Surface and Interface Studies of ZnO using Reactive Dynamics Simulation

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Abstract

About 90% of all chemicals are produced with the help of catalysts, substances with the ability to accelerate reactions without being consumed. Metal oxides play a prominent role in catalysis, since they are able to act reversibly in many chemical processes. Zink oxide (ZnO) is used to catalyse a number of industrially important reactions. For many of these reactions water is present as a reactant, product, or byproduct. The surface structure has a significant impact on the catalytic activity. However, currently, no experimental method simultaneously offers the spatial and temporal resolution to directly follow a catalytic process.

This thesis explores surface structure dependent dynamical behavior for ZnO surfaces, nanoparticles, and water interfaces, using the computational chemistry method Molecular Dynamics, which enables detailed studies of structural and dynamical processes. Quantum mechanical (QM) calculations have been performed to obtain the energetics of the materials as a function of structure. This data has been used to parametrize reactive force-fields (ReaxFF), since the catalytic processes require both far larger and longer simulations than the capabilities of QM calculations on current computers.

The simulations show that when steps are present on the surface, during crystal growth of ZnO, the creation of energetically favorable structures is accelerated. At the ZnO - water interface, structures that favor hydrogen bonding is promoted. At low, monolayer, coverage water adsorbs both molecularly and dissociatively, whereas at high coverage dissociated adsorption is favored. During evaporation from the monolayers, the ratio of dissociated and molecular water is preserved. Surface steps stabilizes the dissociated state as well as increases the rate of dissociation. The dynamical properties of ZnO nanoparticles were explored using Raman measurements and simulation. In both simulation and experiment certain vibrations were suppressed in the nanoparticles, compared to bulk. The simulations show that a narrow surface region lack the bulk-specific vibrations.

Keywords: catalysis, molecular dynamics, force-fields, metal oxide, ZnO, dynamical effects on reactivity

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List of Papers

This thesis is based on the following papers, which are referred to in the text by their Roman numerals.

I  A reactive force field (ReaxFF) for zinc oxide
D. Raymand, A.C.T. van Duin, M. Baudin and K. Hermansson

II  Water adsorption on stepped ZnO surfaces from MD simulation
D. Raymand, A.C.T. van Duin, D. Spångberg, W.A. Goddard III and K. Hermansson

III  Development and validation of a ReaxFF reactive force field for Cu-cation/water interactions and copper metal/metal oxide/metal hydroxide condensed phases
A.C.T. van Duin, V.S. Bryantsev, M.S. Diallo, W.A. Goddard III, O. Rahaman, D.J. Doren, D. Raymand and K. Hermansson
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IV  Water adsorption beyond monolayer coverage on ZnO surfaces and nanoclusters
D. Raymand, T. Edvinsson, D. Spångberg, A.C.T. van Duin and K. Hermansson

V  Hydroxylation structure and proton transfer reactivity at the Zinc Oxide-water interface
D. Raymand, A.C.T. van Duin, W.A. Goddard III, K. Hermansson and D. Spångberg
Submitted

VI  Raman Scattering and Phonon Density of States in Growing ZnO Quantum Dots
D. Raymand, T.J. Jacobsson, K. Hermansson and T. Edvinsson
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1. Svensk sammanfattning

En katalysator är ett ämne som har förmågan att skynda på en reaktion utan att själv förbrukas, en s.k. katalysisk process. Upp till 90% av alla kemikalier produceras genom någon form av katalytisk process. En form av katalys är s.k. heterogen katalys där reaktanterna och katalysatorn har olika aggregations tillstånd, vanligtvis används gasformiga reaktanter tillsammans med en fast katalysator. Metalloxider är en viktig klass av katalysatorer eftersom de har förmågan att agera reversibelt i många kemiska processer, t.ex. som reduktions- och oxidationsmedel samt som jonledare. Dessa egenskaper hjälper till att sänka reaktionsbarriärer i otaliga reaktioner. Metalloxiden zinkoxid har visat sig kunna katalysera flera industriellt viktiga reaktioner, bland annat framställning av metanol och väts. I många processer har zinkoxid förmågan att agera både som syra och bas och kan därigenom katalysera ett flertal reaktioner, t.ex. sönderdelning av vatten. I denna avhandling har zinkoxid studerats med hjälp av dator simuleringar.

Förklaringen bakom ett materials katalytiska funktion anses till stor del vara kopplad till dess ytstruktur. Tyvärr är detaljerad information om ytans struktur svåråtkomlig och kunskapen om katalytisk funktion är därför begränsad. Framstegen i experimentella uppställningar har varit stora de senaste åren. Alltmer detaljerad information om atomär ytstruktur kan erhållas från allt bättre mikroskop, och reaktionsmekanismer kan erhållas från olika typer av spectroskopi. Men det är fortfarande ofta svårt att säkert koppla de experimentella observationerna till processer på atomär nivå.

Beräkningar kan ge den nödvändiga informationen om struktur och reaktionsmekanismer som krävs för att förstå katalys som förnärvarande inte kan erhållas på annat vis. En av de mest använda teoretiska metoderna för att studera fasta material och deras ytor är kvantmekaniska beräkningar, från vilka man kan få mycket högkvalitativ information.

Tyvärr kräver denna typ av beräkningar ofta mycket datorkraft och de kvantmekaniska modellsystemen är därför oftast begränsade till att inkludera 100-1000 atomer. Denna begränsning leder till svårigheter i studier av katalytiska processer som ofta är mycket kompexa med många atomer inblandade.

Metoden som använts i denna avhandling är s.k. kraftfälts-beräkningar. I kraftfälts-beräkningar använder man en relativt enkel uppsättning matematiska uttryck för att beskriva interaktionen mellan atomerna i modellsystemet. Uttrycken innehåller ett antal parametrar som anpassas...
så att modellen beskriver de krafter atomerna utövar på varandra. I denna avhandling har två kraftfält utvecklats, ett för interaktionen mellan zink, syre och väte och ett som för koppar, syre och väte. Kraftfältsmodellen som använts här heter ReaxFF och är speciellt utformad för att kunna beskriva olika aspekter av kemiska reaktioner. Parametrarna i ReaxFF modellen har anpassats till data från främst kvantmekaniska beräkningar. Om överrensstämmelsen mellan modellen och referensdata är stor kan man anta att modellen ger en likvärdig beskrivning av atomernas interaktion som den kvantmekaniska. Att beräkna interaktionen mellan atomerna i ett modellsystem med kraftfältet är typiskt 100 000 gånger snabbare än motsvarande beräkning av den kvantmekaniska interaktionen. Därför möjliggör kraftfälts-beräkningar studier av effekter som beror av många 1000-tals atomer.


En speciell typ av ytstrukturs effekt på katalysators reaktivitet har studerats särskilt, s.k. ytsteg. På en verklig yta (till skillnad från en modell yta) är ytsteg ett vanligt förekommande inslag. Typiskt för atomer i en kristall är att deras inbördes ordning upprepas periodiskt i alla riktningar. Detta ger upphov till lager av atomer i den s.k. kristallstrukturen. Vid en yta bryts denna periodiska upprepnings, vilket kan ske på olika sätt. Slutar kristallen helt parallellt med ett av dessa lager erhålls en helt plan yta. Om kristallen slutar lite snett jämfört med lagren erhålls en stegad yta. Ytans profil kan då liknas vid en sågands kurva eller en serie trappsteg, s.k. ytsteg.

Vid simuleringsav tillväxt av en zinkoxid kristall befanns ytstegen påskynda processen att skapa mer stabila ytstrukturer. I gränsytan mellan vatten och zinkoxid befanns stegen underlättade sönderdelning av vatten och en medföljande hydroxyleringen av zinkoxid ytan. Vattenmolekylernas struktur i lagren precis vid zinkoxid ytan visade sig spela en avgörande roll för deras reaktivitet med avseende på sönderdelning av vatten närmast ytan. När zinkoxid täcks av ett enda lager av vatten föreligger stora delar som molekylärt vatten, till skillnad från när ytan täcks av ytterligare vatten då det sönderdelas i högre grad (i lagret närmast zinkoxid ytan). Detta beror på att olika strukturer är fördelaktiga för interaktionen mellan vatten molekylerna i de olika situationerna. Slutssatsen är att strukturer som är fördelaktiga för vattnets interaktion premiersas. Eftersom vatten ingår som reaktant eller produkt i många av de katalytiska processer som sker på zinkoxid ytan så är denna typ av information av särskilt intresse.
Zinkoxidnanopartiklar har även studerats eftersom de anses lovande i en mängd tillämpningar och det är därför intressant att kartlägga deras egenskaper. Hur atomerna vibrerar i ett material bestämmer en mängd av dess egenskaper däribland värmekapacitet. Genom spektroskopiska mätningar observerades det att nanopartiklar av zinkoxid av olika storlekar uppvisa olika egenskaper med avseende på atomernas vibrationer. Genom analys av simulerade zinkoxid nanopartiklar, kopplades denna effekt till att vissa vibrationer som finns i kristallin zinkoxid inte är möjliga i partiklarnas ytregion. Eftersom ytans relativa bidrag till partikelns egenskaper minskar med ökande storlek, så påverkas partikelns egenskaper proportionellt mot dess storlek.
2. Introduction

It is estimated that $\sim 90\%$ of all chemicals are produced using some catalytic process [1]. Catalysts offer alternative reaction paths associated with lower activation barriers compared to uncatalysed reactions. However, they do not alter the equilibrium of a chemical reaction. Another important property a catalyst may have is to increase the selectivity of a chemical reaction, thus increasing the yield of the desired product. In heterogeneous catalysis the reactants and the catalysts are in different phases, typically the reactants are gaseous and the catalysts solids. Among the advantages of heterogeneous catalysis is the ease of separating the resulting product from the catalyst. Metal oxides are an important class of catalysts since they have the ability to act reversibly in several processes such as acid-base and redox reactions, and oxide-ion diffusion.[2, 3]

Historically, the design of catalysts has largely been an engineering technique, where combinations of so-called modifiers are systematically combined and tested for catalytic effect. The catalytic modifiers are additives that are used to perform specific tasks in the catalytic reaction. Metals and metal oxides are common examples of modifiers. The addition of a particular modifier to a catalyst is often based on empirical observation and the mechanism behind its catalytic function is rarely understood [4]. For example, in the control of car emissions platinum is used to oxidize carbon monoxide and unburned hydrocarbons in combination with ceria which acts as an oxygen buffer/conductor, but their exact roles are disputed [5, 6]. This combinatorial method of improvements results in unsystematic advancements of the catalysts and clearly has limitations that can only be overcome by a more fun-

Figure 2.1: A schematic view of a copper nanoparticle supported on the ZnO(10\overline{1}0) surface.
damental understanding. Such understanding is provided by surface science techniques.[1]

In this thesis, the work has focused on aspects of zinc oxide (ZnO). Today, ZnO or ZnO-containing materials are used in heterogeneous catalysis to produce many chemicals, such as methanol from CO and H\textsubscript{2} and hydrogen via the water-gas shift (WGS) reaction (H\textsubscript{2}O + CO \rightarrow H\textsubscript{2} + CO\textsubscript{2}). In both these cases ZnO is typically used together with copper since the combination achieves far higher activity than each component separately. [2, 5, 7]

It is commonly accepted that elementary reaction steps of a catalytic process are promoted by certain structural features on the surface called active sites, e.g. steps, vacancies, and metal clusters [4]. Fig. 2.1 schematically shows how a copper metal cluster supported on ZnO catalyst could look. The characterization of these surface active sites is an important step towards understanding catalytic activity. However, structure determination of a surface is difficult because of the lack of surface sensitive experimental techniques. There are several fundamental problems in studying the structure of metal oxide surfaces. Metal oxides are typically good electrical insulators and many of the experimental techniques used in surface science rely on the emission, transmission or adsorption of charged particles, e.g. transmission electron microscopy (TEM). These techniques need a certain amount of conductivity in the sample in order to avoid problems of surface charging. Moreover, samples are usually prepared by cleaving single crystal samples along a specific crystallographic plane to create surfaces with the desired orientation. This is difficult since unintentional cleaving of the crystal along a slightly different plane may result in a sample with radically different properties. [2, 3] Currently no experimental technique simultaneously offers the temporal and spatial resolution needed to directly follow the elementary steps of a catalytic process, which renders the interpretation of measured quantities difficult. Despite these difficulties there has been tremendous progress in recent decades in surface sensitive experimental techniques and in the analysis of the data they produce. Among these there are direct methods of studying the surface structure, for example, scanning tunneling microscopy (STM) and indirect spectroscopic methods like infrared spectroscopy (IR) (where the signal has to be assigned to various structures of e.g. adsorbates on the surface). These have enabled researchers to get insight into the surface structure of the metal oxides, with and without adsorbed molecules [1].

Computational chemistry plays an increasingly important role in surface science and therefore also in the understanding of catalysis. The reason is that computational methods are able to offer structural information at the atomic level for processes occurring at the short time-scales of the individual reaction steps. Computational methods therefore constitute a valuable complement to experimental techniques. [8]

Quantum-mechanical (QM) electron structure calculations provides a solid base for understanding chemistry at the atomic level from first-principles and
offers powerful predictive capabilities. Among other things, QM-methods pro-
vide a way to sample the potential energy surface (PES) for various model
systems. From the PESs it is possible to derive several properties e.g. geometric
ground state structure, relative stability of different crystal phases, surface
energies, and reaction paths. In particular, the type of bonding involved in a
chemical process can be elucidated using QM-methods. Unfortunately, these
methods are rather limited in the number atoms they can describe simultane-
ously by the speed of current computers. QM-methods are typically capable
of describing 100-1000 atoms for up to a few tens of picoseconds. It is thus
not possible to use QM-calculations alone to study many catalytically impor-
tant features, since models including these require larger systems and longer
time periods than is afforded by current computers.

One possible way to extend the time- and length-scales offered by QM-
methods is to replace the complex QM description of the interaction between
atoms with simpler analytical formulas. In such a method, it is critical to
transfer as many as possible of the features offered by the computationally
expensive, but chemically versatile QM-methods to the more limited analyti-
cal formulas. The success or failure of this transfer depends on the ability of
the formulas to retain the important features of the QM-description. This ap-
proach of substituting analytical formulas for the QM description of the PES
is called the force-field method and is part of a strategy called multiscale mod-
eling [8]. The guiding idea behind multiscale modeling is to transfer detailed
information from computationally expensive methods to coarser methods that
are able to model larger systems for longer time periods. Fig. 2.2 shows a
schematic picture of the hierarchy that constitutes multiscale modeling.

![Hierarchy of overlapping methods in computational chemistry with re-
spect to the time- and length-scales they are able handle.](image)

*Figure 2.2: Hierarchy of overlapping methods in computational chemistry with re-
spect to the time- and length-scales they are able handle.*
In this thesis the ReaxFF reactive force-field model [9] has been used. ReaxFF was designed to include many of the features necessary to describe catalytic processes. The model is designed to handle the breaking and reformation of bonds, handle charge transfer, and describe metallic, covalent, and ionic bonding, simultaneously. The mixed nature of the bonding in metal oxides is likely important for the catalytic effect, and therefore the inclusion of these features in the model may be critical for its performance. For example, the chemical bonding in ZnO is partly covalent and partly ionic in character [5]. Creating a ZnO surface can therefore be seen as cutting nearest-neighbor bonds and creating dangling bonds, where the surface Zn and O can act as Lewis-acid and Lewis-base sites, respectively [10]. This feature is likely to be partly responsible for the activity of ZnO as a catalyst.

The work presented in this thesis is part of a greater research project aimed at building a model for hydrogen (H₂) production through the WGS reaction catalyzed by a Cu/ZnO-catalyst. This necessitates a model that can handle all important interactions between the following elements H, C, O, Cu, and Zn. Hydrogen is an industrially important chemical used in the synthesis of many chemicals. It may gain even more importance since it has been proposed as an alternative to petroleum based fuels used in vehicles [11]. Hydrogen is typically produced through a process called steam reforming, where methane reacts with water to produce carbon monoxide and hydrogen. To increase the yield and purify the resultant hydrogen gas, the carbon monoxide is removed by allowing it to react with additional water through the WGS reaction [12]. Therefore special attention has been devoted to aspects of the Cu/ZnO catalysed WGS reaction, since information on the atomic/molecular level (structure, dynamics, reactivity) related to the role of ZnO may be vital in the optimization of catalyst functionality.

In this thesis project, the primary goal has been to cast light on a number of structural, dynamical, and mechanistical issues related to ZnO, the ZnO surface, the ZnO-water interface, and to ZnO nanoparticles and their surfaces. The Copper/Copper Oxide/Water system has also been explored. Six papers are included in this thesis. Papers I-III focus on force-field development and Papers IV-VI on large-scale, long-time simulations at realistic temperatures beyond the limitations of standard QM-methods. As an example, Fig. 2.3 shows a snapshot from a 13 ns long simulation of the liquid water-ZnO interface, using a model consisting of 1392 atoms.

In Paper I, a force-field for pure ZnO was developed by making it reproduce a data-set which describes the important features of the ZnO: ZnO in its normal form crystallizes in the wurtzite type structure and at high pressures ZnO transforms to the rocksalt type structure [13]. ZnO is relatively hard with a bulk modulus of 140 GPa [14] and has a high melting point (Tₘ=2250 K [15]). The surface is dominated by four low-index faces: the non-polar (10 ¯10) and (11 ¯20) faces which are parallel to the c-axis, and the polar (0001) and (000¯1) faces which are perpendicular to the c-axis [2]. It has been shown in
Figure 2.3: A snapshot of the ZnO-water interface from a molecular dynamics simulation included in Paper V. The upper part shows liquid water and the lower part the ZnO(6170)-surface. Zinc atoms are colored gray and hydrogens white. Oxygens are colored red except in OH-groups where they are blue.

FTIR and HRTEM investigations [16] that for ZnO powders, the (10¯10) and the (11¯20) faces together account for about 80% of the total surface area. The resulting force-field was used to study ZnO crystal growth and evaluate the dynamic behavior of bulk ZnO by calculating the vibrational mean square amplitudes of the Zn and O ions at different temperatures. In Paper II, the force-field model was extended to include the interactions between ZnO and water. This extended force-field was used to study the structure of water monolayers on flat and stepped ZnO surfaces at two temperatures, 300 K and 600 K. The force-field was also used in Papers IV-VI. In general, the interaction of catalytic metal oxide surfaces with water is of interest since they are almost always hydroxylated in real environments [17]. In particular, the water-ZnO interaction is especially interesting, since water plays an integral role in many of the reactions catalyzed by ZnO [7]. Water on metal oxides can adsorb molecularly or dissociatively and the type is known to depend on the structure of the surface [18]. Determining which type is predominant important, since the dissociation products (OH, H, and O) are chemically very different from water [19]. It is difficult to identify whether water is adsorbed molecularly or dissociatively using experimental techniques. The difficulties lie in the similarity between the vibrational spectra of H\textsubscript{2}O and OH bound to the surface: The O-H stretching vibrational band is broad and the frequencies of both OH and H\textsubscript{2}O surface groups change depending on their surroundings. Several interesting features of the ZnO-water interface have previously been published by Meyer et al. [20, 21, 22]. In particular, these authors observed an especially favorable hydrogen-bond pattern within water monolayers on the ZnO(1010) surface, consisting of alternating molecular and dissociated water ordered into a 2×1-pattern (with respect to
the surface unit cell). The structural reason behind is that in the mixed case, the dissociated water is stabilized by hydrogen bond donation from a neighboring water molecule. The formed surface hydroxyl is additionally stabilized by accepting a hydrogen bond from the hydrogen transferred to a nearby oxygen of the ZnO-lattice.

In **Paper III**, a force-field for Copper/Copper Oxide/water systems was developed to, among other things, study the dynamic nature of the structure of Cu\(^{2+}\) in aqueous solution, which is interesting since the d\(^9\) electronic configuration of the copper ion suggest the possibility of a Jahn-Teller effect. Many studies into the structure of aqueous Cu\(^{2+}\) have been published, using various experimental techniques and theoretical methods [23]. The structure proposed for aqueous Cu\(^{2+}\)-complexes usually vary between 5-fold or 6-fold and no clear consensus has been reached. The development of the Cu/O/H force-field is also a necessary step towards a model for the WGS reaction.

Metal oxide-liquid water interfaces are interesting and challenging since the structure and dynamics of the interface region strongly differs from the aqueous and solid bulk phases. These differing properties are mainly determined by surface specific chemistry [24], i.e. the ability of the metal oxide surface to order the water molecules through adsorption patterns that depend on surface structure. The liquid water-ZnO interface is present in many contexts, for instance in the electrode/electrolyte interface of ZnO photovoltaics and in the synthesis of ZnO nanoparticles in aqueous solution. **Paper IV** presents a broad study of ZnO surfaces covered with water, nanoparticles in the nanometer-range, both clean, covered with water, and immersed in water. In **Paper V** a detailed study of the ZnO-liquid water interface is presented where the interface was studied with respect to structural features of the first adsorption layer and its connection to H transfer reactivity.

Nanoparticles exhibit many features not present in bulk material because of e.g. their high surface to volume ratio. ZnO nanoparticles have a wide range of applications [13, 25, 26, 27]; these include catalysis and gas-sensing where the surface area enhancement is particularly important. **Paper VI** is a combined experimental and theoretical study of ZnO nanoparticles. Simulations were performed for nanoparticles in the same size range as those synthesized for the experiments. This enabled direct comparisons between theory and experiment, thereby aiding the interpretation of experimental observations. Differences between the ion dynamics of the surface and bulk regions were explored. The largest 7 nm particle (15084 atoms) that was simulated is shown in **Fig. 2.4**.
Figure 2.4: The 7 nm ZnO wurtzite nanoparticle used in Paper VI to model the vibrational behavior in nanoparticles ranging in size from 1 to 7 nm in diameter.
3. Method

A multitude of methods are used in computational chemistry and as presented in Fig. 2.2, these can be ordered into a hierarchy with respect to the time and length scales of the systems they are able to handle. The complexity afforded by a particular method has clear implications for the computational expense of using it and thus the size of the system that is feasible to model with available computer resources. At the base are quantum mechanical (QM) methods which explicitly describe the electron interaction. However, the computational expense of these electronic methods often limit their applications to calculations of finding the minimum energy structure of a system (along with the many features associated with determining the electron structure). Section 3.2 gives an introduction to the QM methods used in this thesis.

One way to reduce the computational expense is to remove the explicit description of electrons and treat them implicitly using the atoms as the smallest possible unit, i.e. an atomistic approach. In such a model the interaction between the atoms can be provided by a collection of analytical formulas, force-fields, substituting an explicit description of the bonding through electron interaction. Compared to QM-methods, force-fields are typically orders of magnitude less expensive in computational time. The force-fields contain a number of parameters which are adjusted (using a fitting routine) to enable them to reproduce properties from either experimental data or QM data, or both. This data set of properties will hereafter be referred to as a training set. The main drawback of using force-fields is that they are only guaranteed to capture the properties toward which they were initially trained, which limits their predictive power. A nicer way to express it would be to say that using a force-field is a methodical way of using the data in the training set to study new (model) systems. This means that the training set has to be chosen carefully in order for the force-field to become versatile.

The comparatively low computational cost of using force-field models makes it easier to use methods that rely on the sampling of a large number of configurations, for example in the modeling of systems at finite temperatures. Modeling systems at finite temperature is collectively called simulation [28] and there are two major techniques: Monte Carlo and Molecular Dynamics (MD). In Monte Carlo simulation, random configurations are generated and evaluated using a set of criteria. For instance, in Metropolis Monte Carlo the generated configuration is accepted if it is lower in energy than the previous one or accepted with a probability of \( \exp(-\Delta E/RT) \) if the energy
increases. These Metropolis criteria ensures that the accepted configurations obey a Boltzmann distribution. The desired properties are calculated for each accepted configuration and averaged. One limitation of Monte Carlo simulation is that the configurations are not correlated in time. MD simulation is a technique of generating configurations that are connected in time making it possible to calculate time-correlated properties. Section 3.1 gives a more detailed description of MD simulation.

The aim of this thesis is to cast light on a number of structural, dynamical, and mechanistical aspects related to heterogeneous catalysis and therefore MD simulations was chosen as method. The majority of the time spent in this Ph.D. project has been devoted to parametrize ReaxFF force-fields for use in MD simulations. All simulations have been performed using either the ReaxFF software package written by Prof. Adri van Duin [9] or GRASP by Aidan P. Thompson [29]; the latter utilizes the force evaluation routine from the former. The simulations were analyzed to obtain the results presented in the papers using mostly in-house written software and scripts.

### 3.1 Molecular Dynamics Simulations

In an MD simulation the individual positions of the atoms in a model system is propagated using Newton’s equations of motion [30]. It is therefore not only possible to derive static equilibrium properties using MD, like the average structure, but also time-correlated properties like diffusion constants, velocity auto-correlation functions, and other dynamic properties that have a dependence in time. Moreover, non-equilibrium processes can be studied, e.g. crystal growth and evaporation from a liquid surface, to mention two examples related to this thesis work.

In the model system a set of atoms interact through a many-body potential function, i.e. the PES. The MD simulations performed in this thesis work rely on classical mechanics, and as such neglects quantum effects like zero point vibrations. In a classical description the motion of an atom is determined by the Newton’s law of mechanics ($force = mass \times acceleration$) or in a more general way:

$$\frac{\partial^2 \mathbf{r}_i(t)}{\partial t^2} = -\frac{1}{m_i} \nabla \phi(\mathbf{r}_i(t)),\quad (3.1)$$

where $\mathbf{r}_i(t)$ is the position of atom $i$ at time $t$, $m_i$ the mass of the atom, and $\phi(\mathbf{r}_i(t))$ is the instantaneous potential energy of the atom [31]. The force acting on a particle at a certain coordinate is obtained from the negative gradient of the potential function at this coordinate. The potential function, $\phi(\mathbf{r}_i(t))$, can be calculated in different ways, either directly through QM-calculations with the drawback of computational cost, e.g. Car-Parinello MD [32], or through force-fields, the method used in this thesis.
Equation 3.1 is integrated simultaneously for all atoms yielding the trajectory for each atom $i$. It is impossible to analytically integrate the equation since the motion of the atoms are anharmonically coupled. It is therefore numerically integrated using a finite difference method, where the difference is taken in time, i.e timestep $\Delta t$. If the timestep is short enough and the integration includes a sufficient number of steps the calculated trajectory of the model system can be used to calculate equilibrium properties of the system (the ergodic principle).

### 3.2 Quantum-Mechanical Calculations

All QM calculations in this thesis work were performed with the purpose of creating data for use in the parametrizations of force-fields. Common for all QM electronic structure methods is that they explicitly describe electron interaction. They range from very accurate wavefunction based methods which incorporate effects of dynamic and static electron-correlation, like MP2 and CCSD(T), to methods relying on semi-empirical approximations of the electron interaction like extended Hückel. In general, there is an inverse relation between accuracy and computational expense. Density functional theory (DFT) offers a good compromise between accuracy and computational expense for many systems and is commonly used in metal oxide surface chemistry [33]. It is often possible to improve the results of pure DFT by including a fraction of exact exchange [28]. One notable example of these so-called hybrid-functionals is the B3LYP-functional [34, 35], which has been used with success for a large variety of systems. The ReaxFF model [9] was originally developed for hydrocarbons using results from B3LYP calculations, and so are a large part of the ReaxFF-parameters that have since been published. Moreover, the B3LYP-functional has been reported to produce geometric structures and electronic structures of good accuracy for ZnO [36]. For these reasons B3LYP has been used for all the work included in this thesis, except for metals where the PBE-functional [37] was used.

For clusters, the quantum mechanical calculations were performed using the GAUSSIAN03 program [38]. For the periodic systems the following program packages were used, CRYSTAL03 [39] and CRYSTAL06 [40] for metal oxides, and SeqQuest [41] for metals.
3.3 Force-Fields

In the general case, the interaction energy of an N-body system can be written as an expansion of the coordinates \((r_1, \ldots, r_n)\) in the following way:

\[
\phi_{\text{tot}} = \sum_{i=1}^{N} \sum_{j>i}^{N} \phi_2(r_i, r_j) + \sum_{i=1}^{N} \sum_{j>i}^{N} \sum_{k>j}^{N} \phi_3(r_i, r_j, r_k) + \ldots \quad (3.2)
\]

A universal set of analytical functions that manage to approximate \(\phi_{\text{tot}}\) well for a broad range of systems and applications does not exist. Therefore the functional form of the force-field has to be chosen with care since it often has implications for the results. Consequently, even for one and the same class of systems more forms are in use in the literature than can be mentioned here. A few examples of popular potentials in use for the non-electrostatic part of pair interaction energies are the Lennard-Jones potential, the Buckingham potential, and the Morse potential.

In the simplest force-field models the total interaction \((\phi_{\text{tot}})\) is approximated by neglecting higher order interactions \((\phi_3 + \ldots)\), i.e. only the interactions between all pairs of atoms in the system are considered. For example, for a binary system consisting of Zn and O atoms described by a 2-body potential the total interaction would consist of a sum of Zn-Zn, Zn-O, and O-O types of interactions. If the modeled system contains three components, e.g. H/Zn/O, the number of interactions doubles, with three additional types of interactions, Zn-H, O-H, and H-H. However, in most cases the pure 2-body potential fails because the interaction between two atoms is affected by e.g. which other atoms they are bonded to. These non-pairwise contributions are called many-body effects. To improve the description it is possible to add the 3-body interactions explicitly \((\phi_3)\). In the example of the binary system, the total interaction would then also include six additional types of interactions: Zn-Zn-Zn, Zn-Zn-O, Zn-O-Zn, O-Zn-O, Zn-O-O and O-O-O. In general, the number of interactions that needs to be handled increases quickly when the number of components grow, and the increase is greater if more terms in equation 3.2 are used. The equation is therefore truncated to the shortest series that is possible while achieving the desired accuracy of the total interaction energy.

There exists many strategies for including the many-body effects in the force-field. For instance, it is possible to include these effects in an average manner by creating effective potentials, e.g. by fitting a 2-body potential to data that includes many-body effects. These 2-body potentials do not represent the true interaction energy between two particles, but are often able to work well in a limited number of situations. In practice effective potential models are almost always used (regardless of whether a 2-body, 3-body, etc, potential is used), since they facilitate using fewer terms of equation 3.2. There are many additional ways to reduce the number of terms needed and the following three are common: (i) A certain element is described using multiple sets of pa-
rameters, thus capturing effects of different chemical environments (negating the need of a higher order potential term). For example, different parameters for the oxygen-oxygen interaction between water molecules compared to oxygen interactions in metal oxides. (ii) Intra- and intermolecular interactions are treated separately using different functional forms/parameters, or fixed intramolecular distances. Using water as an example this could mean fixing the internal O-H distances but allowing the O-H distances between separate molecules to vary. (iii) The electrostatic interactions are described using fixed charges on the atoms (thereby excluding the possibility of charge redistribution). These ways can allow for a more accurate description of the interactions under certain circumstances while using fewer terms of equation 3.2. But they also limit the type of chemistry that can be studied, i.e. it is problematic to treat reactions.

3.3.1 The ReaxFF reactive force-field

The ReaxFF force-field [9] was originally devised from the outset of a few principles chosen to make the force-field able to handle reactions.

- There should be no discontinuities in energy or force during reactions.
- Potential functions should be able to handle changes in coordination during reactions.
- The force-field should use one unique set of parameters for each element regardless of chemical environment.

In order to achieve this, the interaction model of ReaxFF uses a bond-order/bond-energy relationship. The bond-order approach was originally proposed by Pauling in 1947 [42] and initially implemented by Finnis and Sinclair [43] for transition metals, Abell [44] for lithium and hydrogen, Tersoff [45] for silicon, and Brenner [46] for hydrocarbons. For a bond-order potential, before any interaction can be calculated, the bond-orders for each atom needs to be determined. In the ReaxFF potential, the bond-order of each atom is defined as the sum of a continuous function of the pairwise distances between it and all other atoms in the system. However, in practice the bond-order function is typically quite short-range, limiting the calculation to pairwise distances within a radius of $\sim 3\text{Å}$. The continuous bond-order function is parametrized separately for different pairs of elements. In the ReaxFF potential, one basic assumption is that each element has a preferred bond-order.

The dependence on bond-order enables many-body effects to be captured into otherwise purely 2-body, 3-body, or 4-body interaction terms. For example, the 2-body term in a bond-order potential gives interaction energies between pairs of atoms that not does only depend on the interatomic distances, but also on the local density around each atom (the bond-order of each atom respectively). The ReaxFF potential includes 3-body valence angle terms and 4-body torsional terms, as is also common in force-fields used for organic and
biomolecular molecules. In ReaxFF these terms also depend on bond-order in order to make them go to zero smoothly as bonds break. The ReaxFF force-field makes no distinction between intramolecular and intermolecular interactions. The total potential energy expression of the ReaxFF is partitioned into several energy terms as given in equation (3.3).

\[
E_{\text{system}} = E_{\text{bond}} + E_{\text{over}} + E_{\text{under}} + E_{\text{lp}} + E_{\text{val}} + E_{\text{pen}} + E_{\text{tors}} + E_{\text{conj}} + E_{\text{vdWaals}} + E_{\text{Coulomb}} \tag{3.3}
\]

These partial contributions include bond energies \(E_{\text{bond}}\), under-coordination penalty energies \(E_{\text{under}}\), lone-pairs energies \(E_{\text{lp}}\), over-coordination penalty energies \(E_{\text{over}}\), valence angles energies \(E_{\text{val}}\), energy penalty for handling atoms with two double bonds \(E_{\text{pen}}\), torsion angles energies \(E_{\text{tors}}\), conjugated bonds energies \(E_{\text{conj}}\) and terms to handle non bonded interactions, namely van der Waals \(E_{\text{vdWaals}}\) and Coulomb \(E_{\text{Coulomb}}\) interactions. All terms except the last two are bond-order dependent, i.e. will contribute more or less depending on the local environment of each atom.

The Coulomb energy \(E_{\text{Coulomb}}\) of the system is calculated using an environment-dependent charge distribution described using the electronegativity equalization method (EEM) [47], in which individual atomic charges vary as the system geometry varies. This feature allows ReaxFF to describe charge transfer in chemical reactions (in an average way calculated from three parameters per element). All other non-bonded interactions (short-range repulsion and long-range dispersion) are included in the van der Waals term \(E_{\text{vdWaals}}\) which is described using a Morse potential. The non-bond-order-dependent terms \(E_{\text{Coulomb}}\) and \(E_{\text{vdWaals}}\) are screened by a taper function at long distances and shielded to avoid excessive repulsion at short distances. A detailed description of the equations for each the individual terms in equation 3.3 can be found in Refs. [9] and [48]. The force acting on an atom is obtained by taking the negative gradient of equation (3.3). These treatments of bonded and non-bonded interactions were designed to allow the ReaxFF model to describe bonding in covalent, metallic, ionic, and intermediate materials using a unique set of parameters for each element, thus providing means for transferability.

3.3.2 Parametrization of a ReaxFF force-field
A ReaxFF force-field is parametrized by optimizing its parameters against a training set consisting mostly of QM-derived data (using a least squares procedure). The training set can consist of atomic charges, bond dissociation energies, bond lengths, angle strains, heats of formation, vibrational frequencies, and transition state energies. Experimental data is usually used for the heats
Figure 3.1: Volume-energy relationships for several ZnO polymorphs used in the parametrization of the ReaxFF force-field parameters for Zn and O in Paper I and II. The structures included were 4-coordinated wurtzite and zincblende, 6-coordinated rocksalt, and 8-coordinated caesium chloride. The top half shows the B3LYP reference data along with the unit-cells for each structure, the bottom half shows the ReaxFF model data obtained using the parameters presented in Paper I.

of formation, to be able to combine data calculated using different QM methods, e.g. PBE for metals and B3LYP for metal oxides and molecules. In order for the force-field to become transferable for a particular element, the training set needs to include information about the element in a wide range of compounds, preferably in various aggregation states. The training set should also comprise data for systems with a variety of coordination numbers to provide a good description of the bond-order dependence. This coordination-dependent data can be obtained in many ways e.g. varying the number of ligands in a gas-phase cluster. The method used here was to scan the volume for a particular compound in various crystal structures. Using ZnO as an example, data for the volume-energy relationship was included in the training set for four polymorphs: Wurtzite(4), zincblende(4), rocksalt(6), and caesium chloride(8) (coordination number in parenthesis), c.f. Fig. 3.1.

In order to ensure a good description of the most important parts of the data set, a weighting scheme is employed during the parametrization. For instance, the weights chosen for ZnO prioritized the correct relative order of stability of the 4-coordinated structures (i.e. wurtzite lower than zincblende), rather
than the best possible bulkmodulus of the CsCl-phase of ZnO. The general procedure for parametrizing a ReaxFF force-field is as follows:

(i) Creation of an initial training set of data points (energies, charges, and geometries) from QM calculations.
(ii) Selection of the appropriate number of terms in the ReaxFF energy expression (starting with $E_{\text{bond}}$, $E_{\text{over}}$, $E_{\text{vdWaals}}$, and $E_{\text{Coulomb}}$).
(iii) Giving the force-field parameters initial values based on physical meaning.
(iv) Fitting the force-field model to the training set.
(v) Evaluation of whether the training set is satisfactorily reproduced by the current parameter set or if the energy expression needs to be expanded with additional terms. This may in turn require the training set to be expanded with additional data points, (i).
(vi) Repeating (iv)-(v) until the fit is deemed satisfactory.
(vii) Validation of the potential parameters by comparing properties extracted from the model to experimental and quantum chemical data not used in the training set. If the model performs unsatisfactorily, the training set needs to be expanded and the procedure is repeated from step (ii).

In this thesis the force-field parameters were optimized using a successive one-parameter search technique [49]. As in all cases where a large number of parameters are used in a complicated function with many extreme points, there is no guarantee that the global optimum is found in the optimization. Therefore, many different initial values for the parameters were tested before the optimization resulted in a satisfactory force-field.
4. New force-fields

The force-fields parametrized here are part of a greater research project with a goal to develop a model for the Cu/ZnO water-gas shift catalyst. The strategy to attain such a model consists of smaller steps, to among other things, make use of the parallel development of the ReaxFF force-fields elsewhere. Currently, several research groups contribute to the development of ReaxFF parameters for new elements, adding cross-terms between existing elements, or improving already existing parameters. This was the strategy employed here:

(i) Develop a model for zinc oxide.
(ii) Add the cross-terms to handle interactions between water and zinc oxide, utilizing parameters for water that had recently been developed elsewhere [50].
(iii) Develop a model for Water/Cu/Copper oxide.
(iv) Add the cross-terms to handle interactions between zinc oxide and copper.
(v) Add the cross-terms to handle interactions with carbon species making use of the already available carbon oxidation parameters [51].

The complexity is greatly increased with each step since the number of interactions that need handling grows quickly and the balance governing reactions can be delicate, and especially so when the chemical system involves many species. For example, the equilibrium between different species in a model system will be shifted if the bond being cleaved is erroneously too weak and/or the one being formed too strong, or vice versa. Such problems can be expected to grow when the number of different bonding patterns increases. In addition, the barriers between different states need to be well described since they will determine the timescales of the different reactions. These reaction rates are of particular interest in a catalytic context. These are all important aspects to keep in mind when setting up a training set, parametrizing a force-field, or analyzing data from a simulation.

With respect to force-field development, this thesis work includes the first three steps (i-iii), with a majority of the time spent on the two first steps. In section 6, the initial work on step (iv) will be discussed shortly. The fifth and most difficult step is as of yet untreated and may well in turn be broken down in several more steps.

In Paper I the data in the training set was created with a view to what chemical information for ZnO is relevant to optimize a force-field for use in a surface chemistry context, and performing the necessary QM-calculations. In
Paper II the existing training set was expanded with data points describing the interaction between water and ZnO. In Paper III an initial training set was set up using the same method as in the previous papers and an initial force-field was fitted to it. The initial force-field was used to generate input geometries for additional QM-calculations. Subsequently, the force-field was refitted using this data, and the procedure was repeated until the match between QM-data and force-field data was satisfactory. This iterative approach has long been used in the field force-field development for non-symmetric systems, e.g. for liquids where interactions in non-symmetric geometries play a very important role.

In future ReaxFF force-field developments, using a similar technique as in Paper III to obtain data for the parametrization of interactions between molecules and catalytic surfaces seems favorable. Moreover, this methodology has the ability to find erroneously stable configurations present in the force-field description. Below is a short but more detailed summary of each parametrization.

4.1 ZnO(s) and ZnO surfaces

In Paper I, the goal was to parametrize a model for a broad range of chemical environments of the Zn-O binary system, namely solid-state ZnO and its surfaces, non-stoichiometric ZnO, gas-phase zinc hydroxide clusters, nanoparticles, and Zn-metal. Since the long term target of the model is surface chemistry and catalysis applications, the necessary trade-offs were made to obtain a good surface description.

The training set consisted of the following data: The volume-energy equation of state for a number of Zn metal and ZnO phases, the relation between structure and energy for a number of low-index ZnO surfaces, and bond-length and angle scans in gas-phase zinc hydroxide clusters. Since ReaxFF is a bond-order force-field it is important to include data in the training set that describes the energy profile for bond length variations with different bond-orders (i.e. coordination numbers). For the Zn metal phases, the volume-energy equation of state for the following structures were included: 12-coordinated hexagonally close-packed (hcp) and face-centered cubic (fcc), 8-coordinated body-centered cubic (bcc), and 6-coordinated simple cubic (sc). For the ZnO phases, the following structures were included: 4-coordinated wurtzite and zincblende, 6-coordinated rocksalt, and 8-coordinated caesium chloride. Note that the included surfaces also provide data for lower coordination numbers, for example 3-coordination in the case of wurtzite surfaces. Fig. 3.1 gives a comparison between the equations of state for the four metal oxide polymorphs obtained from the QM calculations and the ReaxFF model. The inclusion of the two 4-coordinated structures (zincblende and wurtzite) and their relative stability, and in particular the
relative stability of their surfaces (wurtzite(10\overline{1}0), wurtzite(11\overline{2}0), and zincblende(100)) provided a description of ZnO and its surfaces. Moreover, the inclusion of the high-pressure rocksalt structure along with two of its surfaces ((100) and (110)) provided a description of configurations that may appear at strained interfaces or in particular for small nanoparticles where the core may experience very large strains to minimize the surface energy. The caesium chloride structure was included for technical reasons, to provide data for 8-coordination. Comparisons between cell axes, mechanical properties, and surface energies from QM calculations, experiment and the ReaxFF model are given in Tables 4.1-4.3. For ZnO, the force-field gives a good description of the cell axes and elastic properties of the more stable ZnO polymorphs, and the correct order of the relative stability of the different polymorphs and their surfaces. For Zn metal, the cell axes, elastic properties, and order of the relative stability of the different polymorphs is satisfactory, especially considering that the Zn metal was not of primary interest for the intended application of the force-field.

**Figure 4.1:** The dissociation profiles for a water monolayer on ZnO(10\overline{1}0) using (left) B3LYP and (right) ReaxFF. The optimized geometries for the fully molecular (1 \times 1)-M, half dissociated (2 \times 1)-HD, and fully dissociated (1 \times 1)-D monolayers are shown. Zn, O, and H are represented by small light gray, large dark gray, and small white spheres, respectively. The two traces correspond to a direct dissociation path from molecular to dissociated adsorption, and a dissociation path via the half-dissociated structure.

### 4.2 ZnO–water

In **Paper II** the force-field model was extended by adding cross-terms for the interactions between ZnO and water. Parallel to the development of the zinc oxide force-field, Duin et al. [50] had developed new oxygen and hydrogen parameters in order to improve the description of water via fitting to a training set consisting of e.g. water dimer configurations, water-binding energies in water clusters of up to 35 molecules, proton transfer barriers in basic and acidic water clusters and barriers and reaction energies for water auto-
Table 4.1: QM results and ReaxFF results (at 0 K) compared to experimental data (at room temperature) for the cell axes, heat of formation (ΔfH), bulk modulii, and elastic constants of the four polymorphs (B1-B4) of ZnO.

<table>
<thead>
<tr>
<th>Property</th>
<th>Wurtzite(B4) P63mc</th>
<th>B3LYP (Paper I)</th>
<th>ReaxFF (Paper I)</th>
<th>ReaxFF (Paper II)</th>
<th>Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>a/Å</td>
<td>3.28</td>
<td>3.28</td>
<td>3.29</td>
<td>3.25 [52]</td>
<td></td>
</tr>
<tr>
<td>c/Å</td>
<td>5.28</td>
<td>5.28</td>
<td>5.30</td>
<td>5.21 [52]</td>
<td></td>
</tr>
<tr>
<td>ΔtHb4/(kcal/mol)</td>
<td>-84.4</td>
<td>-91.2</td>
<td>-83.3</td>
<td>[53]</td>
<td></td>
</tr>
<tr>
<td>Bulk modulus/GPa</td>
<td>136</td>
<td>139</td>
<td>144</td>
<td>141, 143 [54, 14]</td>
<td></td>
</tr>
<tr>
<td>c11/GPa</td>
<td>207.9</td>
<td>222.9</td>
<td>209.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>c12/GPa</td>
<td>113.3</td>
<td>116.3</td>
<td>121.1</td>
<td>121.1 [55]</td>
<td></td>
</tr>
<tr>
<td>c13/GPa</td>
<td>81.4</td>
<td>103.5</td>
<td>105.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>c33/GPa</td>
<td>287.5</td>
<td>212.8</td>
<td>210.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>c44/GPa</td>
<td>52.0</td>
<td>57.1</td>
<td>42.47</td>
<td></td>
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<tr>
<th>Property</th>
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<td>Bulk modulus/GPa</td>
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<td>130</td>
<td>130</td>
<td>This polymorph</td>
<td></td>
</tr>
<tr>
<td>a/Å</td>
<td>4.60</td>
<td>4.60</td>
<td>4.62</td>
<td>does not occur</td>
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</tr>
<tr>
<td>ΔtHb1-ΔtHb4/(kcal/mol)</td>
<td>0.50</td>
<td>1.19</td>
<td>0.97</td>
<td></td>
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<table>
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<tr>
<th>Property</th>
<th>Rocksalt(B3) Fm3m</th>
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<th></th>
<th></th>
<th></th>
</tr>
</thead>
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<tr>
<td>Bulk modulus/GPa</td>
<td>202</td>
<td>227</td>
<td>283</td>
<td>203,228 [14, 56]</td>
<td></td>
</tr>
<tr>
<td>a/Å</td>
<td>4.30</td>
<td>4.26</td>
<td>4.44</td>
<td>4.27 [56]</td>
<td></td>
</tr>
<tr>
<td>ΔtHb3-ΔtHb4/(kcal/mol)</td>
<td>8.57</td>
<td>8.15</td>
<td>7.72</td>
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<table>
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<tr>
<th>Property</th>
<th>Caesium Chloride(B2) Pm3m</th>
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<td>Bulk modulus/GPa</td>
<td>183</td>
<td>327</td>
<td>407</td>
<td>This polymorph</td>
<td></td>
</tr>
<tr>
<td>a/Å</td>
<td>2.68</td>
<td>2.63</td>
<td>2.64</td>
<td>does not occur</td>
<td></td>
</tr>
<tr>
<td>ΔtHb2-ΔtHb4/(kcal/mol)</td>
<td>37.89</td>
<td>43.24</td>
<td>37.58</td>
<td>in nature</td>
<td></td>
</tr>
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Table 4.2: QM results and ReaxFF results (at 0 K) compared to experimental data (at room temperature) for the cell axes, cohesive energy ($E_{coh}$), bulk modulii, and elastic constants of Zn-metal.

<table>
<thead>
<tr>
<th>Property</th>
<th>PBE (Paper I)</th>
<th>ReaxFF (Paper I)</th>
<th>ReaxFF (Paper II)</th>
<th>Experiment</th>
</tr>
</thead>
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<tr>
<td></td>
<td>hcp $P6_3/mmc$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$a$/Å</td>
<td>2.63</td>
<td>2.73$^a$</td>
<td>2.74$^a$</td>
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<tr>
<td>$c$/Å</td>
<td>5.06</td>
<td>4.46$^a$</td>
<td>4.49$^a$</td>
<td>4.95 [57]</td>
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<td>$E_{coh}(hcp)$/kcal/mol</td>
<td>-31.6</td>
<td>-31.0</td>
<td>-31.1 [15]</td>
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<tr>
<td>Bulk modulus/GPa</td>
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<td>87.7</td>
<td>110</td>
<td>64.5-75.1$^b$</td>
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<tr>
<td>$c_{11}$/GPa</td>
<td>193</td>
<td>224</td>
<td></td>
<td>163$^b$</td>
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<td>$c_{12}$/GPa</td>
<td>41</td>
<td>56</td>
<td>31$^b$</td>
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<td>53</td>
<td>48$^b$</td>
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<td>$c_{44}$/GPa</td>
<td>71$^c$</td>
<td>74$^c$</td>
<td>39$^b$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>fcc $F\bar{4}3m$</td>
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<tr>
<td>Bulk modulus/GPa</td>
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<td>3.86</td>
<td>3.87</td>
<td>not occur</td>
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<tr>
<td>$E_{coh}(fcc)-E_{coh}(hcp)$/kcal/mol</td>
<td>1.31</td>
<td>0.00$^a$</td>
<td>0.00$^a$</td>
<td>in nature</td>
</tr>
<tr>
<td></td>
<td>bcc $Im\bar{3}m$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bulk modulus/GPa</td>
<td>84.6</td>
<td>73.5</td>
<td>89</td>
<td>This polymorph</td>
</tr>
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<td>3.06</td>
<td>3.06</td>
<td>3.11</td>
<td>does not occur</td>
</tr>
<tr>
<td>$E_{coh}(bcc)-E_{coh}(hcp)$/kcal/mol</td>
<td>2.71</td>
<td>2.71</td>
<td>2.15</td>
<td>in nature</td>
</tr>
<tr>
<td></td>
<td>sc $Pm\bar{3}m$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bulk modulus/GPa</td>
<td>64.2</td>
<td>30.2</td>
<td>30</td>
<td>This polymorph</td>
</tr>
<tr>
<td>$a$/Å</td>
<td>2.71</td>
<td>2.71</td>
<td>2.77</td>
<td>does not occur</td>
</tr>
<tr>
<td>$E_{coh}(sc)-E_{coh}(hcp)$/kcal/mol</td>
<td>6.00</td>
<td>6.62</td>
<td>6.11</td>
<td>in nature</td>
</tr>
</tbody>
</table>

$^a$ Zn-Zn-Zn angle terms for pure Zn were not included, and therefore ReaxFF will preserve the ideal $c/a$ ratio ($(8/3)^{1/2}$) of a close packed crystal. This also means that the volume-energy relationship for the fcc and hcp phases will be identical.

$^b$ Experimental values taken from the review article by H.M. Ledbetter[58]

$^c$ These hcp-specific stresses are not correctly reproduced for the reason stated in $^a$. 

31
dissociation. The new oxygen parameters were substituted for the old and the remaining parameters in the ZnO force-field were refitted to the training set from Paper I. Before the refit, the training set was also expanded with QM data points describing the interaction between water and ZnO.

For the selection of relevant adsorption structures of water on ZnO, the study of Meyer et al. [22] was used as a reference. Starting from a large number of initial configurations they had found nine separate adsorption structures for a single water molecule on the ZnO(10\overline{1}0)-surface using geometry optimization with the PBE-functional and a plane-wave basis-set. Here, to remain consistent with the previous data in the training set, the structures of Meyer et al. were used as initial guesses for B3LYP calculations. Additionally, several water dissociation profiles were computed. The new data thus entered into the training set were adsorption structures, adsorption energies, and dissociation profiles. Fig. 4.1 depicts the relative stability of three different adsorption structures for a water monolayer on ZnO(10\overline{1}0) (fully molecular, fully dissociated, and half dissociated) and the dissociation profiles connecting them. The re-fit resulted in only minor changes of the properties produced by the ReaxFF model (as shown in Tables 4.1-4.3), namely a small deterioration of the mechanical properties and a small improvement of the cell axes and surface energies.

4.3 Cu, Cu$_2$O, CuO, Cu$^{2+}$–water

Paper III describes the development of a force-field for Cu/O/H-interactions. The training set comprised geometries, energies, and charges for [Cu(H$_2$O)$_n$]$^{2+}$-clusters, [CuOH(H$_2$O)$_n$]$^+$-clusters, Cu-metal as well as CuO, and Cu$_2$O crystalline phases. An initial force-field was fitted against the training set and MD-simulations of aqueous Cu$^{2+}$ were performed. From
these simulations a number of 

\[ \text{[Cu(H}_2\text{O)}_5]^{2+} \] -structures were extracted and used as input for QM-calculations. The new QM-data were subsequently added to the training set and the force-field was refitted. The procedure was repeated one additional time, this time extracting \[ \text{[Cu(H}_2\text{O)}_6]^{2+} \] -structures. In the second comparison between the QM-data and the force-field, the model was found to be satisfactory and no further re-parametrization was deemed necessary. The Cu/O/H force-field developed here uses the same O/H parameters as the force-field presented in \textbf{Paper II}. Its development is therefore a necessary step towards the creation of a model for the Cu/ZnO WGS catalyst, which will require consistent parameters for Zn/Cu/O/H.
5. Results

The force-fields described in Chapter 4 were developed to be able to describe the interactions between Zn/O/H and Cu/O/H in a consistent way for a variety of bonding situations. These versatile force-fields were used to cast light on a number of structural, dynamical, and mechanistical aspects related to the ZnO-water interface, to ZnO nanoparticles, and ZnO surfaces, as well as the solvation of Cu$^{2+}$ in water. With the new force-fields it thus became possible to go beyond the limitations of standard QM-methods and perform large-scale, long-time simulations for complicated and interesting systems.

Figure 5.1: The final snapshots taken after 300 ps of MD simulation of crystal growth via ZnO sputtering onto the polar oxygen-terminated ZnO(0001) surface. The figure to the left started from a flat surface and to the right started from a stepped surface. Crystal growth is seen to proceed faster towards non-polar surface orientations if a step is present. Here Zn and O are represented by light gray spheres and dark gray spheres, respectively, and the periodic images have been shaded.

5.1 Atomic vibrations in ZnO(s) and ZnO crystal growth

Vibrational properties of bulk ZnO and the surface mechanisms for crystal growth on the polar oxygen terminated wurtzite(0001) surface were studied in Paper I.
Crystal growth was studied following the simulated deposition procedure devised by Kubo et al. [59], who had previously also studied ZnO crystal growth on the ZnO(0001)\(^1\) surface. In Paper I the following procedure was used: Two surface models were constructed: With and without a surface step. The simulations were performed at 700 K. During 30 ps of deposition, ZnO dimers were made to emerge at regular 2 ps intervals with random velocities (the velocities were distributed on a half sphere with radius 900 m/s) from an emitting source located 20 Å above the surface. In addition to the original procedure in Ref. [59], the deposition was repeated ten times for each surface model, and in each case the surface was allowed to relax after the deposition during an additional 300 ps. Inspecting the resulting trajectories revealed that the growth mechanism alters with the presence of a step; if a step was present the surface structure was able to grow faster from its initial polar wurtzite(0001) facet towards a different non-polar surface facet. This behavior is observed in nine of the ten simulations. On the flat surface, the incoming dimers are randomly distributed over the surface leading to the growth of an additional (0001)-layer in eight of the ten simulations. Fig. 5.1 shows snapshots from the end of the ZnO crystal growth simulations, the left hand side is the resulting structure starting from a flat surface and the right hand side starting from a stepped surface.

The dynamics in bulk ZnO was explored via anisotropic vibrational mean square amplitudes (\(\langle u^2 \rangle\)), which were calculated at three different temperatures for the Zn atoms and O atoms, respectively. The ReaxFF model produces values that grow linearly with temperature which is typical for a ceramic material. The values were compared to \(\langle u^2 \rangle\) values from diffraction experiments and good agreement between ReaxFF model and experimental data was found, c.f. Fig. 5.2.

5.2 Structure and reactivity of ZnO-water interfaces

The structure of solid-liquid interfaces is challenging to probe using experimental techniques. With a force-field model it is possible to simulate the interface and extract properties that can be compared to results from indirect experiments such as spectroscopic and pH-measurements, as in the present case. Paper II, Paper IV, and Paper V explore the water-ZnO interface. In Paper II the structure of water monolayers on ZnO surfaces (flat and stepped) were studied at different temperatures. Paper IV presents a broad study of ZnO surfaces covered with water — many layers, nanoparticles in the nanometer-range, clean, covered with water, and immersed in water. Paper V is a more detailed study of the ZnO-liquid water interface; here the water structure (molecular or dissociated) in the first adsorption layer and its

\(^1\) Here the naming convention of Ref. [59] was used, i.e. the oxygen-terminated surface perpendicular to the c-axis was designated as (0001).
connection to H transfer reactivity was explored. The system descriptions for the ZnO–water simulations are given in Table 5.1. Below is a short summary of the results.

### 5.2.1 H$_2$O structure on the ZnO-surface

Simulations of the water-ZnO interface was performed for water monolayer coverage at 300 K and 600 K, and the liquid water interface at 300 K. In the monolayer simulations, on ZnO(1010)-terraces the 1:1 equilibrium between molecular:dissociated water in the water monolayer previously found both by STM experiments and PBE-calculations [20], is reproduced. The monolayer simulations in this thesis were started from either a fully molecular or fully dissociated water layer and in both cases the 1:1 equilibrium on ZnO(1010)-terraces is reached quickly (< 10 ps) at 300 K. At an elevated temperature (600 K), the monolayer starts to break down through evaporation. However, the 1:1 ratio persists, since water reassociates to compensate for water-loss due to desorption. At both temperatures the reason for this is that it is possible to form a more favorable hydrogen-bonded network in mixed molecular/dissociated monolayers compared to fully molecular or dissociated layers.

At higher water coverage, a higher level of dissociation was found compared to at monolayer coverage. This in agreement with Hirschwald [62], who concluded from IR-spectroscopic measurements that water dissociates in the first adsorption layer on the ZnO surface. The main reason for this increase in dissociation is the supply of more water molecules, enabling a new hydrogen-bonding pattern involving water molecules outside the first adsorption layer. In this H-bond pattern, many of the Zn-OH hydroxyls do not accept hydrogen bonds from the H transferred to the surface (as is the case for the

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**Figure 5.2:** Atomic vibrational mean square amplitudes for wurtzite ZnO(s). ReaxFF and experimental values from neutron (Albertsson et al. [52]) and x-ray (Schultz et al. [60] and Kihara et al. [61]) diffraction.
Table 5.1: Slab models for flat and stepped ZnO surfaces used with ReaxFF in Papers II and V. Values are given per repeating unit.

<table>
<thead>
<tr>
<th>Surface Normal</th>
<th>No. of Zn sites</th>
<th>Surface Area (Å²)</th>
<th>Steps Width of (10\overline{1}0)-terrace (rows)</th>
<th>Step conc. of slab of water (steps/Å)</th>
<th>Thickness of slab (Å)</th>
<th>Thickness of water layer (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(10\overline{1}0)</td>
<td>48</td>
<td>19.9×21.6</td>
<td>0 6</td>
<td>0.000</td>
<td>14.9</td>
<td>22.4</td>
</tr>
<tr>
<td>(6\overline{1}70)</td>
<td>56</td>
<td>21.6×21.6</td>
<td>1 5</td>
<td>0.046</td>
<td>15.3</td>
<td>18.9</td>
</tr>
<tr>
<td>(5\overline{1}60)</td>
<td>48</td>
<td>21.6×18.4</td>
<td>1 4</td>
<td>0.054</td>
<td>15.2</td>
<td>23.0</td>
</tr>
<tr>
<td>(4\overline{1}50)</td>
<td>40</td>
<td>21.5×15.1</td>
<td>1 3</td>
<td>0.066</td>
<td>17.7</td>
<td>26.0</td>
</tr>
<tr>
<td>(3\overline{1}40)</td>
<td>64</td>
<td>21.6×23.8</td>
<td>2 2</td>
<td>0.083</td>
<td>11.6</td>
<td>18.9</td>
</tr>
<tr>
<td>(2\overline{1}30)</td>
<td>48</td>
<td>21.5×17.5</td>
<td>2 1</td>
<td>0.114</td>
<td>19.6</td>
<td>23.3</td>
</tr>
<tr>
<td>(1\overline{1}20)</td>
<td>64</td>
<td>21.6×22.8</td>
<td>4 0</td>
<td>0.174</td>
<td>14.6</td>
<td>16.2</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Surface Normal</th>
<th>No. of atoms in monolayer water models</th>
<th>No. of atoms in liquid water models</th>
<th>Equilibration time for liquid water sim. (ns)</th>
<th>Total sim. time for evaporation sim. (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(10\overline{1}0)</td>
<td>720 (Zn\textsubscript{312}O\textsubscript{288}+(H\textsubscript{2}O)\textsubscript{36})</td>
<td>1344 (Zn\textsubscript{288}O\textsubscript{288}+(H\textsubscript{2}O)\textsubscript{256})</td>
<td>9.1</td>
<td>9.5</td>
</tr>
<tr>
<td>(6\overline{1}70)</td>
<td>792 (Zn\textsubscript{312}O\textsubscript{312}+(H\textsubscript{2}O)\textsubscript{56})</td>
<td>1392 (Zn\textsubscript{312}O\textsubscript{312}+(H\textsubscript{2}O)\textsubscript{256})</td>
<td>9.4</td>
<td>9.2</td>
</tr>
<tr>
<td>(5\overline{1}60)</td>
<td>704 (Zn\textsubscript{30}O\textsubscript{29}+(H\textsubscript{2}O)\textsubscript{36})</td>
<td>1328 (Zn\textsubscript{29}O\textsubscript{29}+(H\textsubscript{2}O)\textsubscript{256})</td>
<td>11.8</td>
<td>9.5</td>
</tr>
<tr>
<td>(4\overline{1}50)</td>
<td>600 (Zn\textsubscript{304}O\textsubscript{240}+(H\textsubscript{2}O)\textsubscript{40})</td>
<td>1248 (Zn\textsubscript{240}O\textsubscript{240}+(H\textsubscript{2}O)\textsubscript{256})</td>
<td>12.6</td>
<td>9.9</td>
</tr>
<tr>
<td>(3\overline{1}40)</td>
<td>832 (Zn\textsubscript{320}O\textsubscript{320}+(H\textsubscript{2}O)\textsubscript{64})</td>
<td>1408 (Zn\textsubscript{320}O\textsubscript{320}+(H\textsubscript{2}O)\textsubscript{256})</td>
<td>9.4</td>
<td>9.0</td>
</tr>
<tr>
<td>(2\overline{1}30)</td>
<td>784 (Zn\textsubscript{320}O\textsubscript{320}+(H\textsubscript{2}O)\textsubscript{48})</td>
<td>1408 (Zn\textsubscript{320}O\textsubscript{320}+(H\textsubscript{2}O)\textsubscript{256})</td>
<td>13.1</td>
<td>9.3</td>
</tr>
<tr>
<td>(1\overline{1}20)</td>
<td>832 (Zn\textsubscript{320}O\textsubscript{320}+(H\textsubscript{2}O)\textsubscript{64})</td>
<td>1408 (Zn\textsubscript{320}O\textsubscript{320}+(H\textsubscript{2}O)\textsubscript{256})</td>
<td>11.6</td>
<td>9.0</td>
</tr>
</tbody>
</table>

All simulations in Paper II were 100 ps long.
All monolayer simulations in Paper V were 5 ns long (1 ns equilibration and 4 ns production)
The productions simulations for the liquid water models in Paper V were all 4 ns long.

monolayer coverage), but instead they accept an H-bond from a second layer water molecule which in turn accepts from the transferred H. This type of water-mediated structure is common on ZnO(10\overline{1}0)-terraces and makes up a double-layer of hydroxyls in the first adsorption layer with water molecules adsorbed on top of them in turn, shown in Fig. 5.3.

5.2.2 Influence of surface steps
The effect of a surface step on the adsorption was studied using seven surface models with surface steps separated by a varying distance. These were created by systematically introducing steps parallel to the (0001)-direction on the ZnO(10\overline{1}0) surface. Both monolayer and liquid water coverages were simulated. From each simulated trajectory the level of dissociation in the water region was calculated (as a function of time). By comparing the result for the different surface models it was found that the presence of steps promoted...
dissociation at all coverages, the steps being almost fully hydroxylated in all cases, while the (10\overline{1}0)-terraces remained hydroxylated to approximately the same degrees as the unstepped (10\overline{1}0)-surfaces (50\% for monolayer, 85\% for higher coverage). In the monolayer simulations at 600 K, water evaporated from the (1010) terraces, but the steps themselves remained hydroxylated. At higher coverage (in the liquid water model), the adsorption structures (highlighted in Fig. 5.3) making up the double-layer structure found on the (10\overline{1}0) surface are less likely to be found if a step is present. To test the stability of the double-layer and the effect of steps on the ability of the surfaces to bind water, the model systems were opened, i.e. subjected to a vacuum, to allow for evaporation. Fig. 5.4 shows the evaporation curves calculated by following the time evolution of the water content for each of the seven model systems during the evaporation simulations.

The simulations showed that, when present, the double layer binds additional water molecules, and therefore a slower desorption rate was observed. The evaporation curves also showed that there was a correlation between presence of steps and desorption rate, since water-mediated structures were affected by their presence.
5.2.3 Proton transfer dynamics

The influence of surface steps on a water dissociation reaction was explored by calculating the free energy barrier for transfer of an H between a Zn-bound water molecule and a surface O. A series of simulations were performed using the previously mentioned surface models (seven in total). The reactivity of the formed hydroxyls and adsorbed water molecules was analyzed and it was found that several criteria had to be satisfied in order for an H to be transferred to the metal oxide or vice versa:

(i) The water/hydroxyl oxygen binds to a single Zn-ion.
(ii) The reactive H of the water molecule points towards a naked surface O-ion. In case of re-association the transferred proton points towards a Zn-bound hydroxyl group.
(iii) The reaction path is not blocked by another water molecule.

**Fig. 5.5** shows three simulation snapshots for the dissociation reaction meeting the above criteria. A probability distribution function for the H transfer was calculated (pdf($r_{O-H}$)) by collecting all O-H distances in the simulations meeting the criteria into a histogram, separately for each of the seven model systems. From each distribution function the potential of mean force (PMF) was obtained according to eqn. 5.1.

$$ PMF(r_{O-H}) = -k_B T \ln(pdf(r_{O-H})) $$ (5.1)
Figure 5.5: Snapshots of a water dissociation reaction meeting the criteria defined to analyze the reactivity of the adsorbed water molecules with respect to hydroxylation of the ZnO surface. The dissociating water molecule and the accepting O(ZnO) are highlighted. Zn, O(ZnO), O(H₂O) and H are represented by small gray spheres, large red spheres, large blue spheres, and small white spheres, respectively.

Fig. 5.6 shows the PMF-curve calculated for the (10{10})-surface along with the barrier.

Figure 5.6: PMF-curve for O-H distances in water adsorbed on the ZnO(10{10})-surface meeting a set of criteria determined to be necessary for being able to transfer H to the surface. The barrier for this type of dissociation is indicated. The curve is calculated from a MD-simulation at 300 K.

As previously mentioned the steps were found to promote the hydroxylated state. The PMFs also showed that the barriers for dissociation became successively smaller when more steps were present. The barrier for dissociation as a function of step concentration is presented in Fig. 5.7. On the most highly stepped surfaces the barrier is only 2 kJ/mol or smaller.

An important conclusion from the simulations was that no dissociation or H transfer reactions between water molecules is observed outside the first ad-
sorption layer on ZnO, indicating that these reactions can only proceed on the metal oxide surface (in the time-scales of the simulations), i.e. if the reactions were catalyzed by the surface.

**Figure 5.7:** Dissociation barrier (obtained from potential of mean force) plotted against step concentration, using data from the final 4 ns of simulation time for each surface. For each system, 13 to 17 ns of simulation time was required (equilibration and production). The value for the (11\(\bar{2}0\))-surface is plotted as 0 kJ/mol since no barrier was observed. Block averages were used to estimate the standard error of the mean for the dissociation barriers and the error bars are plotted with a 95% confidence interval.

### 5.2.4 ZnO nanoparticles and water

The relaxation and reconstruction of ZnO nanoparticles was studied by simulating nanoparticles that were initially terminated by low-index surfaces: ((10\(\bar{1}0\)), (11\(\bar{2}0\)), (0001), and (000\(\bar{1}\))). Four separate cases were simulated: two clean nanoparticles of different sizes at 300 K and 1500 K, respectively, one covered with water at 1500 K, and one immersed in water at 300 K. In two of the cases (clean and covered with water), simulations at T=1500 K show that water is able to catalyze reconstruction of the nanoparticle surface. Even though the simulation of the clean nanoparticle was ten times longer than that of the water-covered nanoparticle, the latter underwent a larger reconstruction and displayed a more spherical shape at the end of the simulation. The polar (0001) and (000\(\bar{1}\)) surfaces were found to reconstruct more extensively compared to the non-polar surfaces in both cases.

For the remaining two cases (two small 1 nm particles, clean\(^2\) and immersed in water, both simulated at T=300 K), large reconstructions were observed for

\(^2\)simulation of the clean 1 nm particle was presented in Paper VI.
the clean particle compared to almost none for the particle immersed in water. Thus water appears to have a stabilizing effect at 300 K (in contrast to at 1500 K). This is most likely due to the ability of water to stabilize the polar surfaces. The effect may explain why ZnO nanoparticles synthesized from aqueous solution are crystalline, even for small particle sizes.

5.3 Dynamics of ZnO nanoparticles

**Paper VI** was a combined experimental and theoretical study of ZnO nanoparticles. The ZnO nanoparticles were synthesized in ethanol solution from zinc acetate and lithium hydroxide and subsequently dried. A series of samples containing successively larger particles in the range 3-9 nm were synthesized. The optical band gap was measured with UV-Vis absorption measurements and the average size of the particles in each sample was determined using a relation between size and the band gap. Raman spectroscopic measurements for the ZnO nanoparticles showed a systematic increase in the intensity of a Raman-active optical phonon at $\sim 436 \text{ cm}^{-1}$ with particle size.

To help explain the experimental vibrational observation, MD simulations were performed and phonon density of states (DOS) calculated for ZnO nanoparticles in the size range 1-7 nm (diameter). **Fig 5.8** shows the measured Raman spectra and the calculated phonon DOSs. All MD simulations were performed at 300 K. During the equilibration (also at 300 K) the structures of the particles were relaxed, by allowing for the potential energy to decrease and finally converge to within 0.5 kJ/mol per ZnO unit. The phonon DOSs were calculated by taking the Fourier transform of the velocity autocorrelation function obtained from the production stage of the MD simulations. **Table 5.2** lists the particle sizes, percentage of surface atoms, and simulation times.

In agreement with the Raman experiments, the calculated total phonon DOSs show a mode at $\sim 450 \text{ cm}^{-1}$ which increases in intensity with particle size (the upper row of **Fig. 5.8**). To assist the analysis, separate phonon DOSs were created for the core and the surface regions of each nanoparticle. The surface region was defined as the atoms in the outermost 5 Å shell (approximately the length of the $c$-axis of the ZnO unit cell).

First of all, the surface and the core DOS differ (the lower row in **Fig. 5.8**), reflecting the fact that the local structure and bonding at the surface is modified both by surface reconstruction and relaxation, and by the loss of neighbors. For example, the intensity of the 450 cm$^{-1}$ mode was found to be suppressed in the surface region compared to the core region. Moreover, the partial phonon DOSs from each of the regions, surface or core, were found to be largely unaffected by particle size. For all but the smallest 1 nm particle (which lacks a core under the definition used), the core DOSs are virtually identical.
Figure 5.8: Top left: Raman spectra of ZnO nanoparticles (and a background measurement of Zn(Ac)$_2$·H$_2$O). Top right: Phonon DOSs showing intensity at $\sim 450$ cm$^{-1}$ increasing with size. Bottom left and right: Surface and core phonon DOSs.

and the surface DOSs display a modest intensity increase at $\sim 450$ cm$^{-1}$ as the particles grow (smaller than the increase in the total DOSs).

It was thus concluded that the increasing intensity in the total phonon DOSs was primarily related to the increasing ratio of core to surface atoms as the particle grows. Lastly, in the comparison between the calculated DOSs and the experimental spectra, it should be noted that the calculated DOSs is the projection of the whole phonon dispersion curve, while the measured Raman spectra refers to $\vec{q} = 0$ only.

5.4 Structure of Cu$^{2+}$ in aqueous solution

In Paper III the Cu/O/H force-field was used to give additional insight concerning the coordination number and geometry of Cu$^{2+}$-ions in aqueous solution. Fig. 5.9 shows the Cu-O radial distribution function and O-Cu-O angular distribution calculated from a simulation of a [Cu(H$_2$O)$_{216}$]$^{2+}$ system at 300 K. The radial distribution function displays two distinct peaks at 1.94 Å and 2.27 Å. Integration of the peaks results in four and two water molecules,
Table 5.2: Details of the MD simulations of ZnO nanoparticles at 300 K: Particle characteristics and simulation times.

<table>
<thead>
<tr>
<th>Nanoparticle diameter</th>
<th>Stoichiometry</th>
<th>Number of atoms</th>
<th>Surface atoms</th>
<th>Core atoms</th>
<th>Fraction of surface atoms (%)</th>
<th>Equilibration time</th>
<th>Production time</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 nm</td>
<td>Zn_{24}O_{24}</td>
<td>48</td>
<td>48</td>
<td>0</td>
<td>100</td>
<td>125 ns</td>
<td>4 ns</td>
</tr>
<tr>
<td>2 nm</td>
<td>Zn_{232}O_{232}</td>
<td>464</td>
<td>417</td>
<td>47</td>
<td>90</td>
<td>15 ns</td>
<td>1 ns</td>
</tr>
<tr>
<td>3 nm</td>
<td>Zn_{644}O_{644}</td>
<td>1288</td>
<td>942</td>
<td>346</td>
<td>73</td>
<td>10 ns</td>
<td>300 ps</td>
</tr>
<tr>
<td>4 nm</td>
<td>Zn_{2107}O_{1407}</td>
<td>2814</td>
<td>1694</td>
<td>1120</td>
<td>60</td>
<td>5 ns</td>
<td>200 ps</td>
</tr>
<tr>
<td>5 nm</td>
<td>Zn_{2728}O_{2728}</td>
<td>5456</td>
<td>2789</td>
<td>2667</td>
<td>51</td>
<td>1 ns</td>
<td>200 ps</td>
</tr>
<tr>
<td>6 nm</td>
<td>Zn_{4744}O_{4744}</td>
<td>9488</td>
<td>4230</td>
<td>5258</td>
<td>45</td>
<td>1 ns</td>
<td>200 ps</td>
</tr>
<tr>
<td>7 nm</td>
<td>Zn_{7542}O_{7542}</td>
<td>15084</td>
<td>6022</td>
<td>9062</td>
<td>40</td>
<td>1 ns</td>
<td>100 ps</td>
</tr>
<tr>
<td>bulk</td>
<td>Zn_{1680}O_{1680}</td>
<td>3360</td>
<td>-</td>
<td>-</td>
<td>0</td>
<td>200 ps</td>
<td>100 ps</td>
</tr>
</tbody>
</table>

Surface atoms are defined as those whose mean position during the production simulation is in the outermost 5 Å shell of the particle. Core atoms are the remaining ones.

Time until potential energy had converged within 0.5 kJ/mol per ZnO unit.

respectively, i.e. the copper ion displays a distorted 6-fold coordination with this force-field. The angular distribution calculated for the six water molecules in the first hydration shell shows two peaks at 90° and 176°. These two results, along with visual inspection of selected snapshots, confirm that the Cu-ions display a Jahn-Teller distorted 6-fold coordination in the simulation.

To further confirm the equilibrium structure, a series of MD simulations were performed starting from different initial coordination numbers and geometries for the Cu^{2+}-ions, namely four-fold square planar and five-fold square pyramidal. Several simulations were performed for each case. The 4-fold to 5-fold transition was found to be fast (< 15 ps), whereas the 5-fold to 6-fold transition was found to be considerably slower, sometimes lasting during the entire simulation (125 ps).

Since the 5-fold to 6-fold transition was found to be slow, it is reasonable that during a long simulation 5-fold coordinated complexes exist for extended time intervals, even if the simulation is otherwise dominated by 6-fold coordination.
Figure 5.9: Results from an MD-simulation of a \([\text{Cu(H}_2\text{O)}_{216}]^{2+}\) system at 300 K. Left: Cu-O radial distribution function \((g(r))\) and its integral \((n(r))\). Right: O-Cu-O angular distribution for the six water molecules in the first hydration shell.
6. Concluding remarks and future work

The work presented in this thesis has extended the possibilities of studying ZnO surfaces, ZnO nanoparticles, ZnO-water interfaces, and aqueous Cu$^{2+}$-ions by developing reactive force-field models fitted to results from QM-calculations. The force-field approach has allowed studies of scientific problems that are difficult to address using experimental techniques and standard QM-methods. These models were used to simulate systems containing thousands of atoms, during several nanoseconds at several temperatures. Important steps were taken towards creating a model for the study of the Cu/ZnO water-gas shift catalyst. Following are the key conclusions of this thesis.

The newly developed force-fields were able to satisfactorily reproduce experimental bulk and surface properties of ZnO. Simulations of the water-ZnO system show that structures that promote hydrogen bonding are favored. Steps on the ZnO surface were found to increase the level of hydroxylation by stabilizing the hydroxylated state and decreasing the barrier for water dissociation. At monolayer coverage an equilibrium of 1:1 molecular:dissociated water was present on ZnO(10\bar{1}0) surfaces and terraces. At elevated temperatures the equilibrium persists during evaporation, i.e. dissociated water reassociates to compensate for water-loss due to desorption. At higher water coverage a higher level of hydroxylation was found compared to monolayer coverage due to increased possibilities of hydrogen-bonding favoring the hydroxylated state. Moreover, on ZnO(10\bar{1}0) surfaces and terraces, a double-layered adsorption structure consisting of hydroxyls bonded directly to the ZnO surface and additional water molecules adsorbed on top of the hydroxyls was found.

Raman spectroscopic measurements for ZnO nanoparticles in the size range of 3-9 nm showed a systematic increase in the intensity of certain Raman-active optical phonons with particle size. To help explain the experimental observation, MD simulations were performed and phonon density of states (DOS) calculated for ZnO nanoparticles in the size range 1-7 nm. It was found that the intensity of certain vibrational modes were suppressed in the surface compared to the core, including the modes previously observed using Raman. Therefore, it was concluded that the increasing intensity was related to the increasing ratio of core to surface atoms as the particle grows.

The future work in this project is centered around obtaining a working model for the Cu/ZnO catalyst. Before this is accomplished, several additional steps needs to be taken. Work has been started to combine the Cu/H/O and the
Zn/O/H force-fields (they already share parameters for O and H) and a training set of data for Zn/Cu clusters and Zn and Cu containing gas-phase hydroxide clusters was constructed. To test the model, adsorption structures and energies for single Cu-atoms were calculated using the force-field. These were subsequently re-calculated using quantum-mechanics. Unfortunately, some discrepancies were found that might influence the results, thus a larger training set was deemed necessary. The development process for the Cu/Zn/O/H force-field is thus currently in step (v) in the scheme listed in section 3.3.2. This can be seen as a variant of the methodology employed in Paper III.

In spite of these deficiencies, the force-field was used to address the question of how the surface morphology of a copper particle was affected by supporting it on a ZnO surface. From these preliminary simulations there were clear indications that the shape of the Cu particle was indeed affected by the structure of the Cu/ZnO interface. However, for the reasons stated above, the force-field needs to be finalized before conclusive results can be presented. The immediate future work on the model thus consists of extending the training set and refitting the force-field to it.
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