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A. Caro, D. A. Crowson, M. Caro

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Classic many body potential for concentrated alloys, and the inversion of order in Fe-Cr.

A. Caro,^{1,*} D.A. Crowson,^{1,2} and M. Caro¹

¹*Chemistry and Materials Science Directorate, Lawrence Livermore National Laboratory, Livermore, CA 94551*

²*Virginia Polytechnic Institute and State University, Blacksburg, VA 24061*

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Atomistic simulations of alloys at the classic - or empirical - level face the challenge to correctly model basic thermodynamic properties. In this work we propose a methodology to generalize many-body classic potentials to incorporate complex formation energy curves. Application to Fe-Cr allows us to correctly predict the order vs segregation tendency in this alloy, as observed experimentally and calculated with *ab initio* techniques, providing in this way a potential suitable for radiation damage studies.

Computational Materials Science is nowadays a standard approach to study complex problems in solids. Besides *ab initio* techniques, a great interest exists for classic approaches adequate for large number of atoms, as needed in studies of large crystalline defects with long range interactions. The requirement of accurate, predictive simulation tools points towards the necessity of models for the interactions that are able to reproduce important fundamental properties of materials. Usually the models used are known as 'many body' potentials, grouped in large categories as the Embedded Atom Models and the Second Moment Approximation [1]. Most of the vast amount of work done using these classic potentials addresses either pure elements or intermetallic compounds, only a few address concentrated alloys.

Based on the enormous success of these many body potentials for large scale atomistic simulations of materials [2, 3], there has been a continuous progress in the field since its inception, extending the models towards increasingly complex materials like bcc, covalent, ordered compounds and dilute alloys. In this paper, we focus on concentrated alloys with complex heat of formation, and provide a methodology to address arbitrarily complex systems. This methodology is applied to Fe-Cr, a system of interest in fission and fusion technology as structural material with good mechanical, thermal, and radiation properties. Computer simulation studies of radiation damage in these alloys require models that can adequately predict alloy stability / microstructure evolution under large doses.

The so-called many body potentials share in common a description of the total energy in terms of the sum over atom energies, themselves composed of two contributions, namely embedding and pair potential terms. For heteroatomic systems, let's say binary alloys involving elements A and B, it reads

$$E = \sum_i^N [F_{\alpha_i}(\sum_{j \neq i} \rho_{\alpha_i \beta_j}(r_{ij})) + 1/2 \sum_{j \neq i} V_{\alpha_i \beta_j}(r_{ij})] \quad (1)$$

where α , β stand for elements A or B sitting at sites i , j ; F 's are the embedding functions for either type of

elements, and V 's and ρ 's are the pair potentials and densities between α - β pairs. Alloy properties are therefore described by the functions ρ_{AB} and V_{AB} . Depending on the model considered, the density functions do not always include the cross term ρ_{AB} . Different expressions for the embedding energies, densities, and pair potentials englobe a large diversity of similar models.

In recent papers we addressed the problem of alloy description with atomistic models from the perspective of thermodynamics rather than the properties of a single impurity. We developed numerical tools to calculate free energies of the relevant phases and applied them to a couple of systems, namely Au-Ni [4] and Fe-Cu [5]. Both these systems share in common the fact that the formation energy of the alloy is a rather symmetric function of the composition and, as it is shown below, a standard approach using a cross pair potential term was enough to reproduce their properties. We found that alloy models fitted to properties of the dilute limit usually show erroneous behavior in the concentrated case. For Fe-Cr in particular, this problem is at the core of the limitations of the classic potentials due to the highly non-symmetric formation energy, that even change sign at low Cr concentration [6].

Focusing our attention on disordered alloys, the strategies to develop alloy potentials have been at least twofold: perform a global optimization of all functions in Eq.(1) together to match the targeted properties of A, B and AB systems, or start by developing potentials for pure A and pure B, and then fit the alloy properties by adjusting the cross terms in that equation. By far, most of the work done on alloys has used the dilute heat of solution as the key alloy property to fit, but in general, the description of concentrated alloys require more information than that contained in this sole quantity.

A convenient way to analyze alloy properties with independence of the pure elements is to discuss excess quantities, i. e. quantities measured with respect to the linear interpolation between the two constituents. Ideal solutions, by definition, have null excess quantities, while real alloys depart from linearity. To construct models that de-

part from linearity, we can use either or both terms in Eq(1). It is important to notice that even without using a cross density, the embedding term always introduces a heat of formation, i. e. a non-linearity of energy vs composition, through the non-linear functions $F_\alpha(\rho(x))$.

In this work we follow the strategy of taking potentials from the literature for the pure elements, and adjust the alloy terms, focusing on non-linearities built upon the pair potential cross term alone, using a representation that minimizes the non-linear contribution of the embedding term. We start with a preparation of the two pure element potentials in a way that is adequate for our purpose, that is, the effective representation with normalized densities, namely

$$\begin{aligned}\rho &= \rho^{orig} / \rho_{eq}^{orig} \\ F(\rho) &= F^{orig}(\rho^{orig}) - F^{orig'}(\rho_{eq}^{orig}) \cdot \rho^{orig} \\ V_\alpha(r) &= V_\alpha^{orig}(r) - 2F^{orig'}(\rho_{eq}^{orig}) \cdot \rho^{orig}(r)\end{aligned}\quad (2)$$

where the superscript *orig* stands for original, the subscript *eq* for equilibrium values, and the prime ' for derivative. These transformations do not alter the properties of the pure elements but have the advantage of minimizing the contribution of the embedding term to the formation energy of the alloy, as is discussed below, and allows us to combine potentials for pure elements coming from different sources with incommensurate magnitudes.

In this work we use the Fe potential reported in [7] and the Cr potential reported in [8]. For these particular potentials the transformations (2) drop the contribution of the embedding term to the formation energy down to 1 meV/atom at $x \simeq 0.5$, making it negligible in front of the target value for this alloy ~ 100 meV/atom, [6]. This in practice leaves the pair potential as the sole contributor to the formation energy.

The free energy of a random solid solution phase of an alloy with composition x at temperature T is conveniently expressed as:

$$g(x, T) = g_{id}(x, T) + g_{mix}(x, T) + \Delta g(x, T) \quad (3)$$

where g_{id} is the compositional weighted free energy of the pure components, given by $g_{id}(x, T) = (1-x)g_A(x, T) + xg_B(x, T)$, and g_{mix} is the entropy of mixing for a random alloy, $g_{mix}(x, T) = kT((1-x)\ln(1-x) + x\ln(x))$. The excess Gibbs energy of mixing is conveniently expressed by a Redlich - Kister expansion [9] as:

$$\Delta g(x, T) = x(1-x) \sum_{p=0}^n L_p(T)(1-2x)^p \quad (4)$$

where L_p is the p^{th} -order binary interaction parameter; in general it is a function of temperature. Due to the complexity that represents fitting potentials to actual temperature dependent functions, in what follows we shall

adopt two important simplifications: neglecting the excess vibrational entropy and assuming that the formation energy does not depend on T . This simplifies Eq.(4) to:

$$\Delta g(x, T) \cong \Delta H(x) = x(1-x) \sum_{p=0}^n L_p(1-2x)^p \quad (5)$$

For Fe-Cr the formation energy has recently been calculated *ab initio* [6] together with a rough estimate of the bulk modulus B and lattice parameter of the alloy a_0 . These calculations contain several simplifications, as Fe and Cr both have magnetism, and are therefore not to be considered as the definitive values classic models have to reproduce, but as first estimates upon which classic models can be developed. From those results we shall consider that $B(x)$ and $a_0(x)$ are just given by the linear interpolation between the constituents, assumption based on the errors reported in [6] and the small departure from the ideal behavior. Therefore the formation energy will be our single target function to be reproduced.

From Fig(5) in Ref[6] the formation energy of bcc ferromagnetic Fe-Cr alloys can be reproduced by a Redlich-Kister expansion, Eq 5, to 4th order in $(1-2x)$. Table I gives the corresponding coefficients in [eV].

TABLE I: Values of the Redlich-Kister expansion coefficients, Eq. 5, corresponding to ΔH_{Fe-Cr}^{mix} from Ref [6], in eV.

L_0	L_1	L_2	L_3	L_4
0.41566	0.0814134	-0.0101899	0.267659	-0.248269

To find the functional form of the cross potential we need an analytic model for the alloy. We adopt a model in which the species that sits on site i can either be A or B , but both are embedded in the same average environment, as discussed by Ackland and Vitek [2] :

$$\begin{aligned}E^{ran} &= x_A^2 \sum V_{AA}(r_{ij}) + c_B^2 \sum V_{BB}(r_{ij}) \\ &+ 2x_A x_B \sum V_{AB}(r_{ij}) + x_A F_A(\tilde{\rho}_A) + x_B F_B(\tilde{\rho}_B)\end{aligned}\quad (6)$$

with $\tilde{\rho}_A = \tilde{\rho}_B = x_A \sum \rho_A(r_{ij}) + x_B \sum \rho_B(r_{ij})$.

It is now easy to see that in the effective representation, Eqs. (2), the contribution of the embedding terms to the excess energy of mixing, ΔE^{emb} , is small:

$$\Delta E^{emb} = x_A(F_A(\tilde{\rho}) - F_A(\rho_0)) + x_B(F_B(\tilde{\rho}) - F_B(\rho_0)) \quad (7)$$

By making a Taylor development of F around ρ_0 and using Eq.(2) we see that the contribution is quadratic in $(\tilde{\rho} - \rho_0)$:

$$\begin{aligned}\Delta E^{emb} &= x_A(F_A''(\rho_0)(\tilde{\rho} - \rho_0)^2) + x_B(F_B''(\rho_0)(\tilde{\rho} - \rho_0)^2) \\ &\ll E^{emb}\end{aligned}\quad (8)$$

The contribution to the excess energy from the pair potential terms is (replacing for short $\sum V_{AA}(r_{ij})$ by v_A , and so on, and $x_B = x$, $x_A = 1-x$),

$$\Delta E^{pair} = x(1-x)\{2v_{AB} - (v_A + v_B)\} \quad (9)$$

We now introduce our proposition for the alloy potential based on the following points: *i*- Taking advantage of the result Eq. (8) we build up the non-linearity upon the pair potential alone (this is a simplification adopted for this case in particular; it can easily be removed in other cases and use either or both contributions); *ii*- we assume that V_{AB} is a function of both (x, r) that it can be separated into a product $h(x)u_{AB}(r)$, we then choose,

$$V_{AB}(x, r) = h(x) \frac{1}{2} (V_{AA}(r) + V_{BB}(r)) \quad (10)$$

This election of the cross pair potential allows us to describe any type of formation energy curves, giving an ideal solution for $h(x) = 1$, a regular solution with positive or negative heat of mixing for $h(x) \gtrless 1$, and an arbitrary complex heat of mixing for $h(x)$ a polynomial on x . We also see that without introducing a polynomial on x we can not go beyond symmetric formation energies (i. e. only L_0 in the expansion 4). Eq. 10 also shows that if the target function is a fourth order Redlich-Kister polynomial, so will $h(x)$ be. It provides then with a hint on what kind of function to use in the optimization procedure.

We replace now $V_{AB}(r_{ij})$ in Eq. 6 by $h(x) \frac{1}{2} (V_{AA}(r_{ij}) + V_{BB}(r_{ij}))$ and by minimizing the difference between this expression for the energy and the target formation energy (Eq. 5 and Table II), at the lattice parameter that minimizes the energy, we find the coefficients of $h(x)$, reported in Table 11.

TABLE II: Coefficients of the 4th order polynomial $h(x)$ in Eq. 10, with values extracted from a global minimization as explained in the text

h_0	h_1	h_2	h_3	h_4
0.883644	-0.059302	0.644634	-1.342524	0.918932

It is interesting to point out that if Eq. 8 gives a really small contribution, as is the case for these two pure element potentials in the effective representation, we can neglect altogether the contribution of the embedding terms and then, equating Eqs. 5 and 9 instead of minimizing a target function, we can define $h(x)$ the composition dependence of the cross potential through an identity, namely:

$$(h(x) - 1)(v_A + v_B) \simeq \sum_{p=0}^n L_p^\phi (1 - 2x)^p \quad (11)$$

The formation energy, the lattice parameter and the Bulk modulus of the resulting alloy are shown in Figs. 1. The Bulk modulus shows a small softening with respect to linearity of about 5 GPa at $x \simeq 0.5$, that in terms of the absolute value of B represents a change of 3%. The lattice parameter is linear within 0.1%. The formation energy in turn shows a curve indistinguishable from the

target function extracted from Ref. [6]. In summary, the potential reproduces extremely well the energy, lattice parameter, and bulk modulus.

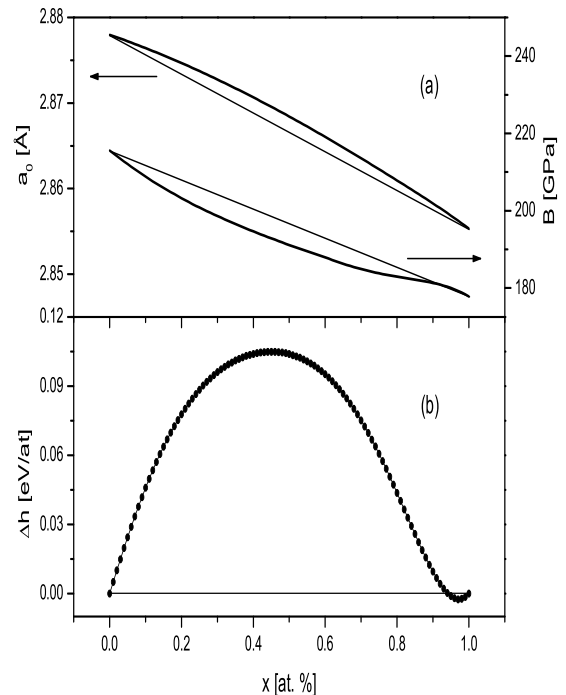


FIG. 1: Variations of Bulk modulus B, and lattice parameter a_0 (a), and formation energy of the alloy (b) as a function of Fe composition. Thin straight lines represent the linear interpolation corresponding to the ideal solution. Maximum departures for B and a_0 from ideal behavior are 2.5% and 0.1% respectively

Figure 2 shows that the polynomial $h(x)$ that results from the fitting procedure is a smooth function of x , close to $y = 1$, and that it crosses the line $h = 1$ at $x \simeq 0.94$, the composition at which the alloy behaves as ideal, as expected.

The final requirement for practical applications is to define the concentration x to be used in a simulation. There is some alternatives to choose $x(r)$ and a sound choice is to define the composition to be used in the cross term involving atoms at location i and j through the partial B-density (i. e. the component of the total density at atom i originated by B atoms at sites j) as,

$$x_{i,j} = \frac{1}{2}(x_i + x_j) = \frac{1}{2} \left(\frac{\rho_B^i}{\rho^i} + \frac{\rho_B^j}{\rho^j} \right) \quad (12)$$

This definition provides a well behaved function, adequate for force calculations [10].

Application of this potential requires small modifications to the standard EAM programs to implement the calculation of $h(x)$ and the derivatives of $V_{AB}(x, r)$.

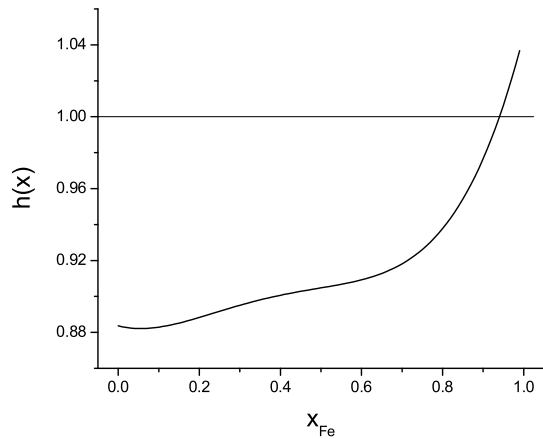


FIG. 2: Polynomial $h(x)$ representing the composition dependence of the cross potential versus Fe composition, according to Eq. 11

To test the new potential and its ability to predict ordering tendencies in the alloy, we run Monte Carlo simulations at 500K and determined the Warren-Cowley [9] short range order parameter of the first neighbor shell. Results are reported in Figure 3, together with the experimental results from Ref. [11]. Inversion of order in transition-metal alloy has been predicted long ago, with a change in sign at $x = 0.25$ for the case of Fe-Cr [12]. First measurements found it at $x = 0.10$ [11]. With the *ab initio* data used to develop this potential, change in ordering tendency occurs at $x = 0.06$, where the formation energy is zero. Also, with the maximum strength of the negative formation energy being only a few meV/atom, the maximum order obtained at 500K is only -0.025 , while the experimental result reports a value at a higher temperature (700K) that is close to its maximum possible value $-x/(1-x) \simeq -0.05$.

In conclusion, this is the first potential designed to adjust a complex behavior of a real alloy, namely an intricate heat of solution as reported by [6]. Even if the target function is probably not the definitive *ab initio* result for this alloy, the procedure proposed in this work can be used to reproduce any function of the composition. It is important to note that in this work, because we choose only one function to fit, the determination of the polynomial $h(x)$ Eq. 11 was the result of an optimization of an easy target function, while in the general case, all targeted properties, i. e. energy, B , a_0 , and others, have to be determined simultaneously by an optimization procedure as is usually done with empirical potentials, and that the natural way to achieve this is by considering the r -dependent part of the cross potential to also be an unknown function with parameters to be determined, instead of the simple average potential used here.

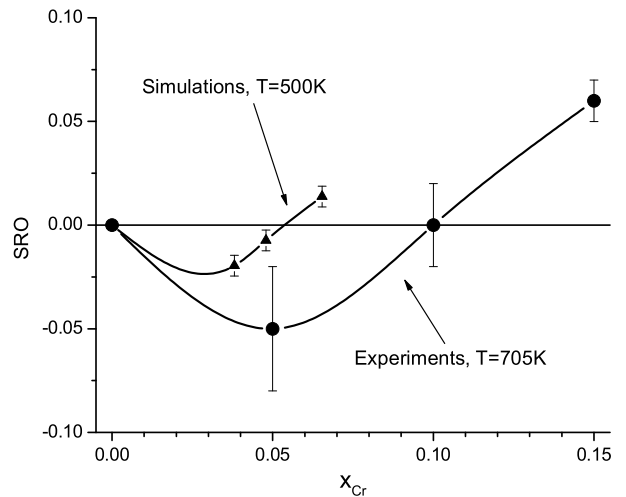


FIG. 3: Short Range Order parameter versus Cr composition as calculated by Monte Carlo simulations with the new potential and experimental measurements from [11]

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* Electronic address: caro2@llnl.gov

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