

A Final Report

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STUDY OF THE EMBEDDED ATOM METHOD OF ATOMISTIC
CALCULATIONS FOR METALS AND ALLOYS

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Technical Summary

Solids have been studied by atomistic modeling since the earliest availability of computers for scientific research. By the mid sixties, it was understood that models for metals based on reasonably short ranged two-body forces coupled with a global volume dependent contribution to the crystal energy yielded surprisingly good results for bulk calculations, but were unsatisfactory at surfaces. Little progress was made until the early eighties, when Daw and Baskes developed the Embedded-Atom Method (EAM) based on density functional theory and intended primarily for tight-packed transitional metals, and Finnis and Sinclair developed a model based on tight binding theory and intended primarily for bcc transition metals. The underlying mathematical format of both approaches is the same, and provides an extension of the earlier models through a function which in practice provides a measure of local volume dependence. The primary purpose of this research project was to investigate the implications of this mathematical format and to use the resulting insight to correlate the known physical input data with computed results of properties that are difficult to access experimentally. Embedded-Atom Method terminology is used, but this research is applicable as well to the Finnis-Sinclair model.

The approach taken was to design simple EAM models based on analytic functions and to study both the constraints on the functions caused by the physical input data for fitting specific metals and the relations between the functions and the calculated properties. The functions can then be used as a bridge to correlate the physical input data with the properties computed with the EAM models. The majority of calculations were carried out for tight-packed metals (fcc and hcp), but bcc models were also studied.

A simple EAM model requires three types of functions to be fully specified: an electron density function and an embedding function for each atom species present, and a pair potential for each type of two-body interaction present. For comparison of different EAM models, a "normalized" form was defined in which the energy from two-body forces and from the embedding function are independently in equilibrium in the perfect crystal at equilibrium.

There were fifteen published paper from this research project, and so just a few generalizations will be listed:

- The vacancy formation energy and the surface energy are correlated so that if the vacancy formation energy is given correctly, the surface energy will be smaller than the best experimental values.
- Calculated results are relatively insensitive to the electron density function, as long as it is smooth and monotonically decreasing.

- Defect formation energies are proportional to the average shear modulus and are almost independent of the bulk modulus and the cohesive energy.
- The fcc shear anisotropy ratio is normally greater than two in EAM models, in agreement with most fcc metals but not with aluminum.
- As a function of c/a ratio, the hcp structure is only stable in a narrow window. The fcc lattice is more stable if c/a is greater than ideal (1.63), and the bcc lattice is more stable if c/a is less than about 1.58.
- The two-body potential well must be broad in the vicinity of first and second neighbor distances for the bcc structure to be more stable than a tight-packed structure. This broadening also must occur to fit the elastic constants in a bcc structure. Thus, a bcc model fit to bcc elastic constants will be stable relative to fcc, while a fcc model fit to fcc elastic constants will be stable relative to bcc.
- There is a transformation which can change both the embedding function and the two-body potential such that the overall model is unchanged. If it is assumed that two-body potentials between different species in alloys can be constructed analytically from the pure metal functions, and that alloy models retain the same transformation invariance as pure metals, then the alloy potentials are uniquely determined.
- The analytic alloy potentials derived by the above procedure give a good account of the heats of formation of stoichiometric compounds of Cu, Ag, Au, Ni, and Pt, but consistently give values too high for compounds involving Pd.
- Binary alloy heats of formation are determined primarily by the relative size and the cohesive energy of the two elements. If both of these quantities are smaller for one metal than the other, there is a tendency for negative heats of formation, while if one is smaller and the other larger, there is a tendency for positive heats of solution.
- The primary model parameter determining whether the fcc or hcp lattice structure will be more stable is the range of the two-body and electron density interactions.
- The calculated intrinsic fcc stacking-fault energy is only slightly less than the extrinsic (experimental results on this point are not clear), and both increase with increasing vacancy formation energy, decreasing atomic volume and shear modulus, and are insensitive to the bulk modulus and the cohesive energy.
- Equations for the concentrations of vacancies and antisite defects in ordered alloys in thermodynamic equilibrium at and near stoichiometry were derived as functions of defect energies.

List of Publications

- Johnson, R. A., "Interatomic Potential Development in Materials Science," in Computer Simulation in Materials Science, R. J. Arsenault, J. R. Beeler, Jr., and D. M. Esterling, eds. (American Society for Metals, Metals Park, Ohio 1987), pp. 29-44.
- Johnson, R. A., "Analytic Nearest-Neighbor Model for FCC Metals," Physical Review B, Vol. 37 (1988), p. 3924.
- Johnson, R. A., "Relationship Between Defect Energies and Embedded Atom-Method Parameters," Physical Review B, Vol. 37 (1988), p. 6121.
- Oh, D. J., and Johnson, R. A., "Simple Embedded Atom Method Model for FCC and HCP Metals," Journal of Materials Research, Vol. 3 (1988), p. 471.
- Oh, D. J., and Johnson, R. A., "Embedded Atom Method Model for Close-Packed Metals," in Atomistic Simulation of Materials, V. Vitek and D. J. Srolovitz eds. (Plenum, New York, 1989), p. 233.
- Oh, D. J., and Johnson, R. A., "A Semi-Empirical Potential for Graphite," in Atomic Scale Calculations in Materials Science, J. Tersoff, D. Vanderbilt, and V. Vitek eds. (Symposium Proceedings Vol. 141, Materials Research Society, Pittsburgh, PA, 1989), p. 51.
- Johnson, R. A., and Oh, D. J., "Analytic Embedded Atom Method Model for BCC Metals," Journal of Materials Research, Vol. 4 (1989), p. 1195.
- Johnson, R. A., "Alloy Models with the Embedded-Atom Method," Physical Review B, Vol. 39 (1989), p. 12554.
- Oh, D. J., and Johnson, R. A., "Relationship Between c/a Ratio and Point Defect Properties in HCP Metals," Journal of Nuclear Materials, Vol. 169 (1989), p. 5.
- Johnson, R. A., "Implications of the Embedded-Atom Method Format," in Many-Atom Interactions in Solids, R. M. Nieminen, M. J. Puska, and M. J. Manninen eds. (Springer Proceedings in Physics Vol. 48, Springer-Verlag, New York, NY, 1990), p. 85.
- Johnson, R. A., "Phase Stability of FCC Alloys with the Embedded-Atom Method," Physical Review B, Vol. 41 (1990), p. 9717.
- Brown, J. R., and Johnson, R. A., "Antiphase Boundary Calculations for the L₁₂ Structure using an Embedded Atom Method Model," Materials Research Society Symposium

Proceedings, Vol. 209 (1991), p. 71.

Johnson, R. A., "Many Body Effects on Calculated Defect Properties in HCP Metals," Philosophical Magazine A, Vol. 63 (1991), p. 865.

Johnson, R. A., "Stability of Tight-Packed Metals with the Embedded-Atom Method," Journal of Materials Research, Vol. 7 (1992), p.

Johnson, R. A., and Brown, J. R., "Vacancies and Antisite Defects in Ordered Alloys," Journal of Materials Research,

Future Directions

These comments include thoughts on extensions to the present form of most EAM models, and on the application of EAM calculations to technologically significant problems.

The electron density function depends only on distance and can be thought of as the lowest-order term in an expansion of many-body terms. It is spherically symmetric and cannot account for any angular dependence as occurs in covalent bonding, for example. Baskes and others have investigated orientational effects, primarily in attempts to tailor the EAM to covalent crystals. In these modified models, the electron density sensed by a given atom is not just determined by the proximity of neighboring atoms, but is modified by the angles between pairs of neighboring atoms. These contributions probably have little effect on fcc metals, but they should be applicable to bcc metals. The problem is that the standard physical input data for bcc metals can be fit (albeit somewhat awkwardly) without these terms, so that adding more parameters adds arbitrariness to the fitting procedure and a lack of uniqueness to the resulting model. Alternatively, three-body potential energy terms could be used. The transformation invariance mentioned in the technical summary provides some relation between these two approaches, and it seems preferable to leave the orientational dependence with the electron density.

Another approach, which is related to the above, involves thinking of the electron density as an expansion of a volume dependent term (as in present models) with "s" type symmetry, a polarization term with "p" type symmetry, a shear term with "d" type symmetry, and a term with "f" type symmetry. This last term differentiates between fcc and ideal hcp by symmetry alone. Again there is the problem with too many adjustable parameters, but Baskes has produced a model which in essence contains these terms in a simple way without additional adjustable parameters (work is to be published). This effort should be continued.

Both of these approaches eliminate the transformation invariance that was employed in developing alloy potentials. Thus, a deeper understanding of interactions in alloys is necessary to apply these extensions to the EAM to alloys.

As long as a realistic perception of the meaning of the results of atomistic calculations is maintained, present EAM models can be used for studying numerous problems in materials. Of course, this is presently being done at many sites. More work is probably being carried out on Al alloys than any other metal, and this requires some caution because Al is a difficult metal to model and it is not certain that present models adequately portray the real character of Al. Another area of technological importance which presently seems to be neglected is the study of ultrafine particles in which the majority of atoms sense the presence of a surface or an interface, i.e., very small particles, fine needles or whiskers, and thin flakes or foils.

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