MOLECULAR DYNAMICS SIMULATIONS OF AGGREGATION
OF ANATASE (TITANIUM DIOXIDE) NANOCRYSTALS

A Dissertation in
Chemical Engineering
by
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Abstract

A quantitative understanding of the forces between colloidal nanoparticles would benefit numerous applications in sensing, nanoelectronics, composite materials, nanofluids, optics, and catalysis, which could exploit the unique properties associated with their small sizes. In applications involving crystallization, the aggregation of nanoparticles can be important. Recent experiments on specific materials, including anatase-$\text{TiO}_2$, have documented the phenomenon of oriented attachment, in which nanocrystals approach one another and merge along specific crystallographic directions to form twinned or single-crystalline structures. The ability to direct crystallization through oriented attachment is an exciting prospect that could allow for the creation of new nanostructures with well-defined sizes and shapes. To realize the full potential of oriented attachment for achieving the controlled synthesis of anatase nanocrystals, insight into its origins, which are not currently clear in all cases, would be beneficial.

This dissertation employs molecular dynamics simulations to resolve the issues regarding anatase nanoparticle aggregation in a vacuum and in aqueous environments. By utilizing both symmetric and asymmetric nanocrystals, the majority of the observed synthesized anatase shapes have been covered. MD simulations have been carried out to determine the aggregation pathway of such nanocrystals, and by repeating the simulation with different initial configurations, the directional alignment of these nanocrystals has been discovered in vacuum environment. Also, by performing force, energy, dipole-dipole interactions, and other sorts of calculations, the origins of the preferred alignment of anatase nanocrystals in vacuum has been discovered.

Oriented attachment was first discovered in experimental studies for the crystallization of anatase nanocrystals under hydrothermal aqueous conditions. For the aqueous anatase nanoparticles, the Bandura-Kubicki force field has been tested against results from first-principles calculations based on density-functional theory
and refined to describe the binding of $\text{H}_2\text{O}$, $\text{H}^+$, and $\text{OH}^-$ to various crystal faces. Hence, the parameters for the available force fields have been modified to be used for anatase nanocrystals. Since MD is a very strong tool that allows solving larger systems with many water molecules, it has become possible to study the aggregation mechanism of anatase nanocrystals in an aqueous environment. Also, the difference in water adsorption on anatase surfaces under ambient and hydrothermal conditions has been studied, while hydration effects have been quantified.
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Chapter 1

Introduction

1.1 Background

1.1.1 Applications of Titanium Dioxide

Titanium dioxide (TiO$_2$) is the naturally occurring oxide of titanium that is a technologically important material in many industrial and scientific applications. TiO$_2$ is a very versatile material because of its high optical index, refraction and transparency across visible wavelength range [15, 16], innate semiconducting and electrical properties [17], biocompatibility [18, 19], and photocatalytic properties [20–24]. Because of its high refractive index [25] TiO$_2$ is one of the whitest materials known to exist on Earth, distinguished as "titanium white". Production statistics in 2007 [26] show that over 5.7 million tons of TiO$_2$ were converted to TiO$_2$ pigment. Titanium dioxide is widely used to provide whiteness and opacity to products such as paints [27], papers [28], food [29], and toothpastes [30] because of its biocompatibility. Since titanium dioxide reflects light so well, it is also used in cosmetic and skin care products especially in sunblock, where it helps protect the skin from ultraviolet light [31–36]. TiO$_2$ is also recently used in gas sensors, protective coatings, and optical coatings for its environmental benefits [37].

Besides its applications due to its high opacity, TiO$_2$ has particular technological significance in photocatalytic processes. Because of its high photocatalytic activity, TiO$_2$ has received enormous attention in the past couple decades, which started by the discovery of Fujishima and Honda in 1972 [38] of the photocat-
alytic splitting of water on TiO$_2$ electrodes, where the collected hydrogen was used as a fuel [38, 39]. Due to the novel and enhanced photocatalytic properties of nanosized titanium dioxide particles, TiO$_2$ has also found application in solar cell devices [40]. By understanding the fundamental processes and enhancing the photocatalytic efficiency of TiO$_2$, several new applications identified. These applications are mostly widespread environmental cleaning technologies such as water purification, wastewater treatment, air purification and deodorizing, and water disinfection [41–47].

TiO$_2$ can also form hydroxyl radicals in the presence of ultraviolet light and water vapor, which oxidize, or decompose organic compounds. Therefore, TiO$_2$ can be used as a self-cleaning coating material for paints, cements, windows, plastics, tiles, or other products, and in the presence of light, the majority of grease, dirt and organic contaminants are decomposed and can easily be swept away by water (rain). The same procedure has been applied for making products that are effective in adsorbing and decomposing several major malodorous gases such as ammonia, hydrogen sulphide and acetaldehyde, and volatile organic compounds [45,46]. TiO$_2$ can also be used in the manufacturing of anti-fogging glass, where it prevents formation of small droplets of water and instead the water forms a continuous flat sheet, so that there is no fogging. An obvious application is commonly found in side-view car mirrors [41].

1.1.2 Polymorphs of Titanium Dioxide

It has been reported in the literature that TiO$_2$ exists in eleven different polymorphs [48] with distinct photocatalytic activities [49]. The multiplicity of polymorphs that TiO$_2$ forms under varying chemical, temperature and pressure conditions also makes it an interesting material to study. The major polymorphs of TiO$_2$ that are profoundly found in nature and are among the low-pressure forms of this material, are anatase, rutile, and brookite [1,50–53]. Because of the dominance of rutile and anatase in industrial applications of TiO$_2$, these two polymorphs are of interest in this study. In both polymorphs of TiO$_2$, titanium has a coordination number of six and their structures is tetragonal. Their lattice parameters and the space group anatase and rutile polymorphs belong to, is listed in Table 1.1. It
should be noted that the number of shared edges in anatase and rutile structures are different, so that anatase has four shared edges, while rutile has only two as shown in Figure 1.1. Evans [54] has shown that the number of shared edges is inversely related to the bulk stability of that polymorph. This explains the fact that rutile is the most thermodynamically stable of all TiO\textsubscript{2} polymorphs at ambient pressures and temperatures.

Table 1.1: Bulk properties of anatase and rutile polymorphs of titanium dioxide [8–10].

<table>
<thead>
<tr>
<th>Crystal structure</th>
<th>System</th>
<th>Space group</th>
<th>Lattice constants( Å )</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Anatase</td>
<td>Tetragonal</td>
<td>(D_{4h}^{19} - I4_1/amd)</td>
<td>3.785 3.785 9.514</td>
<td></td>
</tr>
<tr>
<td>Rutile</td>
<td>Tetragonal</td>
<td>(D_{4h}^{14} - P4_2/mnm)</td>
<td>4.594 4.594 2.959</td>
<td></td>
</tr>
</tbody>
</table>

Anatase is known to be the metastable phase and may transform to rutile at high temperatures and pressures [55–58]. Meanwhile, anatase has attracted great interest since it exhibits the highest activity among other polymorphs of TiO\textsubscript{2} in the photocatalytic processes [1,59]. Therefore, nowadays it is the main material applied in photovoltaic cells, \textit{e.g.}, dye-sensitized solar cells [60]. Moreover, it has been reported experimentally and theoretically [57, 58, 61], that for TiO\textsubscript{2} nanocrystal sizes up to about 14 nm, nanocrystals appear to prefer the metastable anatase phase rather than the rutile form. This can be explained by the fact that the faces enclosing the equilibrated crystal shape are the ones that are thermodynamically and energetically the most stable atomic planes in the lattice. In certain simplified cases, the planes with low Miller indices \((hkl)\) are considered to be the most stable faces. However, in order to precisely distinguish such planes, an accurate knowledge of the surface energies \(\sigma_{s(hkl)}\) for all the crystal planes is required. \(\sigma_{s(hkl)}\) is defined as the excess energy per unit area of the surface lattice layer, when it is compared
Figure 1.1. The tetragonal bulk unit cell of rutile and anatase, both with basic building units of slightly distorted octahedra. The bond lengths and angles of the octahedrally coordinated titanium atoms are indicated and the stacking of the octahedra in both structures is shown on the right side [1].

with the same layer in the bulk lattice. By calculating or experimentally obtaining the values for these energies, the equilibrium crystal morphology will possess Gibbs’ condition for minimum total surface energy for a given volume [Eq. (1.1)], where $A_{(hkl)}$ is the surface area of the $(hkl)$ crystallographic face.

$$\sum_{hkl} \sigma_{s(hkl)} A_{(hkl)} = \text{minimum.}$$ (1.1)
In 1901, Wulff [62] made a proposal about the shape of a crystal, which is being widely used over the decades. According to Wulff, one can define the shape of a crystal by knowing vectors of length $l_{(hkl)}$, each of which is drawn normal to the corresponding $(hkl)$ face. Therefore, based on the Gibbs’ condition for minimum surface energy, these vectors have a length that is directly proportional to $\sigma_{s(hkl)}$. Hence, if the surface energies of various planes are known then it is feasible to draw out the morphology from a set of vectors of known lengths and angular intercepts [63]. The calculated Wulff construction of anatase and rutile nanocrystals is shown in Fig. 1.2 [3,5], with the relative surface formation energies (Table 1.2) [3]. The higher stability of anatase nanocrystal than that of rutile is explained by the lower average surface energy of the anatase polymorph, and the very stable (101) surfaces that are dominant in anatase Wulff shape. Therefore, it is important to know the environmental conditions (such as temperature and pressure) of synthesis of TiO$_2$ nanocrystals along with the size distribution of the particles.

Figure 1.2. The equilibrium shape of TiO$_2$ crystals using the Wulff construction based on calculated surface energies. (A) Rutile and (B) Anatase [2,3].
Table 1.2: Comparison of DFT calculated surface energies in $J/m^2$ [3].

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<th></th>
<th>Anatase</th>
<th>Rutile</th>
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<tbody>
<tr>
<td>(101)</td>
<td>0.45</td>
<td></td>
</tr>
<tr>
<td>(001)</td>
<td>0.98</td>
<td>(110)</td>
</tr>
<tr>
<td>(100)</td>
<td>0.63</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>0.35</td>
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</table>

1.1.3 Manufacturing of Nano-sized Titanium Dioxide

For manufacturing nanosized titanium dioxide particles, there exists two major approaches, sol-gel synthesis [58], and vapor synthesis [64]. Rutile TiO$_2$ nanoparticles may be manufactured on a large scale by the oxidation of titanium tetrachloride (TiCl$_4$) vapor, this approach is called ”chloride” process [64]. This process is generally carried out in a flame reactor, where the following reaction takes place,

$$TiCl_4(gas) + O_2(gas) \rightarrow TiO_2(solid) + 2Cl_2(gas)$$

It has been shown that water vapor that can be readily available in the flame process from the combustion of hydrocarbons in the reactor [65]. Temperature of the flame plays an important role in the size of produced nanoparticles. Also, based on the regions in the flame, which represent the temperature zones [66], different polymorphs of titanium dioxide may be produced. Several studies show that anatase polymorph of titanium dioxide will transform into rutile at moderate temperatures [51, 67, 68]. This transition temperature may vary by the size of particle, impurities, and the synthesis mechanism of the nanoparticle [24,67].

On the other hand, the majority of anatase nano-crystals are produced by the other method, which is called the sol-gel mechanism, or wet-process [58]. It is a heterogeneous chemical reaction and is generally carried out at high temperature and pressure. High temperature is important because most low temperature syntheses produce predominantly amorphous or poorly crystalline anatase [69], which are not desirable in most applications of anatase. The solvent, which is generally
hydrothermal water, and the stabilizing agent used in this technique greatly influence the size and phase of the forming particles [70]. It has been reported that by controlling temperature and $pH$ during hydrothermal treatment, different TiO$_2$ phases may be produced [68]. In this process, all reactants, products, and byproducts are environmentally friendly and very stable in the air. Also, this technique is used to synthesize high quality crystalline anatase nano-crystals with narrow particle size distribution [69].

1.1.4 Oriented Attachment of Anatase Nano-crystals

It has been shown that agglomeration of TiO$_2$ nano-particles often occurs during their preparation by either hydrothermal or dry synthesis. It is basically due to the extremely large surface area and high surface free energy of these nano-particles [68, 71]. Although, scientists have found new ways of preparation for decreasing such attachments [72, 73], in most cases large agglomerates are generated during the synthesis and distribution of nano-particles. Moreover, in most industrial applications of TiO$_2$ nano-crystals, aggregation of colloidal nano-particles plays an important role [18,19,22,40]. Thus understanding the mechanism of aggregation in nano-crystals is essentially important for obtaining knowledge about the final structure and properties of the material.

Crystallization of particles is typically understood in terms of Ostwald Ripening, where crystallites grow by the addition of atoms [74]. In contrast to this classical mechanism of crystal growth, nano-crystals may assemble via spontaneous self-organization between neighboring particles. It has been observed experimentally that some nano-particles aggregate along an alternative growth pathway (oriented attachment mechanism) in which nano-crystals approach one another and merge along specific crystallographic directions to form twinned or single-crystal structures [75–77]. This oriented attachment provides the ability to direct crystallization that could allow for the creation of new nanostructures with well-defined sizes and shapes.

Recent experimental studies have revealed the potential of mainly semiconducting nanocrystals in growing through the oriented attachment mechanism and leading to a variety of final structures including nanowires [78–84], rods [85, 86],
multipods [87–90], prisms [91–93], cubes [94], etc [95, 96]. Making new particles with well-defined sizes and shapes is among the most interesting areas of material science or solid state physics [97]. To realize the full potential of oriented attachment for achieving the controlled synthesis of a broad range of nanomaterials, insight into its origins, which are not currently clear in all cases, would be beneficial.

In reality, most applications of titanium dioxide take place in an aqueous environment. For instance, TiO$_2$ is used for medical applications such as dental and bone implants because of its resistance to corrosion, nontoxicity and being biologically and chemically inert [98]. Also, because of its unique photocatalytic properties, TiO$_2$ is one of the best semiconductors used for photoinduced splitting of water to hydrogen and oxygen using visible light [38,99]. Also, the most important application of anatase nanocrystals is when they are being used in dye-sensitized solar cells, where they are in direct contact with the electrolyte solvent [40]. Last but not least is its ability to enable photocatalytic degradation of environmentally harmful organic compounds in polluted water and air [46,100,101]. As most applications of TiO$_2$ involve an aqueous environment, the reactivity of TiO$_2$ surfaces with water is of great importance for understanding the nature of the photocatalytic processes occurring on these surfaces [102,103].
1.2 Summary of Chapters

This dissertation focuses on the oriented attachment of anatase–TiO$_2$ nanocrystals, first in vacuum and then in aqueous environments. As it is described in Chapter 2, MD simulation is the strongest tool for examining the dynamics of aggregation for such nanocrystals with their specific sizes (and the number of atoms available in the simulation boxes). The details of the computational models that have been used in these sets of simulations are fully addressed in Chapter 2. Considering such background studies, it has been decided to apply MD simulations to investigate oriented attachment in the sintering of anatase nanocrystals, primarily in a vacuum environment [Chapter 3]. These simulations indicate that electrostatic forces between under-coordinated atoms on the edges between nanocrystal facets drive the oriented aggregation. Although dipole-dipole interactions have been inferred to be the driving force for aggregation in previous studies [76, 77, 81], it has been found that oriented attachment rarely occurs along the direction of the dipole - even when the permanent dipole moment is as large as 250 Debye. Although the dipole-dipole interaction is the leading term in the multipole expansion of the electrostatic potential [104] for neutral particles, such as those studied here, higher order, multipole moments (e.g., quadrupole, octapole, etc.) can also contribute to the electrostatic potential.

After comparing such results with the ones obtained by experimental studies of colloidal (hydrothermal) anatase [75], it is found that the simulated aggregates resemble some of the experimental images obtained with high-resolution transmission electron microscopy. However, in the experimental study, aggregation occurred primarily on other facets [75] than what is observed in Chapter 3, and such events are in the minority here. Given the substantial differences between the experimental (colloidal) and simulation (vacuum) environments, this discrepancy is perhaps not surprising. Therefore, to fully address experimental observations, it is necessary to take into account the aqueous environment surrounding the nanoparticles.

Based on the observations made in Chapter 3, the presence of water molecules during the agglomeration of anatase–TiO$_2$ nanocrystals is a critical issue. Therefore, we have continued our studies to examine the oriented attachment of such particles in an aqueous environment. However, many theoretical, and experimen-
tal studies have focused on the investigation of water reactivity on the most stable surface of rutile polymorph, which is (110) surface, while there has been less attention on anatase. Therefore, all the MD simulations for anatase nanoparticles in water are done by applying potential parameters that are provided for rutile (110) surface [105], and lack of proper parameters for simulating adsorption of water on anatase-nanocrystal surfaces is greatly sensed.

In this work, we have been able to identify the best parameters describing the interactions between anatase surfaces and water molecules. Although the detailed information for such approach has been reported in Chapter 4, it can been said in summary that by having the parameters obtained for clusters of TiO$_2$, along with an accurate picture of adsorbed water on such surfaces provided by either experimental works [106–110] or by first-principles calculations [111,112], we have been able to refine the existing parameters to be used for anatase phase of TiO$_2$. Also, we have been able to test the adsorption of water on the most important rutile surface [the (110) surface] and we have shown that the results obtained for this polymorph is also within acceptable limits, and the new parameters can adequately describe the interaction of molecular or dissociated water molecules on this surface. We have compared both water adsorption energy and geometry of molecular water or only geometry for dissociated water on each of the surfaces and have shown that the results are in close agreement with experimental works [106–110] or by first principle calculations [111,112].

The last chapter (Chapter 5) is dedicated to our observation for water adsorption on a single anatase nanocrystal at both room temperature and pressure and also hydrothermal conditions (the conditions at which anatase nanocrystals are manufactured by sol-gel synthesis). As it is fully addressed in Chapter 5, adsorption of water on different sizes and shapes of anatase nanocrystals has been examined, and these results are compared to the ones obtained for bulk water layering on anatase (101) surface. As is explained in Chapter 5, the simulations of nanocrystal aggregation in water are computationally demanding, which would need more computational source and time to be performed.
Chapter 2

Methods

2.1 Abstract

The goal of this chapter is to show the superiority of MD simulations for the case of this work and to introduce available MD algorithms. Also the reasons for choosing the specific potential for titanium dioxide particles and water molecules, which are being applied in the further calculations are mentioned. In addition, the first steps in the preparation of applied nanocrystals in this research work are summarized here.
2.2 Introduction

In order to understand the properties of molecular clusters in terms of their structure and the microscopic interactions between them, applications of atomic-scale simulations, specifically molecular dynamics (MD) is very helpful. As its name suggests, MD brings in aspects of dynamics, the study of why assemblies of molecules move as they do, as well as their thermodynamics. To do so, in MD simulations, the classical equations of motion are solved numerically and step-by-step, where it is assumed that the atoms move according to the Newton’s equations of motion, given by

\[
m_i \ddot{r}_i = f_i \tag{2.1}
\]

\[
f_i = -\frac{\partial}{\partial r_i} U(r_i) \tag{2.2}
\]

where, \(m_i, f_i,\) and \(U(r_i)\) are the mass, force, and the total potential energy of atom \(i,\) respectively. Therefore, it can be said that MD is a computational method for evaluating the thermodynamics and transport properties of materials by solving the classical equations of motion. This is very helpful in our studies, where we are trying to understand the specific mode of nanoparticle aggregation, the so-called oriented attachment mechanism, that the movement and approach of atomic clusters is very important. The size of the systems that we are working with are large enough, so that it makes first-principle studies an impossible choice. Hence, MD simulation is the best choice regarding the accuracy and time issues.

2.3 The MD Algorithm

The general idea of MD simulations is to iteratively numerically integrate the coupled systems of ordinary differential equations of motion, for which there exists several methods. However, in order to have an algorithm that has the capabilities of (i) being able to cope with both short and long timescales; (ii) calculating the forces as infrequently as possible [this is an expensive step]. There are various equivalent versions of the Verlet algorithm, including the original method [velocity Verlet], and a ”leapfrog” form [leapfrog Verlet].
2.3.1 The Velocity Verlet Algorithm

The velocity Verlet is usually the default integration algorithms, because of its simplicity and time reversibility. The algorithm generates trajectories in the microcanonical (NVE) ensemble in which the total energy [kinetic plus potential] is conserved. The total energy fluctuates dramatically in the course of a simulation if the timestep is too large or the potential cutoff is too small. The velocity Verlet algorithm has two stages, at the first stage it requires values of position \( r \), velocity \( v \) and force \( f \) at time \( t \). The first stage is to advance the velocities to \( t + \frac{1}{2} \Delta t \) by integration of the force and then to advance the positions to a full step \( t + \Delta t \) using the new half-step velocities:

\[
\bar{v}(t + \frac{1}{2} \Delta t) \leftarrow \bar{v}(t) + \frac{\Delta t}{2} \bar{f}(t) \tag{2.3}
\]

where \( m \) is the mass of a site and \( \Delta t \) is the timestep.

\[
\bar{r}(t + \Delta t) \leftarrow \bar{r}(t) + \Delta t \bar{v}(t + \frac{1}{2} \Delta t) \tag{2.4}
\]

Between the first and the second stage a recalculation of the force at time \( t + \Delta t \) is required since the positions have changed.

\[
\bar{f}(t + \Delta t) \leftarrow \bar{f}(t) \tag{2.5}
\]

In the second stage the half-step velocities are advanced to to a full step using the new force.

\[
\bar{v}(t + \Delta t) \leftarrow \bar{v}(t + \frac{1}{2} \Delta t) + \frac{\Delta t}{2} \frac{\bar{f}(t + \Delta t)}{m} \tag{2.6}
\]

2.3.2 The Leapfrog Verlet Algorithm

Although leapfrog Verlet scheme is a little simpler and faster than the velocity Verlet, it is not time reversible and does not have the numerical stability the velocity Verlet scheme has. Furthermore, all kinetic related properties have approximate estimators due to the half a step phase offset between velocity and position. The leapfrog Verlet algorithm is performed in one stage. It requires values of position \( r \) and force \( f \) at time \( t \) and velocity \( v \) at half a timestep behind: \( t - (1/2) \Delta t \).
At first, the forces are recalculated at time $t$ (from time $t - \Delta t$) since the positions have changed from the last step:

$$\bar{f}(t) \leftarrow \bar{f}(t - \Delta t) \quad (2.7)$$

The velocities are advanced by a timestep to $t + (1/2)\Delta t$ by integration of the new force.

$$\bar{v}(t + \Delta t) \leftarrow \bar{v}(t - \frac{1}{2}\Delta t) + \Delta t \frac{\bar{f}(t)}{m} \quad (2.8)$$

where $m$ is the mass of a site, and then the positions are advanced to a full step $t + \Delta t$ using the new half-step velocities

$$\bar{r}(t + \Delta t) \leftarrow \bar{r}(t) + \Delta t \bar{v}(t + \frac{1}{2}\Delta t) \quad (2.9)$$

MD simulations normally require properties that depend on position and velocity at the same time (such as the sum of potential and kinetic energy). The velocity at time $t$ is obtained from the average of the velocities half a timestep on either side of timestep $t$:

$$\bar{v}(t) \leftarrow \frac{1}{2} \left( \bar{v}(t - \frac{1}{2}\Delta t) + \bar{v}(t + \frac{1}{2}\Delta t) \right) \quad (2.10)$$

The instantaneous kinetic energy, for example, can then be obtained from the atomic velocities as

$$E_{\text{kin}}(t) = \frac{1}{2} \sum_{i=1}^{N} m_i \bar{v}_i^2(t) \quad (2.11)$$

However, in order to calculate the force acting on each atom in the Verlet algorithms, a potential energy $U(\mathbf{r})$, is usually being used. Function $U(\mathbf{r})$, where $\mathbf{r}$ represents the position vector, is given by the sum of all intra and intermolecular interactions, the latter being defined semi-empirically by force fields also known as interaction potentials. In a force field method, the molecules are described by a "ball and spring", with atoms having different sizes and "softness" and bonds having different lengths and "stiffness" [113]. The bonding information for force fields are obtained explicitly by using data from experiments and other higher level
computational data (i.e. \textit{ab initio} methods).

2.4 Force Field

To carry out MD simulations for this work, the interactions between \textit{Ti} and \textit{O} atoms are needed, to study the aggregation of TiO$_2$ nanoparticles in a vacuum. Also, in an aqueous environment, there exists \textit{Ti}, \textit{O}, \textit{O}_W [oxygen site of water], and \textit{H}_W [hydrogen site of water], where the interaction potentials of all species must be known. In order to choose the best potentials for describing the atomic interactions of a system, it should be considered that the conceptual and computational simplicities are of great importance. At the same time, the potential model should be reliable in terms of its transferability across various polymorphic phases of titanium dioxide. Therefore, an interatomic potential that not only reproduces the crystallographic structures of the polymorphs, but also various physical properties across a range of conditions is generally preferred for MD simulations.

2.4.1 Force Field for the Titanium Dioxide Particle

For modeling TiO$_2$ polymorphs, a large number of potentials have been reported in the literature [9, 11, 114–121]. Collins and Smith [122] have done a thorough survey of nine most promising force fields and have concluded that the Matsui-Akaogi force field [11] is the most suitable for classical molecular dynamics simulations of TiO$_2$ for a wide range of temperatures. It was shown that compared to the other force fields [122], Matsui-Akaogi gives the closest results to the experimental data for lattice energy, polymorphic structures, electric and dielectric constants, and relative surface energies of TiO$_2$ polymorphs [122]. The suitability of this potential has been demonstrated in a broad variety of applications [13, 120, 123–128], including that of Dubrovinskaia \textit{et al.}, who used it to predict a new high-pressure phase of TiO$_2$ that was confirmed experimentally [128]. The Matsui-Akaogi force field has also been shown to perform similarly to a more complex and computationally demanding variable charge model [9, 48, 129].

A two-body rigid-ion Matsui-Akaogi force field is selected to describe the interactions between \textit{Ti} and \textit{O} sites in TiO$_2$ nanoparticles [11]. In this potential, the
interaction energy $U$ between atoms $i$ and $j$ separated by a distance of $r_{ij}$ has the form

$$U(r_{ij}) = A_{ij} \exp\left(-\frac{r_{ij}}{\rho_{ij}}\right) - \frac{C_{ij}}{r_{ij}^6} + \frac{q_i q_j}{r_{ij}}.$$  \hspace{1cm} (2.12)

The Matsui-Akaogi force field assigns partial charges $q$ of +2.196 and −1.098 to titanium and oxygen, respectively ($q_O = -q_{Ti}/2$). These effective charges were obtained by Traylor et al. by fitting to the experimentally observed phonon dispersion of rutile [130]. Among the three terms of this force field, the first two terms in Eq. (2.12) constitute a Buckingham potential, and the last one corresponds to the electrostatic potential. Both Buckingham, which may be interpreted as the non-polar part of the interaction, and electrostatic potentials, which is due to the atomic charges, are non-bonded energies.

Buckingham potential representing van der Waals energy of the system is zero at large distances and becomes very repulsive at short interatomic distances. However, at intermediate distances, this value is negative, indicating a slight attraction caused by the induced dipole-dipole interactions. A general function form of van der Waals energy that fits these conditions is a summation of a repulsive energy ($E_{\text{repulsive}}(R)$) and an attraction term ($-C/R^6$). It is not possible to theoretically derive the functional form of the repulsive interaction, as it is only required that it goes to zero as $R$ goes to infinity, and it should approach zero faster than the $R^{-6}$ term. There are several forms available for this term, however, from electronic structure theory, it is known that the repulsion is due to overlap of the electronic wave functions, and furthermore that the electron density falls off approximately exponentially with the distance from the nucleus. There is therefore, justification for choosing the repulsive part as an exponential function, and the general form of the "$A \exp(-R/\rho) - C/R^6$" function is known as "Buckingham" potential. Also, employing three parameters in the Buckingham potential makes it a better choice for the repulsion part than a two-parameter term. The parameters for the Buckingham potential, $A_{ij}$, $\rho_{ij}$ and $C_{ij}$, were adjusted to reproduce the reported elastic constants of rutile, along with the observed crystal structures of rutile, anatase, and brookite [11]. The values of these parameters are listed in Table 2.1.
Table 2.1: Parameters for the Buckingham potential of the Matsui-Akaogi force field [11].

<table>
<thead>
<tr>
<th>Ion-Ion</th>
<th>A, kcal/mol</th>
<th>ρ, Å</th>
<th>C, kcal Å(^6)/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti − Ti</td>
<td>717654</td>
<td>0.154</td>
<td>120.997</td>
</tr>
<tr>
<td>Ti − O</td>
<td>391053</td>
<td>0.194</td>
<td>290.392</td>
</tr>
<tr>
<td>O − O</td>
<td>271719</td>
<td>0.234</td>
<td>696.941</td>
</tr>
</tbody>
</table>

2.4.2 Force Field for Water Molecules

Water is the most important solvent with applications in nearly every aspect of our lives. Due to its polarity and safety, it has become the number one choice of solvent. In order to do MD simulations of water molecules, it is necessary to have a force field that best describes the paired potential interactions in water.

Hence, for the aqueous solution, water was tested to be adequately represented by the rigid, nonpolarizable SPC/E model [12], relying only on the non-bonded interactions. It is a three-site model, which assigns partial charges to one oxygen and two hydrogens for calculating electrostatic energy by Coulomb’s law, and applies a Lennard-Jones (LJ) potential to the oxygen site to define the dispersion and repulsion. This potential is represented by Eq. (2.13); where \( r_{ij} \) is the distance between atoms \( i \) and \( j \), and the other parameters are listed in Table 2.2. The \( O − H \) distance in each water molecule is constrained to 1.03 Å and the \( H − O − H \) angle in each molecule is maintained at 109.47° by constraining the \( H − H \) distance to 1.633 Å.

\[
U(r_{ij}) = 4\epsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + \frac{q_i q_j}{r_{ij}}.
\]  

(2.13)
Table 2.2: Parameters for the SPC/E water model [12].

<table>
<thead>
<tr>
<th>Site</th>
<th>$q_i$, e</th>
<th>$\sigma_i$, Å</th>
<th>$\epsilon_i$, kcal/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>$O_W$</td>
<td>-0.8476</td>
<td>3.166</td>
<td>0.1554</td>
</tr>
<tr>
<td>$H_W$</td>
<td>+0.4238</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

This model is known to accurately reproduce the water density, water structure, and diffusivity over a wide range of temperature [12]. The SPC/E model, as most water models used in simulations, does not allow for dissociation of water molecules. However, for an anatase nanocrystal with the (101) surface being the majority of exposed crystal facets [3, 57, 58, 131–137], there is good experimental and theoretical evidence that the (101) surface is quite unreactive. In particular, water is found to adsorb without dissociation on a clean anatase (101) surface [58, 59, 103, 112, 138]. On the other hand, for the minority (001) surface, there is several data provided by first-principles calculations and experimental studies that show water molecules undergo spontaneous dissociative adsorption on clean anatase (001) surface [4,58,112,139–142]. This matches the reported observations of the presence of dissociated water at the surface of anatase nanoparticles, which cannot be explained if only the majority (101) surface is considered [4]. Hence, in this work, we will also consider dissociated water on the (001) facets of our nanocrystals via addition of charged groups (hydroxyl and hydrogen ions) on the (001) surface, the details of which will be discussed in Chapter 4.

2.4.3 Force Field for the Water-Particle Interactions

Having identified two models for anatase nanoparticle and water, only the interaction potentials involving the water and anatase surfaces is needed to do the simulations of anatase nanocrystal aggregation in water. Currently, many theoretical, and experimental studies have focused on the investigation of water reactivity on the most stable surface of rutile polymorph, which is (110) surface, and there
has been less attention on anatase phase. Therefore, all the MD simulations for anatase nanoparticles in water are done by applying potential parameters that are provided for small clusters of TiO$_2$ [105], and lack of proper parameters for simulating adsorption of water on anatase-nanocrystal surfaces is greatly felt.

In order to find MD parameters for anatase-water interaction, we have started with the \textit{ab initio} derived interaction parameters for Ti and O$_W$, and O$_{TiO_2}$ and O$_W$ reported by Bandura and Kubicki, which was later refined by Predota \textit{et al.} [13, 14]. These parameters are summarized in Table 2.3. Then, we have modified these parameters and derived accurate interaction potentials so that our simulations become a better match of first-principles calculations and experimental works available for anatase surfaces [103, 106–112, 136].

The \textit{ab initio} derived interaction parameters for TiO$_2$ and H$_2$O reported by Bandura and Kubicki [13] suggest that there is no interaction between anatase slab atoms and water hydrogen atoms except for electrostatic interactions. The interaction potentials describing the non-coulombic O$_{TiO_2}$–O$_W$ interactions are considered to be the same as O$_W$–O$_W$ interactions. Since the Bandura potential was not tested for surfaces of anatase, it is unclear whether it can adequately describe water interactions in our system. Fortunately, water adsorption to various anatase surfaces has been studied with \textit{ab initio} DFT calculations by Barnard and colleagues [58], as well as by Selloni \textit{et al.} [103,111,112,143,144]. These studies show the tendency of water molecules to be adsorbed molecularly on the (112) and (101) surfaces, which are of interest here. Also, these studies provide detailed information on the binding energies and geometries of adsorbed water. Selloni \textit{et al.} [59] used DFT to describe H$_2$O binding to stepped (101) surfaces of anatase and these results have relevance to water binding at nanocrystal edges. There are also some experimental works [106–110] that confirm the results obtained by DFT calculations.
Table 2.3: Interaction parameters for water oxygen and Ti and O atoms approximated by Matsui-Akaogi and SPC/E potentials [13].

<table>
<thead>
<tr>
<th>Ion-Ion</th>
<th>A, kcal/mol</th>
<th>ρ, Å</th>
<th>C, kcal Å⁶/mol</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti − O₆W</td>
<td>28593.02</td>
<td>0.265</td>
<td>148.000</td>
<td>BK parameters [13,14]</td>
</tr>
</tbody>
</table>

To carry out the simulations of water adsorption on an anatase nanoparticle, force field parameters derived for interactions between dissociated water molecules and terminating anatase surfaces are needed. As mentioned before, water has not shown a tendency for dissociation on a clean anatase (101) surface, however, it is predicted by both experimental and theoretical studies, that water would first dissociate on a (001) surface, and molecular water will be layering on the -OH and -H groups adsorbed primarily on the (001) surface [5]. According to Bandura and Kubicki [13], several modifications need to be made for running MD simulations of dissociated water on rutile (110) surface. These modifications include changing the charges of H and O of hydroxyl group and H of hydrogen group, along with titanium and oxygen sites of the surface and bulk, and also changing the Buckingham parameters for each set of pair interactions. However, in our case of simulating anatase nanoparticle aggregation in an aqueous environment, surface and bulk atoms may change positions, which makes it impossible to perform simulations with varying charge and force field parameters. Therefore, we have carried out the simulations of dissociated water adsorption on anatase (001) surface and rutile (110) surfaces, so that we may identify a new set of parameters with less complexity. We ran such simulations by dissociating water molecule into -OH and -H groups manually. The advantages of applying the derived new set of parameters for water adsorption simulations on anatase nanoparticles are listed in Chapter 4.
The Daresbury Laboratory molecular dynamics code, DL-POLY version 2.20 [145, 146] was applied to run all MD simulations carried out in this study, including the ones for anatase nanoparticle aggregation and molecular/dissociated water adsorption on anatase surfaces. This package is designed to facilitate MD simulations by providing the ability to run on a parallel architecture, and provide a great variety of thermostats, barostats and force fields including the Matsui-Akaogi potential and SPC/E water model. DL-POLY uses Verlet’s algorithm in conjunction with multiple timestep method, to integrate Newton’s laws of motion over time. The obtained trajectories are printed out in a preferred way, facilitating study of the exact pathway for the alignment of each nanoparticle before aggregation.

2.5 Preparation of Anatase Nanoparticles

![Diagram of equilibrated structures of large and small symmetric nanoparticles with Wulff shapes.](image)

Figure 2.1. Equilibrated structures of the large (a) and small (b) symmetric nanoparticles with Wulff shapes. Oxygen atoms are shown in red (dark) and titanium atoms are shown in white (light).

After choosing the most appropriate force fields available for MD simulations of anatase nanoparticle aggregation, the next step is to prepare nanocrystals for
Figure 2.2. Equilibrated structures of a large nanoparticle that is truncated on the (001) facet (a), and two nanocrystals that are truncated on the (112) facet [(b) and (c)]. Oxygen atoms are shown in red (dark) and titanium atoms are shown in white (light). The gray arrows represent the relative magnitudes and directions of the nanocrystal dipole moments.
this study. The nanoparticles studied in this research work are made uniquely, so that they are below the critical size of transition from rutile to anatase (as mentioned in Chapter 1), while being electronically neutral. Considering the fact that the synthesis method for such particles varies (ref. Chapter 1), the resulting nanocrystals may have different shapes. The most common structure seen for anatase nanocrystals in this size range is the one predicted by Wulff construction, which has a symmetric truncated tetragonal bipyramidal shape as shown in Figure 1.2. However, it has been observed by TEM images that during the synthesis, under specific environmental conditions [i.e. high pH values, or the type of organic additives in the colloidal solutions] some asymmetric shapes of anatase nanocrystals may form [1,10,23,57,57,132].

Therefore, in this study all shapes of anatase nanocrystals that have the highest probability of being made during the synthesis are considered. We have divided them into two categories, symmetric and asymmetric. The nanoparticles in the former group maintain their Wulff construction predicted by first-principles calculations based on density-functional theory (DFT) [3,135], and also by several experimental studies [1,75,147]. To generate the nanoparticles, the preferred shape with the desired size is cut out of a larger lattice that is constructed using the lattice parameters summarized in Table 1.1 for anatase. Excess titanium ions or oxygen ions are removed from the surface (or additional ones are added to the surface) to obtain charge balance and ensure neutrality. As shown in Fig. 1.2, nanocrystals with symmetric Wulff shapes have mainly (101) surface with a small amount of (001) facets. We consider Wulff-shaped nanoparticles of two different sizes: large nanoparticles that contain 3774 Ti and O atoms [Fig. 2.1(a)]; and small nanoparticles with 816 atoms [Fig.2.1(b)]. The length-to-width ratios of these nanocrystals were selected to approximately match those predicted in the DFT study by Barnard and Zapol [135].

In addition to symmetric Wulff shapes, we considered three asymmetric nanocrystals, shown in Fig. 2.2 (a), (b), and (c), which mimic possible off-Wulff shapes that could occur during crystal growth. Unlike the symmetric nanoparticles, these asymmetric nanoparticles possess permanent dipole moments. Thus, we can study the importance of dipole-dipole interactions, which have been proposed to be effective in oriented attachment [76,77,81,148,149]. We have calculated the
dipole moments, $\mu$, of each nanocrystal by the following equation:

$$\mu = \sum_i q_i \mathbf{r}_i$$

(2.14)

where $q_i$ and $\mathbf{r}_i$ are the charge and position vector of ion $i$, respectively. In the asymmetric nanoparticle shown in Fig. 2.2(a), the general Wulff shape is maintained but one of the (001) facets is truncated more, so one side is shorter than the Wulff length. This particle consists of 2958 atoms, and its dipole moment is $\mu \approx 35$ Debye. The nanoparticles shown in Fig. 2.2(b) and (c) each have a (112) truncation. Although the (112) facet is not a terminating plane in the Wulff shape, it has been observed experimentally that some synthesized anatase nanocrystals have a small (112) facet [1,10,23,57,57,132]. The nanocrystals in Fig. 2.2(b) and (c) consist of 3141 and 3528 atoms and they possess dipole moments of 250 and 75 Debye, respectively.

As mentioned before, we employed the DL-POLY package [146], version 2.20 for all the simulations. Here we used the Verlet leapfrog algorithm, with a time step of 0.5fs, to integrate Newton’s equations of motion. The constructed nanocrystals were equilibrated for a time period ranging between 250ps and 2ns in the canonical ensemble at a temperature of 573K. This specific temperature is chosen based on the sintering temperature of anatase nanocrystals in the dry synthesis method [64].

For the symmetric nanoparticles, the equilibration was repeated three times using different initial velocity distributions and the results were independent of the initial condition. All nanocrystals essentially retained their initial shapes throughout the equilibration period, while we calculated the dipole moment $\mu$ of each nanoparticle. Due to their symmetric shapes, the dipole moments of the Wulff-shaped nanocrystals in Fig. 2.1(a) and (b) are zero. The three asymmetric nanoparticles in Fig. 2.2(a), (b), and (c) possess permanent dipole moments, which converged to values of 35, 250, and 75 Debye, respectively, after a 2ns equilibration period.
2.6 Summary

To understand nanoparticle forces and aggregation, application of atomic-scale simulations are very helpful. MD is a very helpful tool for understanding the forces and aggregation of nanoparticles esp. in the presence of solvent. Therefore, by step-by-step numerically integrating the classical equations of motion, MD is capable of solving problems that are currently challenging for first-principles simulations. Also, as its name suggests, MD calculates force and the interaction potential between nanoparticles as a function of their separation [150–155]. To date, even the most sensitive experimental methods do not allow measurement of these parameters. Therefore, MD simulations of nanoparticle aggregation provides proof for the atomic-scale phenomena [124,156–161], which has been obtained from experiment. Hence, MD simulations can be very helpful in resolving key phenomena that govern nanoparticle assembly.

There are several methods for MD simulations, the most important of which is the Verlet algorithm. In order to calculate forces acting on each atom in this algorithm, a force field is needed to calculate potential energy of the system. There are several force fields available for TiO\(_2\) and water, however, we have chosen Matsui-Akaogi and SPC/E models, which best describe the interactions in the above-mentioned materials, and they are among the simplest models. The anatase-water interactions, however, are not easy to calculate, mainly because there is no force field/parameters available for this type of interactions. Therefore, in this study we will be finding new parameters to be used for MD simulations of anatase-water systems, the details of such calculations are reported in Chapter 4.

In the last part of this chapter the nanocrystals that are used in the current study are shown, with their information regarding the number of atoms and the dipole moment of each one of them. Some of these nanoparticles are symmetric and have their Wulff structure, and the rest are asymmetric that are observed to be formed during the synthesis of anatase nanoocrystals. It has been shown that these nanocrystals retain their original shapes during the equilibration period at 573K.
Chapter 3

Oriented Attachment of Anatase Nanocrystals in Vacuum Environment

3.1 Abstract

We use classical MD simulations to study the aggregation of various titanium dioxide [anatase] nanocrystals in vacuum. In all cases, we observe a strong tendency for the nanocrystals aggregate along specific crystallographic directions, in the oriented attachment mechanism. Oriented attachment is driven by electrostatic forces between under-coordinated O and Ti surface atoms, which exist primarily on the edges between nanocrystal facets. Although some of the nanocrystals possess significant dipole moments, dipole-dipole interactions do not direct aggregation, implying that higher-order multipole moments are the driving force for oriented attachment.
3.2 Introduction

Aggregation of nanosized clusters occurs in materials synthesis through both colloidal and vapor-phase routes and, thus, plays a role in determining structure. In many cases, nanoparticles aggregate randomly, to produce irregular or fractal-like clusters, on which the classical descriptions of particle growth are based via Ostwald ripening [162]. However, nanocrystals can also approach one another and merge along specific crystallographic directions, in the oriented attachment mechanism [75–77,163]. The ability to direct crystallization through oriented attachment is an exciting prospect that could allow for the creation of new nanostructures with well-defined sizes and shapes. Several experimental studies have shown that modified shapes of nanocrystals can be formed for specific materials under unique environmental conditions [78–85,87,88,90–96].

Oriented attachment growth has first been observed in TiO$_2$ by Penn and Banfield [75], in SnO$_2$ by Leite et al. [164], in FeOOH by Banfield et al. and Penn et al. [165,166], in Fe$_2$O$_3$ by Penn et al. [166], in ZnO by Oskam et al. [162], in CoOOH by Penn et al. [166], and ZnS by Ocana et al. and Huang et al. [167,168]. Mechanism of oriented attachment has also been found in PbSe by Cho et al. [79], in ZnWO$_4$ by Liu et al. [169], in CuO by Lie et al. [170], in BiPO$_4$ by Geng et al. [171], in CdTe by Tang et al. [81], in ZrO$_2$ by Chen et al. [172], and in PbS by Zhang et al. [173]. One of the important qualities of most of these materials is that they are relatively insoluble, which decreases the rate of random contact. Hence, oriented attachment becomes a strong factor for the aggregation of such particles. It has been shown that both mechanisms may operate simultaneously, with the dominant pathway changing with solution chemistry, particle surface condition, and temperature [168]. However, to this end, a thorough insight into the origins of the oriented attachment mechanism is not observed.

Due to the unique and useful properties of titanium dioxide, this material has found a significant role in several applications in industry [see Chapter 1]. In most of these applications, the attachment of nanocrystals is of great importance for the efficiency of the devices. In order to improve such devices, it is necessary to have a detailed understanding of the alignment of TiO$_2$ nanocrystals. Moreover, it has been shown by experimental and theoretical works that for TiO$_2$ nanocrystal sizes
up to about 14 nm, nanocrystals appear to prefer the anatase phase rather than the rutile form [57,58,61]. This can be explained by the lower average surface energy of the anatase polymorph, and the very stable (101) surfaces that are dominant in anatase equilibrium crystal shape [Wulff shape as in Fig. 1.2].

Therefore, in this study, which is focused on the aggregation of TiO$_2$ nanocrystals in vacuum, we will be applying anatase structure for building the nanocrystals. Also, by studying the aggregation of nanoparticles in vacuum, we isolate the role of intrinsic forces between the nanoparticles.

Oriented attachment was discovered in experimental studies of the crystallization of colloidal anatase [75]. In a colloidal system, oriented attachment could originate from intrinsic forces between nanoparticles, such as dipole-dipole interactions [76,77,81], or from selective adsorption and surface chemistry of liquid-phase molecules at the nanoparticle-liquid interface [76,77,84]. It is also possible that a synergistic interplay between these various phenomena could lead to a directional preference for aggregation [76,77,79,81,174].

### 3.3 Simulation Methods

#### 3.3.1 Force Field Selection

In order to run the simulations, we need a strong tool, which accurately and efficiently predicts the motion of nanocrystals. As discussed in Chapter 2, atomic-scale investigations could contribute significantly to understanding oriented attachment. Although understanding the forces and dynamics between nanometer-sized particles especially in the presence of solvent] is currently challenging for first-principles simulations, classical molecular dynamics (MD) can simulate nanoparticle aggregation [124, 156–160, 175] and furnish many details of this process that are not accessible experimentally.

We expect the long-range interaction between two TiO$_2$ nanoparticles that are separated by more than a few Ångstroms to be dominated by the electrostatic [or Madelung] potential. In quantum-mechanical embedded-cluster calculations, for example, the long-range electrostatic potential is often described classically, by a set of point charges placed on the ions [176–180]. Here, we use the Matsui-Akaogi
force field [11] to describe this interaction. The details and advantages of this force field over the other reported force fields for TiO$_2$ have been summarized in Chapter 2. The force field parameters are also listed in Table 2.1.

### 3.3.2 Simulation Details

To simulate nanoparticle motion, we employed the DL-POLY package [146], version 2.20. We used the Verlet leapfrog algorithm, with a time step of 0.5 fs, to integrate Newton’s equations of motion. A nanocrystal was constructed and equilibrated for a time period ranging between 250 ps and 2 ns in the canonical ensemble at a temperature of 573K. This specific temperature is chosen based on the sintering temperature of anatase nanocrystals in the dry synthesis method [64].

All nanocrystals essentially retained their initial shapes throughout the equilibration runs. During the equilibration, we calculated the dipole moment $\mu$ of each nanoparticle, which is given by $\mu = \sum_i q_i r_i$, where $q_i$ and $r_i$ are the charge and position vector of ion $i$, respectively. Due to their symmetric shapes, the dipole moments of the Wulff-shaped nanocrystals in Fig.2.1 (a) and (b) are zero. The three asymmetric nanoparticles in Fig.2.2 (a), (b), and (c) possess permanent dipole moments, which converged to values of 35, 250, and 75 Debye, respectively, after a 2ns equilibration period.

Subsequent to equilibration, we replicated the nanocrystals and placed them in different initial configurations corresponding to various center-of-mass separations and orientations relative to one another. We studied 50 different initial configurations for the symmetric nanoparticles and 40 for the asymmetric nanoparticles. Initially, the crystals were always sufficiently far apart that they could rotate freely without touching. We simulated the two-particle systems in the micro-canonical (NVE) ensemble. This can be regarded as a realistic environment under vacuum or low-pressure experiments, where heat transfer is slow.

In these set of simulations, no periodic boundary conditions are applied to ensure simulation of isolated nanoparticles. This is the most appropriate way to mimic the low-pressure conditions prevailing in the reactors of the chloride process. The cutoff is chosen such that all the ions in the system are included in force and energy calculations. The total simulation times in the two-particle runs ranged
between 1.0 and 5.0 ns, which is too short to study the entire sintering process, but is long enough to observe the approach, coalescence, and initial restructuring of the nanocrystals after coalescence. Furthermore the potential energy reaches a plateau by this time, indicating that the system is entering a quasi-steady state.

Hence, we have been able to determine how every nanocrystal shape aggregates under such environmental conditions. It should be noted that in our studies, we have only tested the systems of two identical nanoparticles. However, we would expect to have the same mechanism for systems consisting of more than two particles, or the ones with different shapes and sizes.

3.4 Results and Discussions

3.4.1 Aggregation Simulations

The aggregation mechanism shown for the large, symmetric nanoparticles in 3.1 is representative of that observed in 47 out of 50 total trajectories for the symmetric nanoparticles - in eight out of ten for the large nanoparticles and in 39 out of 40 for the small nanoparticles, and in 34 out of 40 total trajectories for the asymmetric nanoparticles. Fig. 3.1(a) shows the initial configuration, where the center-of-mass separation is $\sim 8.5$ nm. After 100 ps [Fig. 3.1(b)], the particles have already adopted the relative orientation that they assume upon aggregation.

Aggregation begins when an (001) surface of one particle contacts the edge between two (101) surfaces of another particle [Fig. 3.1(c)]. More specifically, one of the oxygen atoms on the edge between two (101) facets initially contacts one of the under-coordinated Ti atoms on the (001) surface of another particle. Subsequently, another O-Ti pair comes into contact and the aggregation occurs in a zipper-like fashion. After the particles have “zipped” together, one of the particles tilts, so that its (101) facet contacts the (001) facet of the other particle [3.1(d)], and a long-time restructuring process ensues.

During this long time, the nanoparticles essentially retain their initial shapes, while atoms that reside at the interface between them appear to be rearranging themselves slowly over time. Thus, aggregation occurs via a so-called “hinge” mechanism, which serves to join under-coordinated oxygen and titanium atoms.
Figure 3.1. Snapshots of the aggregation of the large symmetric nanocrystals. These figures are taken (a) at the beginning of the simulation; (b) after 100 ps; (c) after 160 ps and; (d) after 1.0 ns. Oxygen atoms are shown in red (dark) and titanium atoms are shown in white (light).
on the particle facets and edges. It is worth mentioning that in three out of 50 simulations for symmetric nanoparticles, aggregation occurred when the (101) surface of one particle contacted the edge between two (101) surfaces of the other particle. After this, one of the particles tilts to bring two (101) surfaces of the particles into contact.

![Figure 3.2](image.png)

**Figure 3.2.** Temperature and configurational energy variation with time for the aggregation process of two large nanocrystals with initial temperatures of 573K under NVE ensemble [Temperature is shown in red (dark) and configurational energy in green (light) colors].

Fig. 3.2 shows the temperature and configurational energy profiles during the aggregation simulation for large anatase nanocrystals. In all cases, the configurational energy drops when the two nanoparticles come into initial contact. This phenomenon is caused by the creation of a new low potential energy pairs as the ions of nanoparticles move closer to each other. Meanwhile, it is observed that there is a rapid increase in temperature simultaneously as the nanoparticles come in contact with each other. As one of the nanoparticles tilts, the cumulative surface area decreases, which leads to a decrease in the overall potential energy.

In order to conserve the total energy of an adiabatic system, the kinetic energy of the system must increase in accordance with the increase in the temperature of
Figure 3.3. Temperature and configurational energy variation with time for the aggregation process of two small nanocrystals (a), asymmetric nanocrystals (b) with initial temperatures of 573K under NVE ensemble [Temperature is shown in red (dark) and configurational energy in green (light) colors].
the system. The temperature rise is about 12K for the large nanocrystal. Similar profiles for the aggregation of the small and asymmetric particles are shown in Figures 3.3 (a), and 3.3 (b), respectively. For these simulations, the observed temperature rise is different from that found for the large nanocrystal. The comparison between $\Delta T$’s shows that the temperature rise upon aggregation decreases with increasing particle size, which is in accordance with the temperature being related to the average kinetic energy per particle. Therefore, we can conclude that a given decrease in total potential energy occurs when the nanocrystals aggregate, which in turn translates to an increase in temperature.

### 3.4.2 Force calculations in Aggregation Processes

To resolve the origins of the observed directional preference for aggregation, we first note that the interaction energy between the two nanoparticles is dominated by the electrostatic term in Eq. (2.12): The total electrostatic interaction is always at least ten times larger than the total Buckingham potential in our simulations. Although it is tempting to equate the dispersion-like term in the Buckingham potential with a van der Waals force, the values of the $C$ parameters in Eq. 2.1 are larger than the value of $C_6$ that would be inferred from the Hamaker constant for titanium dioxide [181]. Thus, these $C$ parameters can be regarded as fitting parameters for the Matsui-Akaogi potential and we can conclude that attractive dispersion forces are negligible compared to electrostatic forces.

In Fig. 3.4, we show the relative magnitude of the inter-particle force [intraparticle forces are not included in Fig. 3.4] on each atom when the two large, symmetric nanoparticles are in the initial stages of aggregation. Here, we see that the largest forces occur for atoms that direct oriented attachment: those on the edge between two (101) surfaces of the particle on the left in Fig. 3.4 and an (001) surface of the particle on the right. These large forces occur on two-coordinated O atoms along the edges between two (101) surfaces and for four- and five-coordinated Ti atoms on the (001) surface.

In the bulk, Ti atoms are six- and O atoms are three-coordinated, while on the facets, Ti atoms may be four-, five-, or six- coordinated and both two- and three-coordinated O atoms can be found. However, four-coordinated titanium
Figure 3.4. The magnitude of the inter-particle force on each atom when two large nanoparticles are in the initial stages of aggregation. Forces are shown relative to the minimum observed force, which takes the value of one.

Atoms only exist on two edges of the (001) facet, and the two-coordinated oxygen atoms that exist on the edges between two (101) facets have the highest density in the symmetric nanoparticles. The high O density makes aggregation favorable along this edge. Thus, electrostatic interactions between under-coordinated Ti and O atoms drive the aggregation. It is worth mentioning that we monitored the dipole moment as a function of time as the particles approached each other and aggregated. For both the symmetric and asymmetric nanoparticles, this quantity remained essentially constant, fluctuating about its permanent value.

Interestingly, asymmetric nanoparticles exhibit similar aggregation mechanisms to the symmetric ones, despite the fact that these particles possess permanent dipole moments. The asymmetric nanocrystals in 2.2(a) have a high density of
Figure 3.5. (a) Electrostatic map around the asymmetric nanoparticle in 2.2(c), and (b) Coordination number of atoms on the outer surfaces of the asymmetric nanoparticle.
Figure 3.6. (a) Electrostatic map around the small symmetric particle 2.1(b), (b) Electrostatic map around the asymmetric nanoparticle in 2.2(a), and (c) Electrostatic map around the asymmetric nanoparticle in 2.2(b).
two-coordinated oxygen atoms on two of the edges between the (001) and (101) surfaces. While this high density occurs in the symmetric nanoparticles, one of the (001) facets is larger in the asymmetric nanoparticles, so that the length of this edge is comparable to the length of the long edges between two (101) surfaces, which are also rich in two-coordinated O. As for the symmetric nanoparticles, two of the edges between the (001) and (101) surfaces contain four-coordinated Ti. Due to restructuring of the edges of the large (001) facet [which is evident in the curvature of the edges in Fig. 2.2(a)], the number of four-coordinated Ti atoms is the same on the edges of the large and small (001) facets and they have a nearly equal propensity for aggregation. Therefore, in addition to exhibiting the mechanism seen for the symmetric nanoparticles in five trajectories, the nanoparticles in Fig. 2.2(a) also aggregate when two edges between (001) and (101) facets contact in two out of eight trajectories. We did not observe aggregation along the direction of the dipole for these nanoparticles.

The asymmetric nanoparticles in Fig. 2.2 (b) and (c) contain (112) facets, which were observed to be the preferred facets for nanoparticle aggregation in experimental studies of the growth of colloidal anatase [75]. Additionally, both of these nanoparticles have dipole moments and the nanoparticle in Fig. 2.2(b) has a large dipole moment ($\mu = 250$ Debye) along the (112) facet. Despite this, these nanoparticles aggregated along the dipole moment in only one out of 32 trajectories. In 19 out of 32 trajectories, the aggregation mechanism for these nanoparticles was identical to that for the symmetric ones. Also, the high density of two-coordinated oxygen atoms on the edge between the (112) and (101) surfaces on these nanoparticles makes this edge another alternative for the initial aggregation. In eight trajectories we observed initial aggregation via the edge between the (112) and (101) surfaces and the (001) facet. In half of these 8 runs, when the particles have “zipped” together, one of the particles tilts, so that its (112) facet contacts the (001) facet of the other particle. However, in 4 out of 32 total simulations the aggregation was observed to initialize between two (101) facets, or one (101) and one (112) facet.

To clarify the aggregation mechanism, we created maps of the electrostatic potential surrounding the nanocrystals. We set up a grid of points in the plane parallel to each nanoparticle facet and obtained the electrostatic potential by summing the
electrostatic interactions between a charge and the nanocrystal ions at each grid point. In Fig. 3.5 (a) we see that the electrostatic potential is the most negative around the intersection of the (112) and (101) surfaces and at the edges between two (101) facets, which can be linked to the high density of two-coordinated O atoms in these areas [cf., Fig. 3.5 (b)]. As we saw for the symmetric nanoparticles, the four-coordinated titanium atoms are located on the (001) facets, where the electrostatic potential is the most positive. The electrostatic map of other symmetric and asymmetric nanoparticles are shown in Fig. 3.6, which again match the corresponding coordination number of the atoms at the edges.
3.5 Summary

In this chapter we study the aggregation phenomena between nanoparticles in vacuum. The reason we chose vacuum for starting our simulations is because of the fact that we can ignore the solvent effect and retain the intrinsic particle-particle interactions.

Therefore, we have made systems of two identical anatase nanocrystals and studied the aggregation mechanism of them under micro-canonical ensemble. This is considered a realistic environment for vacuum or any low-pressure experiment, when heat transfer is slow. Eventually the nanoparticles aggregate, which leads to a decrease in the potential energy, that results in an increase in the kinetic energy that translates into a rise in temperature.

Furthermore, our simulations indicate that electrostatic forces between undercoordinated atoms on the edges between nanocrystal facets drive oriented aggregation. Although dipole-dipole interactions have been inferred to be the driving force for aggregation in previous studies [76, 77, 81], we find that oriented attachment rarely occurs along the direction of the dipole - even when the permanent dipole moment is as large as 250 Debye. Although the dipole-dipole interaction is the leading term in the multipole expansion of the electrostatic potential [104] for neutral particles, such as those studied here, higher order, multipole moments [e.g., quadrupole, octapole, etc.] can also contribute to the electrostatic potential. Our results imply that these high-order multipoles dominate the electrostatic potential and that they are created by under-coordinated surface atoms.

Comparing our results to those in experimental studies of colloidal [hydrothermal] anatase [75], we find that our simulated aggregates resemble some of the experimental images obtained with high-resolution transmission electron microscopy. However, in the experimental study, aggregation occurred primarily on (112) facets [75] and such events are in the minority here. Given the substantial differences between the experimental (colloidal) and simulation (vacuum) environments, this discrepancy is perhaps not surprising. Our studies indicate that to fully address experimental observations, it is necessary to take into account the aqueous environment surrounding the nanoparticles, which includes dissociation of water and the hydroxylation of nanoparticle surfaces. Nevertheless, our studies do underline
a potentially significant driving force for oriented attachment that our conclusions may generally extend to such systems.
Chapter 4

Water Adsorption on Titanium Dioxide Surfaces

4.1 Abstract

One of the areas attracting increased attention of scientists, is understanding the origins of aggregation of anatase nano-clusters in an aqueous environment when used in industrial devices. Knowing that molecular dynamics (MD) simulations is a very strong choice for studying such mechanisms, there exists a difficulty of identifying the most appropriate force field capable of predict the aggregation dynamics. Although a method for describing the interactions of titanium dioxide nanocrystals has been found, the only calculated parameters are the ones that are obtained by Bandura and Kubicki (BK) with DFT studies for molecular cluster Ti(OH)$_4$(H$_2$O), and there exists a lack of data for larger systems, especially anatase phase. Therefore, in this study we test the capability of the BK potential to describe the binding of water to relevant surfaces of TiO$_2$.

We investigate the binding energies and conformations of molecularly adsorbed water on the (101) and (112) surfaces of anatase and the (110) surface of rutile. We find that the BK potential overbinds water on these surfaces and we suggest a set of Buckingham parameters for the Ti-O$_W$ interaction and LJ parameters for the O-O$_W$ interaction that yield binding energies and conformations in good agreement with first-principles DFT results [13,59,112]. We apply the re-parametrized
potential to describe the structure of water monolayers, bilayers, and trilayers on anatase (101) and we achieve good agreement with \textit{ab initio} MD [103]. In addition to adsorbing molecularly, water can dissociate on the (001) surface of anatase and on the (110) surface of rutile. Also, dissociative adsorption of water on anatase (001) surface leads to breakage of the bond between under-coordinated Ti and O atoms of the surface. This new structure was not observed by applying available parameters refined by Predota \textit{et al.} [14]. Therefore, we have suggested a new set of parameters for dissociative adsorption of water on anatase (001) and rutile (110) surfaces, so that the confirmation of the final structure matches those of DFT studies [13,112].
4.2 Introduction

Titanium dioxide (TiO$_2$) is a technologically important material in many industrial and scientific applications, most notably, in solar cell devices [40], photocatalysis [22–24], gas sensors [37], and biomaterials [18,19]. As described in Chapter 1, several polymorphs of titanium dioxide with distinct crystallographic structures have been found in nature [48]. Among its most common polymorphs, (which are rutile, anatase, and brookite) the bulk phase of rutile is the most thermodynamically stable of all at ambient pressures and temperatures. However, anatase has attracted great interest because it has exhibited the highest activity in many applications of TiO$_2$-based devices [1, 59]. Moreover, it has been reported experimentally and theoretically [57,58,61], that for TiO$_2$ nanocrystal sizes up to about 14 nm, nanocrystals appear to prefer the metastable anatase phase rather than the rutile form, because of its lower surface energy.

Fig. 1.2 shows the equilibrium shapes of rutile and anatase TiO$_2$ crystals based on calculated surface energies, [3,5,112] together with major low-indexed surfaces. Anatase nanocrystals typically expose (101) surface, which is the most stable surface of anatase, with small amounts of (001), while rutile has (110) surface as its major terminating surface. It has been shown that some synthesized anatase nanocrystals may have (112) facet as their terminating surface, although to a lesser extent than the other two surfaces [1,10,23,57,132].

The exposed surface of sintered TiO$_2$ nanocrystals plays a very important role in its application. For instance, when it is used as a photoactive material in the photocatalytic processes [22–24, 182], or as electrodes with a high effective surface area with the electrolyte solution [60,183], or in solar cell devices [40]. As most of these applications of TiO$_2$ nanocrystals involve an aqueous environment, the interactions between nanocrystal surfaces with water are critically important for understanding the nature of the photocatalytic processes occurring on these surfaces. Therefore, the H$_2$O–TiO$_2$ interaction has been extensively studied in the last twenty years. Among the three most stable polymorphs of TiO$_2$, the interaction of water with rutile and anatase TiO$_2$ has been extensively studied.

Considering the fact that currently many theoretical, and experimental studies have focused on the investigation of water reactivity on the most stable surface
of rutile polymorph, which is (110) surface, and there has been less attention on anatase phase, all MD simulations for anatase nanoparticles in water are done by applying potential parameters that are examined for rutile (110) surface [105]. In order to overcome the lack of proper parameters for simulating adsorption of water on anatase-nanocrystal surfaces, we have performed few thousands of simulations to optimize available parameters for clusters of TiO$_2$ to be suitable for carrying out MD simulations of anatase-TiO$_2$ particles. As in MD simulations a semi-empirical force field is used, the parameters of this potential must be fixed so that they reproduce the same results as the very accurate, yet time-consuming first principle studies. Therefore, we have compared an extensive literature survey to find the best first principle data, which matches well with the experimental studies, to be able to optimize the parameters of the force field we are applying.

In order to obtain a thorough understanding of the interaction of water with different TiO$_2$ surfaces, we have reviewed several literature studies on water adsorption on various anatase/rutile TiO$_2$ surfaces. One of the most important issues that significantly affects the H$_2$O–TiO$_2$ interaction, is the coordination numbers of surface atoms and their mutual distance [5]. The mechanism is proposed to be as the following: H$_2$O is almost always adsorbed on the under-coordinated titanium atoms of surface, through Ti-O bonding, while hydrogen bonding occurs between unsaturated oxygen atoms of the surface and water hydrogens [1,5,184].

In almost all cases of water adsorption on different TiO$_2$ surfaces that we have studied, the most important question has been whether water will dissociate over TiO$_2$ surfaces or not. The reason for this significance is that the produced hydrogen and hydroxyl groups greatly alter the particle surface chemistry [5]. The structure of adsorbed water molecules on TiO$_2$ surfaces depends on a combination of parameters such as, symmetry and corrugation of the underlying surfaces, the spacing between surface adsorption sites, and the relative strength of water-water and water-surface interactions [103,184], along with surface reconstruction and defects [e.g. oxygen vacancies, etc.] [5].

In order to find the best set of data for water adsorption on different TiO$_2$ defect-free surfaces, we have studied several theoretical studies carried out by different methods, e.g. density functional theory (DFT) [with various exchange-correlation functionals] [185–191], Hartree-Fock (HF) [192,193], etc.. As such, it is
valuable to summarize the results of the theoretical studies and examine and compare results obtained with different computational strategies to be able to identify the best available results.

4.2.1 H₂O/Anatase Interaction

Currently, many theoretical and experimental studies have focused on the investigation of water reactivity on the most stable surface of rutile polymorph [(110) surface], and there has been less attention on anatase phase, even though anatase–TiO₂ has higher reactivity in photocatalytic applications [24]. As described before, anatase particles obtained from available preparation procedures [summarized in Chapter 1], mainly terminate to the (101) surface, together with a small amount of (001) surface. Therefore, we have studied adsorption of water on these important surfaces, and for doing so, we have first gathered the important information from first-principle studies and experimental results, to be able to match our results against them. Below is a summary of this literature survey.

4.2.1.1 H₂O/Anatase(101)

Since the majority of the terminating surfaces of anatase nanocrystals are (101) surface, its interface with water has been of a great importance, and several studies have focused on it [1, 24, 58, 59, 103, 107–109, 111, 112, 136, 143, 144, 194–199]. Comparing the number of publications devoted to the adsorption or layering of water on the (101) surface, it is worth mentioning that Selloni and her group along with other scientists have obtained valuable results and broadened the knowledge on this matter. From what they have reported, it is concluded that water is adsorbed molecularly on a clean defect free (101) surface. They have also found that water is always adsorbed on the surface so that its oxygen forms a bond with a surface Ti₅c atom and both hydrogens of water form hydrogen bonds with the surface oxygen atoms (O₂c) [59, 112, 194]. Molecular adsorption of water on (101) surface was also supported by a dynamic simulation at 160K [112] and experimental works [temperature-programmed desorption (TPD) and XPS] [107].
The adsorption energy of water on (101) surface calculated by several theoretical works, confirming the molecular adsorption of water on this surface is summarized in Table 4.1. It is observed that the calculated adsorption energies are in the range of $0.56 - 0.84\,\text{eV}$, which is in an excellent agreement with experimental observations $[0.5 - 0.7\,\text{eV}]$ [58,107].

Besides, there are experimental studies [basically TPD] carried out to demonstrate the multi-layered water adsorption on anatase (101) surface [107]. It has been shown that there exists three desorption peaks for water at 160K, 190K, and 250K, which correspond to multi-layered water, water adsorbed to O$_{2c}$, and water adsorbed to Ti$_{Sc}$, respectively [107]. There are also some theoretical studies that are in agreement with this experimental result. Tilocca et al. carried out several dynamic simulations, where they have found the adsorption energies for the first, second and third layers $[0.69\,\text{eV}, 0.65\,\text{eV} \text{ and } 0.56\,\text{eV}, \text{respectively}]$ [103]. In addition, Tilocca et al. have shown that the first mono-layer of adsorbed water is mostly interacting with anatase surface, and is not involved in the network of

Table 4.1: Calculated water adsorption energies ($E_{mol}$) by published theoretical studies on anatase (101) surface. The coverage $\theta$ is a fraction of one mono-layer of water.

<table>
<thead>
<tr>
<th>Method</th>
<th>$\theta$</th>
<th>$E_{mol}$, eV/mol</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>DFT-PW91</td>
<td>$1/2$</td>
<td>0.71</td>
<td>[136]</td>
</tr>
<tr>
<td>DFT-PW91</td>
<td>$1$</td>
<td>0.82</td>
<td>[136]</td>
</tr>
<tr>
<td>DFT-PW91</td>
<td>$1/4$</td>
<td>0.84</td>
<td>[197]</td>
</tr>
<tr>
<td>DFT-PW91</td>
<td>$1$</td>
<td>0.77</td>
<td>[197]</td>
</tr>
<tr>
<td>DFT-PW91</td>
<td>$1$</td>
<td>0.56</td>
<td>[200]</td>
</tr>
<tr>
<td>DFT-PW91</td>
<td>$1$</td>
<td>0.75</td>
<td>[194]</td>
</tr>
<tr>
<td>DFT-PW91</td>
<td>$1/4$</td>
<td>0.78</td>
<td>[111]</td>
</tr>
<tr>
<td>DFT-PW91</td>
<td>$1$</td>
<td>0.72</td>
<td>[112]</td>
</tr>
<tr>
<td>DFT-PBE</td>
<td>$1$</td>
<td>0.75</td>
<td>[199]</td>
</tr>
</tbody>
</table>
hydrogen bonds, as the rest of the water molecules are. Since a good number of studies have focused on the adsorption of water on a defective anatase (101) surface, it is worth mentioning that dissociation of water can occur in the presence of bridging oxygen vacancies [59]. The role of defects in water dissociation has also been studied and it is shown that water can dissociate spontaneously along the ridges on the (101) surface [59,199].

4.2.1.2 $\text{H}_2\text{O}/\text{Anatase(001)}$

As shown in Table 1.2, anatase (001) surface has a much higher surface energy compared to anatase (101) surface [and therefore, higher reactivity], mainly because all surface atoms [$\text{Ti}_{5c}$ and $\text{O}_{2c}$] are unsaturated [3]. Regarding water adsorption on this surface, it is worth mentioning that all theoretical and experimental studies [4,112,141,194,196,201–204] show water dissociation, when this surface is exposed to less amount of water, as listed in Table 4.2, whereas at one mono-layer coverage a mixed molecular/dissociative adsorption state may occur [112].

Table 4.2: Calculated water adsorption energies ($E_{\text{dis}}$) by published theoretical studies on anatase (001) surface. The coverage $\theta$ is a fraction of one mono-layer of water.

<table>
<thead>
<tr>
<th>Method</th>
<th>$\theta$</th>
<th>$E_{\text{dis}},\text{eV/mol}$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>DFT-PBE</td>
<td>1/2</td>
<td>1.17</td>
<td>[203]</td>
</tr>
<tr>
<td>DFT-PW91</td>
<td>1/3</td>
<td>1.11</td>
<td>[203]</td>
</tr>
<tr>
<td>DFT-PW91</td>
<td>1/6</td>
<td>1.25</td>
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<td>1/2</td>
<td>1.73</td>
<td>[196]</td>
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<td>DFT-PW91</td>
<td>1/4</td>
<td>1.71</td>
<td>[136]</td>
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<tr>
<td>DFT-PW91</td>
<td>1/4</td>
<td>1.59</td>
<td>[112]</td>
</tr>
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<td>DFT-PW91</td>
<td>1/2</td>
<td>1.44</td>
<td>[112]</td>
</tr>
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<td>1</td>
<td>1.01</td>
<td>[112]</td>
</tr>
<tr>
<td>DFT-PBE</td>
<td>1</td>
<td>1.05</td>
<td>[136]</td>
</tr>
</tbody>
</table>
It has been proposed by Gong et al. that the high reactivity of (001) surface is mainly due to its surface O$_{2c}$ atoms [203]. It has also been shown [112] that the dissociative adsorption of water leads to a shorter Ti-O$_{2c}$ bond, and also to the cleavage of the surface Ti$_{3c}$-O$_{2c}$ bonds, with the formation of two Ti-OH bonds, which results in a much lower energy for the hydrated surfaces [203]. The length of the hydrogen bonds formed during the dissociative adsorption is found to be shorter than those of molecular adsorption, which confirms the preference of dissociative adsorption over the molecular adsorption [112].

![Figure 4.1](image). Water dissociation over (1 × 4) reconstructed anatase (001). (A) Reconstructed (001); and (B) Water dissociation. [4, 5].

Another difference of the reactive (001) surface is its tendency for reconstruction. It has been observed that at UHV condition, an annealed anatase (001) surface undergoes a (1 × 4) reconstruction, which is proposed to be related to its high surface energy via the existence of highly reactive Ti$_{4c}$ [205–207] [see Fig. 4.1]. As shown in Fig. 4.1, dissociation of water molecules occurs rapidly at the Ti$_{4c}$ species of a reconstructed (001) surface, with a higher adsorption energy than that
on \((1 \times 1)\) \((001)\) surface \[208\]. However, no water dissociation has been reported in the trenches of \((1 \times 4)\) reconstructed surface \[208\]. Several experimental studies, \textit{i.e.} photoelectron spectroscopy \[4\] that confirm such observations by theoretical calculations.

\section*{4.2.2 H}_2\text{O}/Rutile Interaction}

\subsection*{4.2.2.1 H}_2\text{O}/Rutile(110)}

Being the majority of the terminating surfaces of rutile nanocrystal, \((110)\) surface is one of the most studied systems, such that over the last decades, a magnitude of experimental and theoretical studies have focused on this surface \[1,184,209–218\]. Although, when it comes to the studies of water dissociation on this surface, there is still considerable controversy. In almost all experimental studies \[1,210–217\] it is observed that water adsorbs molecularly, at low coverages, on a defect free rutile \((110)\) surface, while in the computational community there is a dispute \[6,7,13,14,105,141,201,219–253\], which is basically because of the fact that there is little difference between the molecular and dissociative adsorption energies. Therefore, the theoretical methods that are used to obtain this adsorption energy play an important role \[5\].

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{diagram.png}
\caption{Dissociated configuration of water on defect free rutile \((110)\) surface. (A) Single water molecule (side view); and (B) One mono-layer coverage \[6\].}
\end{figure}
There have been several cluster simulations done for rutile-(110) surface, however, because of the small size of these clusters they may not represent the adsorption of water accurately, mainly because of the effects of the edge atoms [141,201,219,225]. However, cluster methods may improve significantly by applying first-principles simulations. Lindan et al. [6], used generalized gradient approximation (GGA) with BP88 functional for periodic slabs, to model the adsorption of water on rutile (110) surface. However, they also observed water dissociation on a (2 × 1) periodic slab with three-titanium layers [6]. According to Lindan et al. [6], when water dissociates on a defect free (110) surface, the -OH and -H groups form bonds with five-coordinated titanium atoms (Ti\textsubscript{5c}) and two-coordinated oxygen atoms (O\textsubscript{2c}), respectively [see Fig. 4.2(A)].

Thereafter, Lindan et al. [222] applied 3- and 5-titanium layers slabs with a full mono-layer of water to investigate water adsorption on rutile (110) surface. They reported that a mixed molecular/dissociative configuration is the most favorable adsorption state, as shown in Fig. 4.2(B). Later, by applying a 5-titanium layers slab and the RPBE functional, it was reported that the dissociation of an isolated molecule on rutile (110) surface is exothermic [237]. It was proposed that the main reason for experimentally observing only molecular adsorption is an energy barrier of about 0.25-0.45 eV for water dissociation on rutile (110) surface below 160K. Hence, they suggested that at low temperatures and low coverages, water molecules do not have enough kinetic energy and therefore, mobility to find adjacent sites or defects. They also concluded that the hydrogen bonds between neighboring molecules can lower the dissociation barrier.

Since there was no sign of dissociated water molecules on a defect free rutile (110) surface in the experimental studies [high resolution electron energy loss spectroscopy (HREELS) and TPD] [212], the above-mentioned theoretical calculations were lacking completeness. Later, Bates et al. [224] found that at one mono-layer water coverage on a thicker slab (5- and 6-titanium layer slabs) with a (1×1) surface unit cell, molecular adsorption is the dominant adsorption state [224]. Meanwhile, Schaub et al. showed that water dissociation on rutile (110) surface is endothermic [227], and found that by applying a small unit cell for the calculations, not all the intramolecular interactions will be included. They found that the dissociation result obtained by Lindan et al. was because of the small (2 × 1) super cell area.
that was employed in their calculations. However, it should be noted that Schaub et al. used a thin slab in their calculations, which is known to provide inaccurate results. Also, it is difficult to compare the results obtained by Lindan et al. and Schaub et al. as each group is employing different functionals and slab thicknesses.

Figure 4.3. Convergence of the molecular and dissociative water adsorption energies with slab thickness at full monolayer coverage (left) and for single water molecules (right). The calculation was based on a \((4 \times 2)\) super cell. The solid black lines represent results from full relaxations with water adsorbed symmetrically on both sides of the slab. The calculations in which water was adsorbed only on one side of the slab with the bottom two trilayers fixed at the bulk positions and the broken surface bonds at the bottom of the slab saturated with pseudo-hydrogen atoms are shown by the red dashed lines. [7].

Schaub et al. [227] also considered a larger super cell, \((2 \times 2)\) for their studies and reached the same conclusion that molecular adsorption is more favorable. A few years later, Harris et al. [236] considered 3- to 9-titanium layers slabs for a \((2 \times 2)\) super cell, and confirmed the preference of molecular chemisorption on rutile \((110)\) surfaces.

Finally, Kowalski et al. [7] calculated the adsorption energies of water in different thickness slabs ranging from 3 to 12-titanium layers. They employed PBE functional for one-monolayer and 1/8 mono-layer of water in a \((4 \times 2)\) super cell
[their results are shown in Fig. 4.3]. By DFT–PBE studies, Kowalski et al. showed that molecular adsorption is preferred over the dissociative adsorption, while at low coverages they become energetically degenerate.

Besides the thickness, the size of the super cell is also important and has been widely studied. The main reason for choosing a small super cell is because of the benefit in the time and costs, although computational accuracy also needs to be taken into account. Considering the interactions between adsorbates, a $(1 \times 1)$ cell is shown to be small [5], and it has become important to extend the super cell along both $(x, y)$ directions. Based on the extensive literature review by Sun et al. [5], a $(2 \times 2)$ super cell should give results similar to those with a larger area, such as $(4 \times 2)$ super cells.

Table 4.3: Calculated water adsorption energies by published theoretical studies on rutile (110) surface. $E_{\text{mol}}$, $E_{\text{dis}}$, and $E_{\text{mix}}$ represent molecular, dissociative, and mixed states of water adsorption given in eV/molecule [the preferred adsorption is indicated by bold numbers]. The coverage $\theta$ is a fraction of one mono-layer of water. Also, the number of titanium layers in each slab is given by N.

<table>
<thead>
<tr>
<th>Method</th>
<th>N</th>
<th>$\theta$</th>
<th>$E_{\text{mol}}$</th>
<th>$E_{\text{dis}}$</th>
<th>$E_{\text{mix}}$</th>
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<td></td>
<td></td>
<td>[6]</td>
</tr>
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<td>0.99</td>
<td>1.10</td>
<td>0.91</td>
<td>[222]</td>
</tr>
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<td></td>
<td>0.98</td>
<td>[224]</td>
</tr>
<tr>
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<td>3</td>
<td>1/4</td>
<td>0.56</td>
<td>-0.23</td>
<td></td>
<td>[227]</td>
</tr>
<tr>
<td>DFT-RPBE</td>
<td>3</td>
<td>1/2</td>
<td>0.40</td>
<td>0.42</td>
<td></td>
<td>[231]</td>
</tr>
<tr>
<td>DFT-RPBE</td>
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<td></td>
<td>0.37</td>
<td>[231]</td>
</tr>
<tr>
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<td>1.27</td>
<td></td>
<td>[232]</td>
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<td>0.42</td>
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<td>DFT-RPBE</td>
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<td>0.64</td>
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<td>0.37</td>
<td>[231]</td>
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Continued on Next Page...
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<thead>
<tr>
<th>Method</th>
<th>N</th>
<th>$\theta$</th>
<th>$E_{mol}$</th>
<th>$E_{dis}$</th>
<th>$E_{mix}$</th>
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<td>1.14</td>
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<td>0.87</td>
<td>0.83</td>
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<td>0.79</td>
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<tr>
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<td>DFT-PW91</td>
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<td>DFT-PBE</td>
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<td>DFT-PBE</td>
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</tr>
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<td>0.81</td>
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<td>1/8</td>
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<td></td>
<td>1.04</td>
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</table>
In order to have a better understanding of the previously conducted theoretical studies, various calculated results have been collected in Table 4.3. These results correspond to the ones obtained by periodic slab models, which are thicker than 3-titanium layers, and are thus more reliable. Also, the adsorption energies obtained by cluster models are not listed here. By comparing the results obtained from first-principle studies to the ones found by the experimental works [211,212,214], it appears that PW91 and PBE are the most accurate functionals.

Although static calculations are conveniently used for a maximum of one monolayer of water, dynamic simulations have to be employed for systems containing several layers of water. In order to start a classical MD simulation, a suitable force field must be chosen. Among several water models that have been developed, TIP3P and SPC/E are often used for the water/TiO\textsubscript{2} system [13,14]. For describing the interactions between Ti and O atoms in TiO\textsubscript{2}, the Matsui and Akaogi force field is found to be the best potential [11,13,14]. The interface of water with TiO\textsubscript{2} surfaces is also simulated using Matsui and Akaogi potential for the Ti-O\textsubscript{water} interaction [13]. Predota et al. studied the water/rutile-(110) for both hydroxylated and non-hydroxylated surfaces [14]. They showed that water molecules will form their first layer on top of surface Ti\textsubscript{5c} sites and the second layer above the surface O\textsubscript{2c} atoms. They also found that after the second layer, the water structure takes the same structure as for the bulk water. The same structure for two-layer water adsorbed on a rutile (110) surface was also confirmed by Mamontov et al. [105,247].

Skelton et al. [244] also carried out MD simulations to simulate the interface of water/rutile-(110), with the modified TIP3P water potential. Their results showed a two-layer water structure, which is consistent with the positions of two layers in other simulations [13,14]. These various force field MD simulations predict similar results, which are also in agreement with in situ X-ray crystal truncation rod (CTR) measurement [159]. However, in the MD simulations, there exists no water exchange between the first layer and the other layers, while experimental studies indicated that such exchange is feasible [254]. Because TIP3P and SPC/E models do not allow for the dissociation of water molecules, and considering the fact that first principle MD simulations can describe the adsorption and dissociation of water molecules, several first principles MD simulations have been carried out.
It has been shown by some first principle MD studies that partial dissociation of water may occur on rutile-(110) surface. However, because of the limits of first principle studies, it is not economic to use thick slabs for such simulations or run long enough simulations. Because the results of the simulations also depend on the computational methods and models, it is still difficult to unambiguously determine whether dissociative adsorption is favorable with respect to molecular adsorption [5]. Recently Cheng et al. [251] carried out first principle simulations of water multi-layers on rutile (110) surface with the GGA-PBE functional and a 5-titanium layers slab, and reported a dissociation free energy of 0.6 eV, suggesting that dissociative adsorption is unlikely on a defect free aqueous (110) surface.

Therefore, the key aspect of doing simulations of water/TiO$_2$ systems, is to find an optimized way to describe the interactions in such systems.

4.3 Simulation Methods

4.3.1 Force Field Selection

In order to find the best parameters describing the interactions between anatase surfaces and water molecules, an accurate picture of adsorbed water on such surfaces is needed. This data may be provided by either experimental works [106–110] or by first principle calculations [111,112]. Density functional theory (DFT) studies provide the structure and energetics of water adsorption on anatase surfaces, from which, it may be concluded that the favored adsorption mechanism of water on (101) and (112) surfaces is molecular adsorption, while a combination of molecular and dissociative adsorption is favorable for the (001) surface [111,112]. Although first principle studies may provide accurate results, because of their limitations, they may only be able to cover the very beginning of the adsorption process [e.g. first few picoseconds].

Besides these calculations, few X-ray photoelectron spectroscopy (XPS) and temperature-programmed desorption (TPD) studies [106,107,109,110,257] of anatase nanocrystals exist, which confirm the theoretical prediction of molecular adsorption of water on (101) facet. However, due to the difficulty in obtaining
sufficiently large high-quality anatase nanocrystals, experimental studies on well-characterized anatase surfaces are scarce [4]. Hence, by applying the strong tool of MD simulations, it would be possible to predict the behavior of anatase nanocrystals in a water environment. In this work we are deriving new parameters for the interactions between water and anatase surfaces for the first time, which will be further used to describe the layering of water surrounding anatase crystal surfaces. These new parameters will provide more accurate results for the simulation of the above-mentioned interactions.

To carry out simulations, the Daresbury laboratory code, DL-POLY version 2.20 [146], has been used. Knowing that the Matsui-Akaogi potential [11] is the most suitable force field available for classical molecular dynamics simulations of TiO$_2$ for a wide range of temperatures [122], we have selected it to describe the interactions between Ti and O ions by Eq. (2.12). The values of Buckingham potential parameters are listed in Table 2.1.

As described in Chapter 2, in the aqueous solution, water was tested to be adequately represented by the rigid, nonpolarizable SPC/E model [12], where the total interaction energy between oxygen and hydrogen sites of water are calculated by Eq. (2.13). The parameters of this potential are listed in Table 2.2.

To describe interactions between TiO$_2$ and water, Bandura and Kubicki (BK) adopted a hybrid force field combining elements of Eq’s 2.12 and 2.13 [13]. Their force field was refined by Predota et al. [14] and we adopt the refined version here. They assumed that the interaction between an H atom in water (H$_W$) and a Ti or O atom in TiO$_2$ is purely electrostatic, while the non-bonded interaction between oxygen atoms in water (O$_W$) and oxygen atoms in TiO$_2$ can be described by the SPC/E force-field [2.13] with $\epsilon_{O-W} = \epsilon_{O-Ow}$ and $\sigma_{O-Ow} = \sigma_{O-Ow}$. They used the Matsui-Akaogi potential to describe bonding between O$_W$ and Ti, introducing three additional parameters: $\sigma_{Ti-Ow}$, $\rho_{Ti-Ow}$, and $C_{Ti-Ow}$ [cf., Eq. 2.12]. They obtained these parameters by fitting to the structure and vibrational frequencies of the molecular cluster Ti(OH)$_4$(H$_2$O) predicted in first-principles density-functional theory (DFT) calculations with the generalized gradient approximation (GGA) B3LYP functional. Parameters for their force field are listed in Table 4.5.

Also, for the interactions between TiO$_2$ and hydrogen and hydroxyl groups, BK potential has a very complicated form, which assigns several partial charges
and interaction parameters differently to surface and bulk species. This form may not be successfully adopted for all kinds of simulations, where the surface and bulk atoms may change their positions during the course of simulations. Meanwhile, this potential has been refined by Predota et al. [14], where they have assigned different charges to hydrogens in the hydrogen and hydroxyl groups. Also, the charge of under-coordinated oxygen bound with the hydrogen group, which will be referred to as the bridging oxygen \((O_B)\), is different from the bulk oxygen charge. The values for these charges are chosen so that the system of slab and hydrogen and hydroxyl groups are electronically neutral [see Table 4.9]. Another restriction that is implied in this potential is the fixed bond lengths that are set for Ti–O and O–H, the values of which are reported in Table 4.10. Also, an angle bending potential is introduced to both Ti–O–H angles, where \(E_{\angle Ti-O-H} = (1/2)k(\theta - \theta_0)^2\) with \(k=0.6124 \text{ eV/rad}^2\) and \(\theta_0=90.85^\circ\). As for the interaction parameters, it is assumed that the interactions between Ti–OH, O–OH, and O–O_{OB} are described by the Matsui-Akaogi potential, with the parameters listed in Table 4.8, while considering electrostatic interactions among all species of the system. Because the BK was not tested for surfaces of anatase, it was unclear whether it could adequately describe water interactions in our system. As such, in this research work we studied whether BK would appropriately describe anatase-water interactions.

### 4.3.2 Simulation Details

We perform two different types of calculations: energy minimization, to obtain binding energies and conformations, and molecular dynamics (MD) simulations to quantify structural properties of water multi-layers. The Daresbury laboratory MD simulation code, DL-POLY version 2.20 [146], has been used for these calculations. We utilize periodic slabs to represent various TiO_2 surfaces. As we will discuss below, the vacuum spacing, thickness, and lateral dimensions of the slabs have been adjusted to match corresponding DFT calculations. For all periodic simulations, a cutoff radius was applied for van der Waals interactions, equal to half of the shortest side of the slab. In addition, we have applied standard Ewald sum to correct the long-ranged electrostatic energies of the system. Also, NVT ensemble has been applied in all cases, where we employ Nose-Hoover thermostat with a
relaxation time of $\tau=0.5$ps. Water molecules were made rigid by applying three constraints for bond lengths $[O-H=1.03 \text{ Å}, \text{ and } H-H=1.68 \text{ Å}]$, using SHAKE algorithm. A timestep of 0.1fs is used in all simulations, while the trajectories are written at every 1ps.

4.4 Results and Discussions

4.4.1 Water Adsorption on Anatase

We consider three surfaces of anatase: the (101), (001), and (112). The adsorption of water on anatase has been studied by first-principles DFT calculations [58, 103, 108, 111, 112, 136, 144], as well as experimentally [107, 109, 143]. These studies show the tendency for water molecules to adsorb molecularly on the (112) and (101) surfaces, and its preference to initially dissociate on the (001) surface. In our discussion below, we first address molecular adsorption and we subsequently progress to dissociation.

4.4.1.1 Anatase (101)

![Diagram of Anatase (101) surface](image)

Figure 4.4. Anatase (101) surface, with half of the thickness shown. Red and gray circles represent O and Ti atoms, respectively.

The (101) surface of anatase is the most favored energetically [1] and it is, therefore, a good target for testing and improving the BK force field. To model this surface, we employ a periodic $(2 \times 1)$ slab with 4 layers of titanium, an area
of $(10.24 \times 7.57) \, \text{Å}^2$ per layer, a vacuum spacing of $\sim 15 \, \text{Å}$, and the composition $\text{Ti}_{16}\text{O}_{32}$. These slab dimensions were chosen to match those in first-principles calculations \cite{111,112}, so we could achieve good agreement regarding the convergence of the calculations. The structure of the relaxed (101) surface is shown in Fig. 4.4, where we see that it contains both coordinatively unsaturated 2(5)-fold O(Ti) (O$_{2c}$ and Ti$_{5c}$) and fully saturated 3(6)-fold O(Ti) (O$_{3c}$ and Ti$_{6c}$).

To study $\text{H}_2\text{O}$ adsorption, we place one water molecule parallel to the surface with its nucleophilic end 2.7 Å above one of the four Ti$_{5c}$ sites and the hydrogens in various random configurations. The water coverage, evaluated with reference to the number of surface Ti$_{5c}$ sites, is 0.25 monolayer (ML) to match DFT studies \cite{111,112}. Water molecules were adsorbed on one side of the slab only. During structural optimizations, atoms in the bottom layer of the surface slab were fixed to their bulk equilibrium positions, while water and the rest of the slab atoms were allowed to move until the maximum force on any atom was below 0.01 eV/Å. All of the different initial configurations of the water molecule lead to the same final configuration. We calculate the adsorption energy $E_a$ using the general expression

$$E_a = -\frac{1}{N_W} (E_{S+W} - E_S) ,$$

where $N_W$ is the number of water molecules, $E_{S+W}$ is the energy of the slab with water adsorbed on it, and $E_S$ is the energy of the bare slab.

\textbf{Figure 4.5.} Binding configuration for an adsorbed water molecule on anatase (101). Red and gray spheres represent O and Ti atoms, respectively, while white spheres represent hydrogens. The dashed lines indicate H-bonds between the water molecule and surface O$_{2c}$. 
Figure 4.5 shows the binding configuration of water on anatase (101). This is the binding configuration predicted by our re-parametrization of the BK potential, which we will discuss below – although we note that the binding configurations predicted by our potential, the BK potential, and DFT calculations are all qualitatively similar. As shown in Fig. 4.5, the water molecule binds via its oxygen to a Ti\textsubscript{5c} surface atom and associates with nearby O\textsubscript{2c} surface atoms via H bonds. We note that while our force field does not explicitly include a hydrogen-bonding potential, the attraction between positively charged hydrogens and negatively charged oxygens significantly affects the binding conformations of adsorbed water. We refer to this attraction as a hydrogen bond when the O–H bond length is less than 2.4 Å, the distance between the two involved oxygens is less than 3.3 Å, and the angle between the vectors connecting the oxygens to the H is less than 30°. This definition was also adopted by Tilocca and Selloni [144] in their studies of water near anatase surfaces. Table 4.4 lists adsorption energies and key structural parameters of an adsorbed water molecule on anatase (101) from DFT, experiment, the BK force field, and our modified force field. From Table 4.4, we see that while the lengths of the O-Ti\textsubscript{5c} and the H-O\textsubscript{2c} bonds predicted by the BK potential are in excellent agreement with DFT, the BK potential significantly overbounds the H\textsubscript{2}O molecule. Thus, we modified the BK potential to improve its agreement with DFT and experiment.

There are several options to improve the agreement between the potential and DFT. First, in the interest of preserving the transferability of the potential, we maintain fixed partial charges on the 4 different species involved (Ti, O, O\textsubscript{W}, and H\textsubscript{W}) that are set by the SPC/E and Matsui-Akaogi force fields. This means that to improve the water-TiO\textsubscript{2} interaction our options are as follows: (1) We can increase the repulsion between O\textsubscript{W} and Ti by increasing $A$ or $\rho$ in Eq. 2.12. (2) We can decrease the attraction between O\textsubscript{W} and Ti by decreasing $C$ in Eq. 2.12. (3) We can modify the LJ potential parameters between O\textsubscript{W} and O by changing $\sigma$ and/or $\epsilon$ in Eq. 2.13. (4) We can introduce LJ potentials to describe interactions between H\textsubscript{W} and O and/or Ti. To expand on this point, there are some theoretical studies [258,259] demonstrating that the lack of repulsion between H\textsubscript{W} and the negatively-charged site of a solid cluster (O in the case of TiO\textsubscript{2}) can be compensated by applying a LJ potential between H\textsubscript{W} and O.
Table 4.4: Structural parameters and adsorption energies \((E_a)\) of \(\text{H}_2\text{O}\) on anatase (101).

<table>
<thead>
<tr>
<th>Method</th>
<th>(E_a), eV</th>
<th>(\text{O}<em>\text{W}-\text{Ti}</em>\text{5c}, ) Å</th>
<th>(\text{H}<em>\text{W}-\text{O}</em>\text{2c}, ) Å</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>DFT-GGA</td>
<td>0.78</td>
<td>2.284</td>
<td>2.164</td>
<td>[111]</td>
</tr>
<tr>
<td>DFT-GGA</td>
<td>0.82</td>
<td></td>
<td></td>
<td>[136]</td>
</tr>
<tr>
<td>DFT-GGA</td>
<td>0.56</td>
<td>2.28</td>
<td></td>
<td>[58]</td>
</tr>
<tr>
<td>EXP (TPD)</td>
<td>0.69</td>
<td></td>
<td></td>
<td>[107]</td>
</tr>
<tr>
<td>EXP (TPD)</td>
<td>0.57-0.72</td>
<td></td>
<td></td>
<td>[109]</td>
</tr>
<tr>
<td>BK potential</td>
<td>1.21</td>
<td>2.29</td>
<td>1.90</td>
<td>[13,14]</td>
</tr>
<tr>
<td>Modified potential</td>
<td>0.78</td>
<td>2.59</td>
<td>2.32</td>
<td>This work</td>
</tr>
</tbody>
</table>

To test these options, we obtained binding energies and conformations for water in an iterative grid search in the acceptable range of parameters for these force fields. In this search, we began with a coarse parameter grid and we successively refined the grid in regions where the agreement between the potential and the DFT binding energies and conformations was the best. We find that increasing \(\rho\) for the \(\text{O}_\text{W}-\text{Ti}\) interaction in Eq. 2.12 and increasing \(\sigma\) for the \(\text{O}_\text{W}-\text{O}\) interaction in Eq. 2.13, as indicated in Table 4.5 yields the most satisfactory agreement with DFT calculations and experiment. We considered adding LJ potentials to describe the interaction between \(\text{H}_\text{W}\) and \(\text{O}\), but found that the improvements are negligible considering the complexity introduced by this set of interactions. Hence, we decided not to include such interactions. The results from the new set of parameters are listed in Table 4.4, where we see much better agreement between the potential and first principles values for the binding energy of water without a significant change in its binding configuration.
Table 4.5: Interaction parameters for water oxygen and Ti and O atoms approximated by Matsui-Akaogi and SPC/E potentials [14].

<table>
<thead>
<tr>
<th>Ion-Ion</th>
<th>A, eV</th>
<th>ρ, Å</th>
<th>C, eV Å^6</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti − O_w</td>
<td>1238.72</td>
<td>0.265</td>
<td>6.41</td>
<td>[14]</td>
</tr>
<tr>
<td>Ti − O_w</td>
<td>1238.72</td>
<td>0.276</td>
<td>6.41</td>
<td>This work</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Ion-Ion</th>
<th>σ, Å</th>
<th>ϵ, eV</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>O − O_w</td>
<td>3.166</td>
<td>0.0067</td>
<td>[14]</td>
</tr>
<tr>
<td>O − O_w</td>
<td>3.446</td>
<td>0.0067</td>
<td>This work</td>
</tr>
</tbody>
</table>

To further test the potential, we studied the monolayer and multi-layer structures for water on anatase (101) surface using energy minimization and MD simulations. Tilocca and Selloni also studied these structures using first-principles calculations [103,144] and their results serve as a second benchmark for the potential. To match their results, we used a periodic (2 × 1) slab with 4 layers of titanium, an area of (10.24 × 7.57) Å^2 per layer, and a vacuum spacing of ∼15 Å. Additionally, to achieve better statistics on possible disordering of water layers in MD simulations, we also probed a (4 × 2) slab with an area per layer of (20.48 × 15.14) Å^2. At monolayer (ML) coverage, there is one water molecule for every 5-coordinated Ti atom on the surface. This corresponds to 4 and 16 water molecules on the small and large slabs, respectively.

We first investigated the minimum-energy structure for a monolayer of water on anatase (101). The optimized structure is shown in Fig. 4.6. Similar to DFT results [103,144], we observe that water molecules adsorb with their oxygens near the Ti_{5c} atoms. We find one H bond between adsorbed water and surface oxygen for each water molecule and no H bonds among the water molecules, the later being consistent with DFT results [103,144]. In the ML configuration, the water
dipole vectors form a zigzag pattern along the [1\overline{1}0] direction, such that the dipole vectors of water molecules in adjacent [010] rows make an angle of $\sim 60^\circ$. The angle between the plane of a water molecule and the surface plane is $\sim 38^\circ$, compared to the $25^\circ$ angle seen in DFT [144]. Also, in DFT the binding energy per molecule drops 0.05 eV from the value at 0.25 ML to 0.69 eV [144], while the binding energy here remains equal to the value at 0.25 ML. Despite these differences, the qualitative agreement with DFT is very good.

![Figure 4.6. Top-down view of the optimized structure for 1 ML of water on anatase (101). Red bonds/spheres represent O atoms, white spheres represent hydrogen atoms of the water molecules, and gray bonds represent Ti atoms.](image)

To study dynamical properties of the water monolayer, we conducted an MD simulation at 160 K. We chose this temperature to match ab initio MD results [103,144], as well as temperature-programmed desorption (TPD) results [107]. In these simulations, the equilibration time was 2 ns and the subsequent production run was 8 ns. During the production run, we occasionally observe that water molecules can be promoted to the second layer, so that their oxygen site forms a hydrogen bond with the hydrogen site of an adjacent water molecule. The second-layer water molecules can also form hydrogen bonds with water molecules in a neighboring row, giving rise to a third layer. The rise and fall of first-layer water molecules is infrequent and it occurs over a time scale of several picoseconds.

To better analyze the dynamic structure of the monolayer, we calculated the distribution $p(z)$ of perpendicular distances $z$ between the oxygen sites of the
water molecules and the plane formed by the five-fold Ti surface atoms as an average taken every 1 ps for the entire production run. The resulting distribution is shown in Fig. 4.7(a), where we see that there are three peaks for a monolayer of water, centering around \( \sim 2.3 \) Å, \( \sim 3.4 \) Å, and \( \sim 4.4 \) Å. The first and the largest peak represents the water molecules that remain in the proximity of their original adsorption sites. At \( \sim 2.3 \) Å, this peak is located closer to the surface than the O\(_W\)-Ti\(_{5c}\) bond length for a water molecule at 0.25 ML coverage (cf., Fig. 4.4). Similarly, Tilocca and Selloni find a peak at \( \sim 2.0 \) Å, which is also closer to the surface than their O\(_W\)-Ti\(_{5c}\) bond length at 0.25 ML and consistent with the fact that our potential predicts a longer O\(_W\)-Ti\(_{5c}\) bond length than DFT. The smaller second and third peaks in Fig. 4.7(a) represent transient water molecules in second and third layers. These results do not match those obtained in \textit{ab initio} MD [103,144], where only one peak is seen corresponding to the first layer. While the origins of this discrepancy may lie with shortcomings of the potential, we note that the small supercell sizes in the \textit{ab initio} MD simulations, which consider only 4 water molecules in a monolayer, may prohibit this phenomenon. Also, the time scale for second-layer promotion exceeds the 7 ps duration of the \textit{ab initio} MD simulations. Thus, we observe second-layer promotion in 10-ns MD runs, but when we conducted 3-ps equilibration and 4-ps production runs with our potential, as was done with \textit{ab initio} MD [144], we only observed one peak associated with a monolayer.

We also quantified the average number of the H bonds per water molecule as an ensemble average in our MD simulations. Here, we find an average of 0.93 and 0.71 H bonds per molecule for H-O\(_{2c}\) and H-O\(_W\), respectively. This is in contrast to the \textit{ab initio} MD study, where they found 0.61 and 0.03 for these quantities [144]. As for \( p(z) \), part of the discrepancy lies with differences in the time scales probed by us (10 ns) and \textit{ab initio} MD (7 ps). Indeed, we find no H bonds among the water molecules at 0 K, consistent with the low DFT value, and 1 water-surface H bond per molecule. Thus, we see a tendency for the potential to overestimate water-surface H bonding compared to first principles.

In addition to the ordered monolayer structure, Tilocca and Selloni investigated water bilayers and trilayers [103,144], which we can also investigate to further test the force field. The optimized structure of the water bilayer from the force field is
Figure 4.7. Distribution of the perpendicular distance between the plane formed by surface Ti5c and the water oxygen atoms for a water monolayer (a), bilayer (b), and trilayer (c) during an 8-ns MD simulation at 160K. The horizontal lines shown for bilayer adsorption [(b)], represent the perpendicular distance between the plane formed by surface Ti5c and the water oxygen atoms at zero Kelvin.

shown in Fig. 4.8. Here, we observe that water molecules in the first layer have a configuration that is qualitatively similar to that observed for the monolayer, where the water oxygens reside close to the five-fold Ti surface atoms and the water-dipole vectors form a zigzag pattern along the [\bar{1}01] direction. A quantitative difference between first-layer water of the bilayer and monolayer water is that the angle between the alternating dipole vectors is \( \sim 77^\circ \) in first-layer bilayer water, compared to \( \sim 60^\circ \) for a monolayer of water (cf., Fig. 4.6). As we see in Fig. 4.8(a), this change can be understood in terms of hydrogen bonding between first- and second-layer water molecules.

As we see in Fig. 4.8, water molecules in the second layer of the bilayer adopt two different configurations in rows that run along the [010] direction and alternate along the [\bar{1}01] direction. In one of the rows (row 1), one of the hydrogen sites of a second-layer water molecule bonds with a bridging surface oxygen, while the oxygen forms two H-bonds with first-layer water hydrogens. The other hydrogen of
Figure 4.8. Top (a) and side (b) view of the optimized structure of the water bilayer on anatase (101). Red spheres/bonds represent oxygens in TiO$_2$ and first-layer water, green spheres represent oxygens in second-layer water, gray bonds represent Ti atoms, and white spheres represent hydrogen. Dotted lines represent hydrogen bonds between water molecules (a) and between water molecules and surface oxygen atoms (b). The lengths of the different H-bonds (units of Å) are indicated.

this water points up from the surface and is not involved in any hydrogen bonds. In the alternate row (row 2), both hydrogen sites of a water molecule form H-bonds: one with the closest surface bridging oxygen atom and the other with the closest water molecule in the first layer. Additionally, the oxygen atom of this water is involved in an H-bond with first-layer water. Thus, we observe an alternating-row structure for water molecules in the second layer. An alternating-row structure for the bilayer was also seen in DFT calculations [103, 144] – although apparently in that structure the water molecules in row 2 form two hydrogen bonds with O$_{2c}$, instead of coordinating with other adsorbed water molecules.

As for the monolayer, we ran MD simulations for the bilayer at 160 K to obtain the height distribution of the water oxygens $p(z)$. This is shown in Fig. 4.7 (b), where we see two well-defined peaks at $\sim 2.3$ and $\sim 3.4$ Å, and a low and broad peak further away from the surface. Also indicated in Fig. 4.7 (b) are the heights of water oxygen atoms in the zero-temperature bilayer. The two peaks at 2.58 and 2.84 Å are associated with first-layer water, while the peaks at 4.14 and 4.26 Å correspond to second-layer water in the alternating rows, as can be seen in Fig.
These water layers are placed at the same perpendicular distances for water oxygen and 5-coordinated titanium atoms, as the peaks observed in the simulation of a mono-layer of water on the slab. Unlike the ab initio MD simulations, the oxygen atoms of water molecules in the second layer are all in the same height compared to the under-coordinated titanium atoms of the surface. We hypothesize that this discrepancy is also related to the difference in the H bonds that was discussed previously. Therefore, the second peak observed in our simulations has about the same number of water molecules as of the first layer, and the small difference between the length of the first and the second peaks is related to the water molecules that have left the second layer in order to form the third layer.

In the case of MD simulations of bilayer (BL) of water molecules, all water molecules in the system lose their symmetry, making H bonds among themselves or with the surface, or both. However, the under-coordinated titanium atoms of the surface are still being covered by the oxygen site of water molecules, and there is H bonds between water molecules and all surface 2-fold oxygen atoms. It should be noted that during energy minimization simulation, water molecules in the second layer, were in a higher position compared to the MD simulations. This asymmetric structure is in agreement with the ab initio MD simulations, where it is explained that the H bonds between these layers is the reason for such disorder.

Subsequently, we have calculated the number of H bonds in BL simulations during the energy minimization period and actual MD simulations. For the energy minimization simulation we have observed formation of 0.5 H bonds per water molecule with the surface, this is because all water molecules in the second layer make one hydrogen bond with the 2-fold oxygen site of the surface. Also, the number of H bonds per water molecule among other water molecules is 1, this value corresponds to one hydrogen bond between half of water molecules in the first layer with the hydrogen of water molecules in the second layer, along with one, and two hydrogen bond(s) between oxygen(s) in the second layer (different rows), and hydrogens of the first layer, as shown in Fig. 4.8. For the asymmetric layering of water molecules at 160K, the value for the number of H bonds per water molecule between water and surface does not change, which means it is still 0.5. However, this bond is shared almost half and half between the hydrogen of water.
molecules that were originally placed in the first layer and the ones in the second layer. It was also observed that water molecules form H bonds among themselves, when there is about 1.44 hydrogen bonds for each water molecule in the system.

Like *ab initio* MD simulations, we continued our work by adding a third layer of water molecules to the ordered bilayer configuration, to see how this will affect the arrangement of water molecules. To do so, we replicated the configuration of water molecules in the first layer, and transferred them to an upper position compared to the second layer of water. After the equilibration period, we observed that water molecules in the first layer are changing their configurations compared to the ML and BL simulations. Therefore, in the final trilayer (TL) configuration, water molecules in the first layer took alternating positions in each row, where the hydrogen atoms in one row were facing the two-fold oxygen atoms of the surface, while making an H bond with the oxygen sites of water molecules in the second layer. Meanwhile, water molecules in the next row were having one of their hydrogens facing the surface oxygen [or in two out of 8, also forming an H bond with the oxygen site of water molecules in the second layer], and the other one engaging in an H bond with the water molecules in the third layer. Existence of the combination of these two configurations is in agreement with the *ab initio* MD results, although the alternation of them is not exactly the same. Also, for the water molecules in the second layer, we observed two different configurations, where one of the water hydrogens was having an H bond with the two-fold surface oxygen and the other one forming an H bond with the water oxygen in the third layer. At a higher distance from the surface, water molecules in the third layer bound together with hydrogen bonds, which is also observed in *ab initio* MD studies. The equilibrium structure of the tri-layer of water obtained by our energy minimization simulations is shown in Fig. 4.9.

In Fig. 4.7 (c), where the perpendicular distances between water oxygen and 5-coordinated titanium atoms are graphed for tri-layer of water, four layers of water can be detected. The first layer of water has the highest number of water molecules, showing that some of the water molecules in the second layer are now bound stronger to the ones in the first layer via a network of H bonds, and therefore, their distances from the surface is now in the same range of the first layer molecules. Thus, we observe a much longer peak for the first layer of water, as it was seen in
Figure 4.9. Top (a) and side (b) view of the optimized structure of the water trilayer on anatase (101). Red spheres/bonds represent oxygens in TiO$_2$ and first-layer water, green spheres represent oxygens in second-layer water, and blue spheres represent oxygens in third-layer water, gray bonds represent Ti atoms, and white spheres represent hydrogen. Dotted lines represent hydrogen bonds between water molecules and surface oxygen atoms (b). The lengths of the different H-bonds (units of Å) are indicated.

the \textit{ab initio} MD studies. Also, the fourth peak for water molecules is at \( \approx 5.5 \, \text{Å} \), which is in agreement with their studies.

4.4.1.2 Anatase (112)

Figure 4.10. Anatase (112) surface, where red and gray spheres represent O and Ti atoms, respectively.
As another test of the potential to describe the molecular adsorption of water on anatase surfaces, we investigated water adsorption on anatase (112). To model this surface, we employ a periodic (2 × 1) slab with 4 layers of titanium, an area of (10.70 × 5.45) Å² per layer, and a vacuum spacing of ~15 Å. These slab dimensions were chosen to match those in first-principles DFT calculations [111], so we could achieve good agreement regarding the convergence of the calculations. The adsorption of one water molecule on this periodic slab corresponds to a coverage of 0.25 ML. In DFT calculations [111], water was found to adsorb molecularly via bonding of O\textsubscript{W} to Ti\textsubscript{5c} with an additional H bond between H\textsubscript{W} and O\textsubscript{2c}. An illustration of the binding configuration predicted by our potential is shown in Fig. 4.11 and we note that this is similar to that predicted by DFT [111]. The binding energy and key bond lengths for water on anatase (112) are listed in Table 4.6. As for anatase (101), we see that the BK potential predicts significantly stronger binding than experiment – although the key bond lengths are closer to DFT than our potential. We achieve satisfactory agreement with the DFT binding energy, while qualitatively capturing bond lengths. As for anatase (101), we predict longer bond lengths than DFT, which is a consequence of reducing the BK binding energy with the re-parametrized potential. We also capture the correct trend that the binding of water on anatase (101) is weaker than on (112).
Table 4.6: Structural parameters and adsorption energies ($E_a$) of $H_2O$ on anatase (112).

<table>
<thead>
<tr>
<th>Method</th>
<th>$E_a$, eV</th>
<th>$O_{W-Ti_{5c}}$, Å</th>
<th>$H_{W-O_{2c}}$, Å</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>DFT-GGA</td>
<td>1.18</td>
<td>2.13</td>
<td>1.57</td>
<td>[111]</td>
</tr>
<tr>
<td>BK potential</td>
<td>1.58</td>
<td>2.07</td>
<td>1.60</td>
<td>[13,14]</td>
</tr>
<tr>
<td>Modified potential</td>
<td>0.92</td>
<td>2.35</td>
<td>1.89</td>
<td>This work</td>
</tr>
</tbody>
</table>

4.4.1.3 Anatase (001)

In addition to adsorbing molecularly, water can dissociate on anatase. For example, several theoretical and experimental studies [4, 58, 59, 112, 139–142] indicate that water dissociates on the anatase (001) surface at sufficiently low coverages. The SPC/E water model does not describe the dissociation of water. Nevertheless, we describe the binding of H and OH to TiO$_2$ surfaces to form surface hydroxyl groups, and we can describe their interactions with molecular water. This approach has been taken by Predota et al. [14] in their simulation studies of rutile (110) in contact with water containing dissolved electrolyte ions.

When water dissociates on anatase (001), two types of surface hydroxyls may be formed: a terminal hydroxyl, in which the OH binds to a surface Ti atom via an O-Ti bond, and a bridging hydroxyl, in which the H binds to a bridging surface oxygen to form an adsorbed OH group. In the BK potential, the partial charges for O and H atoms in terminal ($O_T$ and $H_T$) and bridging ($O_B$ and $H_B$) hydroxyl groups are unique and different from those in SPC/E water or TiO$_2$. Their values are listed in Table 4.9. Bond lengths of these different groups are fixed to the values in Table 4.10 and a harmonic potential is applied to describe bending of the Ti–O–H bond angle, details of which have been given earlier in this chapter. The bridging and terminal oxygens interact with all oxygen and titanium atoms of TiO$_2$ via the Matsui-Akaogi potential, and all species of the system have electrostatic interactions.
In order to carry out simulations for anatase (001) surface, we first created a periodic slab of (001) surface to match the ones represented in DFT studies [112], under identical starting conditions so that we can compare our results against them. We employed a periodic (2×1) slab with 4 layers of titanium, an area of (7.57×7.57) Å² per layer, and a vacuum spacing of ≈15 Å. The equilibrated structure of anatase (001) surface is shown in Fig. 4.12(a), where both coordinatively unsaturated 2(5)-fold O(Ti) (O_{2c} and Ti_{5c}) are present on this surface. According to the observations of DFT studies [112], by having one water molecule (0.25 ML) on a clean (001) surface, not only will the water molecule immediately dissociate into hydrogen and hydroxyl groups, but also the two unequivalent hydroxyl groups (terminal and bridging) break the bond between O_{B} and Ti_{5c}. An illustration of the binding configuration predicted by our potential is shown in Fig. 4.12 (b) and we note that this is similar to that predicted by DFT [112].

![Figure 4.12](image)

**Figure 4.12.** Anatase (001) slab after energy minimization MD simulations (a), and atomic structure for dissociated water adsorbed this surface (b). Red and gray spheres represent O and Ti atoms, respectively, and white circles represent hydrogens.

By applying the refined parameters reported by Predota *et al.* [14], it was not possible to obtain results even close to the ones obtained by DFT studies. Also, it should be noted that in Bandura and Kubicki’s simulations [13], the surface slab atoms have different charges and interactions with other slab atoms or hydrogen or hydroxyl groups. In our studies, we did not follow their pattern as it adds to the complexity of the system, which would create time restrictions that we would like to reduce by performing MD simulations rather than DFT calculations. Therefore,
we started with the most general interaction parameter of BK potential for Ti$_{5c}$
and O$_T$, and by adjusting it and other parameters of the system [listed in Table
4.8 and discussed below], we have been able to find results that are in a very good
agreement with DFT studies [112].

In order to find the best parameters for the dissociative adsorption of water,
we apply the same procedure we used for molecular adsorption. Consistent with
molecular water simulations, we have several parameters that can go through mi-
nor changes for the adjustment of H$^+$ and OH$^-$ configuration on the studies TiO$_2$
surfaces. In addition to the previously-mentioned Buckingham and SPC/E pa-
rameters, the charges of hydrogen and oxygen atoms in H$^+$ and OH$^-$ can also be
changed, as has been the case in most MD simulation studies [13, 260, 261]. By
knowing the contributions of each of these parameters to the final geometry of the
system, we have run several hundred simulations, using same procedure as for the
molecular adsorption, in order to find the best set of parameters and charges.

Table 4.7: Structural parameters of dissociated H$_2$O on
anatase (001) surfaces.

<table>
<thead>
<tr>
<th>Method</th>
<th>O$<em>{OH}$-Ti$</em>{5c}$, Å</th>
<th>H-O$_2$, Å</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Modifies potential</td>
<td>1.73</td>
<td>1.39</td>
<td>This work</td>
</tr>
<tr>
<td>DFT-GGA</td>
<td>1.93</td>
<td>1.31</td>
<td>[112]</td>
</tr>
<tr>
<td>SCC-DFTB</td>
<td>1.82</td>
<td>1.71</td>
<td>[140]</td>
</tr>
</tbody>
</table>
Table 4.8: Interaction parameters for Ti and O atoms and oxygen of hydroxyl group approximated by Matsui-Akaogi and SPC/E potentials used in this work.

<table>
<thead>
<tr>
<th>Ion-Ion</th>
<th>$A$, $eV$</th>
<th>$\rho$, Å</th>
<th>$C$, $eV$ Å$^6$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Ti - O_{OH}$</td>
<td>13667.46</td>
<td>0.194</td>
<td>12.57</td>
<td>[14]</td>
</tr>
<tr>
<td>$Ti - O_{OH}$</td>
<td>13667.46</td>
<td>0.187</td>
<td>12.57</td>
<td>This work</td>
</tr>
<tr>
<td>$O - O$</td>
<td>11771.46</td>
<td>0.234</td>
<td>30.19</td>
<td>[14]</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Ion-Ion</th>
<th>$\sigma$, Å</th>
<th>$\epsilon$, $eV$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$O - O_{OH}$</td>
<td>3.366</td>
<td>0.0067</td>
<td>This work</td>
</tr>
</tbody>
</table>

Table 4.9: Charges of all atoms of TiO$_2$ surfaces and hydrogen and hydroxyl groups, derived by Predota et al. [14].

<table>
<thead>
<tr>
<th>Atom</th>
<th>Charge</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Ti_{5c}$</td>
<td>+2.196</td>
</tr>
<tr>
<td>$Ti_{6c}$</td>
<td>+2.196</td>
</tr>
<tr>
<td>$O_{5c}$</td>
<td>-1.098</td>
</tr>
<tr>
<td>$O_T$</td>
<td>-1.008</td>
</tr>
<tr>
<td>$O_B$</td>
<td>-1.035</td>
</tr>
<tr>
<td>$H_T$</td>
<td>+0.459</td>
</tr>
<tr>
<td>$H_B$</td>
<td>+0.486</td>
</tr>
</tbody>
</table>
Therefore, started our simulations by applying Matsui-Akaogi interaction parameters found for Ti and O\textsubscript{OH} by Bandura and Kubicki [13,14]. Also, to simulate the van der Waals interactions between O and O\textsubscript{OH}, we have used Lennard-Jones potential. However, it must be noted that this is not the same pair potentials used in the previous studies [13,14]. In the current study, we did not consider any van der Waals interactions between hydrogen atoms and any other species of the system, while electrostatic interactions were employed for all atoms in the simulation box and corrected by the use of standard Ewald sum method. In our set of simulations, we have restricted the hydrogen atoms of the system to either bridging or terminating oxygens via bond constraints. The magnitude of these bond lengths are adopted from the previous DFT studies [112], where Vittadini et al. have found dissociation of water molecules on anatase (001) surface. Therefore, we have fixed O\textsubscript{T}–H\textsubscript{T} as 1.0 Å, and O\textsubscript{B}–H\textsubscript{B} to 1.1 Å. In our simulations, there is no bond constraint between Ti and oxygen atoms of any kind, which means the hydroxyl groups are allowed to change position and hop onto any surface titanium atom. This change in position was not observed during our energy minimization simulations, however, it might be the case for the simulations at higher temperatures or the ones with bulk water molecules surrounding such surfaces. These energy minimization simulations were performed under NVT ensemble by applying Nose-Hoover thermostat with a relaxation time of 0.5ps. The cutoff radius is set to half the smallest length of the simulation box, and a timestep of 0.1fs is used to run the simulations, while the trajectories and energies of the system are written every 10000 timesteps to have data available every picosecond.

One of the most important achievements of trying different charges for oxygen and hydrogen atoms, was regarding the reconstruction effect that has been observed experimentally and theoretically for a clean (001) surface [4,205,206]. When a water molecule is adsorbed on a (001) surface, the bond between the surface O\textsubscript{2c} and Ti\textsubscript{5c} breaks, and two hydroxyl groups which are bound together by a hydrogen bond, will form on adjacent Ti sites on the surface. This phenomena can not be seen when the charges of hydrogen and oxygen of H and OH groups are low. Therefore, we have assigned partial charges $q$ of $-1.2$ and $+0.6$ to oxygen and hydrogen, respectively ($q_H = -q_O/2$), these values are consistent with few other MD simulations [261]. Also, by increasing $\rho$ by about 0.007 Å from this
value in BK’s potential and \( \sigma \) by approximately 0.2 \( \text{Å} \) from the same parameter in SPC/E model, we have been able to find a new configuration for the dissociated water molecule on anatase (001) surface, which is very similar to the one obtained with first-principle studies (the bond lengths are within 8 percent of the reported values).

Table 4.10: Surface Ti–O and O–H bond lengths suggested by Predota et al. [14].

<table>
<thead>
<tr>
<th>Bond</th>
<th>Ti(_T)–O(_T)</th>
<th>O(_T)–H(_T)</th>
<th>Ti(_B)–O(_B)</th>
<th>O(_B)–H(_B)</th>
</tr>
</thead>
<tbody>
<tr>
<td>length, ( \text{Å} )</td>
<td>1.895</td>
<td>0.983</td>
<td>2.02</td>
<td>0.994</td>
</tr>
</tbody>
</table>

4.4.2 Water Adsorption on Rutile (110)

It should be noted that there exists a considerable dispute between experimental and theoretical works regarding whether water dissociation occurs over a clean (110) surface. Most experimental studies indicate that water adsorbs molecularly on rutile (110) surface [211,212,214]. Meanwhile, many theoretical studies (mostly first principle studies) report that water adsorption energy for dissociative water is slightly smaller than for molecular adsorption, which suggests that water will dissociate to \( \text{H}^+ \) and \( \text{OH}^- \) on a clean rutile (110) surface [6, 220, 231, 232, 234]. However, Kowalski et al. [7] have recently tested the effect of slab thickness on the behavior of adsorbed water on (110) surface, and by using DFT-PBE functional, they have shown that at monolayer coverages of water on a 8-layer (110) slab, molecular adsorption of water is energetically more favorable than dissociative adsorption [7]. Therefore, in this research, we have used two sizes of rutile (110) surface in order to study both molecular and dissociative adsorption of water on rutile (110) surface, with our newly derived parameters and compare the results against the DFT studies.

Therefore, we began with molecular adsorption, and employed a periodic \((8 \times 2)\)
Figure 4.13. Rutile (110) slab, with half of the thickness shown (a), and atomic structure for molecular state of a mono-layer of adsorbed water molecule on rutile (110) surface (b). Red and gray spheres represent O and Ti atoms, respectively, and white spheres represent hydrogens. The dashed lines indicate H-bonds between water molecule and surface O$_{2c}$.

slab with 8 layers of titanium, an area of (25.98 $\times$ 11.836) Å$^2$ per layer, and a vacuum spacing of $\sim$15 Å. These slab dimensions were chosen to fit the criterion found for molecular adsorption of water on rutile (110) surface, by first-principles calculations [7]. The structure of the relaxed (110) surface is shown in Fig. 4.13 (a), where both coordinatively unsaturated 2(5)-fold O(Ti) (O$_{2c}$ and Ti$_{5c}$) and fully saturated 3(6)-fold O(Ti) (O$_{3c}$ and Ti$_{6c}$) atoms are present.

After the surface was relaxed, we placed both a mono-layer and half a mono-layer of water molecules with their oxygen sites facing the under-coordinated titanium atoms of the (110) slab. Water molecules were adsorbed on one side of the slab only. During structural optimizations, atoms in the bottom layer of the surface slab were fixed to their bulk equilibrium positions, while water and the rest of the slab atoms were allowed to move until the maximum force on any atom was below 0.01 eV/Å. We began our study with several initial configurations for water molecule on the slabs, and performed energy minimization MD simulations, which all lead to the same molecular adsorbed state for each surface.
Table 4.11: Calculated and experimental structural parameters and adsorption energies ($E_a$) of H$_2$O on rutile (110) surface.

<table>
<thead>
<tr>
<th>Method</th>
<th>$\theta$</th>
<th>$E_a$, eV</th>
<th>O-Ti$_{5c}$, Å</th>
<th>H-O$_{2c}$, Å</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>BK potential</td>
<td>1</td>
<td>1.38</td>
<td>2.22</td>
<td>1.75</td>
<td>[13,14]</td>
</tr>
<tr>
<td>Modified potential</td>
<td>1</td>
<td>0.82</td>
<td>2.64</td>
<td>2.17</td>
<td>This work</td>
</tr>
<tr>
<td>DFT-GGA</td>
<td>1</td>
<td>0.84</td>
<td>2.17</td>
<td>1.73</td>
<td>[13]</td>
</tr>
<tr>
<td>DFT-GGA</td>
<td>1</td>
<td>0.82</td>
<td>2.30</td>
<td>1.67</td>
<td>[262]</td>
</tr>
<tr>
<td>DFT-GGA</td>
<td>1</td>
<td>0.82</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DFT-PW91</td>
<td>1</td>
<td>1.13</td>
<td></td>
<td></td>
<td>[224]</td>
</tr>
<tr>
<td>DFT-PW91</td>
<td>1</td>
<td>1.03</td>
<td></td>
<td></td>
<td>[236]</td>
</tr>
<tr>
<td>DFT-PBE</td>
<td>1</td>
<td>0.87</td>
<td></td>
<td></td>
<td>[248]</td>
</tr>
<tr>
<td>DFT-PBE</td>
<td>1</td>
<td>0.86</td>
<td></td>
<td></td>
<td>[249]</td>
</tr>
<tr>
<td>DFT-PBE</td>
<td>1</td>
<td>0.82</td>
<td></td>
<td></td>
<td>[7]</td>
</tr>
<tr>
<td>MD</td>
<td>1</td>
<td>1.09</td>
<td>2.20</td>
<td>1.79</td>
<td>[13]</td>
</tr>
<tr>
<td>EXP (TPD)</td>
<td>0.61-1.04</td>
<td></td>
<td></td>
<td></td>
<td>[214]</td>
</tr>
<tr>
<td>BK potential</td>
<td>1/2</td>
<td>1.55</td>
<td>2.15</td>
<td>1.83</td>
<td>[13,14]</td>
</tr>
<tr>
<td>Modified potential</td>
<td>1/2</td>
<td>1.08</td>
<td>2.48</td>
<td>2.38</td>
<td>This work</td>
</tr>
<tr>
<td>DFT-PW91</td>
<td>1/2</td>
<td>0.78</td>
<td></td>
<td></td>
<td>[236]</td>
</tr>
<tr>
<td>DFT-PW91</td>
<td>1/2</td>
<td>0.87</td>
<td></td>
<td></td>
<td>[236]</td>
</tr>
<tr>
<td>DFT-PW91</td>
<td>1/2</td>
<td>1.05</td>
<td></td>
<td></td>
<td>[246]</td>
</tr>
<tr>
<td>DFT-PW91</td>
<td>1/2</td>
<td>0.94</td>
<td></td>
<td></td>
<td>[246]</td>
</tr>
<tr>
<td>DFT-PW91</td>
<td>1/2</td>
<td>1.01</td>
<td></td>
<td></td>
<td>[246]</td>
</tr>
<tr>
<td>DFT-PW91</td>
<td>1/2</td>
<td>0.95</td>
<td></td>
<td></td>
<td>[248]</td>
</tr>
<tr>
<td>DFT-PBE</td>
<td>1/2</td>
<td>0.76</td>
<td></td>
<td></td>
<td>[248]</td>
</tr>
<tr>
<td>DFT-PBE</td>
<td>1/2</td>
<td>0.86</td>
<td></td>
<td></td>
<td>[7]</td>
</tr>
</tbody>
</table>

As shown in Fig. 4.13 (b), the water molecules bind to the surface via an O-Ti$_{5c}$ bond with a surface Ti$_{5c}$ atom and one H-bond with a nearby surface O$_{2c}$. The
binding energy and key bond lengths for water on rutile (110) are listed in Table 4.11. As for anatase surfaces, we see that the BK potential predicts significantly stronger binding than experimental results – although the key bond lengths are closer to DFT than our potential. We achieve satisfactory agreement with the DFT binding energy, while qualitatively capturing bond lengths. As for anatase (101), we predict longer bond lengths than DFT, which is a consequence of reducing the BK binding energy with the re-parametrized potential.

By comparing our results with the available experimental results and first-principle calculations [7, 13, 58, 200, 214, 220], we may conclude that by applying the parameters found for anatase phase, we have been able to decrease the difference between the adsorption energies obtained with first-principles and our MD studies, while preventing a dramatic change in the adsorbed water configuration (the bond lengths are within 20 percent of the reported values).

In the last part of this study, we focused on the dissociation of water on rutile (110) surface, by applying our parameters found for anatase (001) surface for this surface of rutile and showed the accuracy of such parameters compared to the DFT results. As discussed before, on thin and small slabs of rutile (110) surface, water molecules prefer to dissociate. Therefore, we have made a small periodic (2 × 1) slab with 4 layers of titanium, an area of (6.495 × 5.918) Å² per layer, and a vacuum spacing of ∼15 Å. The structure of the relaxed (110) surface is shown in Fig. 4.14 (a), where we see that it contains both coordinatively unsaturated 2(5)-fold O(Ti) (O_{2c} and Ti_{5c}) and fully saturated 3(6)-fold O(Ti) (O_{3c} and Ti_{6c}).

As with anatase (001) surface, we manually separate H^+ from OH^- in two water molecules and place them on both sides of the (110) slab to match the initial configurations of DFT studies [13]. During structural optimizations, all species in the system were allowed to move until the maximum force on any atom was below 0.01 eV/Å. We start with different initial configurations for H^+ and OH^- on the slabs, which all lead to the same adsorption state.

The structural parameters of the dissociation of water on rutile (110) surface is given in Table 4.12, while the configuration is shown in Fig. 4.14 (b). As listed in Table 4.12, our modified potential is capable of describing the dissociation of water molecules on rutile (110) surface, and the deviation of the observed bond lengths from the DFT studies is about 5%.
Figure 4.14. Rutile (110) slab after energy minimization MD simulations (a), and atomic structure for dissociated water adsorbed this surface (b). Red and gray spheres represent O and Ti atoms, respectively, and white spheres represent hydrogens.

<table>
<thead>
<tr>
<th>Method</th>
<th>$O_{OH}$-Ti$_{5c}$, Å</th>
<th>$H$-$O_{2c}$, Å</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Modified potential</td>
<td>1.77</td>
<td>2.05</td>
<td>This work</td>
</tr>
<tr>
<td>DFT-GGA</td>
<td>1.83</td>
<td>1.94</td>
<td>[13]</td>
</tr>
<tr>
<td>F-P MD</td>
<td>1.90</td>
<td>1.8</td>
<td>[6]</td>
</tr>
</tbody>
</table>
4.5 Summary

In conclusion, in this work a new set of parameters for Matsui-Akaogi potential in MD simulations has been derived to explain the interactions between both molecular water and dissociated H and OH groups, and anatase nanocrystals. These results are compared to DFT studies and the experimental data with the same operating conditions, and we have achieved very good agreement with those data. We have also compared adsorption of a complete monolayer, bilayer and trilayer of molecular water on anatase (101) surface, which is the majority of the exposed surfaces of this nanocrystal, and have found a perfectly ordered layer of water formation on the (101) surface. This result matches with the DFT conclusions [112], however, because of the much longer time that is maintained by MD simulations, we managed to make further observations of water molecule layering.
Chapter 5

Anatase Nanocrystals in Water

5.1 Abstract

In this chapter we start with MD simulations of water molecules layering around large surfaces of anatase-(101) and rutile-(110) under ambient temperature and pressure. Such simulations are beneficial for understanding the strength of water molecules binding on the most important surfaces of rutile and anatase nanocrystals. Thereafter, we will show how water molecules layer around an anatase nanocrystal at both ambient and hydrothermal conditions. For this study, we will consider both symmetric [with Wulff construction], and asymmetric nanocrystals. Therefore, we will be able to show the difference in water adsorption on different anatase terminating surfaces, which will in turn help in defining the aggregation areas of anatase nanocrystals in water. Nevertheless, we will show how water adsorption is less pronounced under hydrothermal conditions, discussing the higher tendency of aggregation compared to the ambient conditions. We will also explain the importance of water molecules in the aggregation mechanism of such nanocrystals, by calculating energies associated with the solvent molecules. Finally, we will show a typical simulation system of two anatase nanocrystals in water under ambient conditions.
5.2 Introduction

Although oriented attachment of nanocrystals has been observed in several experimental studies, the origins of this mechanism are not well understood. In order to have a better insight, the interfacial region between a solid and a liquid phase should be studied. The amount of research done on TiO$_2$ nanoparticles [1] shows the importance of this material in science and technologic applications. As summarized in Chapter 1, TiO$_2$ nanoparticles are shown to be insoluble in water and are used in several applications as colloids [30, 38, 40, 46, 98–101, 127, 127, 263].

Considering the available techniques for such investigation, MD has proven to be a very strong tool for studying the fundamentals of water adsorption at the atomic level, as explained in Chapter 2. It should be noted that in the literature there are few simulations specified for the study of nanoparticle-liquid interfaces [105, 150, 264]. It was shown in the previous chapters that anatase nanocrystals that are being studied in this work, are stable in vacuum and will retain their equilibrium shape through out the simulation period. Therefore, we will first investigate the stability of such nanocrystals in an aqueous environment. Also we will study water orientation on anatase $(101)$ and rutile $(110)$ surfaces, that are the majority of the terminating surfaces in both nanocrystals. Finally we will study the adsorption of water on anatase nanocrystals.

We will obtain density profiles of water at ambient and hydrothermal conditions on each nanocrystal. Also, the effect of water on each nanocrystal is compared to the effect of nanoparticles on each other. This way we will be able to illustrate the importance of water on the aggregation and alignment of anatase nanocrystals in this solvent. Moreover, we will be adding hydrogen and hydroxyl groups to the preferred sites proposed by theoretical and experimental studies, and will consider the new interaction parameters that we have derived in the previous chapter.

5.3 Simulation Methods

5.3.1 Force field Selection

After finding the suitable force field parameters for anatase-water interactions employing Matsui-Akaogi and SPC/E models [see Chapter 4], simulating water layer-
ing on anatase nanocrystals becomes more accurate. As explained in the previous chapter, the pair potential interactions between titanium and oxygen species in the system are described by Matsui-Akaogi force field [11], by Eq. (2.12), and force field parameters are listed in Table 2.1. According to Chapter 2, for the aqueous solution water was tested to be adequately represented by the rigid, nonpolarizable SPC/E model [12], where the total interaction energy between oxygen and hydrogen sites of water are calculated by Eq. (2.13). The parameters of this potential are listed in Table 2.2. To model the interactions between the water molecules and the titanium and oxygen atoms in the nanoparticles we have used our newly found parameters, summarized in Table 4.5. Also, no interaction between species in the simulation box and the water hydrogen atoms are considered, other than electrostatic interactions.

5.3.2 Simulation Details

The reason for choosing water as solvent in this set of simulations, is mainly due to the manufacturing processes of TiO$_2$ nanoparticles, which is generally done under hydrothermal conditions [72, 73, 265–269]. By using DL-POLY [version 2.20] to carry out the simulations, the time to run simulations decreases because of the capability of this package in performing simulations on a parallel architecture. DL-POLY uses Verlet's leapfrog algorithm in conjunction with multiple time step method, to integrate Newton's equations of motion over time.

Two different environmental conditions are considered for this type of simulations. The first is ambient temperature and pressure, under which anatase nanocrystals are most prevalent. The second one is the hydrothermal condition, under which anatase nanocrystals are manufactured. The hydrothermal temperature is reported to be 523K [75], and the corresponding pressure is 5 kbar. This pressure value was originally obtained by simulating a periodic box of water molecules, with approximately 15000 water molecules employing SPC/E water model. In order to fill the box with water molecules, we used *wateradd* utility provided by DL-POLY version 2.20. The density of water was tested for few pressure values in the range associated with 523K, and 5 kbar was proven to be the best value in order to have density of water equal to $1 \text{ g/cm}^3$. For simulations at room
temperature and pressure [ambient], the values of 300K and 1bar are used. The same box of water molecules was chosen to simulate bulk water at the ambient conditions, where SPC/E model was shown to be successfully reproduce density of water.

In order to carry out the simulations for anatase nanocrystals in water, the equilibrated water box at either environmental condition was emptied in the middle to make room for the particle. Then nanoparticles, which were initially built for vacuum simulations [see Chapter 2], were equilibrated in a vacuum environment at 300K, and 523K. Thereafter, we placed the nanoparticles in the emptied space in the middle of each box of water. These simulations are first carried out under the $NPT$ ensemble for 250ps, which is shown to be sufficient time for the water molecules to arrange in the box and the volume of the box is fixed for the applied temperature and pressure, maintaining appropriate density of water. The thermostat and barostat applied for such simulations was Berendsen with a relaxation time of 0.5ps, and 0.4ps, respectively. By choosing these values, we have been able to maintain pressure and temperature at their target value with very small fluctuations during the course of simulation. Then, the water adsorption simulation is followed by 1250ps under $NVT$ ensemble that is shown to be long enough for the water molecules to layer around nanocrystal surfaces.

The simulation boxes in these set of simulations have periodic boundary conditions in x, y and z directions. The size of the box is chosen such that the interaction between the nanocrystal and its own image in the neighboring box is negligible. For all simulations a time step of 0.25fs is used and statistical data is collected every 4000 time steps. The standard Ewald summation method [270,271] is utilized for long-range corrections of electrostatic interactions.

### 5.4 Results and Discussion

In this series of simulations we have considered our smallest anatase nanocrystal, with 816 atoms representing the symmetric nanoparticles, and two asymmetric nanocrystals with the total of 3141, and 2865 atoms, with a terminating (112) surface. Figures 5.1, 5.2, and 5.3 show the snapshots of these systems in water, respectively. In order to make sure that the neighboring nanocrystals are not inter-
acting with each other, \( \approx 14000 \) water molecules are provided in each simulation box, creating a cubic box of water with a edge length of about 75 Ångstroms.

**Figure 5.1.** Snapshot of the small symmetric nanoparticle [shown in Fig. 2.1 (b)] in water. Titanium and oxygen atoms of the nanocrystal are shown in large gray and red spheres, respectively, and oxygen and hydrogen atoms of water molecules are represented by small red and white spheres.

### 5.4.1 Water Ordering on Anatase and Rutile Surfaces

It was shown in Chapter 4 that water molecules tend to make ordered layers on a clean anatase (101) surface. Also, the formation of one to three layers of water on this surface was shown in Fig. 4.9. Therefore, in this chapter, before starting the simulations of water adsorption on anatase nanocrystals, we have performed similar layering simulations of water, this time with a wider gap between the neighboring slabs in z-direction and an appropriate number of water molecules, so that it would
Figure 5.2. Snapshot of the asymmetric nanoparticle shown in Fig. 2.2 (c) in water. Titanium and oxygen atoms of the nanocrystal are shown in large gray and red spheres, respectively, and oxygen and hydrogen atoms of water molecules are represented by small red and white spheres.

resemble bulk water configuration at room temperature. By these simulations, we would be able to predict the adsorption and dynamics of water molecules on the most important anatase surface.

In order to better evaluate the potential parameters that we found for the interactions between TiO$_2$ surfaces and water molecules in the Matsui-Akaogi force field, we performed bulk water adsorption on the most important rutile surface, as well. Therefore, we have used slabs with surface areas of $(40.96 \times 30.28) \text{ Å}^2$ for anatase (101), and $(25.98 \times 23.67) \text{ Å}^2$ for rutile (110) surfaces. The gap between neighboring slabs in z-direction is approximately $40 \text{ Å}$, which contains about 600-1000 water molecules on either surface. A total time of 1ns has been
specified for the energy minimization period, where the slab configuration was
relaxed by minimizing the atomic force. As in previous calculations, convergence
was assumed when the maximum component of the residual force was less than
0.01 eV/Å.

Subsequent to equilibration, we carried out MD simulation at 300K, to test
the hydrophilicity of each surface at room temperature. A total time of 2ns was
specified for the settlement of temperature at 300K, and the observations were
made after this period of time, which has continued for 8ns. As in Chapter 4,
we have calculated the perpendicular distances between the oxygen site of water
molecules and 5-coordinated titanium atoms of surfaces during 8ns of MD simulation at 300K. The final structures of slabs after 10ns of MD simulations are shown in Fig. 5.4, and Fig. 5.5. The distribution graph \( p(z) \) of bulk water molecules on both surfaces are shown in Fig. 5.6. These results show that two significant layers of water are formed on TiO\(_2\) surfaces, with a much smaller peak representing a third layer of water. Both density peaks are very sharp, illustrating the ordered [or crystallographic] characteristic of anatase-(101) and rutile-(110) surfaces. The distances of these distinct peaks for water oxygen from the under-coordinated titanium atom of surface are in agreement with the those obtained for three layers
Figure 5.5. Equilibrium structure of bulk water arrangement on rutile (110) surface at 300K. Titanium, oxygen, and hydrogen atoms are represented by gray, red, and white spheres, respectively.

of water on anatase-(101) surface [see Chapter 4], which is at about 2.3 Å , and 3.4 Å , respectively. The number of H bonds per under-coordinated oxygen of the surface, between H–O₂c was shown to be 1, in line with the values obtained for the same surface, but with less amount of water molecules. The number of H bonds per water molecule among bulk water was calculated to be approximately 2.18, this value is equal to the one we calculated for a box of water with 15000 water
Figure 5.6. Distribution $p(z)$ of the perpendicular distance from the surface Ti$_{3c}$ sites of the water oxygen atoms for bulk water adsorption at room temperature and pressure on anatase (101) surface (a), and rutile (110) surface.
molecules at ambient temperature, confirming the bulk properties of water in the middle region of the simulation area.

Furthermore, we have made solvent density profile images, where we show water ordering on anatase-(101) and rutile-(110) surfaces. It has been shown by other MD simulations that solvent ordering influences the type and frequency of nanoparticle aggregation [272]. Hence, it is important to study these profiles before starting the aggregation simulations.

Plots of the ordered water molecules around the surfaces are shown in Fig. 5.7, and Fig. 5.8. Here, we see that water density is the highest in the first water layer immediately adjacent to the nanocrystal surfaces, followed by the second layer, while the third layer of water is weakly defined on anatase-(101) surface and barely exists for rutile-(110) surface, consistent with other MD simulations [14].

In the density profile of water on anatase-(101) surface, the first layer of water
corresponds to water layering in the steps on this surface, which has the highest density of under-coordinated titanium atoms. The oxygen site of water is in the registry of the 5-coordinated titanium atom on this surface [the under-coordinated species on this surface are shown in Fig. 4.4], while water hydrogens in the second layer are forming H bonds with the surface O$_{2c}$. The third layer of water is formed while making a network of hydrogen bonds between water molecules in the first, and second layers and the rest of the water molecules in the bulk. The rest of the water molecules are in random order, while having hydrogen bonds with each other. As the (101) surface made for this study is two-sided, the same mechanism occurs for the layers of water molecules on the opposite side of this slab.

Also, when water molecules are arranging on a clean rutile-(110) surface, they are going through the same process. Under-coordinated oxygen and titanium atoms on rutile-(110) surface [as shown in Fig. 4.13] are the main adsorption
sites for water molecules. Water molecules arrange themselves so that their oxygen sites bond with Ti\textsubscript{5c}, while hydrogen sites exhibit hydrogen bonds between the oxygens of the slab and those in the second layer of water.

### 5.4.2 Water Density Profiles on Anatase Nanocrystals

![Figure 5.9](image)

**Figure 5.9.** Solvent density relative to the bulk water density in the simulation box surrounding the terminating surfaces of anatase nanocrystal with 816 atoms [shown in Fig. 5.1] at ambient temperature and pressure [300K and 1bar].

Although the plots shown in the previous section illustrate the ordering of bulk water on TiO\textsubscript{2} surfaces, the layering at the edges, which are readily available for the nanocrystals, does not exist in such slab simulations. Also, the solvent density profiles surrounding nanocrystals, may provide helpful information about the regions of initial contact between nanocrystals. When Sathiyarayanan et al. [272] studied the aggregation of two silver nanoparticles, they showed that solvent layering and ordering within the first layer of solvent was disrupted by the
Figure 5.10. Solvent density relative to the bulk water density in the simulation box surrounding the terminating surfaces of anatase nanocrystal with 816 atoms [shown in Fig. 5.1] under hydrothermal conditions [523K and 5kbar].

edges of nanoparticles, which lead to a low free-energy barrier on the end facets, and therefore, they observed the majority of aggregations initializing in those areas.

Hence, we have provided water density profiles for our anatase nanocrystals, where we have made a contour image surrounding our nanocrystal, to be able to compare water adsorption on different facets and edges of our symmetric and asymmetric nanocrystals at ambient and hydrothermal conditions. Figures, 5.9, 5.10, 5.11, 5.12, 5.13, and 5.14 show the contour images of water density profiles for: symmetric nanocrystals at ambient and hydrothermal conditions, asymmetric nanocrystals shown in Fig. 5.2 at ambient, and hydrothermal conditions, and finally asymmetric nanocrystals shown in Fig. 5.3 at ambient, and hydrothermal conditions, respectively. In order to see water layering on (112) surface, we have rotated the asymmetric particles and have shown the projected water density in
Figure 5.11. Solvent density relative to the bulk water density in the simulation box surrounding the terminating surfaces of anatase nanocrystal with 3141 atoms [shown in Fig. 5.2] at ambient temperature and pressure [300K and 1bar].

that direction. Therefore, we will be able to compare preference of water in layering on (112) surface compared to (101) and (001) surfaces.

As shown in Figures 5.9, 5.10, 5.11, 5.12, 5.13, and 5.14, water ordering on the (101) surface of anatase nanocrystal, is in agreement with observations for a clean (101) slab. These images show how water molecules form their first layer on the steps of the (101) surface, while the second layer of water is formed with the hydrogen bonds between the under-coordinated oxygen atoms of the surface and the oxygen of water molecules.

These figures show the preference of water layering on a stable (101) surface, rather than the high-energy (001) surface. It should be noted that water is shown to prefer a mixture of molecular/dissociative adsorption on anatase-(001) surface, which means after dissociation of few water molecules on the surface, the rest
Figure 5.12. Solvent density relative to the bulk water density in the simulation box surrounding the terminating surfaces of anatase nanocrystal with 3141 atoms [shown in Fig. 5.2] under hydrothermal conditions [523K and 5kbar].

of water molecules will be molecularly adsorbed on this surface. We would have been able to study water adsorption on (001) surface, if we had manually placed hydrogen and hydroxyl groups on the preferred sites of this surface. So, by applying SPC/E water model, we would have been able to study the molecular adsorption of water molecules on the hydroxylated (001) surface. This is one of the simulations that needs to be done in the future.

As for the (112) surfaces, we conclude, similarly to (101) surface, water prefers to arrange around this surface, and the density of water layering on anatase-(112) surface is approximately 3 times higher than for anatase-(001) surface. However, the best layering of water and its highest density have been on the most stable (101) surface, which is about 5 times higher than the (001) surface.

Also, by providing water density profiles for each nanocrystal at two different
environmental conditions [ambient and hydrothermal], we are capable of comparing the two conditions under which anatase nanocrystals stay during the course of synthesis. The density of water surrounding anatase terminating surfaces under the hydrothermal condition are approximately 30 % lower than the ones obtained at the ambient temperature. This suggests less tendency of water molecules to be adsorbed on anatase at hydrothermal conditions, which leads to less ordering of water as compared to the ambient conditions. Therefore, it is more probable that anatase nanocrystals prefer to aggregate under the hydrothermal conditions, where water does not tend to cover the terminating surfaces as strongly.

Figure 5.13. Solvent density relative to the bulk water density in the simulation box surrounding the terminating surfaces of anatase nanocrystal with 2865 atoms [shown in Fig. 5.3] at ambient temperature and pressure [300K and 1bar].
Figure 5.14. Solvent density relative to the bulk water density in the simulation box surrounding the terminating surfaces of anatase nanocrystal with 2865 atoms [shown in Fig. 5.3] under hydrothermal conditions [523K and 5kbar].

5.4.3 Nanocrystal Alignment in the Presence of the Second Nanocrystal

After 1.5ns of equilibration for the symmetric and asymmetric nanocrystals in water, we created systems of two identical nanocrystals in water. Using DL-POLY version 2.20, we started NPT simulations at both ambient and hydrothermal conditions, for 250ps, during which the volume of simulation box has achieved its equilibrium value. The simulations were continued in a canonical ensemble for 750ps, while water molecules were moving throughout the simulation box and around the nanocrystals. However, the anatase nanocrystals, which were at all times covered by at least one layer of water molecules, did not move as much as they could in vacuum simulations. Also, we did not observe a directional alignment of these nanocrystals, indicating that the total time of simulation was short.
Fig. 5.15. Solvent density relative to the bulk water density for anatase nanocrystal with 3141 atoms [shown in Fig. 5.2] at ambient temperature and pressure [300K and 1bar], when it is rotated to have a view of layering on anatase (112) surface.

Fig. 5.19 shows a snapshot of a simulation that is run for two symmetric nanocrystals under ambient conditions. In order to make it less crowded, we have only included a thin slice of water molecules in the box, which are represented by their oxygen site only. As it is seen in Fig. 5.19, during the course of simulation, water molecules are present in the area trapped between two nanocrystals, therefore, we were not able to see any aggregation during the 1ns of simulation period. It may be hypothesized that by running longer simulations, two nanocrystals may face each other in a special way that the attraction between the particles overcomes the water-particle interactions, and two nanocrystals may aggregate.

Due to the difference in the results obtained for anatase nanocrystal aggregation in vacuum [see Chapter 3] with the ones found in the experimental studies [75], there remains a question of the role of water in the aggregation mechanism of such nanocrystals. Although we have studied water adsorption on anatase nanocrystals
and we gained qualitative insight of water affecting the nanocrystal aggregation by forming layers around the exposed surfaces of anatase nanocrystal, a good quantitative study of water effect compared to the direct effect of nanocrystals would be beneficial. Therefore, we have carried out simulations of two identical anatase nanocrystals in water, while saving the configurations and forces of all species in the simulation box at every picosecond. Since we have the configuration of anatase nanocrystals at every picosecond, we have used them and performed simulations of the exact same two nanocrystals, this time in a vacuum.

Hence, we have a record of the energies of the systems of two nanocrystals in the same orientation with water and in vacuum, and also a system of water molecules by themselves. By subtracting the energy of water molecules and the energy of nanoparticles in vacuum from the energy of the same nanoparticles in water, we have been able to calculate the effect of water on these nanoparticles,
Figure 5.17. Solvent density relative to the bulk water density for anatase nanocrystal with 2865 atoms [shown in Fig. 5.3] at ambient temperature and pressure [300K and 1bar], when it is rotated to have a view of layering on anatase (112) surface.

which is also shown by the following equation

$$E_{\text{water-particle}} = E_{\text{total}} - E_{\text{particles}} - E_{\text{water}} \ ,$$

where $E_{\text{water-particle}}$ is the interaction energy between the water and the nanocrystals, $E_{\text{total}}$ is the energy of the system containing all water molecules and both nanocrystals, $E_{\text{particles}}$ is the energy of the system of nanocrystals in vacuum, and $E_{\text{water}}$ is the energy of all water molecules.

Hence, by comparing the energies due to water molecules on nanocrystals and the energy due to the other nanocrystal, we have been able to show that water has a higher impact, while its energy on the nanocrystal is higher by about two orders of magnitude [3000 vs. 10 kcal/mol] compared to the energy of nanocrystals on each other. This implies the significance of water presence in the aggregation
Figure 5.18. Solvent density relative to the bulk water density for anatase nanocrystal with 2865 atoms [shown in Fig. 5.3] under hydrothermal conditions [523K and 5kbar], when it is rotated to have a view of layering on anatase (112) surface.

mechanism of two nanocrystals, and explains the deviation of our results in vacuum compared to the experimental studies carried out in an aqueous environment.
5.5 Summary

In conclusion, it can be said that MD simulations for the adsorption of water on anatase nanocrystals were successfully performed. It was shown that at 300K, the layering of water around (101) surface of nanocrystal matches well with the one observed for the (101) slab. Both of them proved two distinct layers of water on these stepped surfaces. Water molecules are shown to be arranging in a way such that their oxygen site is on top of the under-coordinated surface titanium atom. While the hydrogen sites of water make hydrogen bonds with the under-coordinated surface oxygen.
Also, it was shown that under hydrothermal conditions, water layering is less noticed compared to the ambient condition. Knowing that anatase nanocrystals are synthesized under hydrothermal conditions, makes it more probable for the nanocrystals to aggregate during the synthesis. Furthermore, energy calculations show the importance of water presence in these studies.
Chapter 6

Conclusion and recommendations for Future Studies

In this research we have studied the oriented attachment of anatase nanocrystals in vacuum and aqueous environments. By applying the strong tool of MD simulations, we have been able to fully address the aggregation of nanocrystals in vacuum. We observed that such nanocrystals tend to aggregate along two specific edges, which have the highest density of under-coordinated titanium and oxygen atoms. According to our results, we conclude that the origins of nanoparticle aggregation in vacuum are the higher-order multipole moments, and that the dipole-dipole interactions are not significant in our studies.

Thereafter, we have tested the application of current force field parameters, originally found for clusters of TiO$_2$ by DFT studies, to test how well these parameters can describe the interactions in our anatase systems. In order to do so, we have selected the most appropriate first principle calculation results that describe the adsorption of water on the most important anatase surfaces [(101)], and by using the exact same size and conditions of the surfaces, we have been able to carry out few thousand energy minimization MD simulations, and compare their results against the DFT calculations. In conclusion, we have been able to improve the current parameters of matsui-Akaogi force field to be used in anatase systems. We have calculated the optimized parameters for both molecular and dissociative adsorption states on different anatase surfaces.

Finally by having the best models and parameters, we have been able to show
the layering of water on anatase nanocrystals. The results include two conditions [ambient and hydrothermal] under which anatase nanocrystals may reside during the course of synthesis. The layering of water shows the important role of water in the aggregation mechanism of anatase nanocrystals. We have shown that water molecules form two delicate layers on the majority of anatase terminating surfaces. By calculating the energy due to water molecules on each nanocrystal, and comparing it to the amount of energy due to the other nanocrystal, we have shown the important role of water molecules in such simulations.

Also, we have simulated systems of two nanocrystals in a box of water in order to understand the aggregation or alignment of these nanoparticles. However, during the first 1ns of the simulations, we have only observed very slow motion of nanocrystals, while water molecules are adsorbed on the exposed surfaces. We did not find an ordered behavior of such nanocrystals in water, mainly because the simulation time has been short.

In conclusion, simulating the aggregation of anatase nanocrystals in water takes a much longer time compared to the ones carried out in a vacuum. This is mainly because of the large number of long-ranged electrostatic interactions in the system. In order to shorten this duration, one may use a smaller simulation box, which means less number of water molecules. However, if the box is too small, the neighboring periodic images will have interactions with each other that may not be favorable. So, an optimized size for the simulation box would be the best choice.

Also, for a better comparison with the experimental studies, it would be ideal if the simulations are carried out in systems with different pH values. As hypothesized by Penn and Banfield [75], at the pH values close to the isoelectric point of anatase nanocrystals, the frequency of aggregation via oriented attachment mechanism is higher. Therefore, it would be beneficial to compare the simulations that are performed with addition of ionic species to the system. However, the accuracy of the force field parameters in representing the interactions of such ions with the available species in the simulation box should be tested.

The last but not the least is performing MD simulations for two anatase nanocrystals in an aqueous environment, with proper amount of hydrogen and hydroxyl groups that are manually placed on the predicted sites. By doing so, the shortcoming of SPC/E water model in modeling dissociative water will be mainly
fixed. Then, the effects of having such functional groups that affect the chemistry of the surfaces to a great extend may be evaluated for the aggregation mechanism of anatase nanocrystals.
Bibliography


[54] EVANS, R. (1966) INTRODUCTION TO CRYSTAL CHEMISTRY, CAMBRIDGE UNIVERSITY PRESS.


ODISKS,” ADVANCED MATERIALS, 14(15), pp. 1084+.


PARTICLES,” SCIENCE, 298(5601), pp. 2176–2179.


[104] JACKSON, J. (1975) CLASSICAL ELECTRODYNAMICS, JOHN WILEY AND SONS INC.


TIO2 ANATASE (101) AND (001) SURFACES,” PHYSICAL REVIEW LETTERS, 81(14), pp. 2954–2957.


[131] SHKLOVER, V., M. NAZEERUDDIN, S. ZAKEERUDDIN, C. BARBE, A. KAY, T. HAIBACH, W. STEURER, R. HERMANN,


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