Interatomic Potentials from First-Principles Calculations: the Force-Matching Method

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(June 26, 1993)

Abstract

We present a new scheme to extract numerically “optimal” interatomic potentials from large amounts of data produced by first-principles calculations. The method is based on fitting the potential to ab initio atomic forces of many atomic configurations, including surfaces, clusters, liquids and crystals at finite temperature. The extensive data set overcomes the difficulties encountered by traditional fitting approaches when using rich and complex analytic forms, allowing to construct potentials with a degree of accuracy comparable to that obtained by ab initio methods. A glue potential for aluminum obtained with this method is presented and discussed.

PACS numbers: 34.20.Cf, 61.50.Lt, 64.70.Dv
While first-principles methods for computer simulation in condensed matter are rapidly improving in speed and accuracy, classical interatomic potentials continue to constitute the only way to perform molecular dynamics (MD) or Monte Carlo computations on systems with a very large size (number of atoms $N \sim 10^4$–$10^6$) or for long simulation times ($t \sim$ nanoseconds). With the advent of massively parallel machines and the proper computer codes, simulations on the mesoscopic scale appear feasible, allowing one to address a whole new range of problems in the physics of defects, surfaces, clusters, liquids and glasses. However, obtaining accurate and realistic potentials constitutes a challenging problem. It is now well recognized [1] that fairly elaborate analytic expressions—involving for instance density-dependent terms, angular forces, or moment expansions—are necessary for a realistic description of most materials under different conditions (geometries, structures, thermodynamic phases). A typical potential is thus constituted by a number of functions combined in a complex way, and often nested one into another. Unfortunately, such powerful forms can make the task of fitting a potential to a given material quite formidable and cumbersome. There are often many possible ways to fit a set of experimental quantities within a given analytic framework, and rather arbitrary assumptions on the functions are usually made to reduce the number of parameters to a manageable level. Such assumptions could be the basic reason why potentials apparently good at $T = 0$ sometimes fail at finite temperature, or for geometries or local conditions not considered when the fit was made.

On the other hand, the development of first-principles methods—where forces on atoms are obtained by directly solving the electronic structure problem—has been very vigorous in the last decade [2,3], and evolved to a point where dynamical simulations of systems with $N$ of the order of 100–1000 and times $t$ of the order of picoseconds are within reach for an ever increasing number of physical systems. Therefore, it seems compelling to construct a bridge between these two research lines, making use of the large amount of information that can be obtained by first-principles methods to construct reliable potentials for computations on a much larger scale.

While one possible way to achieve this consists of trying to derive potentials from first-
principles theoretically by exploiting approximation schemes [4,5], we proceed here along
different, somewhat complementary lines. Namely, with realism of the final potential as the
main goal, we present a new method to process a large amount of output of first-principles
calculations (positions and forces), and combine this information with traditional fitting on
experimental quantities, obtaining a potential by a numerical optimization procedure.

We assume that the analytic form of the potential is defined by a number of single
variable functions whose arguments are simply obtained from the atomic coordinates. Such
is the case for essentially all the two-body and many-body potentials currently in use. For
example, a glue potential [6–8]

\[ V = \frac{1}{2} \sum_{ij} \phi(r_{ij}) + \sum_i U \left( \sum_j \rho(r_{ij}) \right) \]  

(1)
is defined by a pair potential \( \phi(r) \), an “atomic density” function \( \rho(r) \), and a “glue function”
\( U(n) \). Other potentials may have functions of bond angles or of other quantities. Let
\( \alpha \) indicate the entire set of \( L \) parameters \( \alpha_1, \ldots, \alpha_L \) used to characterize the functions.
To determine the “optimal” set \( \alpha^\ast \) we try to match the forces supplied by first-principles
calculations for a large set of different configurations with those predicted by the classical
potential, by minimizing the objective function

\[ Z(\alpha) = Z_F(\alpha) + Z_C(\alpha) \]  

(2)
with

\[ Z_F(\alpha) = \left( 3 \sum_{k=1}^{M} N_k \right)^{-1} \sum_{k=1}^{M} \sum_{i=1}^{N_k} |F_{ki}(\alpha) - F_{ki}^\circ|^2, \]  

(3)

\[ Z_C(\alpha) = \sum_{r=1}^{N_C} W_r |A_r(\alpha) - A_r^\circ|^2. \]  

(4)

In \( Z_F \), \( M \) is the number of sets of atomic configurations available, \( N_k \) is the number of atoms
present in configuration \( k \), \( F_{ki}(\alpha) \) is the force on the \( i \)-th atom in set \( k \) as obtained with
parametrization \( \alpha \), and \( F_{ki}^\circ \) is the reference force from first-principles. \( Z_C \) contains contri-
butions from \( N_C \) additional constraints. \( A_r(\alpha) \) are physical quantities as calculated with
parametrization $\alpha$. $A_r^\alpha$ are the corresponding reference quantities, which may be supplied either from the first principles calculation, or perhaps more likely directly from experimental data. $W_r$ are weights which are chosen at convenience.

The $M$ configurations do not need to be related to each other, and in fact it is desirable to include input data relative to different geometries and physical situations (clusters, surfaces, bulk, solid, defects, liquid, etc.) in the attempt to achieve a good potential transferability. In practice, one can use samples from high temperature \textit{ab initio} MD trajectories for various systems, thus obtaining a good representation of the regions of configuration space that they actually explore at finite $T$.

Expression (2) can be seen under two different points of view. If emphasis is given to $Z_F$, then the minimizing potential appears as the “best” approximation of the first-principles system, with $Z_C$ acting as a guide towards the correct region in the space of parameters. In fact, many properties (for instance, the formation energy of a defect) are not easily determined from the forces alone. Moreover, one could include terms aimed at correcting shortcomings of the first-principles method in use. If emphasis is given, instead, to $Z_C$, then the method looks like a conventional fit, but where the $Z_F$ term relieves the researcher from the enormous burden of guessing the shape of the functions constituting the model. $A_r^\alpha$ and $W_r$ can be maneuvered for tuning.

It should also be noted that invariance properties of the Hamiltonian must be recognized and taken care of by imposing additional, dummy constraints. For instance, a glue potential (1) is invariant under the transformations (a) $\rho(r) \rightarrow A\rho(r), U(n) \rightarrow U(n/A)$, and (b) $\phi(r) \rightarrow \phi(r) + 2B\rho(r), U(n) \rightarrow U(n) - Bn$. The two constants $A$ and $B$ are arbitrary and must be fixed by additional conditions, that can be enforced as further quadratic terms in eq. (3), as if they were constraints for physical properties. In contrast with the latter, these terms exactly vanish at the minimum.

In the present realization, the single variable functions constituting the potential are defined as third-order polynomials (cubic splines) connecting a set of points $\beta_i$, preserving continuity of the functions and of their first two derivatives across the junctions. The pa-
rameters $\alpha_l$ are a one-to-one mapping to the points $\beta_l$, chosen on the basis of computational convenience \[9,10\]. In the simplest case, $\beta_l = \alpha_l$. Particular boundary conditions, such as requiring a function and its first derivative to be zero at a cutoff distance $R_c$, are directly incorporated into the parametrization. A number of parameters of the order of 10–20 per function seems to give sufficient flexibility, and in fact using finer grids may give rise to noise problems (oscillations of the functions depending on the input set) in the spline-based formulation.

The computational engine of the method is a multidimensional minimization procedure for the objective function (2). To be prepared to deal with the presence of multiple local minima, we have implemented a simulated annealing algorithm in parameter space (described in \[9,10\]). However, we found it to be necessary only when starting from an initial guess very far from the optimal one. The basin of attraction of the optimal potential is sufficiently broad that a simple quasi-Newton method is adequate to reminimize $Z$ after small adjustments to the values of $A_r^\circ$ and $W_r$, or changes in the set of first-principles configurations. In a typical minimization run, $Z$ is evaluated a few thousand times. The force computations are carried out by using standard MD techniques such as neighbor lists to decrease computer time, and the computational resources can be compared to those requested by a classical MD code. In preliminary tests using MD trajectories generated by classical potentials \[9\], this scheme has proven to be able to reconstruct exactly the original potentials without any further assumption beyond the analytic form—within the precision allowed by the spacing between spline knots, and within the range of the function arguments sampled by the input data.

The first application of the force-matching method presented here is for aluminum. The reasons for this choice are threefold: (i) due to the absence of $d$ electrons, Al can be studied quite easily and accurately with present first-principles methods; (ii) the metallic character suggests the use of the relatively simple glue model \[4\], even if it has well known limitations (lack of angular forces); (iii) in spite of the simpler electronic structure, glue-like potentials obtained so far for Al seem to be less accurate than those for noble metals, and the validity
of glue schemes for Al has been recently questioned [11], making it worthwhile to investigate this issue further.

The potential has been parametrized by a total of \( L = 40 \) parameters (spline knots), of which 14 for \( \phi(r) \) and \( \rho(r) \), and 12 for \( U(n) \). The functions reach zero at \( r = R_c \), and at \( n = 0 \), by means of fixed additional spline knots. The first-principles data used as input have been extracted by trajectories of MD simulations using the local orbital density functional scheme described in [3]. We have processed a total of \( M = 85 \) sets of atomic configurations, of which 7 represent a bulk system with a vacancy (\( N = 107 \)) at \( T = 100 \) K, 10 the same system at 1750 K (undergoing melting), 20 an equilibrated bulk liquid (\( N = 108 \)) at 2650 K, 13 a (100) slab (\( N = 108, 100 \) K), 10 a \( N = 150 \) cluster at 1000 K, 25 the same cluster in the liquid state at 2200 K, for a total of 10633 force vectors included in Eq. (3).

We have used \( N_c = 32 \) additional constraints, 8 of which for the cohesive energy, the equilibrium lattice spacing \( a_0 \), the (unrelaxed) vacancy formation energy, the (unrelaxed) (111) intrinsic stacking fault energy, the (unrelaxed) (111) surface energy, the bulk modulus and the shear moduli \( C_{11} - C_{12} \) and \( C_{44} \), 22 to fit the energy and pressure to the universal equation of state [12] at 11 different lattice spacings \( (a/a_0) = 0.90, 0.94, 0.97, 1.05, 1.11, 1.20, 1.30, 1.40, 1.50, 1.60, 1.75 \), and the remaining 2 are related to the invariance properties of the potential described above. The weights \( W_r \) assigned to the constraints and the cutoff radius \( R_c \) for \( \phi(r) \) and \( \rho(r) \) have been adjusted by a trial-and-error procedure, where potentials were generated by minimizing (2) and then run through a test suite including evaluation of relaxed energies of defects and surfaces, surface relaxations, thermal expansion and a melting point estimate by zero pressure MD simulations. The final potential, shown in Fig. 1, has \( R_c = 5.56 \) Å (between the 3rd and the 4th neighbor shell in the fcc crystal), and corresponds to \( Z = Z_F + Z_C = 0.029 + 0.003 = 0.032 \) (eV/Å)\(^2\). \( \sqrt{Z_F} \approx 0.17 \) eV/Å is the root mean square (rms) deviation of force components, to be compared with the rms force component in the input data, 0.92 eV/Å. Such error is at least one order of magnitude smaller than that typical of empirical models [13]. Some properties of the potential are listed in Table 1.

It should be noted that no constraint was imposed on the phonon frequencies at the zone
boundary, so that they are mostly determined by the force-matching term. Surface energies are somewhat lower than in experiment, although they are higher than those predicted by other potentials of the same class [3]. Surface relaxations are very realistic—in particular, the rather uncommon surface expansion of Al(111) [22] is obtained—except that the contraction of Al(110) is not as large as in experiment. This discrepancy is already present with the first-principle method in use [14], and has been simply transmitted to the potential. The thermal expansion behavior, obtained by MD at zero pressure, is shown in Fig. 2. The melting temperature, corresponding to the discontinuity, has been determined with a precision of about 3 K by achieving solid-liquid coexistence in a constant enthalpy run for a system with 10752 particles, following the technique described in [15]. Thermal and melting properties are in remarkable agreement with experiment.

In conclusion, this first study shows that the force-matching method is a very effective tool to obtain realistic classical potentials with a high degree of transferability for systems which the \textit{ab initio} calculation technology is capable of treating. The number of such systems is rapidly increasing as electronic structure methods are improved and the computing power increases. The numerical optimization procedure at the heart of the method is expected to be well suited to handle easily the rich and complex analytic forms—including angular-dependent terms—required for a realistic modelling of covalent bonds, and considered difficult to fit so far. In fact, it could also be used to compare quantitatively different functional forms, on the basis of their accuracy in reproducing the \textit{ab initio} forces. It would also be of considerable help in the fitting of alloys, where the number of experimental properties available is usually rather limited.

We are indebted to Dave Drabold, Cathy Rohrer, Wei Xu and Sang Yang for useful discussions and suggestions. We especially thank Dave Drabold for providing the \textit{ab initio} data. This work has been carried out under the U.S. Department of Energy Grant No. DOE-BES (0) 76ER01198.
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FIGURES

FIG. 1. The three functions constituting the optimized glue potential for Al.

FIG. 2. Lattice parameter $a$ as a function of temperature for our optimized potential (solid line), compared with experimental data (dotted line). The jumps indicate the volume change on melting. In the liquid region, $a$ is defined as $(4\Omega)^{1/3}$ where $\Omega$ is the atomic volume, as in the fcc crystal.
TABLES

TABLE I. Experimental and calculated (with the optimized potential) values for equilibrium lattice spacing, cohesive energy, bulk modulus, elastic constants, phonon frequencies at the points X, L and K of the Brillouin zone, vacancy formation and migration energies, intrinsic (111) stacking fault energy, surface energy and surface relaxation between the two outmost layers for the (111), (100) and (110) surfaces, melting temperature, latent heat and volume change on melting. All the energies are at $T = 0$ and include relaxation effects.

| Parameter                  | exp. (Å) | calc. (Å) |
|----------------------------|----------|-----------|
| $a_0$                      | 4.032    | 4.032     |
| $E_c$ (eV/atom)            | 3.36     | 3.36      |
| $B$ (MBar)                 | 0.809 $^a$ | 0.809     |
| $C_{11}$ (MBar)            | 1.180 $^a$ | 1.181     |
| $C_{12}$ (MBar)            | 0.624 $^a$ | 0.623     |
| $C_{44}$ (MBar)            | 0.325 $^a$ | 0.367     |
| $\nu_L$ (X) (THz)         | 9.68 $^b$ | 9.29      |
| $\nu_T$ (X) (THz)         | 5.81 $^b$ | 5.80      |
| $\nu_L$ (L) (THz)         | 9.69 $^b$ | 9.51      |
| $\nu_T$ (L) (THz)         | 4.22 $^b$ | 4.02      |
| $\nu_L$ (K) (THz)         | 8.67 $^b$ | 8.38      |
| $\nu_T$ (K) (THz)         | 7.55 $^b$ | 7.50      |
| $\nu_T$ (K) (THz)         | 5.62 $^b$ | 5.34      |
| $E_{vac}^f$ (eV)           | 0.66 $^c$ | 0.69      |
| $E_{vac}^{in}$ (eV)        | 0.62 $^d$ | 0.61      |
| $E_{SF}$ (meV/Å$^2$)      | 7.5–9.0 $^e$ | 6.5       |
| $\gamma_{111}$ (meV/Å$^2$)| 71–75 $^f$ | 54.3      |
| $\gamma_{100}$ (meV/Å$^2$)| 71–75 $^f$ | 58.8      |
| $\gamma_{110}$ (meV/Å$^2$)| 71–75 $^f$ | 64.7      |
| Parameter               | Value            |
|------------------------|------------------|
| \(d_{12} (111)\) (%)  | \(+0.9 \pm 0.7\)  |
| \(d_{12} (100)\) (%)  | \(-1.2 \pm 1.2\) |
| \(d_{12} (110)\) (%)  | \(-8.5 \pm 1.0\) |
| \(T_m\) (K)           | 933.6            |
| \(L_m\) (eV/atom)     | 0.1085           |
| \(\Delta V_m\) (%)    | 6.5              |

\(^a\)Extrapolated classically to \(T = 0\) from data in Ref. [16].

\(^b\)Frequencies at 80 K from Ref. [17].

\(^c\)Ref. [15].

\(^d\)Ref. [19].

\(^e\)Ref. [21].

\(^f\)Estimates for an “average” orientation, Ref. [21].

\(^g\)Ref. [22].

\(^h\)Ref. [23].

\(^i\)Ref. [24]. Ref. [22] reports \(-8.4 \pm 0.8\).
