Effective potentials for quasicrystals from ab-initio data

Peter Brommer* and Franz Gähler
Institut für Theoretische und Angewandte Physik
Universität Stuttgart

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Abstract

Classical effective potentials are indispensable for any large-scale atomistic simulations, and the relevance of simulation results crucially depends on the quality of the potentials used. For complex alloys like quasicrystals, however, realistic effective potentials are practically inexistent. We report here on our efforts to develop effective potentials especially for quasicrystalline alloy systems. We use the so-called force matching method, in which the potential parameters are adapted so as to optimally reproduce the forces and energies in a set of suitably chosen reference configurations. These reference data are calculated with ab-initio methods. As a first application, EAM potentials for decagonal Al-Ni-Co, icosahedral Ca-Cd, and both icosahedral and decagonal Mg-Zn quasicrystals have been constructed. The influence of the potential range and degree of specialisation on the accuracy and other properties is discussed and compared.

Keywords: force matching; quasicrystal; effective potential; molecular dynamics; ab initio

1 Introduction

Large-scale molecular dynamics simulations are possible only with classical effective potentials, which reduce the quantum-mechanical interactions of electrons and nuclei to an effective interaction between the atom cores. The computational task is thereby greatly simplified. Whereas ab-initio simulations are limited to a few hundred atoms at most, classical simulations can be done routinely with multi-million atom systems. For many purposes, such system sizes are indispensable. For example, fracture studies of quasicrystals require samples with several million atoms at least [1]. Diffusion studies, on the other

*e-mail: `p.brommer@itap.physik.uni-stuttgart.de`

hand, can be done with a few thousand atoms (or even less), but require very large simulated times of the order of nanoseconds [2], which also makes them infeasible for ab-initio simulations.

While physically justified effective potentials have been constructed for many elementary solids, such potentials are rare for complex intermetallic alloys. For this reason, molecular dynamics simulations of these materials have often been done with simple model potentials, resulting in rather limited reliability and predictability. In order to make progress, better potentials are needed to accurately simulate complex materials.

The force matching method [3] provides a way to construct physically reasonable potentials also for more complex solids, where a larger variety of local environments has to be described correctly, and many potential parameters need to be determined. The idea is to compute forces and energies from first principles for a suitable selection of small reference systems, and to fit the potential parameters so that they optimally reproduce these reference data. Hereafter, potentials generated in this way will be referred to as fitted potentials. Thus, the force matching method allows to make use of the results of ab-initio simulations also for large-scale classical simulations, thereby bridging the gap between the sample sizes supported by these two methods.

2 Force Matching

As we intend to construct potentials for complex intermetallic alloys, we have to assume a functional form which is suitable for metals. A good choice are EAM (Embedded Atom Method) potentials [4], also known as glue potentials [5]. Such potentials have been used very successfully for many metals, and are still efficient to compute, even though they include many-body terms. In contrast, pure pair potentials show a number of deficiencies when it comes to describe metals [5]. The functional form of EAM potentials is given by

$$V = \sum_{i,j<i} \phi_{k_i k_j}(r_{ij}) + \sum_i U_{k_i}(n_i), \qquad \text{with} \qquad n_i = \sum_{j \neq i} \rho_{k_j}(r_{ij}), \tag{1}$$

where $\phi_{k_i k_j}$ is a pair potential term depending on the two atom types k_l. U_{k_i} describes the embedding term that represents an additional energy for each atom. This energy is a function of a local density n_i determined by contributions ρ_{k_j} of the neighbouring atoms. It is tempting to view this as embedding each atom into the electron sea provided by its neighbours. Such an interpretation is not really meaningful, however. The potential (1) is invariant under a family of "gauge" transformations [5], by which one can move contributions from the embedding term to the pair term, and vice versa, so that it makes little sense to give any of them an individual physical interpretation.

In order to allow for maximal flexibility, and to avoid any bias, the potential functions in (1) are represented by tabulated values and spline interpolation, the tabulated values acting as potential parameters. This makes it unnecessary to guess the right analytic form beforehand. The sampling points can be chosen freely, which is useful for functions which vary rapidly in one region, but only slowly in another region.

The forces and energies in the reference structures are computed with VASP, the Vienna Ab-Initio Simulation Package [6, 7], using the Projector Augmented Wave (PAW) method [8, 9]. Like all plane wave based ab-initio codes, VASP requires periodic boundary conditions. For quasicrystals, this means that periodic approximants have to be used as reference structures. As ab-initio methods are limited to a few hundred atoms, those approximants must be rather small. For the systems studied so far, this was not a major problem, as the relevant local environments in the quasicrystal all occur also in reasonably small approximants. Icosahedral quasicrystals with F-type lattice may be more problematic in this respect. For these, small approximants are rare, and the force matching method requires a sufficient variety of reference structures.

Given the reference data (forces, energies, and stresses in the reference structures), the potential parameters (in our case: up to about 120 EAM potential sampling points for spline interpolation) then are optimised in a non-linear least square fit, so that the fitted potential reproduces the reference data as well as possible. The target function to be minimised is a weighted sum of the squared deviations between the reference data, denoted by the subscript 0 below, and the corresponding data computed from the fitted effective potential. It is of the form

$$Z = Z_{\mathrm{F}} + Z_{\mathrm{C}}, \qquad \text{with} \tag{2}$$

$$Z_{\mathrm{F}} = \sum_{j=1}^{N_A} \sum_{\alpha=x,y,z} W_j \frac{(f_{j\alpha} - f_{0,j\alpha})^2}{\boldsymbol{f}_{0,j}^2 + \varepsilon_j}, \quad \text{and} \quad Z_{\mathrm{C}} = \sum_{k=1}^{N_c} W_k \frac{(A_k - A_{0,k})^2}{A_{0,k}^2 + \varepsilon_k}, \tag{3}$$

where Z_F represents the contributions of the forces $\boldsymbol{f}_j$, and Z_C those of some collective quantities like total stresses and energies, but also additional constraints A_k on the potential one would like to impose. The denominators of the fractions ensure that the target function measures the relative deviations from the reference data, except for really tiny quantities, where the ε_l prevent extremely small denominators. The W_l are the weights of the different terms. It proves useful for the fitting to give the total stresses and the cohesion energies a higher weight, although in principle they should be reproduced correctly already from the forces.

We developed a programme named *potfit*, which optimises the potential parameters to a set of reference data. It consists of two largely independent parts. The first part implements a particular parametrised potential model. It takes a list of potential parameters and computes from it the target function, i.e., the deviations of the forces, energies, and stresses from the reference data. Wrapped around this part is a second, potential independent part, which implements a least square minimisation module, using a combination of a deterministic conjugate gradient algorithm [10] and a stochastic simulated annealing algorithm [11]. This part knows nothing about the details of the potential, and only deals with a list of potential parameters. The programme architecture thus makes it easy to replace the potential dependent part by a different one, e.g., one which implements a different potential model, or a different way to parametrise it.

3 Results and Applications

We generated several fitted potentials for decagonal Al-Ni-Co and icosahedral Ca-Cd quasicrystals, as well as Mg-Zn potentials suitable for both icosahedral and decagonal phases. In a first step, classical molecular dynamics simulations with simple model potentials were used to create reference configurations from small approximants (80–250 atoms). These included samples at different temperatures, but also samples which were scaled and strained in different ways. The approximants were carefully selected, so that all relevant local environments are represented. For those reference structures, the forces, stresses and energies were computed with ab-initio methods, and a first version of the fitted effective potential given by sampling points with cubic spline interpolation was fitted to the reference data. In a second step, molecular dynamics simulations with the newly determined potential were used to create new reference structures, which are better representatives of the structures actually appearing in that system. The new reference structures complemented and partially replaced the previous ones, and the fitting procedure was repeated. This second iteration resulted in a significantly better fit to the reference data. In order to test the transferability of the fitted potentials, further samples similar to the reference structures were created, and their ab-initio forces and energies were compared to those determined by the classical potentials. The deviations were of the same order as the deviations found in the potential fit, which shows that the fitted potentials transfer well to similar structures. For Al-Ni-Co, a force-matched potential is displayed in figure 1. Fitted potentials for Ca-Cd and Mg-Zn are not displayed here for space constraints, but are available from the authors.

The potentials developed for decagonal Al-Ni-Co quasicrystals are intended to be used in high-temperature diffusion simulations [2]. It is therefore important that they describe high temperature states well, which is achieved by selecting the reference structures accordingly. By using high temperature reference structures, the fitted potential is especially trained to such situations. As part of the potential validation, the melting temperature was determined by slowly heating the sample at constant pressure, and the elastic constants of decagonal Al-Ni-Co were determined. We actually have constructed two potential variants: Variant A gives excellent values for the elastic constants (Table 1), but produces a melting temperature which is somewhat too high. Conversely, variant B shows larger deviations in the elastic constants, but gives a very reasonable value of the melting temperature of about 1300 K. It is a general experience that with an effective potential it is often not possible to reproduce all desired quantities equally well at the same time.

In complex intermetallic systems there are many competing candidates for the ground state structure. This is the case also for complex crystalline systems. In principle, the ground state of these can be determined directly by ab-initio simulations, but for large unit cells this is extremely time-consuming, or even impossible. Classical potentials can be used to select the most promising candidates, and to pre-relax them, so that the time for ab-initio relaxation can be dramatically reduced. Potentials used for this purpose must be able to discriminate energy differences of the order of a meV/atom. This has been largely achieved with fitted potentials for the Mg-Zn and Ca-Cd systems, by using mainly near

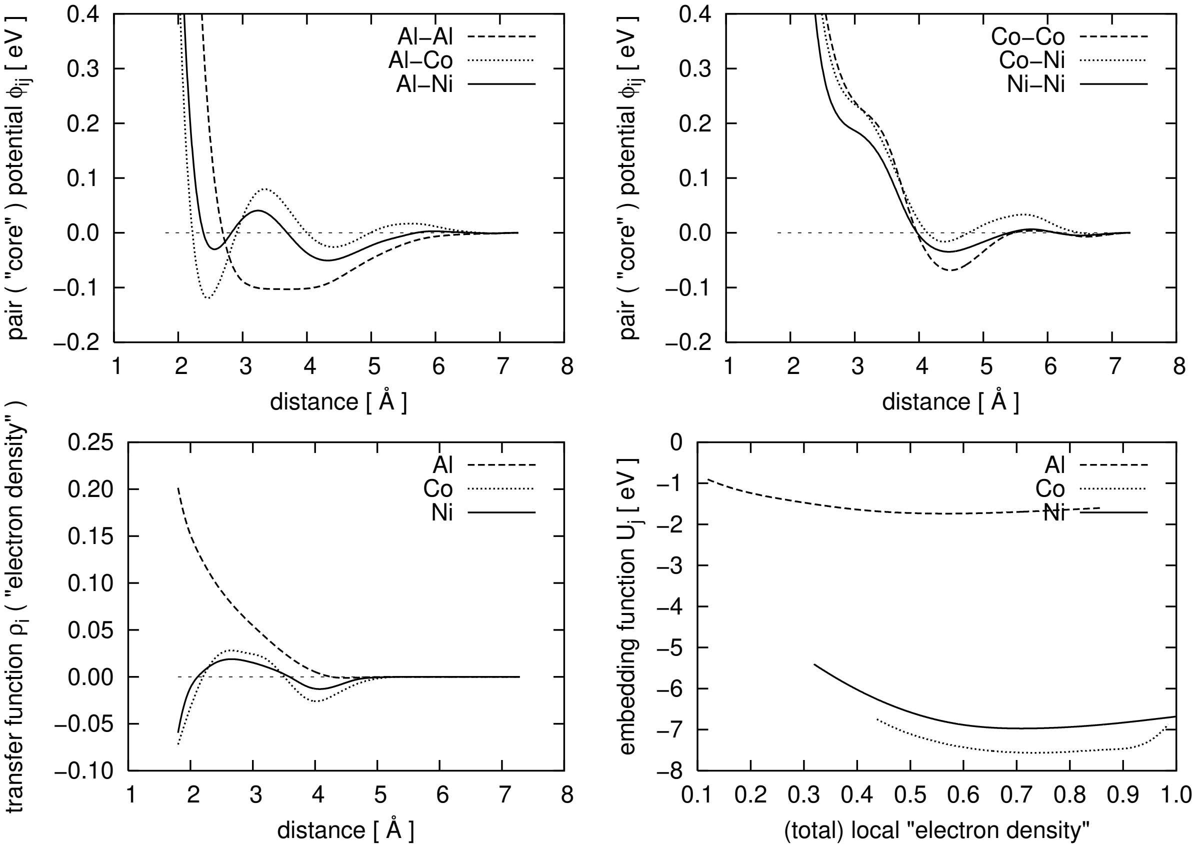

Figure 1: Potential functions for decagonal Al-Ni-Co

ground state structures as reference structures. Also, for this application it is important to choose a small ε_j in equation (3), so that small forces are also reproduced accurately. The so constructed Ca-Cd potentials have been used successfully for structure optimisations [13].

4 Discussion and Conclusion

The selection of the reference structures used for the potential fit largely determines the capabilities of the resulting potential. For a precise determination of the ground state, low temperature structures should be dominant in the reference structures, and it must be assured that even small forces and energy differences are reproduced accurately. For high temperature simulations, on the other hand, typical high temperature structures must be predominant in the reference structures. This opens the possibility to design specialised potentials for certain purposes by a suitable selection of reference structures. It should be kept in mind, however, that a fitted potential can only deal with situations it has been trained to. For instance, one should not expect a fitted potential to handle surfaces correctly, if it was trained only with bulk systems. Clearly, there is always a trade-off between the transferability and the accuracy of a fitted potential. A potential can be

Table 1: Elastic constants of decagonal Al-Ni-Co

[GPa]	c_{11}	c_{33}	c_{44}	c_{66} [a]	c_{12}	c_{13}
Exp. [12]	234	232	70	88	57	67
Pot. A	230	231	55	70	91	91
Pot. B	197	187	49	58	86	84

[a] In decagonal QC: $c_{66} = \frac{1}{2}(c_{11} - c_{12})$

made more versatile by training it with many different kinds of structures, but the more versatile it becomes, the less accurate it will be on average. Conversely, very accurate fitted potentials will probably have limited transferability.

For practical applications, the range of a potential is also an important issue, as it enters in the third power in the computational effort of molecular dynamics. Allowing for a larger potential range results in greater flexibility of the potential, which might improve its accuracy, but this comes at the price of a slower simulation. We therefore need a compromise between speed and accuracy. The potential range should only be increased as long as this can improve the potential quality. In a first step, our fitted potentials were constructed with a fairly generous range of about 7Å. It turned out, however, that especially the transfer function ρ_i did not make effective use of this range, and was essentially zero beyond 5Å. In a second fit we therefore restricted the range of ρ_i to 5Å, without significant loss of accuracy. This is one of the advantages of using tabulated functions: The system itself chooses the optimal functions, including the optimal range.

Force Matching has proven to be a versatile method to construct physically reasonable, accurate effective potentials even for structures as complicated as quasicrystals and their approximants. Our *potfit* programme makes it easy to apply this method to different systems, and is also easy to adapt for the support of further potential models. The potentials constructed so far have successfully been used in high temperature diffusion simulations of decagonal Al-Ni-Co [2], and in structure optimisation of approximants in the Zn-Mg and Ca-Cd systems. Further fruitful applications of the fitted potentials can certainly be expected, and we hope to apply our methods also to other complex alloy systems, where reliable potentials are still lacking.

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