Ab-initio derived force-field parameters for molecular dynamics simulations of deprotonated amorphous-SiO₂/water interfaces

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Abstract

We present a set of Coulomb point charges and van der Waals parameters for molecular dynamics simulations of interfaces between natively deprotonated amorphous SiO_2 surfaces and liquid water, to be used in combination with standard biomolecular force fields. We pay

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particular attention to the extent of negative charge delocalisation in the solid that follows the deprotonation of terminal silanol groups, as revealed by extensive Bader analysis of electronic densities computed by Density Functional Theory (DFT). The absolute charge values in our force field are determined from best-fitting to the electrostatic potential computed ab-initio (ESP charges). Our proposed parameter set is found to reproduce the energy landscape of single water molecules over neutral and deprotonated amorphous SiO₂ surfaces and, after a minor adjustment, over thin oxide films on Si. Our analysis reveals a certain degree of arbitrariness in the choice of the DFT scheme used as the reference for the force-field optimisation procedure, highlighting its intrinsic limits.

1 Introduction

Silica is a constituent of many technologically relevant materials, ranging from rocks to glass and electronic devices. Furthermore, a film of amorphous silicon oxide forms on the surface of all silicon-based electronic components that operate in contact with air, making silica a crucial material also in processes such as the fracture of microelectromechanical systems (MEMS),¹ the wear of silicon tips for atomic force microscopy² and the hydrophilic bonding of silicon wafers.³ As a consequence, a large number of theoretical works (e. g. $^{4-10}$) based on both quantum-mechanical and classical atomistic methods have been performed to study the chemical and physical properties of this complex and polymorph-rich material. In particular, various classical interatomic potentials have been developed to extend the length- and time-scales with respect to those accessible by means of quantum-mechanical simulations. Examples of simple but widely used interatomic potentials, able to capture some properties of bulk silica, are those developed by van Beest et al. (BKS)¹¹ and by Vashishta et al.¹² The former has the simple form of a Buckingham and Coulomb pair potential, while the latter has a two-body and three-body functional form. More recently, more complex force fields have been proposed to improve such descriptions. For instance, an ab-initio based polarizable force field for bulk silica was developed by Tangney et al.¹³ and refined by Kermode et al.¹⁴ Another example is the charge-optimized many body potential recently proposed by Shan et al.¹⁵ for Si/SiO₂ interfaces and amorphous silica.

A particularly challenging task is the development of force fields that accurately describe silica/water interfaces. In its most stable adsorption configuration on silica surfaces, water dissociates, saturating silicon and oxygen dangling bonds with OH groups and H atoms, respectively.¹⁶ For example, the (001) surface of α -quartz features a dense network of geminal, mutually hydrogen-bonded silanols,¹⁷ leading to ordered water layers,^{18,19} whereas the amorphous silica surface is characterized by a typical distribution of isolated, geminal and h-bonded silanols.^{20–22} As they determine the degree of hydrophobicity, these silanol densities and distributions are crucial quantities that govern the behaviour of silica-based materials in a number of important processes. These include, for instance, the stress-corrosion cracking of glass,^{23,24} the potentially toxic dissolution of silica,²⁹ the adhesion of biomolecules to MEMS^{25,26} or biosensor surfaces,²⁸ and the biomineralisation of sponges.²⁷

In the last, biology-related examples, silica/water force fields should be easily usable in combination with existing biomolecular force fields such as AMBER, ³⁰ CHARMM³¹ or OPLS, ³² as well as with specific water models, such as the widely used TIP3P.^{33,34} The Clay force field³⁵ accurately describes the quartz/water interface and uses flexible SPC water, ³⁶ but is not designed to describe bulk silica as all bonding terms other then for the surface hydroxyls are absent. The potential of Lopes et al.³⁷ is a CHARMM model that captures well the properties of crystalline SiO₂ surfaces in combination with the TIP3P water model. Cruz-Chu et al.³⁸ developed a CHARMM water contact angle (CWCA) silica/water potential by fitting the silica's charges and van der Waals parameters to the contact angle of water on an amorphous silica surface. In spite of the similar functional form, the Clay, Lopes and CWCA empirical force fields have been parametrised very differently and a recent comparison of these models for the quartz/water interface can be found in.³⁹ Hassanali et al.⁴⁰ augmented the BKS potential with silanol three-body terms and used it in combination with the SPC/E water model.⁴¹ The potential of Cole et al.⁴² combines the Vashishta potential for silica and the Stillinger-Weber⁴³ potential for silicon in order to describe both silica and natively oxidized silicon in contact with liquid water, modelled with TIP3P. The force field of Pedone et al.⁴⁴ for the hydroxylated silica surface introduces explicit silanol hydrogen-bonding terms to describe silica polymorph surfaces. Fogarty et al.⁴⁵ recently proposed a reactive force field for the silica/water interface that is based on the variable bond order potential ReaxFF.⁴⁶

All of the aforementioned models describe neutral silica/water interfaces. However, this assumption is valid under strong acidic conditions only, since the isoelectric point of SiO₂ lies between 2 and 3. At larger pH values, deprotonation of silanol terminal groups takes place, leading to negatively charged surfaces.^{47,48} To account for realistically charged surfaces at neutral pH, the potential developed by Hassanali et al.⁴⁹ includes additional interaction terms to describe deprotonated O atoms. However, the BKS charges for the Si and O atoms (+2.4 and -1.2 e, respectively) are much larger than those of any of the other force-fields presented above, and appear to poorly perform when used for surface systems.⁵⁰ Indeed, atomic point charges of the surface atoms should be able to reliably reproduce the electrostatic potential in surface proximity calculated by quantum mechanical methods (ESP charges), as done for instance by Lopes et al.³⁷ This would ensure optimal mapping of the true electrostatic interaction energy in terms of a simple Coulomb potential, in line with the approach used to develop biomolecular force-fields. Moreover, the extent of charge redistribution around the terminal O⁻ atoms following silanol deprotonation has never been studied so far, motivating a thorough analysis based on quantum mechanical calculations, as presented in this work.

In our approach, the values of point charges for all atomic species are chosen according to extensive quantum mechanical calculations. The Coulomb interactions between water molecules and surface atoms are then augmented by a Lennard-Jones (LJ) potential to match as closely as possible the energy landscape of water molecules over a number of different surface sites, including deprotonated silanols. This is in line with the potential development for SiO₂ and Si/SiO_x surfaces previously performed by Cole et al.,⁴² which represents the starting point of our work. We would like to stress that our potential is specifically designed to describe amorphous, deprotonated SiO₂ surfaces in contact with liquid water and biomolecules, while we do not attempt to provide a faithful description of the mechanical properties of the silica matrix. Moreover, our simple potential does not allow us to describe any chemical surface reaction, unless used within QM/MM approaches specifically conceived to this purpose.⁵¹

This paper is organized as follows. After a description of the computational methods, we present our results for the ab-initio charge reference calculations on various deprotonated silica surfaces in Section 3. Here, we first carry out a Bader charge analysis⁵² to estimate the delocalisation of negative charge left on the system upon deprotonation. Subsequently, the absolute values of the classical charges in our force field are determined by the ones that best fit the electrostatic potential formed by the ab-initio electronic density (ESP charges). The combined information from both Bader and ESP charges is then used to propose a novel charge prescription for deprotonated silica surfaces. In Section 4, we present a validation of our charge prescription by comparing the energy landscape of single water molecules over larger SiO₂ clusters with reference DFT calculations on multiple adsorption sites and paths. As a final test, we present results for the heat of immersion of a neutral amorphous SiO₂ surface, calculated with different versions of the TIP3P water model, and with different choices of the charges for the surface hydroxyl groups.

2 Computational Methods

DFT calculations The DFT reference data for the validation of the force field are obtained using the PBE⁵³ and PW91⁵⁸ gradient-corrected exchange-correlation functionals and a variety of methods for treating dispersion forces. To perform calculations with the PBE functional and the van der Waals correction of Tkatchenko and Scheffler,⁵⁹ we employ the GPAW code,^{55,56} which uses a grid-based real-space implementation of the projector augmented wave (PAW) method.⁵⁴ A grid spacing of 0.16 Å is used, as suggested by convergence tests on atomisation energies in oxygen-containing molecules. Geometry optimisations are carried out using the fast inertial relaxation engine (FIRE) algorithm⁵⁷ until all forces are smaller than 0.025 eV/Å. Other dispersion-corrected DFT calculations are carried out with the QUANTUM ESPRESSO code,⁶⁰ using ultrasoft pseudopotentials and a 30 Ry cutoff for the plane-waves expansion. In particular, we use

the DFT-D, 61,62 vdW-DF1 $^{63-65}$ and vdW-DF2 66 methods. The Lautrec computer code 67 and the PAW formalism are used to perform the calculations with the PW91 functional. In all calculations the Brillouin zone is sampled by a 2×2 k-point Monkhorst-Pack distribution for the periodically repeated slab models, while only the Γ -point is considered in the calculations of isolated clusters. Spin-polarized DFT calculations are performed on charged systems to check that no spurious polarization arises as a consequence of deprotonation of our slab or cluster models.

MP2 calculations The MP2⁶⁸ calculations are carried out on a small cluster with stoichiometry $Si_4O_{13}H_9$, cut out from the central site of the original cluster used in the DFT calculations, as explained in detail in Section 3.3. The calculations are performed as a series of MP2 single-point energy calculations at each geometry, using the Gaussian03 software package,⁶⁹ along with the $6-31++G^{**}$ basis set^{70,71} and the frozen core approximation.

3 Reference DFT calculations of deprotonated SiO₂ surfaces



Figure 1: Model systems used for the calculation of atomic charge differences after the deprotonation of a terminal silanol group. (a) The (0001) surface of α -quartz in contact with liquid water. (b) A small periodically repeated amorphous SiO₂ slab in contact with liquid water. (c) A deprotonated amorphous SiO₂ cluster carved out from the large amorphous SiO₂ slab shown in (d) and terminated with OH groups to saturate the artificial dangling bonds.

The first question we would like to address is the extent of delocalisation of the negative charge left on a terminal Si-O⁻ group after deprotonation of a surface silanol. This information will be needed to accordingly modify the atomic charges of our force-field around the deprotonated



Figure 2: Differences between Bader charges before and after deprotonation of a terminal OH group for the (0001) surface of α -quartz in contact with liquid water. In plots (a) and (b) we show the atomic charge differences within the first 10 Å around the deprotonated site in order to mask artificially large charges on the bottom side of the slab due to polarisation effects.

surface site with respect to the charges used for the neutral system. To this aim, we perform a series of DFT calculations for three model systems (Fig. 1):

- a periodically repeated slab model of the (0001) surface of α -quartz;
- a periodically repeated model of amorphous SiO₂;
- an amorphous SiO₂ cluster carved out from a large periodically repeated amorphous SiO₂ slab.

From the charge density calculated both for the neutral and for the corresponding deprotonated surfaces, we compute atomic charges according to the Bader "atoms-in-molecules" partitioning scheme, ⁵² and analyse the atom-resolved charge differences. We note that many factors may contribute to non-negligible variations of the resulting charge differences, including in particular (i) the presence or absence of water above the surface; (ii) whether the system is fully relaxed after

deprotonation or the atomic positions are kept in the same configuration prior/after deprotonation; and (iii) the way the DFT calculations account for the presence of a net negative charge in the simulation cell. These questions are addressed in the rest of the Section, starting with the crystalline α -quartz model.



Figure 3: Structural properties of the periodically repeated amorphous system described in section 3.2. The bond angle (a) and bond length (b) distributions (solid lines) are fitted to a gaussian (dashed lines). Reference values for the structural properties are $110^{\circ}\pm10^{\circ}$ and $142^{\circ}\pm25^{\circ}$ for the O-Si-O and Si-O-Si bond angles and 1.62 ± 0.05 Å for the Si-O bond length respectively, whereas 2.2 g/cm³ is reported as the experimental bulk density (all values are taken from ¹²)

3.1 Crystalline SiO₂

We use an orthorhombic supercell of α -quartz oriented with the *z* axis perpendicular to the basal plane (0001) of the hexagonal unit cell, with optimized edge lengths of 10.06×8.71×11.24 Å³. The supercell is periodically repeated in the three Cartesian directions and a 13-Å -thickness vacuum is inserted in the *z* direction. The resulting surfaces are terminated with 2 hydroxyl groups per Si surface atom, and the void is filled with 37 water molecules (Fig. 1(a)). The amount of vacuum and the number of water molecules are chosen to give the density of TIP3P water at 300 K, and to allow for the rearrangement of water to form an orderless hydrogen bond network between top and bottom surfaces upon relaxation. Initially, we fully relax the geometry of the entire system, compute the Bader charges, remove a proton from one of the terminal hydroxyl group and recompute the Bader charges without further relaxation. We then relax all atomic positions of the deprotonated system (both the crystalline slab and the liquid water above it) and compute the

Bader charges once again. The atomic charge differences are shown in the graphs of Fig. 2(a,b) and represented as a colour-code in Fig. 2(c).

It can be seen that the atoms with larger charge differences are localized close to the deprotonated site prior to relaxation of the deprotonated system, but that the charge differences spread over a larger number of atoms, distant from the charged site, as a consequence of relaxation. This is a result of the screening that free H₂O molecules and bound-surface OH groups exert on the deprotonated site while they polarize themselves, re-arranging the hydrogen bond network in order to minimize the electrostatic energy of the system. Indeed, by integrating the charge differences in spherical regions centered on the terminal O^- atom, we see that a substantial amount of charge is taken up by the liquid water, and that this amount increases after relaxing the atomic positions (Fig. 2(d,e)). Notably, the absolute values of charge differences are rather small, even on the deprotonated site, and the negative charge is spread over all atoms of the system. This is clearly shown in Fig. 2(f), where the integral of the charge difference reaches the target value of -1 for distances that include the whole system. This effect is to be considered a general drawback of our ground-state DFT calculations, which tend to overestimate the extent of delocalisation of additional electronic charge as a consequence of the self-interaction error intrinsic in the approximate exchange-correlation functionals.⁷²

3.2 Amorphous SiO₂, periodic system

We produce a periodic amorphous silica system starting from 99 randomly distributed silicon and oxygen atoms in a $9.74 \times 16.87 \times 10.73$ Å³ cell. The bulk structure is initially annealed and cooled using the interatomic potential developed by Vashishta et al.,¹² and following the procedure described in Ref.⁴² We then insert a 10 Å vacuum layer along the *z* direction, saturate the resulting dangling Si and O bonds with OH and H groups, respectively, and perform a further geometry optimisation with DFT. The validity of the resulting surface is checked against structural properties of amorphous silica, as reported in Fig. 3. Seven hydroxyl groups are present on each side of the slab, corresponding to a surface OH density of 4.4 OH/nm², that falls within the experimental range

2.6-4.6 OH/nm².²² After this procedure, the size of the simulation cell is $9.64 \times 16.70 \times 24.12$ Å³, and the empty volume above the surface is filled with 60 water molecules.

The Bader charge differences upon deprotonation are qualitatively similar to those obtained for the crystalline sample. Namely, also in this case a pronounced effect of the polarisation of the liquid water in contact with the surface upon deprotonation, enhanced by the atomic relaxation, is evident (Fig. 4(a,b,c)). In this case, in addition to the calculation of the deprotonated system with a negatively charged unit cell, we perform a calculation in which the proton is removed from its hydroxyl group and added to a water molecule of the liquid, thus preserving the overall cell neutrality. After full relaxation of the system, the Bader charge differences on the atoms close to the deprotonated site are very similar to the previous case (unit cell with net charge of -1 e), as visible by comparing the graphs in Fig. 4(b) and Fig. 4(d). In the charge neutral system (Fig. 4(e)), the atoms near the deprotonated site are polarized during the relaxation. These atoms receive a larger net negative charge and the H₃O in (f) is more postitively charged than in the unrelaxed case.

In order to avoid the influence of water polarisation, we carry out a further calculation of the charge differences in the *absence* of liquid water. To do this, we start from the atomic positions of the surface slab obtained after full minimisation of the neutral system in the presence of water and calculate the Bader charge differences without further relaxation. In this case we obtain larger charge difference values, that amount in particular to -0.13 e for the terminal O^- atom, and to -0.05 e both for the first-neighbour Si atom and a neighbouring surface oxygen atom (Fig. 4(g)). Also in this case a non-negligible amount of charge (-0.15 e) is spread over the entire system. However, the initial drop of the integrated charge difference ((Fig. 4(h)) is indeed limited to the second-neighbour atoms to the deprotonated spot, as also visible from the colour-code analysis in Fig. 4(i).

3.3 Amorphous SiO₂ clusters

As a third system, we consider amorphous SiO_2 clusters carved out of a large amorphous SiO_2 slab, produced as described in Ref.⁴² The clusters are centred on the O atom of a surface silanol group and two different cluster radii of 9 and 11 Å are used (Fig. 1). The clusters are carved paying attention to preserve the integrity of all SiO₄ tetrahedra, and the artificially created dangling bonds are terminated with OH terminal group. This procedure ensured convergence of the electronic structure of the clusters in all cases. For this system, we did not perform any relaxation of the atomic positions (neither before nor after deprotonation of the central OH group), to avoid spurious effects due to the artificial cluster termination.

The results of the atom-resolved charge differences are summarised in Fig. 5. Importantly, no significant differences in the charge values on the atoms close to the deprotonated site are found for the two cluster sizes. Moreover, no significant differences are observed by performing the calculations of the deprotonated system (net charge of -1 e) either under periodic boundary conditions with a uniformly distributed positive countercharge, or under open boundary conditions (Fig. 5(a,b,d,e)). In the latter case, the wavefunctions vanish at the edges of the box and no compensation charges need to be added. For both cluster sizes, the major charge differences are limited, as in the case of the periodically repeated amorphous slab, on the deprotonated O⁻ atom, on its Si first neighbour and its O second neighbour. This is both visible in the graphs and in the colour-code representations in Fig. 5.

3.4 ESP charges for neutral and deprotonated surfaces

In the previous sections, we computed the atomic point charges according to the Bader electron density partitioning scheme, which presents the advantage of being independent of the used basis set (unlike e.g. the Mulliken charges) and of taking into account all valence electrons of the systems. However, the force fields commonly used to perform MD simulations of dissolved biomolecules are constructed using atomic point charges that best-fit the ab-initio electrostatic potential of the molecules outside an exclusion zone close to the atomic cores (so-called ESP)

charges). Generally, the boundary of the exclusion zone is defined as the envelope of spheres centered on the atoms with radii equal to the van der Waals radii of each atomic species. We have computed the ESP charges of all systems presented above before and after deprotonation of the same surface site, in the absence of liquid water over the surfaces, but using the atomic coordinates of the optimised neutral systems in the presence of water. The differences of the ESP charges are reported in the graphs of Fig. 6 for the (0001) α -quartz, the small periodic amorphous SiO₂ slab and the larger amorphous SiO₂ cluster. The results reveal a large scatter of the data, making a precise analysis of the charge differences based on the ESP scheme difficult. However, it is interesting to note that the charge differences on the deprotonated O⁻ atom are consistently in the range -0.12 to -0.2 e, in qualitative agreement (albeit generally larger) with the Bader charge differences obtained for the amorphous systems in the absence of water (about -0.12 e).

As far as the absolute values of the computed ESP charges are concerned, in the case of the neutral, amorphous SiO₂ cluster, we observe little variations of the charges on the atoms of the three species (Si, O, H). For Si, the charges vary from 1.49 to 1.87 e, with an average value of 1.64 e; for O, they vary from -0.70 to -0.97 e, with an average value of -0.83 e; for H, they vary from +0.40 to +0.52 e, with an average value of +0.44 e. Interestingly, the values do not differ for the O atoms bridging two Si atoms or for the O atoms of terminal OH group. Moreover, the average values for O and Si are very close to the values employed in existing force fields, such as the one formulated by Vashishta¹² and later modified by Cole et al.⁴² to describe SiO₂ or oxidized Si surfaces in contact with water (-0.8 and +1.6 e respectively). The absolute values of the average ESP charges are slightly lower in the case of the small amorphous SiO₂ slab (+1.44, -0.73, +0.43 e for Si, O, H, respectively), and even lower in the case of the crystalline surface (+1.33, -0.68, +0.38 e for Si, O, H). Notably, the latter set is quite close to the charges used in the force field for hydroxylated crystalline silica surfaces developed by Lopes et al.³⁷ (+1.08, -0.54, +0.32 e for Si, O, H). Finally, after deprotonation of a terminal OH, we compute absolute values of the ESP charges on the O⁻ atom of -0.89, -0.91, and -1.03 e for α -quartz, the small amorphous slab and the amorphous cluster, respectively.

3.5 Definition of the force field charges

As pointed out in the introduction of this paper, we base our force-field parametrization on the work of Cole et al.⁴² A revision of the parameters introduced in the original publication is necessary for two reasons. First, the original parametrization included an explicit "hydrogen-bond" interaction between the terminal OH groups and the water solvent, specific to the AMBER force field.³⁰ This interaction is now obsolete and not included in the novel AMBER force field versions, nor in other fixed-charges force fields such as e.g. CHARMM.³¹ Secondly, we deal here explicitly with deprotonated O⁻ terminal groups, which require ad-hoc charge modifications. We note that our parametrization will be set up focusing in particular on *amorphous* SiO₂ surfaces, but that we expect it to be reasonably transferable also for crystalline, hydroxylated SiO₂ surfaces.

The analysis of the Bader and ESP charges presented above allows us to formulate the novel parametrization in the following way:

- The charges on the Si and O atoms of the surface slab are kept to their original values of +1.6 and -0.8 e, respectively. This is both consistent with the potential developed by Vashishta et al. to simulate bulk SiO₂ materials and their surfaces, and is now justified by the computed values of ESP charges for amorphous SiO₂ (see above).
- The charge on the H atom of any terminal OH group is set to +0.4 e. This is justified by the computed values of ESP charges and allows us to keep the charges on the O atoms of both the bulk and the surface silanol groups equal to -0.8 e. Accordingly, all Si atoms are equivalent and charged +1.6e.
- Deprotonated, terminal O⁻ atoms are assigned a charge of -1.0 e, i.e. -0.2 e are added to the terminal atom as a consequence of the deprotonation. This value is slightly larger than the differences of Bader charges computed for the amorphous systems (in the absence of water), but is consistent with the larger charge difference values of the ESP charges, and with their absolute values for deprotonated systems.

• After removing a proton (charged +0.4 e) and increasing the negative charge on the terminal oxygen (-0.2 e), another -0.4 e must be distributed over the neighbouring atoms to ensure charge compensation and obtain a net charge value of -1 e. Since our Bader analysis shows that most of the charge delocalisation is limited to the second-neighbours, we decide to assign a charge difference of -0.1 e to both the first-neighbour Si atom and to the three second-neighbour O atoms (whose charges become +1.5 and -0.9 e, respectively). Although this distribution is to some extent arbitrary, and does not follow the computed Bader charge differences quantitatively, we remind that a considerable amount of charge differences in the DFT calculations are spread over the entire system. As this would be difficult to cope with in a force-field set-up, we report the whole changes within the second-neighbour zone, and spread them equally on the Si and O atoms for the sake of simplicity.

In summary, the charges assigned to the surface silanol groups are reported in Fig. 7. Note that the same values can be assigned to neutral or singly-deprotonated geminal $Si(OH)_2$ terminal groups (in the latter case, the O atom of the non-deprotonated OH would have a charge of -0.9 e).

4 Validation of the force field

In this Section, we compare the energy landscapes experienced by single TIP3P water molecules over either amorphous SiO₂ surfaces (clusters) or natively oxidized Si surfaces treated at the forcefield level with corresponding energy landscapes computed by ab-initio (DFT and MP2) methods. In all calculations the atomic positions are kept fixed, and the water molecules are moved rigidly along the direction perpendicular to the surface plane. The water-surface interactions are mapped onto a sum of pairwise Coulomb and Lennard-Jones (LJ) interactions between each pair of atoms *i* and *j* with atomic charges q_i and q_j separated by a distance $r_{ij} = r$:

$$V(r) = \frac{q_i q_j}{r} + \varepsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r} \right)^{12} - 2 \left(\frac{\sigma_{ij}}{r} \right)^6 \right], \tag{1}$$

Table 1: Charges and Lennard-Jones parameters for the interactions between water and SiO₂ surfaces. The parameters used in this work are compared to those of the other force fields, taken from Ref.,³⁹ and adapted to match the AMBER implementation. The units for q, σ and ε are electrons, kcal/mol and Å, respectively.

	Si	OB	OH	Н	OM
		This	work		
q	1.600	-0.800	-0.800	0.400	-1.000
σ	1.600	1.762	1.650	1.000	1.650
Е	0.300	0.261	0.150	0.021	0.150
		Lopes	et al. ³⁷		
q	1.080	-0.530^{a}	-0.540	0.320	
σ	2.000	1.770	1.770	0.224	
ε	0.600	0.152	0.152	0.046	
		Clay	FF ³⁵		
q	2.100	-1.050	-0.955	0.425	
σ	1.853	1.777	1.777	0.000	
ε	1.86×10^{-6}	0.155	0.155	0.000	
		CWO	CA^{38}		
q	0.900	-0.450	-0.660	0.430	
σ	2.147	1.750	1.770	0.224	
ε	0.300	0.152	0.152	0.046	
		Hassanal	li et al. ⁴⁹		
q	2.400	-1.200	-1.200	+0.600	-1.600

^{*a*} The OB charge depends on the selected surface.

where the LJ term is written according to the standard AMBER implementation. The LJ parameters σ_{ij} and ε_{ij} are commonly written as a combination of species-dependent parameters assigned to each atom:

$$\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j}; \ \sigma_{ij} = \sigma_i + \sigma_j.$$
 (2)

We note that different codes use slightly different analytic expressions for the Lennard-Jones interactions and accordingly different combination rules, so that the absolute values of the parameters need to be adapted (rescaled) depending on the specific code used.

In the present work, the atomic charges for the different species of the surface have been defined above (Section 3). For the LJ parameters, we use the ones determined in the original force-field development by Cole et al. A summary of the charges and LJ parameters of the model presented here compared with those of other force fields is reported in Table 1. These parameters can be used with the AMBER package without further rescaling.

4.1 Water over neutral amorphous surfaces

To test the performance of the charges and van der Waals parameters summarized in Fig 7 and Table 1 we compute the energy of a single TIP3P water molecule placed over our largest amorphous SiO_2 cluster (Fig. 1(c)) at increasing surface-molecule distances. We have chosen three different configurations (Fig. 8), in which:

- the H atoms of water point outwards, and the O atom is above the H atom of a central OH terminal group;
- the H atoms of water point inwards, one of each is above the O atom of the same OH group;
- the atomic positions of the water molecule are optimised with the force field in a region of the surface roughly in between three terminal OH groups.

For each configuration, the molecule is rigidly moved along the direction perpendicular to the surface plane. The obtained interaction curves are shown in Fig. 8, compared to reference curves obtained at the level of GGA-DFT (PBE functional), without and with the dispersion correction developed by Lundqvist and coworkers (DF2),⁶⁶ as implemented in the Quantum Espresso code.⁶⁰ We note in passing that other dispersion corrections, and notably the one developed by Tkatchenko and Scheffler (TS),⁵⁹ have been found to agree very well with the DF2 correction. A more thorough comparison between different functional and dispersion corrections will be presented later in Section 4.3 for the case of natively oxidized Si surfaces (see Fig. 11). In addition, for the first two configurations we perform also MP2 calculations of the same interaction curves, although the size of the amorphous SiO₂ cluster is reduced to cope with the greatly increased computational time involved (see insert of Fig. 10 and Section 2).

As visible from our results, there are striking differences between the computed ab-initio curves, which makes the precise definition of a *reference* to a great extent arbitrary. The classically

computed interaction energies perform differently for the two orientations of the water molecule over the three terminal OH groups. In the first case the force-field results agree well with the DF2 reference curve, while in the second case they agree better with the MP2 curve. In the third case, for which the MP2 calculation would be too expensive given the large size of the cluster, the potential reproduces reasonably well the DF2 curve. Compared to the original parametrization of Cole et al. and with the widely used force field by Lopes et al., our potential is generally closer to the ab-initio curves. In particular, it is reassuring to see that the position of the potential energy minimum is well-captured by the parameters summarized above, and also the depth of the potential well is to be considered, in the absence of an *absolute* reference, acceptable. This is remarkable given that no attempt has been made to adjust the values of charges previously defined on the basis of ESP calculations to fit the ab-initio interaction curves.

As a further test, we have computed the interaction energy of a water molecule lying flat on the (x,y) plane parallel to the surface of the large amorphous SiO₂ cluster, placed in a set of 36 positions spanning a discrete 5x5 Å² grid. The results obtained with our force field are compared with DFT calculations at the PBE+DF2 level in Fig. 9. The interaction energy in the potential minimum amounts to -0.18 eV for our force field and -0.20 eV for DFT. The position of the minimum in the force-field map is slightly shifted by about 0.5 Å in the x direction, resulting in an anticipated onset of repulsion when the probing molecule approaches one of the terminal OH group of the surface. However, the overall agreement between the classical results and the DFT reference is very good.

4.2 Water over deprotonated SiO₂

Even more remarkable is the level of agreement that we obtain between the interaction energy of a water molecule with a deprotonated terminal O^- atom of the amorphous SiO₂ surface computed classically and ab-initio (Fig. 10). In this case, as we expect the MP2 scheme to perform better than standard DFT because of the presence of a net negative charge, we perform all calculations for small model clusters and two opposite orientations of the water molecule over the O^- atom (as shown in the insets of Fig. 10). The results show that the chosen set of charges and van der Waals

parameters can be efficiently used to describe deprotonated surface sites, justifying <u>a posteriori</u> the choice made for the values of charge differences arising upon deprotonation. These results also support the approach undertaken here, of determining the extent of the charge difference delocalisation region by means of a Bader analysis and assigning the absolute charge values on the basis of ESP charges.

4.3 Natively oxidized Si surfaces

An important case system that we would like to simulate using the same force-field approach as for amorphous SiO₂ is the natively oxidized Si surface, for which the scheme by Cole et al. had been originally developed. The variability of the oxidation states of the Si atoms in the thin oxide film is taken into account by assigning the O atoms charges equal to -0.8 e and the Si atoms charges $q_{Si} = +0.4N_O$, where N_O is the number of first-neighbour O atoms. In this way, the standard charges of -0.8 and +1.6 e are recovered for four-fold oxygen coordination as in SiO₂.

When we place a TIP3P water molecule near a hydroxylated model of the oxidized Si(001) surface (sample taken from⁴²), we observe that, in the absence of the explicit hydrogen-bond term, the force-field charges for silanol groups previously used in Ref.⁴² (-0.6 and +0.2 e for O and H, respectively) fail to reproduce the reference DFT curves. Namely, for a water molecule with its H atoms pointing upwards placed on-top of the H atom of a terminal OH group we find strong *under*estimation of the interaction, whereas strong *over*estimation is found for the opposite orientation, with the water H atom on-top of the hydroxyl O atom (Fig. 11). Strong underestimation of the adsorption energy is also found for a water molecule in a local energy minimum (as determined by DFT with the PBE functional) over the surface. Unfortunately, the use of the revised charges defined in the present work (Fig. 7) improves only partially the underestimation in the first and third cases, while it makes the overestimation for the second case even worse. Therefore, we are forced to introduce an ad-hoc correction of the silanol charges specific to the case of thin oxide layers.

We obtain acceptable results if we assign to the H, O, and Si atoms of the silanol groups

charges of +0.4, -0.6, and +1.4 e, respectively. With respect to the parametrization of Cole, this corresponds to a shift of +0.2 e from the Si atom to the H atom of silanol. With these charges and the same, *unmodified* van der Waals parameters as reported in Table 1, we obtain a very good agreement between the classical interaction curve and the one computed at the level of PBE+TS vdW-corrected GGA for the third case (local minimum of potential energy). In the first two cases, the classical curves very slightly overestimate the interaction, by an amount that we consider fully acceptable at this level of approximation (see Fig. 11).

To summarise, in the general case of OH groups bound to Si atoms that are coordinated by less than four O atoms, our scheme assigns the charges in the following way:

- O atoms bridging two Si atoms are charged -0.8e;
- Si atoms not bound to any OH group are charged $+0.4N_O$, as before;
- H atoms of terminal OH groups are charged +0.4e;
- O atoms of terminal OH groups are charged -0.6e;
- Si atoms terminated with N_{OH} hydroxyl groups (generally 1) are charged $+0.4N_O 0.2N_{OH}$.

For a final validation test, we have computed interaction energy curves for a water molecule close to a *deprotonated* site of the natively oxidized Si surface. The results are reported in Fig. 12, together with a representation of the chosen system (the molecule is initially minimized at the PBE level and then shifted rigidly along the *z* axis normal to the surface) and the set of charges used for neutral and deprotonated silanols. In the case of deprotonated, terminal O^- atoms, the same corrections as for the case of amorphous SiO₂ are applied, namely -0.2 e to the O^- atom, -0.1 e to the first-neighbour Si and -0.1 e to the second neighbours (either O or Si, depending on the oxidation state of the central Si). The classical curve only slightly overestimates the interaction energy calculated at the PBE+TS, van-der-Waals-corrected GGA level. This is consistent with the curves obtained for the small am-SiO₂ clusters, (Fig. 12) where the PBE+TS interaction energy underestimates the (probably more reliable) MP2 result, and the force field nicely matches the

latter. Therefore, we can safely conclude that the proposed modification of the O and Si charges of silanol groups (+0.2, -0.2 e, respectively) are the *only corrections* to the general SiO₂ force-field scheme necessary to guarantee acceptable transferability to the case of natively oxidized surface. In particular, both the van der Waals parameter set and the charge differences due to OH deprotonation remain unchanged.

As a side observation, we would like to point once again towards the considerable variation of the interaction energies calculated with several dispersion correction schemes and standard GGA functionals (PBE and PW91), visible in particular in Fig. 11. In the absence of chemically accurate ab-initio reference calculations (ideally beyond MP2), which are not easily practicable for systems of this size, we are bound to a putative error bar that can amount to as much as 20% of the total interaction.

4.4 Heat of immersion of amorphous SiO₂

As a final test of the performance of our parameter set, we compute the heat of immersion of the neutral amorphous SiO₂ surface slab shown in Fig. 1(d). In particular, we perform the calculation using three slightly different modifications of the TIP3P water model, namely (i) the original TIP3P, (ii) the so-called modified TIP3P (mTIP3P) where the LJ parameters of the H atoms are explicitly considered, and (iii) the modification by Price and Brooks introduced to take into account small differences in the electrostatic interaction energy calculated with the Ewald method rather than via truncated Coulomb interactions.⁷³ For each water model, we compute the heat of immersion for increasing values of the charges of terminal OH groups, and with the LJ parameters reported in Table 1. The heat of immersion E_{im} is calculated from the difference between the average total energy of the system in contact with water $E_{interface}$ and the average total energies of the two separate components, namely the hydroxylated dry silica surface E_{silica} and the bulk water E_{water} , obtained in MD simulations at constant temperature (300 K) and pressure (1 atm): $E_{im} = (-E_{interface} + E_{silica} + E_{water})/A$, with $A = 1.85 \cdot 10^{-17} \text{ m}^2$ being the total area of the top and bottom surfaces of the silica slab.

Table 2: Calculated heat of immersion of neutral $am-SiO_2$ for different OH charges and TIP3P modifications.

	$E_{im} [\mathrm{mJ/m^2}]$				
OH charges	mTIP3P	TIP3P	TIP3PEw		
-0.6, +0.2	451.1	352.5	340.6		
-0.7, +0.3	276.7	178.1	166.2		
-0.8, +0.4	102.8	4.2	-7.8		

The computed values of E_{im} present a remarkable sensitivity to the surface charges and to the chosen water model, suggesting that absolute heat of immersion values shall be interpreted with great care when performed with even slightly different simulation setups. Interestingly, the strength of the water-surface interaction <u>decreases</u> with increasing charge values of the terminal OH groups, suggesting that electrostatic repulsion dominates the observed behaviour. A precise comparison with experimental values (around 150-250 mJ/m²⁷⁴) is difficult because of the native negative surface charges present in the experiments and the non-trivial contribution of counterions in MD calculations including charged surface models. However, the values computed with the largest charges, as defined in Fig. 7, seem to be acceptable, given the expected increase of the E_{im} values arising from the presence of net charged sites.

5 Conclusions

By using a pragmatic approach, we have developed and validated a transferrable force field for modelling the non-bonded interactions between natively charged amorphous silica surfaces and liquid water. The functional form, consisting of Coulomb and Lennard-Jones interactions, and the combining rules for our force field are chosen to ensure harmonisation with common biomolecular force fields such as AMBER and CHARMM, and builds upon a previously developed model for neutral Si/SiOx/water interfaces.⁴²

A crucial issue in the development of our novel parameter set has been the assignment of atomic point charges, especially for the case of deprotonated silanol groups, based on extensive DFT calculations applied to a range of reference systems. We have found that absolute charge values can be reliably computed using the ESP scheme, as widely employed in the formulation of force fields for biological and other organic molecules. However, to determine the extent of charge (de)localization and the charge differences on neighbour atoms to a deprotonated surface site, the Bader partioning scheme provides the best results. In particular, robust charge difference values are obtained between systems not including liquid water above the surface and without structural minimization of the atomic positions after removal of a proton from a terminal silanol group. Here, the initial atomic position of the neutral system are obtained via full structural optimisation of the surface slab in the presence of bulk liquid water wetting the surface. For the particular case of amorphous SiO_2 , we found that adjustment of the point charges up to the second nearest neighbours around the deprotonated sites is necessary.

Remarkably, without further adjustments, the chosen charge values, combined with previously determined Lennard-Jones parameters for the surface Si and O atoms,⁴² yield a good description of the aqueous interface for both charge-neutral and negatively-charged surfaces. The performance of the parameter set has been validated against adsorption profiles of single water molecules on both neutral and deprotonated surfaces computed by quantum-mechanical methods. Interestingly, the reference adsorption profiles are markedly different for different choices of standard or dispersion-corrected GGA-DFT functionals and for MP2 calculations. As already pointed out previously in this paper, the absence of an obvious quantum reference is to be considered as an intrinsic limit of the approach followed here. Unfortunately, experimental observables on which the potential parameters could be further validated against are hardly available. A possible exception is the measured heat of immersion, whose calculation is however limited by very large sensitivity to the precise simulation setup, the chosen water models and other small parameter variations.

Nevertheless, it is reassuring to see that acceptable agreement between the classical computed interactions and the quantum mechanical curves (as well as the experimental heat of immersion values) could be obtained using our DFT-determined charges <u>without further modification</u>. A minor adjustment of the charge values of terminal silanol groups has been only necessary to ensure good transferability of the potential to natively-oxidized silicon surfaces. Even in this case, however, we

could apply the same charge differences between the neutral and the deprotonated systems, further justifying our ab-initio based approach. We note that in the present work we have chosen deliberately not to attempt a fine-tuning of the Lennard-Jones parameters of the Si and O atoms made available in a previous work,⁴² and to keep these parameters fixed when going from the neutral to the charged surface model. This choice is consistent with the idea of avoiding the specialization of the potential to a very specific situation (for which a fine-tuning of the LJ parameters could be easily performed, if wished), maybe at the expenses of precision, but gaining in simplicity and especially in transferability.

We anticipate that future applications of this force field will aid in progressing our understanding of the biomolecule-inorganic interface for non-idealized surfaces, in particular amorphous and natively charged. Moreover, having tested and validated our approach against other available force fields for SiO_2 /water, which is probably the most widely studied solid/liquid interface, we believe that it can be transferred to a variety of oxide surfaces of biotechnological relevance, including e.g. titanium, aluminium, zinc or iron oxides.

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Figure 4: Bader charge differences for a periodically repeated amorphous SiO_2 slab in contact with water and in vacuum. For the system in contact with water, both a charged (a-c) and an overall neutral systems are considered (d-f).



Figure 5: Differences between Bader charges before and after deprotonation of a terminal OH group calculated on semi-spherical amorphous SiO_2 clusters carved out of a large amorphous surface slab. The deprotonated OH group is located at the center of the flat cluster surface. The plots refer to two different cluster radii and boundary conditions.



Figure 6: ESP charge differences before/after deprotonation of a terminal silanol group on the three considered systems.



Figure 7: Summary of the atomic point charges assigned to silanol groups of neutral and deprotonated SiO_2 surfaces



Figure 8: Validation of the potential parameters for neutral am-SiO₂. The three different configurations are described in detail in the text.



Figure 11: Validation of the potential parameters for the neutral, natively oxidized Si(001) surface.



Figure 12: Validation of the potential parameters for the deprotonated, natively oxidized Si(001) surface.