Abstract

A new method for deriving Embedded Atom Model (EAM) type interatomic potentials from electronic structure calculations has been proposed, for application to metallic solids. Density Functional Theory (DFT) has been utilized to calculate the electronic charge densities of a crystal at various lattice constants, while for the description of the effective embedding function we consider both the embedded atom’s charge density and those corresponding to the neighboring atoms. The calculated charge densities can be expressed conveniently by a three-dimensional fitting to an appropriate superposition of atomic orbitals. Al as a prototypical metallic solid has been used for application of the method, and validate the approach by reproducing adequately experimental data for cohesive energy, bulk modulus, surface energies, elastic constants and dynamical properties at finite temperatures, obtained by MD simulations.

Introduction

The embedded-atom method (EAM) became a popular method for computing many static and dynamical properties of metallic systems via computer simulation techniques. Molecular dynamics (MD) and Monte Carlo (MC) simulations have established this approach as one of the most reliable methods for describing metals and alloys without recourse to computationally expensive quantum mechanical approaches. The method is empirical, as it relies on the use of experimental data for fitting the necessary parameters for the description of a specific material. However, several deficiencies have appeared in many cases. It was first realized that in terms of the usual EAM approach, the properties of an impurity are supposed to be fully characterized by the cross-pair interaction and the corresponding embedding potential, while the on-site local density of the embedded atom remains unchanged. In this sense, the embedding function is designed for the description of the embedded atom only, while the total charge density is characteristic of the local environment, which is a reasonable approximation in the case of bulk stoichiometric materials but is an oversimplification in the cases of impurities or point defects, where the local electronic structure results from the host and the embedded atom specific characteristics that may be significantly altered in a foreign environment relative to its own bulk value. The problem becomes more important when dealing with binary or ternary alloys, while the non-stoichiometric multi-element nano-structured metallic materials remain an impervious challenge. In addition, it is still difficult to construct a faithful potential in the cases of nanoscale objects with non-stoichiometric local structure, due to the lack of relevant experimental information.
The aim of the present work is the construction of a theoretical potential model within the framework of the EAM theory, able to capture the interactions between the components of a specific local environment, with the parameterized functions based only on \textit{ab-initio} calculations. We used the density functional theory (DFT) to calculate the “real” densities of the valence electrons that are subsequently utilized for the evaluation of the effective embedding parameters as a function of the electronic densities of the embedded atom.

**Charge density**

A straightforward estimation of the total charge density for the bulk material at equilibrium could be approximated by superposing the free atom electron density. However, this procedure yields charge density deviations that at certain points may be large up to 15% in Al crystal. The situation is improved when the charge density is fitted by superposing the spherically symmetric charge distributions of each atom since Al is a 3s metal, the form of \( \rho(r) \) was taken from the expression for the 3s-electronic wave function:

\[
\rho(r) = (a_0 + a_1 r + a_2 r^2)^2 \exp(-r/c)
\]

with \( a_0, a_1, a_2 \) and \( c \), fitting parameters. All fits in this work have been performed using the MERLIN package\(^4\). As it is seen on Fig. 1 this calculation resulted in deviations for the charge density from the DFT data that it at most 7% at a distance of 0.7Å from the atom positions.

Further, we have utilized the obtained parameters for the partial charge density functions in a procedure to reproduce the charge density from DFT in some specific cases such as single vacancy, divacancy, (100) surface and adatom on (100) surface without relaxation. Fig. (2) shows representative sections for those cases. The results show satisfactory agreement with the results for the electron density obtained by \textit{ab initio} calculation, although some important features could be noted. The values of the charge density at the vacancy position in Fig (2a) is slightly overestimated. Then in Fig (2d) the shape of the peaks for 001 section (where negative direction of the x-axis points toward the bulk) has inverse behavior comparing to DFT result. Both deviations could be related to the proposed model, which is not able to redistribute the “released” electrons due to the vacancy or surface existence and as result the total number of electrons is not conserved. Besides, the weighting factor (utilized in this work) for the \( P \) angular momentum term is positive which is the most likely reason for the inverse behavior in the case of the adatom. A negative value is supposed to improve the results for this particular case, nevertheless in this work we have chosen this specific set of parameters which describe at best the whole region of fitted lattice constants, not only at equilibrium.
Representative charge density for a horizontal section at the top of the Al fcc basis cell as result of *ab initio* DFT calculation (a), superposition of spherically symmetrical functions for the case of free atom (b), 3D fitting procedure with spherical symmetry (c) spherical and *P* angular momentum contribution (d) with corresponding absolute error to density, calculated by DFT.
Representative sections of selected directions for unrelaxed: (a) single vacancy; (b) divacancy; (c) (001) surface and (d) single adatom on (001) surface. The position of the vacancy in Fig. (2.a) is at origin as well as in Fig. (2.b) and additional one at ~5.5 a.u. in 110 direction for the divacancy case. In Fig. (2.c) origin lies at arbitrary atomic position on the (001) surface and 111 direction represent the charge density profile toward the substrate. In Fig. (2.d) the position of the adatom is at origin and the negative distances for 001 direction refers to substrate charge densities. Open circles, squares and triangles refer to the results from DFT, while lines represents the results from the proposed model for charge density description.

Seeking to assign physical meaning to $\rho(r)$, it could be easily noted that it is very short ranged, acquiring practically zero values even at first neighbor distances. Direct utilization of the DFT charge distribution, for instance for a spherically symmetric charge density in the case of a free atom, leads to unreasonable results for the pair-wise term and the embedding function. This is a consequence of the short-ranged nature of the charge density that leads to extremely weak many-body correlations due to the fact that in the original theory the “embedded” atom is considered as a point object and the “density” as an effective host density at that point. In terms of this formalism, it is impossible to describe adequately the real interaction that results from the electronic interactions. To overcome this deficiency we consider the embedded atom $i$ as a soft sphere, consisting of the associated electronic cloud that is introduced into the “bath” of the host electrons.
(\overline{\rho}_i \). Consequently, the charge density, \( \rho(r) \), is obtained by integrating the atomic and the host charge densities and appears as a measure of the effective interaction (through the embedding function) of the embedded atom with the host density.

\[
\rho_i^{\text{eff}} = \frac{1}{2} \sum_{j \neq i} \int_{\Omega} P_i(\vec{r}) P_j(\vec{r} - \vec{r}_j) \, d\vec{r}
\]

(2)

where \( P_i(\vec{r}) \) is the partial contribution to the charge density of atom \( i \) at position \( \vec{r} \) and \( \Omega \) is the integration volume. Eq. (2) could be considered as an expression of the effective interaction between atoms \( i \) and \( j \) determined by their electronic intermixing. In the case of only spherically symmetrical partial contributions to the charge density, Eq. (2) reduces to the following expression:

\[
\rho_i^{\text{eff}} = \frac{1}{2} \sum_{j \neq i} \int_{\Omega} \rho_i^{a(0)}(\vec{r}) \rho_j^{a(0)}(\vec{r} - \vec{r}_j) \, d\vec{r}
\]

(3)

When \( p \) electrons have to be included, Eq. (2) is rewritten in a more general form:

\[
\rho_i^{\text{eff}} = \frac{1}{2} \sum_{j \neq i} \int_{\Omega} \frac{Q_i(\vec{r}) Q_j(\vec{r} - \vec{r}_j)}{\overline{\rho}_j(\vec{r}_j, \vec{r})} \, d\vec{r},
\]

(4)

where \( Q_i(\vec{r}) + Q_j(\vec{r} - \vec{r}_j) = (\overline{\rho}_i(\vec{r}_i, \vec{r}))^2 \) and \( \overline{\rho}_j(\vec{r}_j, \vec{r}) \) is the charge density at the position \( \vec{r} \) due to the existence of atoms \( i \) and \( j \). Eq. (4) reduces to Eq. (2) in the case of spherically symmetric partial densities.

**Application to Al**

The method has been applied in the bulk Al case that we chose because of the great availability of EAM models (for comparison reasons) and the simplicity of its outer electron shells ([Ne]3s\(^2\)3p\(^1\)) that simplify the DFT calculations and permit easier description of the charge distributions. For the calculation of total-energies and electronic densities to be fitted, we used the HARES\(^5\) DFT code, which is a first-principles Real-space Electronic Structure method\(^6\), including the valence electrons only with the Perdew-Zunger\(^7\) parameterization of the exchange-correlation energy in the framework of the local-density approximation\(^8\) (LDA). We performed calculations for a wide range of lattice constants in the interval 6.0-9.4 a.u., with a spacing of 0.1 a.u. for the real space grid and sufficiently dense grid of k-points in reciprocal space [10x10x10] generated with the Monkhorst-Pack scheme\(^9\), taking into account the full symmetry of the point group for the fcc crystal.

**Results and discussion**

See the original paper for details.

**Concluding remarks**

This work presents a method for constructing of a new type of embedded atom potential model using only electronic structure information. The model is based on charge
densities obtained by DFT calculations at various volumes that are used for the derivation of an effective charge density, constructed to take into account the contributions of the valence electrons of both the embedded atom and the neighboring host atoms. The method has been applied in the case of Al for which we performed MD simulations and we calculated several thermodynamic quantities that were compared with the available experimental and theoretical data. From the general good agreement we found we conclude that the approach seems to reproduce satisfactorily the behavior of the bulk material and also of the other important features like surface energies, vacancy formation energies, etc. The method is expected to give good description in systems containing impurities, multi-component systems and non-stoichiometric alloys, for which a proper description of the interatomic interactions is still lacking. However, the presented formalism for the EAM potential has to be modified by adding a cross term for the effective charge density corresponding to atomic contributions from different species which is meant to describe the many-body cross correlations. Further, with respect to the computational details, this additional term will affect only the procedure of summation to obtain the total effective charge density for an embedded atom and will not alter the effectiveness of the code.

Keeping in mind that the functionals we are using result eventually in a semi-empirical potential model, it would be interesting to test the validity of the present approach in different elements, having more complicated charge distributions and especially in the cases of alloys and impurities.

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