CHAPTER 6

A Reaxff Reactive Force-field for Proton Transfer Reactions in Bulk Water and its Applications to Heterogeneous Catalysis

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6.1 Introduction

Water is essential to the very existence of life, playing its important role in a myriad of physical, chemical, and biological processes. Despite having a simple molecular structure, it forms one of the most complex substances.^{1–4} Specific interactions amongn water molecules in the condensed phase are responsible for its anomalous behavior. Extensive atomistic simulations have been performed to connect the microscopic structure of water to its macroscopic properties. The accuracy of simulation results strongly depends on the quality of the applied intermolecular potentials. To this end, more than 50 empirical water potentials have emerged in the literature, broadly differing in the

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representation of the intra- and intermolecular energetics and the range of properties that can be reliably reproduced. Comprehensive reviews of ever-growing research effort in this field and comparison of the performance of several popular water potentials can be found in Refs. 5–11.

The existing interaction potentials for water vary from the simplest rigid pairwise additive three-site models to much more complicated flexible polarizable potentials with additional interaction sites, smeared charges and dipoles, fluctuating charges, Drude oscillators, *etc.* The classification of the potentials into pairwise additive (two-body) and polarizable (many-body) depends on whether the interaction energy for an assembly of water molecules contains only a sum of pair potentials or includes many-body correction terms resulting from the polarization of the monomer by its neighbors. The pair and polarizable potentials have their own merits and shortcomings. The former category of potentials implicitly incorporates many-body effects through the use of enhanced charges or monomer dipole moments. They are aimed at reproducing experimental results for the range of temperatures, pressures, and phases considered in their parametrization, and thus regarded as effective models having limited transferability to dissimilar environments (clusters, liquid water, ice). The latter category of potentials can be thought of as transferable potentials expected to perform well across different environments with regard to description of cooperative effects. However, the main practical drawback of this class of models, when fitted at the bottom of the potential well for water clusters, is the necessity to incorporate computationally expensive quantum dynamical simulation protocols for including intermolecular zero-point effects (ZPE) in order rigorously to derive macroscopic thermodynamic observables.¹²

There is growing interest in and need for generalizing water potentials to describe various phenomena in inhomogeneous environments, for example in the context of solvation of neutral and ionic solutes, solute transport, molecular structure of an organic–water interface, protolytic dissociation, *etc.* Owing to the highly complex nature of these processes, there still remains a question as to whether empirical potentials are able to reproduce the aforementioned processes with sufficient accuracy. It has been shown that using polarizable potential models for both water and monatomic inorganic ions is paramount for modeling solvation and transport of ions across organic–water and air–water interfaces.^{13–15} Although the importance of the polarization and charge transfer in the polar and inhomogeneous environments has been recognized, it has been difficult to include these effects explicitly in the broadly applicable polarizable force field. Ongoing research in this area has been recently documented in a special issue.¹⁶ The vast majority of simulations for biomolecular systems are still being performed using non-polarizable force field, which can be especially problematic for describing interactions involving ions, charged residues, and π -electron systems.

Most of the flexible water potentials employ stiff (harmonic) bond-stretching and angle-bending potentials and do not allow for bond forming and breaking. The solvation of single structures, either H_3O^+ or OH^- , in the aqueous solution and at interfaces has been modeled with reasonable success using

non-reactive potentials.^{13–15} However, the important processes of H^+ and OH^- migration via a structural diffusion (hopping) through water cannot be described using such methods. In response to this deficiency, several empirical models for water that can dissociate have been published.^{17–22} However, the dissociative properties of water (if any) have been illustrated only on small clusters and the applicability of these potentials to model charge migration and various protolytic reactions in the aqueous bulk has yet to be tested. Meanwhile, other interesting methodologies to model proton transfer reactions in aqueous solutions have emerged, with a water molecule represented as still undissociable but protonizable moiety.^{23–30}

Voth and coworkers developed a multistate empirical valence bond (MS-EVB) method^{23–25} to simulate proton solvation and transport in water and biomolecular systems. The EVB Hamiltonian matrix constructed on the basis of the chemically relevant protonation configurations is diagonalized in order to determine the excess proton delocalization and shuttling through water molecules for any given nuclear coordinates and time step in the molecular dynamics (MD) run. This approach was successfully applied for investigation of proton transport in bulk water, proton wires, proton channels of biomolecular systems, and polymer electrolyte membranes.²⁶ Lill and Helms introduced the stochastic proton hopping scheme (Q-HOP) that is capable of simulating transport of a single proton in aqueous solutions by combining classical MD simulations with instantaneous proton hopping events.²⁷ Proton transfer probability is calculated on the basis of the distance between donor and acceptor and the environmental influence of the surrounding groups. Surprisingly, these and other^{28–30} developed schemes are not parameterized to describe the dissociation of water and the structural migration of the OH^- , and therefore do not provide dissociation pathways for a variety of base-catalyzed reactions in aqueous solution.

Many of the questions raised here can, in principle, be addressed in the framework of Car–Parrinello³¹ and *ab initio* molecular dynamics where the parametrization of the potential is avoided by solving Hartree–Fock or Kohn–Sham equations at each time step.^{32–36} However, such simulations become computationally intractable for systems with a few hundred water molecules and simulation times of more than 100 ps. Recent controversy on the structural and dynamic properties of liquid water, apart from the limited accuracy of the modern exchange-correlation functionals, raised the issue of using the proper simulation protocols with the sufficient length of equilibration and production runs and the combination of pseudopotentials and basis sets yielding converged results.^{35,36} As such, they provide valuable benchmark data for validation of more approximate methods having much broader applicability for realistic and complex systems.

Our current research centers on the development of a computational approach to model chemical reactions in aqueous solution, which has been a long-standing and almost formidable challenge within the realm of empirical models. The important step toward this goal is to build effective potential for water that can allow for autoionization and intermolecular proton and hydroxyl transfer. In addition, the ability to model water dissociation, both homolytically and heterolytically, can provide all the necessary reaction pathways under different conditions.

The reactive force-field (ReaxFF) platform contains all essential ingredients accurately to model various dissociation pathways and formation of chemical bonds. Since the first publication in 2001 on hydrocarbons,³⁷ ReaxFF has been successfully applied for modeling complex chemical transformations involving high-energy materials,^{38–40} silicon/silicon oxides,⁴¹ polymer decompositions,⁴² metals, and transition metals^{43,44} in the gas phase, in the solid phase, and at the interface. In the present chapter we have extended the ReaxFF method to describe liquid water and reactions involving proton transfer in small clusters and the water phase. Since the ReaxFF water potential is fully compatible with our previous parametrization, considering the interaction between water and other molecules of interest will allow for reactive molecular dynamic simulations of a wide range of complex chemical processes in the aqueous phase.

6.2 Methods

6.2.1 Quantumchemical Methods

The structures and energies for a series of the clusters used in the training set were obtained with the Jaguar 7.0 program package using the X3LYP/6-311G** level of theory. All structures were fully optimized.

6.2.2 Force-field Optimization

The force-field parameterization was performed with the ReaxFF standalone program, using a single-parameter, parabolic approximation fitting procedure. Parameter correlation was accounted for by looping multiple times over the force-field parameters. Each parameter was allowed to modify within a set range, thus ensuring physically realistic and mathematically relevant final values. Forty-five different parameter combinations were obtained by fitting against the static DFT-data – these different combinations were obtained by modifying the weights of the individual training set components and re-parameterization. The results in this manuscript are all from parameter combination 41, which gave the best results for the bulk water dynamical (Section 6.3.2) and static properties (Section 6.3.1).

6.3 Results and Discussion

6.3.1 Force-field Development

The following sections describe the various QM-cases that were either used to parameterize the ReaxFF water description or to validate the potential.

6.3.1.1 Bond Dissociation, Angle Distortion and Charges

To ensure transferability to other ReaxFF descriptions we not only considered O–H bond dissociation but we also trained the ReaxFF parameters against

H–H dissociation in H_2 and O–O single- and double-bond dissociation in the H_2O_2 and O_2 molecules. For these three cases we derived adiabatic QM bond expansion/compression energies, where the expansion was taken all the way to the dissociative limit. Most weight was put on the QM-data close to the equilibrium and to the dissociation energies. Figure 6.1(a–c) shows the QM and ReaxFF results for these cases.

Figure 6.1 QM and ReaxFF bond dissociation energies for the O–H dissociation in H_2O (a), the H–H dissociation in H_2 (b), and the O–O single and double bond dissociation in H_2O_2 and O_2 (triplet) (c).

To defined the ReaxFF angle parameters we performed a QM-simulation on the H_2O molecule where the H–O–H angle was adiabatically distorted from 72° to 134° . Figure 6.2 shows the QM- and ReaxFF results for this angle distortion energy. ReaxFF obtains an equilibrium angle of 103.3° for the isolated water molecule; this angle opens up to a value of 105.6° in the Ice(cmc)-phase.

Figure 6.3 compares the QM/Mulliken and ReaxFF average charges on the oxygen atoms for the H_2O -monomer up to the H_2O -decamer cases and for Ice(pna21). We put a relatively low weight on these Mulliken charges during the force-field optimization, which allowed the charges and polarization to also be determined by the QM-energy data. This resulted in ReaxFF charge distributions that are systematically more polarized than the QM/Mulliken charges. Figure 6.4 compares the ReaxFF and QM/Mulliken charges for the $\text{H}_3\text{O}^+ / [\text{H}_2\text{O}]_6 / \text{OH}^-$ cluster; for this cluster we find that both QM and ReaxFF

Figure 6.2 QM and ReaxFF H–O–H angle strain energies for H_2O .

Figure 6.3 QM/Mulliken charges and ReaxFF charges on oxygen for water clusters and for the Ice(pna21)-condensed phase.

Figure 6.4 QM/Mulliken and ReaxFF oxygen and cation/anion hydrogen charges for a $[\text{H}_3\text{O}]^+[\text{OH}]^-[\text{H}_2\text{O}]_6$ -cluster.

Figure 6.5 QM and ReaxFF water dimer binding energies as a function of oxygen-oxygen distance.

do not completely localize the positive and negative charges on the H_3O^+ cations or OH^- anions. This delocalization of the formal cation/anion charges is more substantial in ReaxFF compared with QM/Mulliken.

6.3.1.2 Water Clusters and Ice Condensed Phase Binding Energies

Figure 6.5 compares the ReaxFF and QM-results for water dimer dissociation. We included the C_s , C_i , C_2 and C_{2v} water dimer configurations in the ReaxFF training. Figure 6.4 shows that ReaxFF properly predicts the dimer stability order ($\text{C}_s > \text{C}_i, \text{C}_2 > \text{C}_{2v}$). ReaxFF overbinds the C_s dimer: it gives a binding energy of $5.9 \text{ kcal mol}^{-1}$ where QM gives $5.0 \text{ kcal mol}^{-1}$. The ReaxFF C_s -dimer

has an equilibrium O–O distance of 2.9 Å, which is in exact agreement with the QM-geometry.

Figure 6.6 shows the ReaxFF and QM binding energies for $[\text{H}_2\text{O}]_n$ clusters, with $n = 2$ to 34. While ReaxFF over-binds the H_2O -dimer it actually under-binds the $[\text{H}_2\text{O}]_3$ to $[\text{H}_2\text{O}]_{11}$ clusters. For larger clusters we find good agreement between ReaxFF and QM. The larger clusters were given a relatively high weight in the force-field fitting, as these are more relevant for a bulk water description. Figure 6.7 shows the QM and ReaxFF binding energies to $\text{H}_3\text{O}^+[\text{H}_2\text{O}]_n$ and $\text{OH}^-[\text{H}_2\text{O}]_n$ clusters. For both the positively as well as the negatively charged clusters we find that for $n = 1$ there is a significant over-binding, related to overpolarization of the one solvating water molecule. With increasing water solvation the ReaxFF results agree well with the QM, indicating that ReaxFF should properly describe both H_3O^+ as well as OH^- solvation in bulk water.

We also tested ReaxFF for the Ice(cmc) and Ice(pna21) binding energies; Figure 6.8 shows that ReaxFF consistently underestimates the QM binding energies by about 10%. ReaxFF predicts an equilibrium density of 0.93 kg dm^{-3} for Ice(cmc) while QM gives an equilibrium density of 0.899 kg dm^{-3} .

6.3.1.3 Reactions

To test and train the ReaxFF parameters for reactive events we considered a number of hydrogen and proton transfer reactions for neutral, cation, and anion systems. Figure 6.9 and Table 6.1 compare the QM and ReaxFF barriers

Figure 6.6 QM and ReaxFF water cluster binding energies as a function of cluster size.

Figure 6.7 QM and ReaxFF water binding energies to $\text{H}_3\text{O}^+[\text{H}_2\text{O}]_n$ and $\text{OH}^-[\text{H}_2\text{O}]_n$ clusters.

Figure 6.8 (a) QM and ReaxFF water binding energies in Ice(cmc), Ice(pna21) and Ice(cmc) with one water vacancy in two different locations. (b) QM and ReaxFF water energies of Ice(cmc) as a function of density.

for a concerted hydrogen shift reaction in $[\text{H}_2\text{O}]_n$ systems, where $n=2$ to 6. These reactions are very relevant for water-catalyzed reactions in, for example, enzymes and on surface catalysis. We find good qualitative and quantitative agreement between ReaxFF and QM for these reactions; both methods agree that the four-water case has the lowest concerted hydrogen-shift barrier, while this barrier goes up substantially, owing to increase angle strain, when fewer water molecules are involved in the concerted event. Increasing the number of water molecules in the water-cycle from four to six leads to a modest increase in barrier.

To test the ReaxFF potential for proton transfer we considered a $\text{H}_3\text{O}^+ - \text{H}_2\text{O}$ dimer (Figure 6.10). In this system, we monitored the barrier for

Figure 6.9 QM and ReaxFF barriers for concerted hydrogen transfer in $[H_2O]_n$ clusters. The inset shows the reaction for $n=4$.

Table 6.1 QM and ReaxFF barriers (in kcal mol⁻¹) for concerted hydrogen transfer in $[H_2O]_n$ as a function of the number of water molecules.

$n(H_2O)$	Barrier(QM)	Barrier(ReaxFF)
2	45.0	64.0
3	25.7	23.8
4	21.9	19.4
5	24.5	27.0
6	28.6	31.9

Figure 6.10 QM and ReaxFF barriers for proton migration as a function of O—O distance in an $[H_2O-H-OH_2]^+$ cluster.

proton transfer at different O–O distances. QM and ReaxFF agree that the global minimum for this dimer is at a O–O distance of 2.8 Å. For this configuration both ReaxFF and QM find proton transfer barriers of around 5 kcal mol⁻¹. Shortening the O–O distance to 2.4 Å increases the overall energy of the system but removes the barrier for proton transfer; at this O–O distance both QM and ReaxFF find that the most stable configuration is with the proton equidistant from both oxygen atoms. An increase in O–O distance to 3.2 and 3.6 Å results in a considerable increase in the proton transfer barrier.

Figure 6.11 shows a similar test case for an anionic system; here we transfer a proton in a OH⁻–H₂O dimer. In this case the most stable configuration of the dimer has a O–O distance of 2.48 Å. In contrast to the H₃O⁺–H₂O case discussed previously, for the anionic dimer the proton is shared between the oxygen atoms in the global energy minimum. At increased O–O distances a barrier to proton transfer appears; this barrier increase to more than 60 kcal mol⁻¹ for an O–O distance of 3.6 Å.

The cases presented in Figures 6.9–6.11 were all considered in the ReaxFF parameterization. After the parameterization we performed two additional validation cases on proton transfer reactions. Figure 6.12 shows the ReaxFF proton transfer reaction energies for two different migration paths in an H₃O⁺[H₂O]₂ system. In path 1, the H₃O⁺ remains solvated by two water molecules, while path 2 results in a 1-fold solvated H₃O⁺ that is about 3 kcal mol⁻¹ higher in energy than the reactant. Figure 6.13 shows that ReaxFF predicts an automatic proton transfer in response to a solvation change, which is a key mechanism for proton transfers in bulk water.

6.3.2 Molecular Dynamics Simulations

6.3.2.1 Density and Cohesive Energy

In order to validate the ReaxFF bulk water description we performed a series of NVT/MD simulations at five different water densities (0.8, 0.9, 1.0, 1.1, and

Figure 6.11 QM and ReaxFF barriers for proton migration as a function of O–O distance in an [HO–H–OH]⁻ cluster.

Figure 6.12 ReaxFF path for indirect (path 1) and direct (path 2) proton transfer in a $[\text{H}_2\text{O}-\text{H}_3\text{O}-\text{H}_2\text{O}]^+$ system.

Figure 6.13 ReaxFF barrier for proton transfer resulting from a forced solvation change in a $[(\text{H}_2\text{O})_6\text{H}_3\text{O}]^+$ system. External restraints were only imposed on the solvating waters.

1.2 kg dm^{-3}). These MD simulations were performed on periodic systems containing 100 water molecules using a Berendsen thermostat with a temperature damping constant of 100 fs. Figure 6.14 (right panel) shows the average potential energy per water molecule obtained from these simulations. We observe that the 1.0 kg dm^{-3} density produces the lowest average potential

Figure 6.14 (left) Mean square displacement vs. time for an 800-water system at density = 1.00 kg dm^{-3} and $T = 300 \text{ K}$. (right) Average cohesive energy versus density for an 800-water system.

energy ($-10.9 \text{ kcal per H}_2\text{O}$); this energy is in good agreement with the experimental heat of vaporization for water ($-10.5 \text{ kcal mol}^{-1}$). These results indicate that these ReaxFF water parameters can reproduce both the cohesive energy and the density of liquid water in an NVT-environment. In MD-simulations with an NPT-ensemble we observe a density decrease for liquid water at room temperature to a value of 0.94 kg dm^{-3} .

6.3.2.2 Diffusion Constants

To determine the water self-diffusion constant and the proton and anion diffusion constants we performed MD/NVE simulations at $T = 300 \text{ K}$ on a 100 water system, a 99 water/ H_3O^+ and a 99 water/ OH^- system at densities of 1.00 kg dm^{-3} . The 99 water/ H_3O^+ and 99 water/ OH^- were performed using a overall neutral simulation box. These simulations were performed for 1 ns with a time-step of 0.25 fs; unfolded system coordinates were saved every 250 iterations (62.5 ps). This yielded 4000 system configurations from which an averaged mean square displacement (MSD) was obtained. For the 100 H_2O system the MSD was obtained by analyzing and averaging the displacement of all the oxygen atoms; for the anion and proton systems both non-reactive and reactive diffusion was taken into account by locating the position of the OH^- or H_3O^+ molecule in the system box, using the ReaxFF bond order information, and by tracking the displacement of the oxygen atom in the anion or proton. From the MSD analysis for the proton and anion diffusion we can clearly observe jumps in the proton or anion coordinates, associated with a proton transfer reaction. Figure 6.14 (left panel) shows the MSD for the water, proton and anion diffusion, resulting in diffusion constants of, respectively, $0.2106 \text{ Å}^2 \text{ ps}^{-1}$, $0.400 \text{ Å}^2 \text{ ps}^{-1}$ and $0.500 \text{ Å}^2 \text{ ps}^{-1}$. While the water and proton diffusion constants are in good agreement with experimental values ($0.2272 \text{ Å}^2 \text{ ps}^{-1}$ and $0.4200 \text{ Å}^2 \text{ ps}^{-1}$),⁴⁵ we find that ReaxFF overestimates the anion diffusion constant (experiment: $0.3200 \text{ Å}^2 \text{ ps}^{-1}$) by almost a factor of 2. We initially speculated that the ReaxFF over-binding between the OH^- and its solvation shell (see Figure 6.7) might have been responsible for this fast anion diffusion rate.

To test this hypothesis we increased the weights of the $\text{OH}^-/[\text{H}_2\text{O}]_n$ QM-data in the ReaxFF training set and re-parameterized the force-fields. While this resulted in a substantial improvement of the ReaxFF reproduction of the $\text{OH}^-/[\text{H}_2\text{O}]_n$ solvation energies, at the expense of the ReaxFF performance for other segments of the training set, MD-simulations with these re-optimized parameters did not result in a marked improvement of the anion diffusion rates.

6.3.2.3 Radial Distribution Analysis

Figure 6.15(a–c) compares the ReaxFF and experimental H–H, O–H and O–O radial distribution functions for a bulk liquid water system. These figures were obtained from a 100 ps 800-water NVE MD simulation at $T = 300$ K. System configurations were saved every 1 ps, resulting in 100 system configurations, from which the average Radial Distribution Function (RDF) were obtained. We observe for all three rdf-pairs that ReaxFF gives a good reproduction of the experimental data.⁴⁶ Of particular relevance for the quality of the bulk water structure obtained by ReaxFF is an accurate reproduction of the O–O radial distribution data, indicating that ReaxFF recognizes the optimal O–O distance for the first (2.8 Å), second (4.4 Å) and third (6.7 Å) solvation shells.

Figure 6.15 ReaxFF and experimental H/H (a), O/O (b), and O/H (c) radial distribution functions for bulk water. The ReaxFF radial distribution functions were obtained for an 800-water system using an NVE-ensemble at a density of 1.00 kg dm^{-3} and a temperature of 300 K.

6.3.2.4 Dynamical Properties as Direct Training Set Entries

The ReaxFF description of water, as given in this manuscript, was revised many times to incorporate different types of chemical reaction involving water. In all those revisions, the force-field optimization was restricted to static properties of water involving energy minimization calculations. However, there were no means to optimize for dynamic properties of water such as the diffusion coefficient, viscosity, *etc.* As such, we simply generated over 40 different parameter combinations that gave similar results for the static cases, tested these parameter combinations for dynamics properties and picked the O/H parameters that gave the best mixture of static and dynamic properties. In order to circumvent this time-consuming force-field development scheme in the future, we recently implemented python script, which allows the user to include both static and dynamic properties of water in force-field optimization calculations. For every force-field parameter which we want to optimize, the python script first performs molecular dynamics simulation to evaluate desired dynamical properties of water and calculates the force-field error. Following this, it performs regular energy minimization computations on all the geometries to evaluate the force-field error from static part. After finishing both MD and EM simulations, it combines both sets of force-field errors. Based on the total error, the script then searches for the optimum value of the parameter using a simple parabolic extrapolation search method, which tries to minimize the total force-field error. The detailed algorithm of the python wrapper is shown in Figure 6.16. This approach of including MD simulations in force-field

Figure 6.16 Schematic overview of a Python-based ReaxFF force-field development scheme, including dynamical properties.

optimization increases the time required for force-field parameterization, but it makes sure that dynamical properties are not compromised during force-field optimization.

6.3.3 Heterogeneous Catalysis

6.3.3.1 Overview of Applications of this ReaxFF Water Description

Water-related reactions are highly relevant to a broad range of heterogeneous catalysis systems, either as a direct contributor to the active site or as an exchange-reaction with the catalysis support, providing a reservoir of protons or hydroxyl-groups for reactions at the active site. Over the last three years, the ReaxFF water model presented here has been integrated in a number of metal/metal oxide descriptions relevant to heterogeneous catalysis. Our first successful metal oxide/water interface calculation involved a Zn/O/H ReaxFF description, which managed to reproduce experimentally observed water dissociation trends involving transitions between surface–zinc oxides and zinc hydroxides,^{47,48} and was later used to simulate the collapse of Zn-based metal organic frameworks (MOFs) in the presence of water.⁴⁹ We also managed to integrate the O/H water parameters presented here with a previously published Si/O description,³⁹ enabling simulations of water dissociation on silica materials.⁵⁰ This silica/water ReaxFF description was recently extended with Ca/O/H parameters⁵¹ and Al/O/H^{52,53} parameters, enabling simulations on clays,⁵⁴ aluminum metal surfaces⁵² and calcium silicates.⁵⁵ Besides the relatively straightforward Ca/H₂O interactions, we also managed to derive ReaxFF parameters for the more complex Cu cations in water; for these copper cations we managed to reproduce the non-classical Jahn–Teller distortion of Cu/water complexes.⁵⁶

Parallel to these metal/metal oxide force-field development efforts, we also extended the first- and second-row elements that can incorporate the water description provided here. These extensions include carbon and nitrogen, in a ReaxFF description for glycine reactions in water,⁵⁷ sulfur, related to the catalytic cleavage of S–S bridges,⁵⁸ and phosphates.⁵⁹ Recently, we have merged the ReaxFF glycine description with a recently developed parameter set for titania/water interactions, enabling reactive simulations of peptides on titania surfaces.⁶⁰

6.3.3.2 Heterogeneous Catalysis Application Example

The long-term structural evolution of catalytic surfaces is very important in the evaluation of new catalyst candidates. Studying this evolution is very difficult using solely *ab initio* methods, owing to their limited size and time scales. ReaxFF, however, provides a sufficient size and time range to study relatively slow structural and chemical changes in the surface and bulk composition of catalysts. An important example of a catalyst that undergoes structural changes

is the iron metal catalyst, which has been used in a wide range of hydrocarbon formation and conversion reactions. Iron metal has a relatively high chemical reactivity – it oxidizes readily and can easily integrate carbon and hydrogen atoms in its structure. As such, iron surfaces very rarely remain metallic during long-term catalytic use, and water-dissociation and -formation reactions provide a key reaction step in these iron surface reconstruction events. In order to simulate these events we have developed a Fe/O/H ReaxFF description,^{61,62} using the O/H water parameters described in this chapter. This Fe/O/H description was trained against metal iron, iron oxide, and iron hydride DFT-data, thus covering a wide range of iron surface chemistry relevant to Fisher–Tropsch and water/gas shift catalytic conversions.

Figures 6.17 and 6.18 show an example of the capability of ReaxFF to describe the dynamic property of water formation and decomposition involving the oxidation of an Fe/FeH cluster. The cluster contains an iron hydride core with a diameter of 12 Å and a bare iron metal shell with a thickness of 6 Å. The total atom number of the cluster is 658 with a Fe/H ratio of 8.68: 1. The cluster was placed in the center of a 40 Å*40 Å*40 Å periodic box surrounded by 300 oxygen molecules (Figure 6.17). After energy minimization, the system was subjected to molecular dynamic simulation in the NVT ensemble for 250 ps at 1000 K. The temperature was controlled using a Berendsen thermostat with a damping constant of 100 fs. The oxygen and hydrogen atoms formed hydroxyl groups soon after the simulation started, as indicated in Figure 6.18. These hydroxyl groups can form water molecules while diffusing over the particle surface. Figure 6.18 also shows the continuous formation and dissociation of water molecules, indicating that the iron oxide surface is actively converted to a surface hydroxide during the simulation. These simulations indicate that ReaxFF can describe the changes in catalytic structure as a function of gas-phase composition.

Figure 6.17 Cross-sections of the initial (left) and final (right) system composition in the iron hydride/O₂ molecular dynamics simulations.

Figure 6.18 Analysis of the $\text{O}_2(\text{g})$, surface hydroxyl groups and gas-phase water molecules as observed during the ReaxFF MD-simulation on iron-hydride conversion in O_2 .

6.4 Conclusions

By parameterization against a large QM-based training set, consisting of bond dissociation energies, angle scans, water-dimer and oligomer binding energies, $\text{H}_3\text{O}^+/\text{water}$ and OH^-/water oligomer binding energies, proton migration barriers and ice binding energies, and equations of state, we have developed a ReaxFF reactive force-field capable of describing proton migration in water. This force-field was tested in molecular dynamics simulations and was found to give an excellent reproduction of bulk water properties, including density, cohesive energy, self-diffusion and structural features. We also found good agreement with experiment for the proton diffusion coefficient, which includes non-reactive as well as reactive aspects; however, we found that the force-field over-predicts the OH^- diffusion. Given that this ReaxFF description can also describe H–H and O–O single and double bonds it can be combined with existing ReaxFF descriptions, enabling large-scale ($> 1\,000\,000$ atoms) nano-second-scale simulations on reactive processes in the water phase. Based on the O/H ReaxFF parameters presented here we have already developed ReaxFF parameters for aqueous-phase simulations on proteins, phosphates, sulfonates, silicates and homogeneous and heterogeneous zinc/copper/iron systems.

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