

On recent developments on the embedded atom method

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Abstract

A recent modification to the embedding function $F(\rho)$ for bcc Lithium by Yuan et al [10] is here generalised and then characterised by a second order linear differential equation. The structure of the generalised function, unlike the embedding functions used hitherto, is sufficiently rich to allow for a Cauchy discrepancy ($C_{12} - C_{44}$) that may be either positive or negative.

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1.0 Introduction

Semiempirical atomistic simulations have become an important tool in the study of the structure and properties of materials. Fundamental to any such study is the choice of the manner in which the constituent atoms interact, i.e., the choice of an appropriate interatomic potential. Simple potentials tend not to have enough flexibility to accurately portray real metals, while more fundamental approaches tend to be too unwieldy to carry out the desired calculations with sufficient efficiency.

A procedure for designing a mathematical model of a metal, called the embedded atom method (EAM), was developed about two decades ago by Daw and Baskes [1, 2]. In this approach, the energy required to place a small impurity atom in a lattice is taken solely as a function of the electron density at that particular site. Each atomic species therefore has a unique energy function which is in turn a function of just the electron density. Results obtained from the EAM have been encouraging in that the model has shown satisfactory agreement with experimental data over a spectrum of problems, often previously intractable.

In the practical application of the EAM three functions must be determined. These are the embedding function $F(\rho)$, the density function $\rho(r)$, and the pair potential $\phi(r)$ between any two constituent atoms.

Efforts to improve the EAM led to the modified embedded atom method (MEAM), developed by Baskes et al [3, 4]. The MEAM parameters are published in [4] for several materials. Although some other versions of MEAM have also been developed [5-9], the theory and parameters of MEAM92 described in [4] are most commonly used.

The main difference between the EAM and MEAM lies in the construction of the density function $\rho(r)$. In the EAM, the electron density at site i , ρ_i , is given by a linear superposition of spherically averaged atomic electron densities from neighbouring atoms to site i , while in the MEAM ρ_i is further augmented by angular dependent terms.

Recently Yuan et al [10] introduced a further modification into MEAM92, by adding a new parameter K into the embedding function $F(\rho)$. This was to enable them overcome the problems they encountered in the calculation of the surface energy of bcc Lithium, if the relaxation of surface atom positions are taken into account. In spite of this modification, the model failed woefully for bcc Vanadium where it predicted a monovacancy formation energy that was 50% larger than the experimental value [11].

In view of these problems encountered by Yuan and Coworkers, we shall in this study focus on the structure of the embedding function itself. It has not enjoyed as much development as the density

function $\rho(r)$. A simple form for the atomic electron density $\rho(r)$, as can be found in various simplified versions of the EAM would suffice for our purpose. However, we have generalised the work of Yuan et al [10, 11] as far as the embedding function $F(\rho)$ is concerned. We furnish in this study a more flexible embedding function $F(\rho)$, characterised by a second order linear differential equation. This study will illustrate the rich structure of our generalised $F(\rho)$.

In the standard EAM [2], the Cauchy discrepancy ($C_{12} - C_{44}$) is determined by the curvature of $F(\rho)$ at the equilibrium electron density ρ_0 . In fact, $C_{12} - C_{44} = F''(\rho_0)V_{11}^2/\Omega_0$ where Ω_0 is the volume per atom and V_{11} is an EAM parameter. Our characterization of $F(\rho)$, in this study, is flexible enough to allow for both positive curvature and negative curvature. This frees our model from the problems associated with the usage of restrictive forms of $F(\rho)$.

The organisation of this paper is as follows. A brief review of the EAM with the relevant equations is given in the next section. In section 3, the embedding function used by Yuan and coworkers [10, 11], is examined and generalized, and applied in Section 4 to bcc Lithium and Vanadium. The results obtained are analysed and discussed, and finally, concluding remarks are given in Section 5.

2.0 Theory

The embedded atom method (EAM) is based on density functional theory, which asserts that the energy of a material can be written as a unique functional of the electron density [12, 13]. In the EAM, the important aspect of the electron density is assumed to be the local electron density at each atomic site, as provided by the surrounding atoms. The total energy is divided into an electrostatic interaction plus an embedding energy, which is the energy required to place an atom in a uniform electron gas. Thus, the total energy of an arbitrary arrangement of atoms is given by

$$E_{tot} = \sum_i F_i(\rho_{h,i}) + \frac{1}{2} \sum_{\substack{i,j \\ (i \neq j)}} \phi_{ij}(R_{ij}) \quad (2.1)$$

where $F_i(\rho)$ is the embedding energy of atom i , $\rho_{h,i}$ is the host electron density at atom i due to the surrounding atoms, $\phi_{ij}(R)$ is a short-ranged electrostatic interaction between atom i and atom j , R_{ij} is the distance between atom i and atom j , and all summations are over all atoms. The host electron density is often approximated by the superposition of atomic electron densities.

Daw [14] has derived the EAM energy form from density functional theory, thereby demonstrating the physical origin of the terms in equation (2.1). Daw's derivation ignores band-structure effects and assumes that the electron density can be approximated by a superposition of atomic electron densities. Both of these assumptions are better approximations for fcc metals than for bcc metals. Jacobsen et al [15] have also derived EAM-type functions from ab initio methods, and their results also suggest that the EAM-type approach might be more appropriate for fcc metals than for bcc metals.

The EAM, in spite of the comments above, has been applied to diverse solids and its ability to accurately describe quite a wide range of material properties is one of the most surprising and powerful justifications of the approach [16]. Equation (2.1) shows clearly the three important functions that feature in the EAM – the embedding function $F(\rho)$, the electron density function $\rho(r)$, and the pair potential $\phi(r)$. The EAM, as initially developed by Daw and Baskes [2], requires quite some tedious numerical fitting to various physical quantities in order to determine the three functions. In the past few years, several efforts [16-20] have been made, within the EAM, to circumvent the tedious numerical fitting required to determine EAM functions. Thus, Idiadi and Obodi [20] derived embedding functions, containing three parameters, of the form

$$F(\rho) = \mu \left[f_0 \left\{ e^{\alpha_f} - e^{-\alpha_f \left(\frac{\rho}{\rho_0} - 1 \right)} \right\} \right]^{\lambda_f} \quad (2.2)$$

or

$$F(\rho) = f_0 \left(\frac{\rho}{\rho_0} \right)^{\lambda_f} e^{-\alpha_f \left(\frac{\rho}{\rho_0} - 1 \right)} \quad (2.3)$$

where $\mu = \pm 1$; and f_0 , α_f , and λ_f , are constants to be determined.

Within the MEAM, Baskes [4] utilized a simple embedding function of the form

$$F(\rho) = A E_0 \left(\frac{\rho}{\rho_0} \right) \ln \left(\frac{\rho}{\rho_0} \right) \quad (2.4)$$

to study several solids. In (2.4), A is the only parameter to be determined and E_0 is the sublimation energy (a known physical quantity). Though (2.4) is simple, the density function $\rho(r)$ utilized in the MEAM still requires very tedious fitting.

Recently Yuan et al [10] applied MEAM 92 to bcc Li but modified (2.4) to the form

$$F(\rho) = A E_0 \left[\ln \left(\frac{\rho}{\rho_0} \right) - K \right] \quad (2.5)$$

where A and K are the only parameters to be determined. Though the modified form (2.5) helped to resolve the problems they encountered with Li, it ran into problems again later with bcc V [11].

Because of the problems stated above and the deficiencies in the MEAM already noted by Baskes [4], coupled with the fact that the Standard EAM is incapable of handling materials for which the Cauchy discrepancy is negative, we pursue a completely different approach in this paper. We pursue our investigations within the EAM and adopt a simple form for the atomic electron density $\rho(r)$, as can be found in various versions of the EAM [16, 17]. However we have generalized the work of Yuan et al [10, 11] as far as the embedding function $F(\rho)$ is concerned, by seeking a more flexible embedding function, in a sense to be made more precise in the next section.

3.0 Construction of more flexible embedding functions: Generalized Model

In our view, the problem with the embedding functions (2.1 -2.5) in the previous Section is that they lack flexibility. We illustrate this point by focussing on the functional form (2.5), which yields, at the equilibrium density ρ_0 , the values

$$F(\rho_0) = -A E_0 K \quad (3.1)$$

$$F'(\rho_0) = A E_0 (1 - K) / \rho_0 \quad (3.2)$$

$$F''(\rho_0) = A \frac{E_0}{\rho_0^2} F \quad (3.3)$$

where a prime denotes differentiation with respect to ρ .

In the Standard EAM [2], the Cauchy discrepancy is given by

$$C_{12} - C_{44} = F''(\rho_0) \cdot V_{11}^2 / \Omega_0 \quad (3.4)$$

where Ω_0 is the volume per atom.

In solids for which $C_{12} > C_{44}$, $F''(\rho_0)$ must be positive definite, but in solids where $C_{12} < C_{44}$ then $F''(\rho_0)$ must be negative. The embedding functions used in various EAM studies do not have this flexibility.

It is clear that the function given by equation (2.5) satisfies a second order linear differential equation of the form

$$\frac{d^2 F}{d\rho^2} - \frac{1}{\rho} \frac{dF}{d\rho} + \frac{F}{\rho^2} = 0 \quad (3.5)$$

In order to accommodate as many different embedding functions as possible into the same class, we immediately generalize (3.5) to the form

$$\frac{d^2 F}{d\rho^2} - \frac{\gamma_1}{\rho} \frac{dF}{d\rho} + \frac{\gamma_0}{\rho^2} F = 0 \quad (3.6)$$

where γ_1 and γ_0 are parameters that can be determined. One solution to (3.6) is the generalized form of (2.5), which is

$$\begin{aligned} F(\rho) &= A E_0 \left(\frac{\rho}{\rho_0} \right)^\lambda \left[\ln \left(\frac{\rho}{\rho_0} \right)^\alpha - K \right] \\ &= \frac{F(\rho_0)}{(-K)} \cdot \left(\frac{\rho}{\rho_0} \right)^\lambda \left[\ln \left(\frac{\rho}{\rho_0} \right)^\alpha - K \right] \end{aligned} \quad (3.7)$$

The condition for (3.7) to be a solution of (3.6) is that

$$\begin{aligned} \frac{A E_0}{\rho^2} \left(\frac{\rho}{\rho_0} \right)^\lambda \left[\ln \left(\frac{\rho}{\rho_0} \right)^\alpha - K \right] \cdot \{ \gamma_0 - \lambda \gamma_1 + \lambda^2 - \lambda \} + \\ + \frac{A E_0}{\rho^2} \cdot \left(\frac{\rho}{\rho_0} \right)^\lambda \{ 2\alpha\lambda - \alpha - \gamma_1 \alpha \} = 0 \end{aligned} \quad (3.8)$$

That is,
$$\left. \begin{aligned} \gamma_0 &= \lambda \gamma_1 - \lambda^2 + \lambda \\ \text{and } \gamma_1 &= 2\lambda - 1 \end{aligned} \right\} \quad (3.9)$$

The function defined by (3.7) is clearly a four parameter model for the embedding function and the parameters are A , K , α and λ or $F(\rho_0)$, K , α and λ . E_0 is the negative of the cohesive energy per atom for the material being studied, and is thus a known physical quantity. From (3.7) one gets for the generalized embedding function the results

$$F(\rho_0) = -A E_0 K \quad (3.10a)$$

$$F'(\rho_0) = \frac{F(\rho_0)}{\rho_0} \left[\lambda - \frac{\alpha}{K} \right] \quad (3.10b)$$

$$F''(\rho_0) = \frac{F(\rho_0)}{\rho_0^2} \left[\lambda^2 - \frac{2\lambda\alpha}{K} + \frac{\alpha}{K} - \lambda \right] \quad (3.10c)$$

where a prime denotes differentiation with respect to the electron density ρ . $F(\rho_0)$, $F'(\rho_0)$, and $F''(\rho_0)$ must be chosen to satisfy the EAM equations [2]. By demanding that the model correctly reproduce the monovacancy formation energy E_{1v}^f , which is given, for bcc metals, by

$$E_{1v}^f = 8F\left(\frac{7}{8}\rho_0\right) - 7F(\rho_0) + E_0 \quad (3.11)$$

we see that we have just enough conditions to completely determine the generalized embedding function $F(\rho)$, given by (3.7).

Infact, the monovacancy formation energy E_{1v}^f is correctly reproduced by (3.7), provided α

and λ together satisfy the equation

$$\lambda = \ln \frac{\left\{ \frac{\frac{1}{8} [E_{1v}^f + 7F(\rho_0) + E_0]}{\left[-\frac{F(\rho_0)}{K} \right] \left[\ln \left(\frac{7}{8} \right)^\alpha - K \right]} \right\}}{\ln \left(\frac{7}{8} \right)} \quad (3.12)$$

In the next Section we shall test out the theory sketched here, on body-centred cubic Lithium and Vanadium.

4.0 Application of Generalized Model to bcc Lithium (Li) and bcc Vanadium (V).

4.1.1 bcc Li

The model parameters for bcc Li, as given by Yuan et al [10], are $A = 0.87$, $K = -1.3933$, $E_0 = 1.65eV$, with

$$\left. \begin{aligned} F(\rho_0) &= 2.0001eV \\ F'(\rho_0) &= 3.4356 eV/\rho_0 \\ F''(\rho_0) &= 1.4355 eV/\rho_0^2 \end{aligned} \right\} \quad (4.1)$$

We show in Table 1 various pairs of α and λ that satisfy equation (3.12) and we see that the pair $\alpha = 0.76$ and $\lambda = 1.0784$ also reproduces fairly well the solution (4.1) of Yuan et al [10].

4.1.2 bcc V

The model parameters for bcc V, as given by Yuan et al [11], are $A = 1.0000$, $K = -0.4629$, $E_0 = 5.30eV$, with

$$\left. \begin{aligned} F(\rho_0) &= 2.45337 eV \\ F'(\rho_0) &= 7.7537 eV/\rho_0 \\ F''(\rho_0) &= 5.30 eV/\rho_0^2 \end{aligned} \right\} \quad (4.2)$$

We show in Table 2 various pairs of α and λ that satisfy equation (3.12). We are unable to find a pair that will yield the values of $F'(\rho_0)$ and $F''(\rho_0)$ as given in (4.2).

Table 1: Model parameters of the generalized embedding function $F(\rho)$ for bcc Lithium that will predict a monovacancy formation energy E_{1v}^F of 0.495eV and $F(\rho_0) = 2.0001eV$

α	λ	$F'(\rho_0) [eV/\rho_0]$	$F''(\rho_0) [eV/\rho_0^2]$
0.1	1.5727	3.2890	2.1093
0.3	1.4263	3.2834	2.0140
0.7	1.1247	3.2544	1.5361
0.76	1.0784	3.2479	1.4313
1.0	0.8903	3.2162	0.9252
1.2	0.7298	3.1823	0.3975
1.33	0.6230	3.1564	0.00
1.4	0.5659	3.1415	-0.2266
1.6	0.3982	3.0932	-0.9467
2.0	0.0512	2.9734	-2.6741

Table 2: Model Parameters of the generalized embedding function $F(\rho)$ for bcc Vanadium that will predict a monovacancy formation energy E_{1V}^F of 2.1 eV and $F(\rho_0) = 2.45337\text{eV}$

α	λ	$F'(\rho_0) [eV/\rho_0]$	$F''(\rho_0) [eV/\rho_0^2]$
0.1	2.3250	6.2341	9.4927
0.5	1.3778	6.0302	5.9292
0.7	0.8551	5.8078	2.3307
0.8	0.5794	5.6614	0.0752
0.803	0.5706	5.6565	0.000
0.81	0.5512	5.6454	-0.1670
0.9	0.2931	5.4892	-2.4818
1.0	-0.0045	5.2890	-5.3365
1.5	-1.7010	3.7769	-23.7240
2.0	-3.8979	1.0370	-46.3969

This explains why the model of Yuan et al [11] is unable to correctly predict the experimental vacancy formation energy of 2.1eV for Vanadium.

It is clear from Tables 1 and 2 that the curvature of our generalised embedding function, i.e. $F''(\rho_0)$, admits both positive and negative values.

It is therefore possible to use the model to treat materials like C_r , S_r , and I_r [21] that have $C_{12} < 44$.

5.0 Conclusion

We have successfully generalized the works of Yuan and co-workers [10, 11] as far as the embedding function is concerned. Apart from its overcoming the problem encountered by Yuan et al [11] for V, the generalized four-parameter embedding function is flexible enough to handle materials for which the Cauchy discrepancy is negative.

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