Development of a ReaxFF Reactive Force Field for
Titanium Dioxide / Water Systems

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Bulk modulus

The bulk modulus of a substance measures its resistance to uniform compression. Based on the EOS, bulk moduli were fitted against these results by using the Rose equation-of-state4 for the three most important phases. As is shown in Figure S1, ReaxFF results reproduce the experimental values within 17% error. Depending on the DFT or experimental methods, the bulk moduli vary within those values. Considering that, a 17% discrepancy is reasonable. Also, the trend from DFT results is also
reproduced by ReaxFF as rutile has highest value followed by brookite and anatase. This can be understood by considering the atomic structure of these phases. In other words, the atoms for rutile are packed in unit cell more densely compared to anatase and brookite, which is responsible for the higher zero-pressure density of rutile.

![Bulk Modulus](image)

**Figure S1:** The bulk moduli of rutile (Expt = 230 GPa\(^3\)), anatase (Expt = 178±1 GPa\(^3\)) and brookite (Expt = 255 GPa\(^3\)) as calculated with DFT (Muscat et al.\(^5\), 2004 for rutile and anatase); Beltran et al.\(^6\), 2006 (for brookite ) and ReaxFF (this work).

*Energy differences between the structures*
Figure S2: Energy differences between the structures (reference: rutile)

Surface formation energies

Figure S3 shows surface energies of 5 different faces, 3 for anatase and 2 for rutile. ReaxFF agreement with DFT is as good as the agreement between DFT calculations from different authors. As is shown above, anatase (101) has the lowest value among the anatase surfaces and rutile (110) has the lower value compared to rutile (101), which makes sense because the most common faces are (101) for anatase and (110) for rutile. The discrepancy between ReaxFF and Hummer et al. reaches up to 57%. Interestingly, ReaxFF overestimates the surface formation energy for anatase, while underestimating it for rutile.
**Figure S3:** Surface formation energies and structures which were used in the DFT references for the 3 anatase and 2 rutile surfaces
Liu et al.\textsuperscript{1} demonstrated that the calculated dissociation preference of water adsorbed on the rutile (110) surface can depend on the thickness of the slab used in the simulation. Figure S4 shows the energy difference between fully associated and partially dissociated configuration for a 2x1 surface unit cell with 1 monolayer (ML) of water as the thickness of the slab changes from 3 to 15 Ti-O layers. A positive or negative energy difference corresponds to fully associated or partially dissociated configuration being preferred, respectively. Figure S4 shows that the DFT\textsuperscript{1} predicts fully associated configuration as the preferred method for water adsorption as the thickness of the slab is increased. Our ReaxFF results also predicts fully associated configuration for the adsorbed water molecules on the rutile (110) surface. ReaxFF predicts much smaller fluctuation, than the DFT, in the energy difference which is around 1.1-2.2 kcal/mol per H\textsubscript{2}O. This can be due to electronic structure effect in the DFT calculations that is not present in the ReaxFF simulations\textsuperscript{7}.

**Figure S4:** Energy difference between fully associated and partially dissociated configuration, for a 2x1 surface unit cell simulation box with 1 ML water, with respect to number of Ti-O layers calculated from DFT\textsuperscript{1} and from ReaxFF. DFT and our ReaxFF both predict fully associated configuration as the preferred method of water adsorption on the rutile (110) surface for thicker layers.
**TiO$_2$ clusters**

A total of 150 bare and hydrated TiO$_2$ cluster structures, mainly based on stoichiometric TiO$_2$ cluster cores of the type (TiO$_2$)$_x$ with $x$ in the range 1 – 28, were included in the optimization of the force field. Suitable cluster structures were identified from the literature on small TiO$_2$ clusters$^8,9$ and model TiO$_2$ nanocrystals$^{10}$. Structural isomers for some of the larger clusters, e.g. (TiO$_2$)$_{16}$ and (TiO$_2$)$_{28}$, were initially generated during the force field development during optimizations, low-temperature MD simulations, or simulated annealing with preliminary force fields, and subsequently calculated by quantum chemical calculations and incorporated into the force field fitting procedure. Quantum chemical cluster data was generally either taken from the literature, or obtained using density functional theory cluster calculations performed with the Jaguar 7.0 program [Jaguar 7.0; Schrodinger Inc.: Portland, OR, 2007]. using the B3LYP hybrid functional$^{11,12}$ and a LACVP** basis set and effective core potential (ECP) combination that provides an all electron 6-31G** basis set for the H and O atoms$^{13,14}$, while the Ti atoms are treated using a Hay-Wadt ECP$^{15}$ for the inner core (Ne) electrons together with a double zeta description of the 12 remaining outer core and valence electrons. This level of quantum chemical theory is consistent with that recently employed for the development of ReaxFF force fields for closely related metal oxide systems such as vanadium oxides$^{16}$.

Two types of 3(TiO$_2$) and 4(TiO$_2$) were picked and bond lengths and angles are presented for comparison between ReaxFF and QM. Also, potential energy differences between pairs of clusters and water binding energies for the selected structures are shown in the Table 10–12. Figure S5 (d) to (g) shows the 4 configurations of TiO$_2$ clusters which were chosen for the comparison between ReaxFF and QM results. Measured bond lengths and angles of selected clusters are shown and comparison is made to the quantum-minimizied clusters for each case. Overall, agreement is good ($\pm 0.1$ Å and $\pm 1.2^\circ$) for cluster structures, potential energies and water binding energies except in a few cases.
(a) 2(TiO\textsubscript{2})-type I  
[Config.2 in Figure S6]

(b) 2(TiO\textsubscript{2})-type II

(c) 3(TiO\textsubscript{2})-type IV

(d) 3(TiO\textsubscript{2})-type(I)
[Config.5 in Figure S6]

(e) 3(TiO\textsubscript{2})-type(II)

(f) 4(TiO\textsubscript{2})-type(I)

(g) 4(TiO\textsubscript{2})-type(II)
[Config.11 in Figure S6]

(h) 10(TiO\textsubscript{2})-type I
[Config.14 in Figure S6]

(i) 10(TiO\textsubscript{2})-type II

(j) 12(TiO\textsubscript{2})-type II
[Config.24 in Figure S6]

(k) 12(TiO\textsubscript{2})-type V

(l) 15(TiO\textsubscript{2})-type II
[Config.28 in Figure S6]
(m) 16(TiO$_2$)-type I

[Reference Structure in Figure S6]

**Figure S5:** Configurations of the TiO$_2$ clusters

Figure S6 shows that the potential energy differences between pairs of structures for Ti-O clusters. The reference structure is (m)16(TiO$_2$)-type(I) in Figure S5 and the differences between the energies of 29 different structures divided by numbers of TiO$_2$ units and that of reference structure divided by 16 are shown. Agreement is good overall. The potential energy difference between QM and ReaxFF decreases as the clusters increase in size, which means that large-scale simulations of TiO$_2$-H$_2$O using ReaxFF should be accurate.
**Figure S6:** Potential energy difference between the selected configurations and the reference structure [(m), in Figure S5] 

(a) (TiO$_2$) (H2O)  
(b) 2(TiO$_2$)2(H$_2$O)  
(c) 4(TiO$_2$)2(H$_2$O)  
(d) 4(TiO$_2$)5(H$_2$O)  
(e) 2(TiO$_2$)3(H$_2$O)

**Figure S7:** Configurations of the hydroxide TiO$_2$ clusters for the water binding energy
Figure S8: Energy conservations with respect to time for 1ML and 3ML of rutile (110)
References


