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

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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 aluminium obtained with this method is presented and discussed.

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 $N \sim 10^4$ – 10^7) 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

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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 dynamical simulations of systems with N of the order of 100–1000 and t of the order of picoseconds are now 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.

Potentials are generally defined by a number of single variable functions whose arguments are simply obtained from the atomic coordinates. For example, a glue potential [6-8]

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

is defined by a pair potential $\phi(r)$, an «atomic density» function $\rho(r)$, and a «glue function» $U(n)$. Other potentials may include functions of bond angles or of other quantities. Let α indicate the entire set of L parameters $\alpha_1, \dots, \alpha_L$ used to characterize the functions. To determine the «optimal» set α^* , 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

$$Z(\alpha) = Z_F(\alpha) + Z_C(\alpha), \quad (2)$$

with

$$Z_F(\alpha) = \left(3 \sum_{k=1}^M N_k\right)^{-1} \sum_{k=1}^M \sum_{i=1}^{N_k} |\mathbf{F}_{ki}(\alpha) - \mathbf{F}_{ki}^0|^2, \quad (3)$$

$$Z_C(\alpha) = \sum_{r=1}^{N_C} W_r [A_r(\alpha) - A_r^0]^2. \quad (4)$$

In Z_F , M is the number of sets of atomic configurations available, N_k is the number of atoms in configuration k , $\mathbf{F}_{ki}(\alpha)$ is the force on the i -th atom in set k as obtained with parametrization α , and \mathbf{F}_{ki}^0 is the reference force from first principles. Z_C contains contributions from N_C additional constraints. $A_r(\alpha)$ are physical quantities as calculated with parametrization α . A_r^0 are the corresponding reference quantities, which may be supplied either from the first-principles calculation, or directly from experiment. W_r are weights which are chosen at convenience. It is desirable to include input data relative to different geometries and physical situations (clusters, surfaces, bulk, defects, liquid, etc.) in the attempt to achieve a good potential transferability. In practice, one can use samples from *ab initio* MD trajectories for various systems, thus obtaining a good representation of the regions of configuration space that are actually explored at finite T .

Invariance properties of the Hamiltonian must be recognized and taken care of by 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*) $\phi(r) \rightarrow \phi(r) + 2B\rho(r)$, $U(n) \rightarrow U(n) - Bn$ [6]. 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. (4) 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 β_i , preserving continuity of the functions and of their first two derivatives across the junctions. The parameters α_i are a one-to-one mapping to the points β_i , chosen on the basis of computational convenience [9,10]. In the simplest case, $\beta_i = \alpha_i$. Particular boundary conditions, such as requiring a function and its first derivative to be zero at a cut-off 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.

The computational engine of the method is a 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, for the application presented below, 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 quasi-Newton procedure is adequate to re-minimize Z after small adjustments to the values of A_r^0 and W_r , or changes in the set of first-principles configurations. In a typical run, Z is evaluated a few thousand times. The force computations are carried out by using standard MD techniques to decrease computer time, and the computational resources can be compared to those required by a classical MD code for a long simulation. 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.

While the main purpose of this letter is to illustrate the force-matching method, we also briefly report about its first application on aluminium. A detailed report will appear elsewhere [10]. The reasons for choosing Al are threefold: i) due to the absence of d electrons, Al can be studied quite accurately with present first-principles methods; ii) the metallic character suggests the use of the relatively simple glue model (1), even if it has well-known limitations (lack of angular forces); iii) in spite of the simpler electronic structure, Al is known to be more difficult to model with glue-like potentials than noble metals. In particular, many existing potentials (see table I) predict values for melting temperature, vacancy migration energy, intrinsic (111) stacking fault energy and surface energies that are too low compared with experiment, and excessive thermal expansion. Discrepancies of about a factor two are not uncommon for these properties. Furthermore, 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 40 parameters, of which 14 for $\phi(r)$ and $\rho(r)$, and 12 for $U(n)$. First-principles data were obtained by trajectories of MD simulations using the local orbital density functional scheme described in [3]. We have processed $M = 85$ 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 10 633 force vectors included in eq. (3). We have used $N_c = 32$ additional constraints, of which 8 for the cohesive energy, the

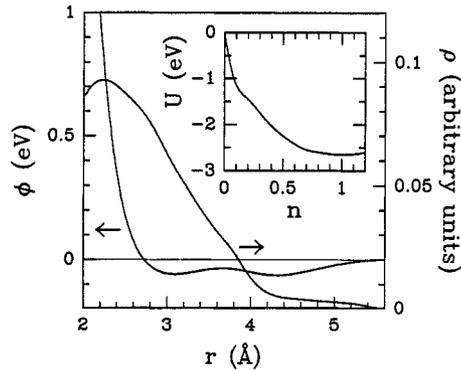


Fig. 1. - The three functions constituting the optimized glue potential for Al.

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 discussed above. The weights W_r assigned to the constraints and the cut-off radius R_c for $\phi(r)$ and $\rho(r)$ have been adjusted by a trial-and-error procedure, where potentials were generated by minimizing Z 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. The final potential, shown in fig. 1, has $R_c = 5.56 \text{ \AA}$, and corresponds to $Z = Z_F + Z_C = 0.029 + 0.003 = 0.032 \text{ (eV/\AA)}^2$. $\sqrt{Z_F} \approx 0.17 \text{ eV/\AA}$ is the root mean square (r.m.s) deviation of force components, to be compared with the r.m.s force component in the input data, 0.92 eV/\AA . For comparison, we have found on the same set of data $\sqrt{Z_F} \approx 0.33$ and 0.41 eV/\AA , respectively, for the potentials in refs. [13, 14]. To verify the stability of the potential against variations in the input data, we have made test runs where the number of configurations included was reduced by factors of approximately 2 and 10. As long as samples from each of the six trajectories used were still present in the set, the optimized potential was extremely close to that obtained from the full set.

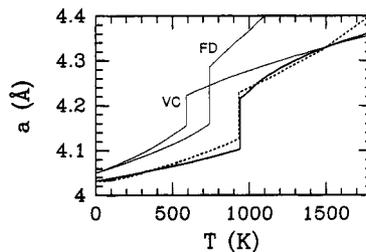


Fig. 2. - Lattice parameter a as a function of temperature for our optimized potential (thick solid line), for the Voter-Chen (VC) [13] and the Foiles-Daw (FD) [14] potentials (thin solid lines), compared with experimental data (dotted line). The jumps indicate the volume change on melting. Uncertainties in the determination of T_M are indicated in table I. In the liquid region, $a \equiv (4\Omega)^{1/3}$ where Ω is the atomic volume, as in the f.c.c. crystal.

TABLE I. – *Experimental and calculated (with the potential optimized in this work, and with those in ref. [13, 14]) 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, thermal-expansion coefficient at room temperature, melting temperature, latent heat and volume change on melting. All the energies are at $T = 0$ and include relaxation effects.*

	Experimental	This work	ref. [13]	ref. [14]
a_0 (Å)	4.032	4.032	4.05 ^(a)	4.05 ^(a)
E_c (eV/atom)	3.36	3.36	3.36	3.58 ^(a)
B (MBar)	0.809 ^(b)	0.809	0.79 ^(a)	0.81
C_{11} (MBar)	1.180 ^(b)	1.181	1.07	1.08
C_{12} (MBar)	0.624 ^(b)	0.623	0.652	0.68
C_{44} (MBar)	0.325 ^(b)	0.367	0.322	0.45
$\nu_L(X)$ (THz)	9.68 ^(c)	9.29	8.55	9.03
$\nu_T(X)$ (THz)	5.81 ^(c)	5.80	5.20	6.23
$\nu_L(L)$ (THz)	9.69 ^(c)	9.51	8.87	9.04
$\nu_T(L)$ (THz)	4.22 ^(c)	4.02	3.70	4.26
$\nu_L(K)$ (THz)	8.67 ^(c)	8.38	7.76	8.30
$\nu_{T1}(K)$ (THz)	7.55 ^(c)	7.50	6.87	7.32
$\nu_{T2}(K)$ (THz)	5.62 ^(c)	5.34	4.80	5.67
E_{vac}^f (eV)	0.66 ^(d)	0.69	0.63	0.62
E_{vac}^m (eV)	0.62 ^(e)	0.61	0.30	0.54
E_{SF} (meV/Å ²)	7.5–9.0 ^(f)	6.5	4.7	2.9
γ_{111} (meV/Å ²)	71–75 ^(g)	54.3	51.4	31.1
γ_{100} (meV/Å ²)	71–75 ^(g)	58.8	53.3	34.1
γ_{110} (meV/Å ²)	71–75 ^(g)	64.7	59.9	36.5
$d_{12}(111)$ (%)	+0.9 ± 0.7 ^(h)	+0.9	–1.6	–0.8
$d_{12}(100)$ (%)	–1.2 ± 1.2 ⁽ⁱ⁾	–1.5	–2.9	–1.7
$d_{12}(110)$ (%)	–8.5 ± 1.0 ^(j)	–4.6	–10.4	–5.4
$(1/a)(da/dT)(10^{-5} K^{-1})$	2.35	1.6	4.2	3.1
T_m (K)	933.6	939 ± 5	590 ± 15	740 ± 10
L_m (eV/atom)	0.108	0.105	0.053	0.098
ΔV_m (%)	6.5	8.4	4.9	9.5

(a) Fitted exactly on a different set of experimental data.

(b) Extrapolated classically to $T = 0$ from data in ref. [15].

(c) Frequencies at 80 K from ref. [16].

(d) Ref. [17].

(e) Ref. [18].

(f) Ref. [19].

(g) Estimates for an «average» orientation, ref. [20].

(h) Ref. [21].

(i) Ref. [22].

(j) Ref. [23]. Ref. [21] reports -8.4 ± 0.8 .

Some properties of the potential are listed in table I. It should be noted that no constraint was imposed on the phonon frequencies at the zone boundary, so that they are mostly determined by force matching. Surface energies are somewhat lower than in experiment, but higher than those predicted by the other potentials. Surface relaxations are realistic—in particular, the rather uncommon surface expansion of Al(111) [21] is obtained—except that the contraction of Al(110) is not as large as in experiment. The thermal-expansion behaviour, obtained by MD at zero pressure, is shown in fig. 2. The melting temperature, corresponding to the discontinuity, has been determined by achieving solid-liquid coexistence, following the technique described in [24]. Thermal and melting properties are in remarkable agreement with experiment. On the other hand, it must be stressed that, by design, this potential is not expected to be accurate for geometries with extremely low coordination—such as small

molecules—which were not included in the input set. As suggested by ref. [11], accuracy on the whole coordination range from 0 to 12 may well be beyond the capabilities of glue schemes.

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 *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. Quantities elaborate to fit with traditional methods, such as thermal properties (related to force anharmonicities), appear to be effectively transferred from the first-principles data. The numerical optimization procedure at the heart of the method is expected to be well suited to handle 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. It would also be of help in the fitting of alloys, where the number of experimental properties available is usually rather limited. Work along these lines is in progress.

* * *

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