi [12] have also provided a characterization of the embedding function $F(\rho)$ through a non-linear diffrential equation for $F(\rho)$. We have since the realized [see reference 3] that such a characterization is not unique. This is not surprising since the EAM equations specify only $F(\rho_o)$, $F'(\rho_o)$, and $F''(\rho_o)$.

The characterisation of Foiles et al [11] is also not unique (see, for instance, Yuan et al [4] for embedding functions with a positive slope). For this study we have therefore decided to drop the characterization of $F(\rho)$ provided by Foiles et al [11], and also the charaterization provided by Idiodi and Obodi [12]. In doing this, we allow ourselves to be guided by the sensible requirement that the material being studied and the six basic EAM equations are all that we need in order determine the nature of $F(\rho)$. To be able to achieve this, we seek a more flexible embedding function, rather than the rigid function often employed in the litrature. The need to have a more flexible embedding function has already been pointed out by Oni-Ojo et al [2] in another study on the EAM. In the next section we determine the EAM parameters for strontium (Sr) a material with $C_{12} < C_{44}$.

3.0 EAM parameters

Table 1 contains the experimental physical contants required in equations (2.1 – 2.6) to determine the EAM parameters. For Sr and Ir, $C_{12} < C_{44}$ but for Rh, $C_{12} > C_{44}$. The situation for Rh is, however, unsettled since theoretical predictions of these same constants (see table III of Ref. [8]) give an oppposite trend (i.e. $C_{12} < C_{44}$)

In an earlier study, Oni-ojo et al [2] proposed a generalized embedding function $F(\rho)$ in the form

$$F(\rho) = AE_o \left(\rho/\rho_o\right)^{\lambda}\left[\ln\left(\rho/\rho_o\right)^{\alpha} - K\right] \tag{3.1}$$

The parameters λ, α, and *k* assist in providing flexibility. From (3.1) one gets the three EAM parameters.

$$F(\rho_o) = -AE_o k \tag{3.2}$$

$$F'(\rho_o) = \frac{F(\rho_o)}{\rho_o}\left[\lambda - \frac{\alpha}{k}\right] \tag{3.3}$$

$$F''(\rho_o) = \frac{F(\rho_o)}{\rho_o^2}\left[\lambda^2 - 2\lambda\frac{\alpha}{k} + \frac{\alpha}{k} - \lambda\right] \tag{3.4}$$

where a prime denotes differentiation with respect to the electron density ρ. The parameter *A* in (3.1) may be set equal to 1 in view of the arguments advanced in Ref. [1]. For this study, we have obtained

results with $A = +1$ and $A = -1$. The parameters λ, α, and k cannot be arbitrarily chosen. Infact, by demanding that the embedding function $F(\rho)$ satisfy equation (2.9), it can be shown that

$$\lambda = \frac{\ln\left\{\dfrac{\frac{1}{12}\left[E_{IV}^{f} + 11\,F(\rho_o) + E_o\right]}{AE_o\left[\ln\left(\frac{11}{12}\right)^{\alpha} - k\right]}\right\}}{\ln\left(\frac{11}{12}\right)} \qquad (3.5)$$

A consistent method of determining the parameters λ, α, and k for all the FCC elements will be more fully discussed else where [14]. For now the constraint provided by (3.5) will suffice for the purpose.

Once the parameters λ, α, and k are known then the EAM parameters $F(\rho_o)$, $F'(\rho_o)$ and $F''(\rho_o)$ can be determined from equations (3.2 – 3.4). The determination of other EAM parameters then follow easily from equations (2.1 – 2.6).

The EAM parameters of Sr for five different sets of the parameters λ, α, and k are shown in Table 2. Model 1 is characterized essentailly by a relatatively high positive value of k, while model 5 has a relatively high value of λ. Model III has a very small value of λ and a negative value of K. Models II and IV lie somewhere in between these three extremes.

We emphasize that all five models yield a negative value for $F''(\rho_o)$. All five models also give positive values for $F'(\rho_o)$. Yuan et al [4] have utilized embedding functions with a positive slope in their studies on bcc metals.

Table 1. Pure metal properities

Lattice constants (in Å), Bulk modulus (in GPa), elastic constants (in GPa) and monovacancy formation energies (in *eV*) have been taken from Ref. [8]. The cohesive energies are from Ref. [13]. The monovacancy formation energy for Sr has been assumed to be approximately 1/3 of the energy, since we are unable to find an experimental value for this material.

	Cohension energy E_o (*eV*)	**Monovacancy formation energy E_{IV}^{f} (*eV*)**	**Lattice constant a (Å)**	**Elastic constants (Gpa)**			**Bulk modulus B (GPa)**
				C_{11}	C_{12}	C_{44}	
Sr	1.72	$E_o/3$	6.08	15	6	10	12
Rh	5.75	1.71	3.80	413	194	184	270
Ir	6.94	1.97	3.84	590	249	262	355

Table 2. EAM parameters for Sr [see Equations (2.1) to (2.2)]

Parameter	**Model**				
	I	**II**	**III**	**IV**	**V**
A	-1	-1	+1	-1	-1
λ	2.012	3.067	0.512	4.13	11.53
α	4	2	1	1.25	0.85
K	4.5	1.25	-.0.7	0.60	0.15
$F(\rho_o)[eV]$	7.74	2.15	1.20	1.03	0.26

Parameter	Model				
	I	II	III	IV	V
$F'(\rho_o)\left[eV/\rho_o\right]$	8.69	3.15	2.34	2.12	1.52
$F''(\rho_o)\left[eV/\rho_o^2\right]$	-5.04	-4.03	-0.26	-2.25	-0.93
$V_{11}[\rho_0]$	0.527	0.59	2.32	0.79	1.2
$W_{11}[\rho_0]$	1.114535	1.347	4.864808	1.828137	2.746086
$V_{12}[\rho_0]$	-0.21323	-0.15583	-0.97338	-0.18788	-0.33252
$\phi_1(r_0)[eV]$	-1.577	-0.64	-0.487	-0.459	-0.329
$\phi'_1(r_0)\left[\frac{eV}{A^o}\right]$	-0.53	-0.216	-0.63	-0.19	-0.216
$\phi''_1(r_o)\left[x10^{16}\frac{eV}{CM^2}\right]$	-0.03978	0.181222	-0.10871	0.196204	0.180578

4.0 (III) Surface energy of Sr

In order to have some measure of the performance of the five different models exhibited in the last section, we shall in this section apply the models to study the (III) unrelaxed surface energy of Sr, which is given by the simple formula

$$\Gamma_{III} = \frac{4}{\sqrt{3}a^2}\left[F\left(\frac{9}{12}\rho_o\right)+\frac{9}{12}\left\{-E_o - F(\rho_o)\right\}+E_o\right]$$

The results obtained for this physical quantity, with the five different models, are shown in table 3.

Table 3. (III) surface Energy Γ_{III} of Sr

	I	II	III	IV	V
Γ_{III} [Ergs.cm^{-2}]	73	117	139	159	261

We are unable to find experimental results or even theoretical calculations, in the literature, with which to compare the results in Table 3. However, if we omit the results of model 1 and model V which are extremes, then the average of the results of model II, III and IV yield a (III) surface energy of (138 $\pm$ 21) Ergs.cm^{-2}.

5.0 Conclusion

In an earlier paper [2], we had asserted that the generalized four-parameter embedding function was flexible enough to handle materials for which the Cauchy discrepancy was negative. This manuscript can be viewed as a demonstration of that assertion. Clear prescriptions on how to fit the value of the parameters A, λ, α, and K will be carried out elsewhere [14] by studying the results obtained for several fcc and bcc metals.

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