Classical Many-Body Potential for Concentrated Alloys and the Inversion of Order in Iron-Chromium Alloys

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Atomistic simulations of alloys at the empirical level face the challenge of correctly modeling basic thermodynamic properties. In this Letter 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 a 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 Letter, 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 heteroatomic systems, let us say binary alloys involving elements *A* and *B*, it reads

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

where α and β stand for elements *A* and *B* sitting at sites *i*

and *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 of 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 nonsymmetric 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 nonlinearity of energy vs composition, through the nonlinear functions $F_\alpha(\rho(x))$.

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 nonlinearities built upon the pair potential cross term alone. To this end, we use a representation that minimizes the nonlinear 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

$$\rho_\alpha = \rho_\alpha^o/\varrho_{\alpha,\text{eq}}^o,$$
$$F_\alpha(\varrho_\alpha) = F_\alpha^o(\varrho_\alpha^o) - F_\alpha^{o\prime}(\varrho_{\alpha,eq}^o)\varrho_\alpha^o, \qquad (2)$$
$$V_{\alpha,\alpha}(r) = V_{\alpha,\alpha}^o(r) + 2F^{o\prime}(\varrho_{\text{eq}}^o)\rho_\alpha^o(r),$$

where the superscript ^{o} stands for original, $\varrho_{\alpha,\text{eq}}^o$ for the density on a lattice site at equilibrium [$\Sigma_{j\neq i}\rho_{\alpha_i}(r_{ij}^{\text{eq}})$], and the prime $^\prime$ 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 allow 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

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

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

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

where L_p is the pth-order binary interaction parameter; in general, it is a function of temperature. Because of the complexity that represents fitting potentials to actual temperature dependent functions, in what follows we 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

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

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 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 $(1 - 2x)$. Table I gives the corresponding coefficients in electron volts.

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 be either A or B, but both are embedded in the same average environment, as discussed by Ackland and Vitek [2]:

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

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

The contribution of the embedding terms to the energy of mixing, ΔE^{emb}, is

$$\Delta E^{\text{emb}} = x_A[F_A(\tilde{\rho}) - F_A(\tilde{\rho} = 1)]$$
$$+ x_B[F_B(\tilde{\rho}) - F_B(\tilde{\rho} = 1)]. \qquad (7)$$

By making a Taylor development of F around $\tilde{\rho} = 1$ and using Eq. (2), we see that this contribution is quadratic in $(\tilde{\rho} - 1)$, and therefore small for small variations in $\tilde{\rho} - 1$:

$$\Delta E^{\text{emb}} = x_A F_A''(\tilde{\rho} = 1)(\tilde{\rho} - 1)^2 + x_B F_B''(\tilde{\rho} = 1)(\tilde{\rho} - 1)^2. \qquad (8)$$

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 ~ 1 meV/atom at $x \simeq 0.5$, making it negligible when compared to the target value for

TABLE I. Values of the Redlich-Kister expansion coefficients, Eq. (5), corresponding to $\Delta H_{\text{Fe}-\text{Cr}}^{\text{mix}}$ from Ref. [6], in eV.

L_0	L_1	L_2	L_3	L_4
0.415 66	0.081 413 4	−0.010 189 9	0.267 659	−0.248 269

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
0.883 644	−0.059 302	0.644 634	−1.342 524	0.918 932

this alloy ~ 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 [replacing for short $\Sigma V_{AA}(r_{ij})$ by v_A, and so on, and $x_B = x$, $x_A = 1 - x$],

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

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 nonlinearity upon the pair potential alone (this is a simplification adopted for this case in particular; it can easily be removed in other cases where TO uses either or both contributions). (ii) We assume that V_{AB} is a function, of both (x, r), that can be separated into a product $h(x)u_{AB}(r)$, and we then choose

$$V_{AB}(x, r) = h(x)\tfrac{1}{2}[V_{AA}(r) + V_{BB}(r)]. \qquad (10)$$

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 cannot go beyond symmetric formation energies [i.e., only L_0 in the expansion Eq. (4)]. Equation (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 $h(x)\tfrac{1}{2}[V_{AA}(r_{ij}) + V_{BB}(r_{ij})]$ and, by minimizing the difference between this expression for the energy and the target formation energy [Eq. (5) and Table I], at the lattice parameter that minimizes the energy, we find the coefficients of $h(x)$, reported in Table II.

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,

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

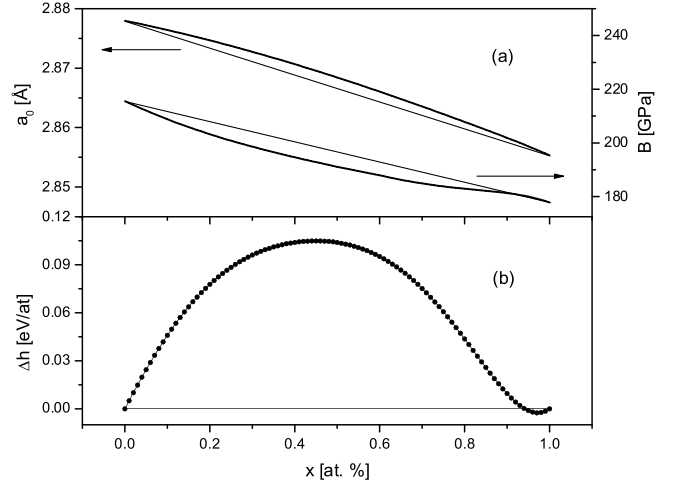The formation energy, the lattice parameter, and the bulk modulus of the resulting alloy are shown in Fig. 1. The bulk

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.

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.

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 $x \simeq 0.94$, the composition at which the alloy behaves as ideal, as expected.
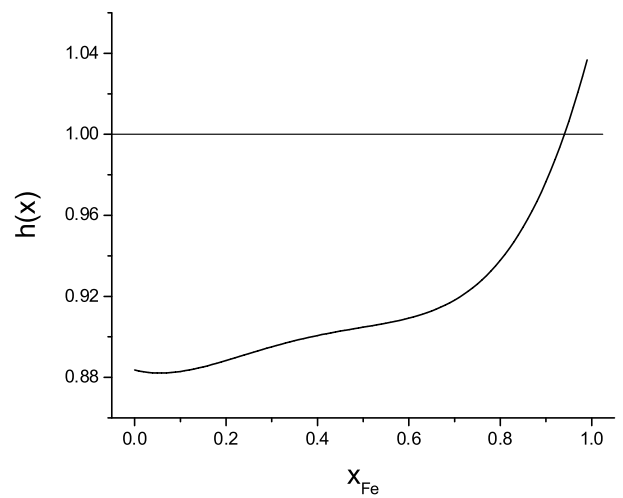

FIG. 2. Polynomial $h(x)$ representing the composition dependence of the cross potential versus Fe composition, according to Eq. (11).
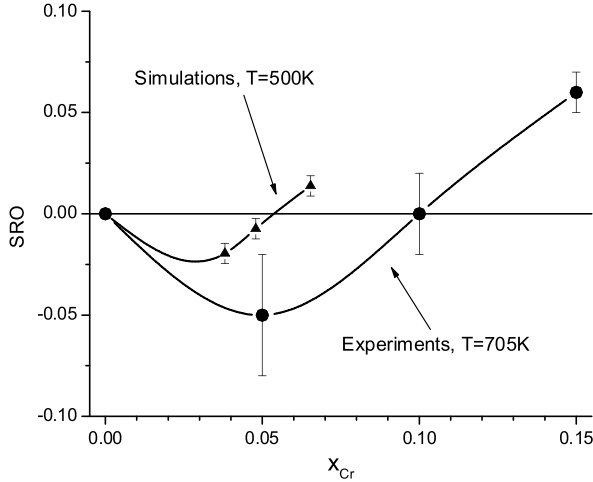
FIG. 3.   Short range order parameter versus Cr composition as calculated by Monte Carlo simulations with the new potential and experimental measurements from [11].

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). The density on a lattice site i, ϱ_i, is given by $\Sigma_l \rho_{\beta_i}(r_{il})$, where the sum runs over the neighbors of i, and β stands for elements A or B sitting at site l. The sum can be decomposed into partial contributions $\varrho_i = \Sigma'_l \rho_A(r_{il}) + \Sigma''_l \rho_B(r_{il}) = \varrho_i^A + \varrho_i^B$, where the $'$ in the sum means neighbors of i occupied by atoms of type A, and similarly $''$ means B occupancy. In this way, the composition to be used in a pair term involving sites i and j can conveniently be defined as

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

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 500 K and determined the Warren-Cowley [9] short range order parameter of the first neighbor shell. We used 500 K 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 700 K.

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 500 K is only -0.025, while the experimental result at even higher temperature is close to its maximum possible value $-x/(1 - x) \simeq -0.05$. 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]. Even if the target function is probably not the definitive *ab initio* result for this alloy, the procedure proposed in this Letter can be used to reproduce any function of the composition.

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