Long-range Finnis–Sinclair potentials for f.c.c. metallic alloys

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ABSTRACT

Many-body, long-range potentials of a Finnis–Sinclair type are formulated for the atomistic description of binary f.c.c. metallic alloys. These potentials are generalizations of the scheme constructed by Sutton and Chen (1990), for the atomistic modelling of f.c.c. elemental metals. The parameters for the alloy potentials are obtained directly from the parameters for the elemental metals, without any further adjustable fitting. Lattice parameters, elastic constants and enthalpy of formation of 45 binary, random f.c.c. alloys are calculated.

§ 1. INTRODUCTION

Models in which cohesion is represented solely by pair potentials lead to the Cauchy relation, $c_{12} = c_{44}$, between the elastic constants (Born and Huang 1968), a condition which does not hold for metals. In the absence of relaxation, pair-potential models overestimate vacancy formation energies by about a factor of two and relaxation improves the estimate only marginally. Pair-potential models also fail to describe the essential qualitative feature of relaxation at metallic surfaces, namely the inward relaxation (e.g. see the papers in Vitke and Srolovitz 1989).

An early extension (Maeda, Vitke and Sutton 1982) of pair-potential models, which improves the description of elastic properties of solids, was the addition of a volume-dependent cohesive energy term, varying with the local atomic volume. Although this scheme was implemented successfully for grain boundary relaxations by Sutton and Vitke (1982), the main difficulty with the approach was the precise definition of a local atomic volume, especially at a free surface.

To overcome some of these problems, three alternative schemes have been proposed, namely the embedded-atom model (EAM) (Daw and Baskes 1984, Foiles, Baskes and Daw 1986), the Finnis–Sinclair (FS) model (Finnis and Sinclair 1984) and the glue model (Ercolessi, Tosatti and Parrinello 1986). In their empirical construction and in their implementation, the models are very similar, although the physical justifications of the models have been presented in different ways by their authors. In all three schemes, the energetics of an arbitrary many-atom system is described by a sum of pair-wise contributions and a cohesive many-body functional.

In the FS model (Finnis and Sinclair 1984), the total energy of the ith atom in an elemental material is written as:

$$E_i^{FS} = \frac{1}{2} \sum_{j \neq i} U(r_{ij}) - \left[ \frac{1}{2} \sum_{j \neq i} \eta(r_{ij}) \right]^{1/2}.$$  (1)

$U(r_{ij})$ is a two-body repulsive interaction between atoms $i$ and $j$, separated by a distance $r_{ij}$. The square-root term, representing the cohesive many-body contribution, is motivated by an analogy (Ackland, Tichy, Finnis and Vitke 1988) with the second moment approximation to the tight-binding model (TBM) where the cohesive energy of a solid varies with the square root of its atomic coordination number (Heine 1980).
The functions $\eta(r_{ij})$ are two-body cohesive pair potentials, which in the framework of TBM can be interpreted as squares of hopping integrals. It is evident from eqn. (1) that both contributions to the total energy depend only upon the interatomic separations, and no angular forces are described.

Recently, Sutton and Chen (1990) developed long-range FS type potentials for ten f.c.c. metals. The long range nature of these potentials is considered essential to model the long-range interaction between a metallic tip in an atomic-force microscope above a metallic substrate (Sutton and Pethica 1990). The potentials were made long range by using simple inverse power forms for the functions $U(r)$ and $\eta(r)$ in eqn. (1). It was shown (Sutton and Chen 1990) that by using an inverse sixth power for $\eta(r)$, the second term on the right of eqn. (1) describes van der Waals pair interactions at long range and many-body unsaturated covalent bonding at short range. For each metal there were four parameters in the potential and it was shown that the potentials gave satisfactory descriptions of the cohesive energy, the lattice parameter and the three elastic constants. It was also shown that the potentials predicted that the f.c.c. crystal structure was always more stable than the b.c.c. structure, but the stabilities of the f.c.c. and h.c.p. crystal structures were indistinguishable.

The FS formalism has recently been extended to the study of alloys. In a detailed study Ackland and Vitek (1990) have applied variants of eqn. (1) to the case of ordered and random substitutional alloys of noble metals (Au, Ag, Cu) with and without local relaxation of atoms. They determined lower and upper bounds for the enthalpy of formation of a random alloy by considering a locally relaxed and an unrelaxed model respectively. For the Ag–Au system, the bounds coincide but for Ag–Cu and Au–Cu systems there are wide ranges of energies between the bounds. The lattice parameters were found to be less sensitive to the assumptions made about the relaxation.

In this Letter, we extend the work of Sutton and Chen (1990) by constructing long-range FS type potentials for binary f.c.c. alloys. The motivation for this work is again the desire to model both long- and short-range atomic interactions between unlike metallic species in the atomic-force microscope. The functions $U$ and $\eta$ entering our potentials are all inverse powers, as opposed to splines employed by most other authors. Apart from the computational efficiency which this choice brings, it has the added advantage that the third derivatives of the potentials are continuous, which is not normally the case for spline functions. Continuity of the third derivatives is essential if the temperature dependence of the potentials is to be incorporated to model thermodynamic properties at elevated temperatures, using the quasiharmonic scheme introduced by Sutton (1989). We have not found it necessary to fit any new parameters for the alloy potentials. Instead we have used a consistent set of four rules (eqn. (11) below) to derive the parameters for interactions between unlike atoms from those reported by Sutton and Chen for the elemental metals. Assuming an unrelaxed random-alloy model, we have calculated the lattice parameters, elastic constants and mixing enthalpies throughout a range of compositions for all 45 binary combinations of the ten f.c.c. metals considered by Sutton and Chen. We have obtained reasonable agreement with experimental data where available.

§2. The potentials

In the work of Sutton and Chen (1990), the total internal energy of a pure metal was expressed in the following FS form:

$$E^{FS} = c \left[ \frac{1}{2} \sum_{i<j} V(r_{ij}) - c \sum_i \rho_i^{1/2} \right].$$

(2)
where

\[ V(r) = \left( \frac{a}{r} \right)^n \]  

and

\[ \rho_i = \sum_{j \neq i} \left[ \frac{a}{r_{ij}} \right]^m. \]  

Here \( n \) and \( m \) are positive integers, \( a \) is the f.c.c. lattice constant and \( \epsilon \) is a parameter with the dimensions of energy. The parameters \( \epsilon, c, n \) and \( m \) were given by Sutton and Chen for the following ten f.c.c. metals: Ni, Cu, Rh, Pd, Ag, Ir, Pt, Au, Pb and Al.

Equations (2)–(4) are readily generalized to describe binary A–B alloys by expressing the Hamiltonian in the following FS form:

\[
\mathcal{H} = \frac{1}{2} \left[ \sum_{i} \sum_{j \neq i} \hat{\rho}_i \hat{\rho}_j V^{AA}(r_{ij}) + (1 - \hat{\rho}_i)(1 - \hat{\rho}_j)V^{BB}(r_{ij}) + \left[ \hat{\rho}_i(1 - \hat{\rho}_j) + \hat{\rho}_j(1 - \hat{\rho}_i) \right] V^{AB}(r_{ij}) \right] \\
- d^{AA} \sum_i \left[ \sum_{j \neq i} \hat{\rho}_j \phi^{AA}(r_{ij}) + (1 - \hat{\rho}_j) \phi^{AB}(r_{ij}) \right]^{1/2} \\
- d^{BB} \sum_i \left[ \sum_{j \neq i} (1 - \hat{\rho}_i) \phi^{BB}(r_{ij}) + \hat{\rho}_i \phi^{AB}(r_{ij}) \right]^{1/2}. \]  

The site occupancy operators \( \hat{\rho}_i \) are defined as follows:

\[ \hat{\rho}_i = \begin{cases} 1, & \text{if site } i \text{ is occupied by an A atom,} \\ 0, & \text{if site } i \text{ is occupied by a B atom.} \end{cases} \]  

The functions \( V^{AA}, V^{BB}, V^{AB}, \phi^{AA}, \phi^{BB} \) and \( \phi^{AB} \) are defined as follows:

\[
V^{AA}(r) = \epsilon^{AA} \left[ \frac{a^{AA}}{r} \right]^m, \quad V^{BB}(r) = \epsilon^{BB} \left[ \frac{a^{BB}}{r} \right]^m, \quad V^{AB}(r) = \epsilon^{AB} \left[ \frac{d^{AB}}{r} \right]^m. \\
\phi^{AA}(r) = \left[ \frac{a^{AA}}{r} \right]^m, \quad \phi^{BB}(r) = \left[ \frac{a^{BB}}{r} \right]^m, \quad \phi^{AB}(r) = \left[ \frac{d^{AB}}{r} \right]^m. \]  

The constants \( d^{AA} \) and \( d^{BB} \) are defined as follows:

\[ d^{AA} = \epsilon^{AA} a^{AA} \quad \text{and} \quad d^{BB} = \epsilon^{BB} a^{BB}. \]  

\( \epsilon^{AA}, \epsilon^{BB}, a^{AA}, m^{AA} \) and \( m^{BB} \) are equated with the parameters \( \epsilon, c, a, m \) and \( n \) of the pure A metal, as tabulated by Sutton and Chen (1990). Similarly, \( \epsilon^{BB}, \epsilon^{AA}, a^{BB}, m^{BB} \) and \( n^{BB} \) are equated with the parameters \( \epsilon, c, a, m \) and \( n \) of the pure B metal. Thus, only the four parameters \( \epsilon^{AB}, a^{AB}, m^{AB} \) and \( n^{AB} \) remain to be determined. These parameters are determined by assuming that the functions \( V^{AB} \) and \( \phi^{AB} \) may be expressed as follows:

\[
V^{AB} = (V^{AA} V^{BB})^{1/2} \quad \text{and} \quad \phi^{AB} = (\phi^{AA} \phi^{BB})^{1/2}. \]  

These relations lead to the following expressions for the remaining parameters:

\[
m^{AB} = \frac{1}{2} (m^{AA} + m^{BB}), \\
n^{AB} = \frac{1}{2} (n^{AA} + n^{BB}), \\
a^{AB} = (a^{AA} a^{BB})^{1/2}, \\
\epsilon^{AB} = (\epsilon^{AA} \epsilon^{BB})^{1/2}. \]  

\[ V^{AB} = (V^{AA} V^{BB})^{1/2} \quad \text{and} \quad \phi^{AB} = (\phi^{AA} \phi^{BB})^{1/2}. \]  

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m^{AB} = \frac{1}{2} (m^{AA} + m^{BB}), \\
n^{AB} = \frac{1}{2} (n^{AA} + n^{BB}), \\
a^{AB} = (a^{AA} a^{BB})^{1/2}, \\
\epsilon^{AB} = (\epsilon^{AA} \epsilon^{BB})^{1/2}. \]  

\[ V^{AB} = (V^{AA} V^{BB})^{1/2} \quad \text{and} \quad \phi^{AB} = (\phi^{AA} \phi^{BB})^{1/2}. \]  

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m^{AB} = \frac{1}{2} (m^{AA} + m^{BB}), \\
n^{AB} = \frac{1}{2} (n^{AA} + n^{BB}), \\
a^{AB} = (a^{AA} a^{BB})^{1/2}, \\
\epsilon^{AB} = (\epsilon^{AA} \epsilon^{BB})^{1/2}. \]
Thus, all parameters in the Hamiltonian, eqn. (5), may be obtained from the parameters for the pure metals which were tabulated by Sutton and Chen (1990). Our assumption that $V^{AB}$ and $\phi^{AB}$ are given by eqn. (10) was made on purely empirical grounds. For example, we found that setting $\epsilon^{AB} = (\epsilon^{AA} + \epsilon^{BB})/2$ led to very unsatisfactory predictions for the lattice parameters of the alloys. A theoretical discussion of arithmetic and geometric means for A–B interactions is given by Calvin and Reed (1971a,b), among others.

§ 3. Application to Random Alloys

3.1. The random-alloy model

We adopt a random f.c.c. alloy model in which sites are occupied by A and B atoms completely randomly, such that the alloy has the required average concentration. No relaxation of the atomic positions is considered, and only the enthalpy at 0 K is calculated. This is the standard random alloy model, as discussed by Ackland and Vittek (1990) for example.

The expectation value, $E'$, per atom of the Hamiltonian given by eqn. (5) of a random $A_xB_{1-x}$ alloy, where $c_A + c_B = 1$, is given by

$$E' = \frac{1}{2} \left\{ \sum_s Z_s [c_A^2 V^{AA}(r_s) + c_B^2 V^{BB}(r_s) + 2c_Ac_B V^{AB}(r_s)] \right\}$$

$$- c_A d^{AA} \left\{ \sum_s Z_s [c_A^2 \phi^{AA}(r_s) + c_B \phi^{AB}(r_s)] \right\}^{1/2}$$

$$- c_B d^{BB} \left\{ \sum_s Z_s [c_B^2 \phi^{BB}(r_s) + c_A \phi^{AB}(r_s)] \right\}^{1/2}.$$

(12)

$r_s$ is the radius of the $s$th coordination shell and $Z_s$ is the corresponding coordination number. Each $r_s$ and the three parameters $\alpha^{AA}$, $\alpha^{BB}$ and $\alpha^{AB}$, must be expressed in the same length scale. We choose the equilibrium lattice parameter $a^*$ of the random alloy as this universal length scale. In this way the energy, $E'$, of the random alloy is expressed as the following function of $a^*$:

$$E' = \frac{1}{2} c_A^2 S_{\text{m}AA} \left[ \frac{a^{AA}}{a^*} \right] + \frac{1}{2} c_B^2 S_{\text{m}BB} \left[ \frac{a^{BB}}{a^*} \right] + c_A c_B S_{\text{m}AB} \left[ \frac{a^{AB}}{a^*} \right]$$

$$- c_A d^{AA} \left( c_A S_{\text{m}AA} \left[ \frac{a^{AA}}{a^*} \right] + c_B S_{\text{m}AB} \left[ \frac{a^{BB}}{a^*} \right] \right)^{1/2}$$

$$- c_B d^{BB} \left( c_B S_{\text{m}BB} \left[ \frac{a^{BB}}{a^*} \right] + c_A S_{\text{m}AB} \left[ \frac{a^{AB}}{a^*} \right] \right)^{1/2}.$$

(13)

The parameters $S_{\text{m}AA}$, $S_{\text{m}BB}$ etc. are dimensionless f.c.c. lattice sums, that are defined as follows:

$$S_{\text{m}AA} = \sum_s Z_s \left[ \frac{a^{AA}}{r_s} \right], \quad \text{etc.}$$

(14)

At each alloy concentration $a^*$ is determined by the variational condition that

$$\frac{\partial E'}{\partial a^*} = 0.$$

(15)
Having determined the equilibrium lattice parameter for the random alloy we may calculate the elastic constants $c_{11}^e$, $c_{12}^e$ and $c_{44}^e$. These constants are given by

$$
\begin{align*}
    c_{11}^e &= \frac{1}{\Omega} \frac{\partial^2 E^*}{\partial e_{11}^2}, \\
    c_{12}^e &= \frac{1}{\Omega} \frac{\partial^2 E^*}{\partial e_{11} \partial e_{22}^*}, \quad \text{and} \\
    c_{44}^e &= \frac{1}{4\Omega} \frac{\partial^3 E^*}{\partial e_{12}^2},
\end{align*}
$$

(16)

where $\Omega$ is the atomic volume, $(a^*)^3/4$, and $e_{11}, e_{22}$ and $e_{12}$ are components of the strain tensor.

The enthalpy of mixing, $\Delta H$, per atom, at 0 K, may also be obtained trivially once $a^*$ is found:

$$
\Delta H = E^* - c_A E^A - c_B E^B,
$$

(17)

where $E^A$ and $E^B$ are the cohesive energies, per atom, of the elemental A and B metals.

### 3.2. Results

The equilibrium lattice parameter, $a^*$, was computed for a range of compositions for the 45 A–B random alloy combinations that may be obtained from the 10 f.c.c. metals considered by Sutton and Chen (1990). Sensible results were obtained in all alloy systems, but in reality solid solutions do not exist in all these systems and therefore we present results only in those systems where comparison with experimental results is possible. Tables of results for all 45 alloy systems are available from the authors on request. The potentials were truncated at a radius of 2 lattice parameters, which encompasses 140 neighbour atoms in 8 coordination shells. It should be noted that since the parameters reported by Sutton and Chen for the pure metals were computed with a cut-off radius of 10 lattice parameters, it was necessary to re-fit the parameters $\epsilon$ and $c$ in eqn. (2). They are given in the table.

In fig. 1 we show a comparison between computed equilibrium lattice parameters and available experimental data for solid solution alloys. Good agreement is obtained except possibly for the Ni–Al system, which may be due to the existence of ordered alloys in the system. Figure 2 shows a comparison between calculated elastic constants and available experimental data for solid-solution alloys. Again, reasonable agreement is obtained, although it is difficult to judge with such a sparsity of experimental data. The calculated enthalpies of mixing are compared with experimental measurements in fig. 3. Here the agreement is not so good, particularly for the Au–Cu system, where the

### Potential parameters $\epsilon$ and $c$ recomputed for a cut-off radius of 2 lattice parameters. The parameters $m$ and $n$ are the same as in Sutton and Chen (1990), and they are given here for completeness.

<table>
<thead>
<tr>
<th>Element</th>
<th>$\epsilon$ (eV)</th>
<th>$c$</th>
<th>$m$</th>
<th>$n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>1.5713 x 10^{-2}</td>
<td>39.755</td>
<td>6</td>
<td>9</td>
</tr>
<tr>
<td>Cu</td>
<td>1.2386 x 10^{-2}</td>
<td>39.755</td>
<td>6</td>
<td>9</td>
</tr>
<tr>
<td>Rh</td>
<td>4.9371 x 10^{-3}</td>
<td>145-658</td>
<td>6</td>
<td>12</td>
</tr>
<tr>
<td>Pd</td>
<td>4.1790 x 10^{-3}</td>
<td>108-526</td>
<td>7</td>
<td>12</td>
</tr>
<tr>
<td>Ag</td>
<td>2.5415 x 10^{-3}</td>
<td>145-658</td>
<td>6</td>
<td>12</td>
</tr>
<tr>
<td>Ir</td>
<td>2.4489 x 10^{-3}</td>
<td>337-831</td>
<td>6</td>
<td>14</td>
</tr>
<tr>
<td>Pt</td>
<td>1.9835 x 10^{-2}</td>
<td>34-428</td>
<td>8</td>
<td>10</td>
</tr>
<tr>
<td>Au</td>
<td>1.2794 x 10^{-2}</td>
<td>34-428</td>
<td>8</td>
<td>10</td>
</tr>
<tr>
<td>Pb</td>
<td>5.5772 x 10^{-3}</td>
<td>45-882</td>
<td>7</td>
<td>10</td>
</tr>
<tr>
<td>Al</td>
<td>3.3307 x 10^{-2}</td>
<td>16-460</td>
<td>6</td>
<td>7</td>
</tr>
</tbody>
</table>
Comparison between experimentally determined (Pearson 1967) solid-solution lattice parameters (Å), shown as points, and lattice parameters computed for the random-alloy model from eqn. (15), shown as solid lines.
Fig. 2

Comparison between experimentally determined (Simmons and Wang 1971) elastic constants (eV Å⁻³), shown as points, and elastic constants computed for the random-alloy model from eqn. (16).

Fig. 3

Comparison between experimentally determined (Hultgren, Orr, Anderson and Kelley 1963) enthalpies of mixing per atom in meV, shown by solid symbols, and computed enthalpies of mixing, shown by lines through open symbols, for the random-alloy model, eqn. (17).
sign of the calculated heat of mixing is wrong at all concentrations. As pointed out by Ackland and Vitek (1990) the enthalpy of mixing is particularly sensitive to whether local relaxation is allowed. In addition to ignoring local relaxation our calculated enthalpies are valid only at 0 K because we have ignored the temperature dependence of the enthalpy of mixing. But the experimental data shown in fig. 3 were all obtained at elevated temperatures. The enthalpy of mixing may also be sensitive to the existence of short-range order in the solid-solution alloys, another effect which is ignored in the random-alloy model. In view of all this it would be surprising if the random-alloy model gave enthalpies of mixing in agreement with experimental measurements. However, we believe this may well be a shortcoming of the random-alloy model rather than our potentials.

§4. Discussion

We have constructed Finnis–Sinclair type potentials for binary f.c.c. metallic alloys which combine a van der Waals attraction at long range with a many-body cohesive interaction at short range. The potentials were constructed specifically for atomistic simulations of interactions, over a wide range of distances, between clusters of unlike atoms. The parameters for potentials describing 45 alloy systems may be obtained directly from those given by Sutton and Chen (1990) for 10 f.c.c. pure metals. Thus, eqn. (11) is an interpolation scheme for generating parameters of potentials for alloys from those of the pure metals.

Using these potentials and the standard model of a random alloy, we obtain a reasonably accurate description of measured concentration dependencies of the lattice parameters and elastic constants of binary alloys which interpolates between the pure elements considered by Sutton and Chen (1990).

Finally, we note that the elastic stability of the alloy systems, characterized by the conditions $C_{11} > 0$, $C_{44} > 0$ and $C_{11} > C_{22}$, is guaranteed by these potentials, thus ensuring a mechanically stable model of binary alloy systems.

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References