



# Creation of models and parametrization of a classical force field for amorphous Al<sub>2</sub>O<sub>3</sub>/water interfaces based on Density Functional Theory



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## ABSTRACT

We present realistic models of amorphous alumina/water interfaces taking into account the chemical termination with hydroxyl groups and chemisorbed water molecules, as predicted by DFT-based MD simulations. On the basis of these models we parametrize a fixed-charges force field to describe the interactions within alumina and across the alumina/water interface, which can be seamlessly combined with biomolecular force fields via straightforward combination rules. The potential parameters are fitted to DFT reference calculations of water/surface interactions and are shown to be very well transferable to organic molecules adsorbing on alumina, in particular amino acid analogues. The correct protonation/deprotonation equilibria of the surface sites in contact with water solutions at different pH values is taken into account and implemented in the surface models and force field parameters via adjustments of the atomic point charges. The ability of our models and force field to predict experimental observables is demonstrated by unbiased calculations of the heat of immersion of alumina powders and of the adsorption free energy of glutathione disulfide on alumina in comparison with experimental data.

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## 1. Introduction

Aluminum oxide (alumina) particles and porous membranes are widely used as adsorbent materials in applications including protein separation and purification systems [1], drug carriers [2] or bio-catalysis [3–5]. All these applications rely on the adsorption of dissolved molecules to the alumina surface, typically from aqueous solutions. Atomistic details of the adsorption interactions are often elusive and difficult to characterize experimentally, although they are important to rationalize the dominant driving forces and thus improve the performance of the technical systems.

As far as atomistic simulations are concerned, most of the available work on alumina/water interfaces has so far employed ideally crystalline surface models [6,7]. However, it is well established that even particles with a crystalline core (e.g.  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>) present a few nm thick amorphous layers of aluminum oxyhydroxide at their outmost surfaces [8,9]. This calls for the development of new realistic models of interfaces between amorphous alumina and large molecules, such as organic drugs or proteins, in water solutions.

In order to achieve this goals, classical force-field potentials enabling the dynamical simulation of systems containing several hundred thousand atoms for at least several hundreds of nanoseconds are needed. Classical force fields describing the interactions in alumina bulk and dry surfaces are already available, either based on fixed charges [10,11] or including polarizability [12] and charge transfer schemes [13]. Potentials mapping the interactions between the surface and its surrounding environment have also been presented, for instance general oxide force fields [14], or parametrized for special cases such as crystalline alumina surfaces [7] or small molecule/small cluster interactions [15]. Moreover, a reactive force field of the 'ReaxFF' type has been developed for alumina/water systems [16], but to date it has not been extended to include also the interaction with organic or biological molecules.

In this work we present a simple fixed-charges potential and its parameter optimization, enabling molecular dynamics simulations of amorphous alumina surfaces in contact with water and dissolved biomolecules. In line with previous own work on oxide surfaces of silicon [17,18], titanium [19,20] and iron [21], surface/water interactions are described by a combination of Coulomb and Lennard-Jones terms, ensuring full compatibility with standard biological force fields such as AMBER [22], CHARMM [23] or OPLS [24] via straightforward combination rules [25,26]. The interactions between Al and O atoms within the oxide are described by

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a Buckingham potential in the original parametrization of Matsui [27], which we use to create models of amorphous  $\text{Al}_2\text{O}_3$  bulk via simulated annealing. This force field has been shown to reproduce well experimental results such as structure, density, bulk modulus, thermal expansion coefficient and melting temperature of alumina [27]. The O–H interactions of surface terminal groups are described with the parameter set of Adiga [28].

All newly determined force field parameters are fitted to reference calculations at the level of dispersion-corrected Density Functional Theory (DFT). DFT is also used to produce small models of amorphous surfaces in contact with water, accounting for the correct surface termination upon mixed dissociative and molecular  $\text{H}_2\text{O}$  adsorption on reactive surface sites. The accuracy of our force field parametrization is tested by comparing the heat of immersion of the surface computed in molecular dynamics simulations with available experimental values. Finally, the transferability of the potential and its ability to predict experimental observables for the case of biomolecule/alumina adsorption is demonstrated by calculating the free energy of adsorption of glutathione disulfide molecules on alumina [6] employing replica exchange with solute tempering combined with metadynamics (RESTmetaD) [20].

## 2. Computational details

The Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) [29] code is used for all calculations based on classical force fields (FF). We use a cut-off of 12 Å for the Lennard-Jones potential and of 8 Å for the Buckingham potential, while the Coulomb interactions are computed by means of the particle-particle particle-mesh Ewald solver [30]. The molecular dynamics simulations to compute the heat of immersion are performed at 300 K in the NVT ensemble, using an integration timestep of 2 fs and a Nosé-Hoover thermostat with a coupling constant of 0.2 ps.

The metadynamics (metaD) simulations are performed using the PLUMED package as a LAMMPS extension [31]. We employ the well-tempered metaD scheme [32,33] with a bias factor of 15 and use the  $z$  coordinate of the center of mass (COM) of the adsorbing dipeptide as the only collective variable. Gaussian hills with height of 0.03 eV and a full width at half-maximum of 0.3 Å are added every 0.5 ps. Furthermore, the replica exchange with solute tempering (REST) method [34] is employed to sample the internal degrees of freedom of the peptide. The combined RESTmetaD simulations are performed as described in [20], with 15 replicas in the NVT ensemble with temperatures between 300 K and 510 K separated uniformly by steps of 15 K, and attempting exchanges between neighboring replicas every 1 ps. The duration of each simulation is 200 ns, and the energies are averaged over the last 100 ns to compute the free energy of adsorption.

The static DFT simulations are performed with the Vienna Ab Initio Simulation Package (VASP) [35], using the PBE GGA exchange-correlation functional [36] and the DF2 correction to account for van-der-Waals interactions [37]. The simulations supercells are sampled with  $\Gamma$ -centered Monkhorst-Pack grids [38] for the integration of the Brillouin Zone. The electron-core interactions are described with the projector augmented wave (PAW) method [39], and the plane-wave basis set is expanded up to a kinetic energy cutoff of 400 eV.

The first-principles molecular dynamics simulation of the amorphous alumina surface in contact with water are performed with the Car-Parrinello scheme [40] as implemented in the LAUTREC code [41,42], using the PW91 [43] GGA functional and a cut-off of 540 eV. We use a fictitious electron mass of 300 au and a timestep of 5.0 au, increasing the mass of the hydrogen atoms to 2 amu. This ensures adiabaticity of the electronic system throughout the dynamics, without addition of an electronic thermostat.

The temperature of the simulation was progressively increased within 0.5 ps and then maintained constant to about  $350 \pm 20$  K by rescaling the atom velocities through a small adaptive (positive/negative) damping term applied to the motion of the atoms, which was updated every 100 timesteps.

## 3. Amorphous $\text{Al}_2\text{O}_3$ bulk structures and surfaces

In this section the strategy for the creation of amorphous alumina surfaces structures including the correct surface termination is introduced and validated. In line with a previous work of Adiga et al. [28], we describe the interactions within the alumina bulk and the terminal hydroxyl group by means of a Buckingham-Coulomb potential of the form:

$$V(r_{ij}) = A_{ij}e^{-\frac{r_{ij}}{\rho_{ij}}} - \frac{C_{ij}}{r_{ij}^6} + \frac{q_i q_j}{r_{ij}} \quad (1)$$

in which the atoms  $i$  and  $j$  are separated by a distance  $r_{ij}$  and the assigned parameters  $A_{ij}$ ,  $\rho_{ij}$  and  $C_{ij}$  are reported in Table 1. As an exception, Al–H and H–H atom pairs only interact through the Coulomb term.

In the original reference [28], the surface hydroxylation was modelled empirically, upon replacement of Al with H atoms in amorphous bulk structures before surface creation and MD annealing. We follow here a difference strategy, in which relatively small models of bulk amorphous structures and dry surfaces are first created with the classical force field, and then allowed to react with bulk water in DFT-based first-principles MD simulations. This allows the chemisorption process of water on reactive surface sites to be described at the full quantum level.

### 3.1. Amorphous bulk structures

Amorphous bulk structures are created with a hybrid ‘melt and quench’ technique following the scheme of Chagarov et al. [44]. Namely, Al and O atoms are randomly placed in the correct stoichiometry in a simulation box at the very low density of 0.9 g/cm<sup>3</sup>. The system is first annealed at 5000 K for 500 ps at constant volume and then the density is gradually increased to 3.2 g/cm<sup>3</sup> over 350 ps. After a further 400 ps equilibration, the system is cooled down to 300 K in 100 ps and further equilibrated for 1 ns. The strategy is applied to four different systems with increasing number of atoms (100, 200, 1000 and 2000 atoms).

In order to compare the obtained structures with other theoretical and experimental data, we calculate the radial distribution function (RDF)  $g_{ij}$  between pairs of atoms  $i$  and  $j$  as

$$g_{ij}(r) = \frac{\langle n_{ij}(r, r + \Delta r) \rangle}{\rho_j 4\pi r^2 \Delta r}, \quad (2)$$

where  $\rho_j$  is the bulk density of species  $j$  and  $\Delta r$  is a chosen step width (0.1 Å in our case). From  $g_{ij}$  we can compute the average first-neighbour distance  $d_{ij}$ , corresponding to the position of the first peak’s maximum, as well as the average nearest-neighbour

**Table 1**

Potential parameters parameter from Matsui [27] and Adiga et al. [28]. Al–H and H–H atom pairs interact only via the Coulomb term. The charges are  $q_{\text{Al}} = 1.4175 e$ ,  $q_{\text{O}} = -0.945 e$  and  $q_{\text{H}} = 0.4725 e$ .

	$A_{ij}/\text{eV}$	$\rho_{ij}/\text{\AA}$	$C_{ij}/\text{eV}\text{\AA}^6$
Al–Al	31570921.75	0.068	14.05
Al–O	28476.91	0.172	34.58
O–O	6462.67	0.276	85.09
O–H	9871.34	0.113	0.71

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