

**MODELLING THERMODYNAMICS OF ALLOYS FOR FUSION APPLICATION**—A. Caro, B. Sadigh, P. E. A. Turchi, M. Caro (Lawrence Livermore National Laboratory), E. Lopasso (Centro Atomico Bariloche, Argentine), and D. Crowson (Virginia Polytechnical Institute)

## OBJECTIVE

This research has two main objectives.

- On one side is the development of computational tools to evaluate alloy properties, using the information contained in thermodynamic functions to improve the ability of classic potentials to account for complex alloy behavior.
- On the other hand, to apply the tools so developed to predict properties of alloys under irradiation.

## SUMMARY

Atomistic simulations of alloys at the empirical level face the challenge of correctly modeling 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.

## PROGRESS AND STATUS

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 work, 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 have 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 hetero-atomic 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  $\alpha, \beta$  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  $\rho$ 's are the pair potentials and densities between  $\alpha-\beta$  pairs. Alloy properties are therefore described by the functions  $\rho_{AB}$  and  $V_{AB}$ . Depending on the model considered, the density functions do not always include the cross term  $\rho_{AB}$ . Different expressions for the embedding energies, densities, and pair potentials enclose 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 have 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 changes sign at low Cr composition [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 requires 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 ideal solution. Ideal solutions, by definition, have null excess quantities and their energy, Eq. (1), is given by the linear interpolation between the two constituents. To construct models that depart from ideality, 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  $F_{\alpha\beta}$ .

In this work, we follow the strategy of using potentials for the pure elements already available in the literature, thereby taking advantage of the continuous progress in the field. We then adjust the alloy terms, focusing on non-linearities built upon the pair potential cross term alone. To this end, we use 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, which for  $\alpha = A, B$  reads:

$$\begin{aligned}\rho_\alpha &= \rho_\alpha^o / \varrho_{\alpha,eq}^o \\ F_\alpha(\varrho_\alpha) &= F_\alpha^o(\varrho_\alpha^o) - F_\alpha^{o'}(\varrho_{\alpha,eq}^o) \cdot \varrho_\alpha^o \\ V_{\alpha,\alpha}(r) &= V_{\alpha,\alpha}^o(r) + 2F_\alpha^{o'}(\varrho_{eq}^o) \cdot \rho_\alpha^o(r)\end{aligned}\quad (2)$$

where the superscript  $o$  stands for original,  $\rho_{\alpha,eq}^o$  for the density on a lattice site at equilibrium, 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 authors with eventually very different and unrelated magnitudes of the densities. In this work, we use the Fe potential reported in [7] and the Cr potential reported in [8].

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

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

where  $g_{ref}$  is the compositional weighted free energy of the pure components, and  $g_{mix}$  is the free energy contribution from the entropy of mixing for a random alloy. 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  $p^{\text{th}}$ -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 the formation energy as 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  $(1-2x)$ . 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]:

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

with  $\tilde{\rho} = x_A \sum \rho_A(r_{ij}) + x_B \sum \rho_B(r_{ij})$ . The contribution of the embedding terms to the energy of mixing,  $\Delta E_{emb}$ , is:

$$\Delta E^{emb} = x_A(F_A(\tilde{\rho}) - F_A(\tilde{\rho} = 1)) + x_B(F_B(\tilde{\rho}) - F_B(\tilde{\rho} = 1)) \quad (7)$$

By making a taylor development we can see that this contribution is small:

$$\Delta E^{emb} = x_A F''_A(\tilde{\rho} = 1)(\tilde{\rho} - 1)^2 + x_B F''_B(\tilde{\rho} = 1)(\tilde{\rho} - 1)^2 \quad (8)$$

For the potentials we use in this work, the transformations (2) in fact drop the contribution of the embedding term to the formation energy down to  $\sim 1$  meV/atom at  $x \sim 0.5$ , making it negligible when compared to the target value for this alloy  $\sim 100$  meV/atom, [6]. This in practice leaves the pair potential as the sole contributor to the formation energy. The contribution to the energy of mixing from the pair potential terms is:

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

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 to use either or both contributions); ii- we assume that  $V_{AB}$  is a function, of both  $(x,r)$ , that 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  $h(x) \neq 1$ , 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 Eq. (4). Eq. (10) also shows that if the target function is a fourth order Redlich-Kister polynomial, so will  $h(x)$  be. It then provides us with a hint as to what functional form to use in the optimization procedure.

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

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

The formation energy, the lattice parameter, and the bulk modulus of the resulting alloy are shown in Fig. 1.

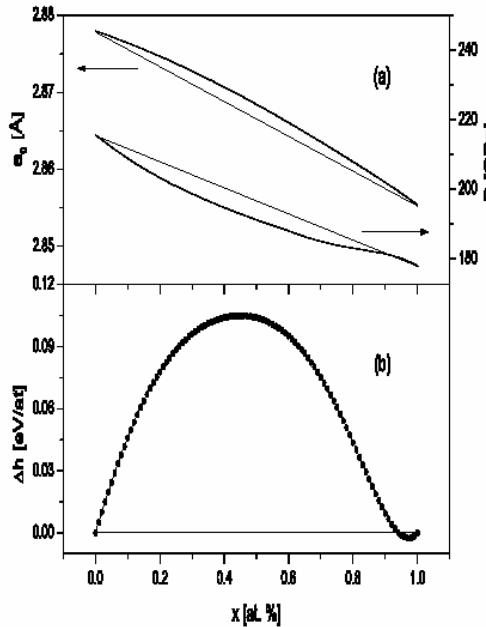


Fig. 1. Variations of bulk modulus  $B$ , and lattice parameter  $a_0$  (a), and formation energy of the alloy (b) as a function of Fe composition. Thin straight lines represent the linear interpolation corresponding to the ideal solution.

The bulk modulus shows a small softening with respect to linearity of about 5 GPa at  $x \sim 0.5$ , 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.

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

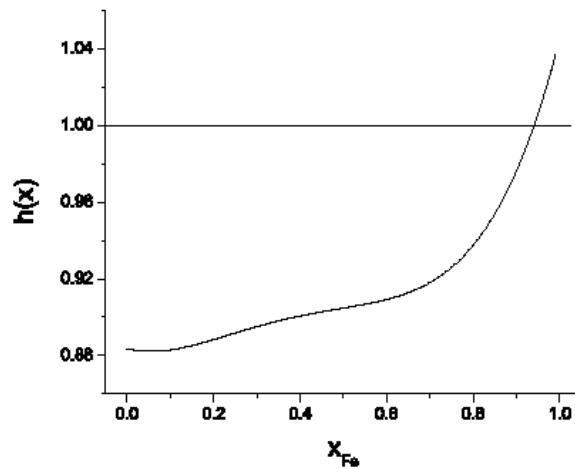


Fig. 2. Polynomial  $h(x)$  representing the composition dependence of the cross potential versus Fe composition, according to Eq. (11).

The final requirement for practical applications is to define the composition  $x$  to be used in a simulation, that for heterogeneous materials becomes a function of position. A sound choice is to use the partial B-density, i.e., the component of the total density at atoms  $i$  and  $j$  originated by B atoms at neighboring sites  $\{l\}$ . In this way, the composition to be used in a pair term involving sites  $i$  and  $j$  can conveniently be defined as:

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

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

To test the new potential and its ability to reproduce the ordering tendencies measured experimentally, we have run Metropolis Monte Carlo simulations in the transmutation ensemble with displacements at 500K and determined the Warren-Cowley [9] short range order parameter of the first neighbor shell. We used 500K because the order is so weak that at 700 K it is comparable to the noise. Results are reported in Fig. 3, together with the experimental results from Ref. [11] at 700K.

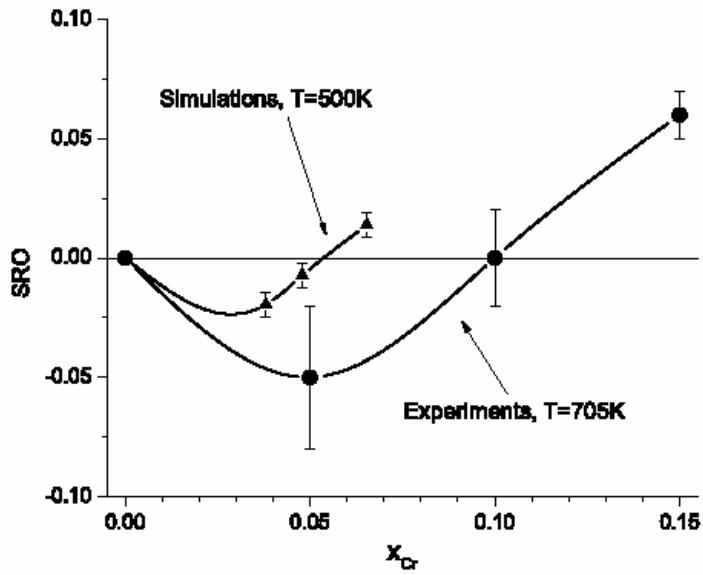


Fig. 3. Short Range Order parameter versus Cr composition as calculated by Monte Carlo simulations with the new potential and experimental measurements from [11].

Inversion of order in Fe-Cr has been predicted long ago, with a change in sign at  $x = 0.25$  [12]. First measurements found it at  $x = 0.10$  [11]. With the *ab initio* data we used to develop the potential, 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 at even higher temperature is close to its maximum possible value  $-x/(1-x) \sim -0.05$ . This discrepancy raises doubts about the accuracy of the *ab initio* prediction.

In conclusion, we present a general procedure to derive a potential for a complex alloy and apply it to the case of Fe-Cr using the heat of solution as reported by [6]. The procedure proposed in this work can be used to reproduce any function of the composition.

The target function is probably not the definitive *ab initio* result for this alloy, given the fact that if the positive side of the formation energy is compared with the database in CALPHAD, Fig. 4, we observe that the experimental maximum heat of formation is about 60 meV/atom, almost half the *ab initio* result. With 100 meV/atom, the miscibility gap would close at 2200K, well inside the liquid phase, in contrast to experiment. This points towards the necessity of a deeper understanding of this alloy, in particular the origin of the ordering vs. segregation tendency, before a definite accurate classic potential could be developed using the methodology proposed here.

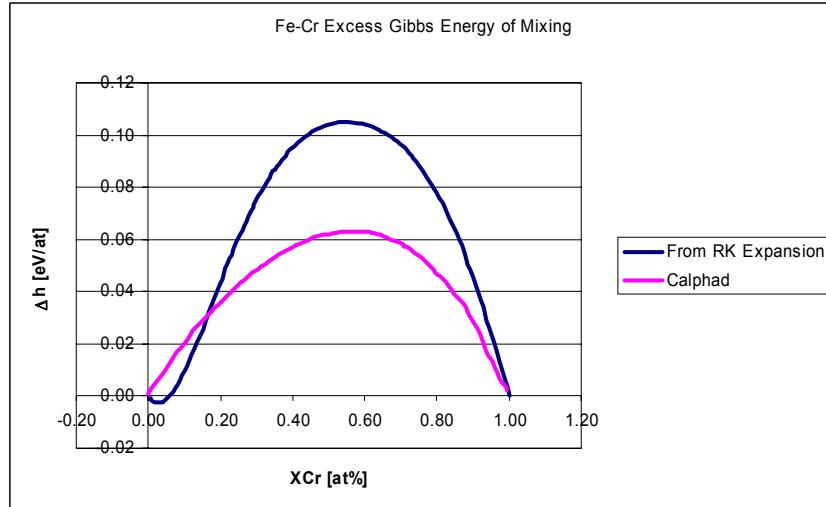


Fig. 4. Comparison between the heats of formation of the Fe-Cr solid solution as in the CALPHAD database and in Ref. [6].

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### Publications

- [1] A. Caro, M. Caro, E. M. Lopasso, P. E. A. Turchi, and D. Farkas, Thermodynamics of Fe-Cu Alloys as Described by the Ludwig-Farkas EAM Potential (submitted).
- [2] A. Caro, D. Crowson, and M. Caro, Classic many body potential for concentrated alloys and the inversion of order in Fe-Cr, Physical Review Letters (in press).