Molecular structure and dynamics of liquid water

Simulations complementing experiments

Daniel Schlesinger
Abstract

Water is abundant on earth and in the atmosphere and the most crucial liquid for life as we know it. It has been subject to rather intense research since more than a century and still holds secrets about its molecular structure and dynamics, particularly in the supercooled state, i.e. the metastable liquid below its melting point.

This thesis is concerned with different aspects of water and is written from a theoretical perspective. Simulation techniques are used to study structures and processes on the molecular level and to interpret experimental results.

The evaporation kinetics of tiny water droplets is investigated in simulations with focus on the cooling process associated with evaporation. The temperature evolution of nanometer-sized droplets evaporating in vacuum is well described by the Knudsen theory of evaporation. The principle of evaporative cooling is used in experiments to rapidly cool water droplets to extremely low temperatures where water transforms into a highly structured low-density liquid in a continuous and accelerated fashion.

For water at ambient conditions, a structural standard is established in form of a high precision radial distribution function as a result of x-ray diffraction experiments and simulations. Recent data even reveal intermediate range molecular correlations to distances of up to 17 Å in the bulk liquid.

The barium fluoride (111) crystal surface has been suggested to be a template for ice formation because its surface lattice parameter almost coincides with that of the basal plane of hexagonal ice. Instead, water at the interface shows structural signatures of a high-density liquid at ambient and even at supercooled conditions.

Inelastic neutron scattering experiments have shown a feature in the vibrational spectra of supercooled confined and protein hydration water which is connected to the so-called Boson peak of amorphous materials. We find a similar feature in simulations of bulk supercooled water and its emergence is associated with the transformation into a low-density liquid upon cooling.
The following papers, referred to in the text by their Roman numerals, are included in this thesis.

I. *Evaporative cooling of microscopic water droplets in vacuo:* Molecular dynamics simulations and kinetic gas theory
   D. Schlesinger, J. A. Sellberg, A. Nilsson, L. G. M. Pettersson
   *Manuscript*

II. *Ultrafast X-ray probing of water structure below the homogeneous ice nucleation temperature*

III. *Benchmark oxygen-oxygen pair-distribution function of ambient water from x-ray diffraction measurements with a wide Q-range*
   L. B. Skinner, C. Huang, D. Schlesinger, L. G. M. Pettersson, A. Nilsson, C. J. Benmore

IV. *Intermediate range molecular correlations in liquid water*
   D. Schlesinger, K. T. Wikfeldt, L. B. Skinner, A. Nilsson, L. G. M. Pettersson
   *Manuscript*

V. *Highly Compressed Two-Dimensional Form of Water at Ambient Conditions*
The following papers are related to but not included in this thesis and are referred to as ordinary references.

A. Microscopic probing of the size dependence in hydrophobic solvation

B. A different view of structure-making and structure-breaking in alkali halide aqueous solutions through x-ray absorption spectroscopy

C. X-ray emission spectroscopy of bulk liquid water in “no-man’s land”

D. X-ray spectroscopy, scattering and simulation studies of instantaneous structures in water
   A. Nilsson, D. Schlesinger, L. G. M. Pettersson
   Eds.: P. G. Debenedetti, M. A. Ricci, F. Bruni
   IOS Amsterdam; SIF Bologna, 2015

E. Anomalous Behavior of the Homogeneous Ice Nucleation Rate in “No-man’s Land”

Author’s contribution

**Paper I:** I performed all Molecular Dynamics (MD) simulations of evaporating droplets and the associated analysis and wrote the major part of the program to find solutions to the Hertz–Knudsen theory describing the evaporative cooling process. I was involved in planning the project and wrote the paper in collaboration with my co-authors.

**Paper II:** I contributed to the temperature calibration with the program discussed in Paper I. I provided simulation data for the SPC/E model and part of those for the TIP4P/2005 model and was involved in the associated structural analysis. I took part in discussions and writing the paper.

**Paper III:** I performed the Reverse Monte Carlo (RMC) simulations in order to determine the O-H contribution to the total RDF. The results were used for the estimate of uncertainties due to the subtraction of this contribution. I was involved in writing the paper.

**Paper IV:** I re-analyzed the experimental data for intermediate-range correlations and compared to existing simulation data. I performed the structural analysis and wrote parts of the paper.

**Paper V:** I performed all MD simulations and their subsequent analyses. I was involved in writing the paper.

**Paper VI:** I performed the major part of the simulations of the TIP4P/2005 model. I contributed with dispersion relations and the system size scaling analysis. I was involved in all discussions and in writing the paper.
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<thead>
<tr>
<th>Abbreviation</th>
<th>Full Form</th>
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<tr>
<td>AFF</td>
<td>Atomic Form Factor</td>
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<tr>
<td>BP</td>
<td>Boson Peak</td>
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<td>DoD</td>
<td>Drop-on-Demand</td>
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<td>DOS</td>
<td>Density Of States</td>
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<tr>
<td>EPSR</td>
<td>Empirical Potential Structure Refinement</td>
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<td>GDVN</td>
<td>Gas Dynamic Virtual Nozzle</td>
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<tr>
<td>H-bond</td>
<td>Hydrogen bond</td>
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<td>HDA</td>
<td>High-Density Amorphous</td>
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<td>HDL</td>
<td>High-Density Liquid</td>
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<tr>
<td>LCLS</td>
<td>Linac Coherent Light Source</td>
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<tr>
<td>LDA</td>
<td>Low-Density Amorphous</td>
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<td>LDL</td>
<td>Low-Density Liquid</td>
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<tr>
<td>LLCP</td>
<td>Liquid-Liquid Critical Point</td>
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<td>LSI</td>
<td>Local Structure Index</td>
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<tr>
<td>MAFF</td>
<td>Modified Atomic Form Factor</td>
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<td>MC</td>
<td>Monte Carlo</td>
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<td>MCT</td>
<td>Mode Coupling Theory</td>
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<td>MD</td>
<td>Molecular Dynamics</td>
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<td>ND</td>
<td>Neutron Diffraction</td>
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<td>PDF</td>
<td>Pair-Distribution Function</td>
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<td><strong>RDF</strong></td>
<td>Radial Distribution Function</td>
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<td><strong>RMC</strong></td>
<td>Reverse Monte Carlo</td>
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<td><strong>SAXS</strong></td>
<td>Small-Angle X-ray Scattering</td>
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<td><strong>SPC/E</strong></td>
<td>water model: Single Point Charge, Extended</td>
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<tr>
<td><strong>TIP4P</strong></td>
<td>water model: Transferable Interaction Potential, 4-Points</td>
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<td><strong>TIP4P/2005</strong></td>
<td>water model: Transferable Interaction Potential, 4-Points (2005 derivative)</td>
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<td><strong>TIP5P</strong></td>
<td>water model: Transferable Interaction Potential, 5-Points</td>
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<tr>
<td><strong>VDOS</strong></td>
<td>Vibrational Density Of States</td>
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<td><strong>VSEPR</strong></td>
<td>Valence Shell Electron Pair Repulsion</td>
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<td><strong>XAS</strong></td>
<td>X-ray Absorption Spectroscopy</td>
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<td><strong>XRD</strong></td>
<td>X-Ray Diffraction</td>
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1. General introduction

This thesis deals with water, seemingly the most natural substance in our everyday life. It is certainly the most important liquid for living organisms and the most common solvent and reactant for chemical reactions taking place on earth. Despite this fact and various scientific efforts, this substance is, in many different aspects, not completely understood on a fundamental level. Water exhibits many anomalies when compared to simple liquids, e.g. argon, due to its extraordinary ability to form hydrogen bonds [1].

1.1 On the significance of fundamental water research

The importance of water to nature and society can hardly be overestimated. In 2010, the United Nations General Assembly explicitly recognized the human right to water and sanitation [2]. Everyone has the “right to sufficient, safe, acceptable, physically accessible and affordable water for personal and domestic use” [3]. According to an estimate by the World Health Organization (WHO), however, “half of the world’s population will be living in water-stressed areas by the year 2025” [4] and the World Economic Forum names water crises one of the most significant long-term risks worldwide in its 2015 Global Risks report [5]. This most concerning perspective holds a high potential for conflicts in different parts of the world and challenges technological developments.

The problem can only be solved in multidisciplinary efforts involving economy, politics, social and natural sciences. Physics and chemistry can, e.g., contribute with waste water treatment and filtering or desalination of sea water. Recent research in this area helps to understand the processes taking place on a molecular level and utilize them, such as simulations of water desalination using nanoporous graphene [6] or membranes with nanotube channels [7].

On a more fundamental level, water research is important to our understanding of atmospheric processes and climate. Important topics in meteorology are the properties of supercooled water which is abundant in the atmosphere, ice nucleation, evaporation and condensation dynamics (see, e.g., the review by Koop in [8]). Water in the supercooled state has extraordinary properties [9]–[11] that are subject to current research and will be discussed below.
in more detail.

One of the most important questions in fundamental water research is that of the role of water for life as we know it. In cells, water is a solvent for the genetic material, proteins and salts. There are numerous active research topics related to the cell-biological relevance of water, e.g. ion hydration, protein hydration, and hydrophobic solvation. Interestingly, the isothermal compressibility and the isobaric heat capacity of water exhibit minima in the physiological temperature range and it can thus be speculated that this is not a coincidence.

1.2 Theories of water

The properties of water are strongly dominated by intermolecular hydrogen bonds (H-bonds). The ability to form H-bonds is caused by the two electron lone-pairs on the oxygen atom inside the water molecule. It can be understood from valence shell electron pair repulsion (VSEPR) theory, that the two lone-pairs on the oxygen atom and the two covalent bonds to the hydrogens repel each other giving rise to hybridization of the $2s$ and $2p$ orbitals and thus the bent shape of the molecule and the tetrahedral geometry $[12; 13]$. A water molecule can thus accept one H-bond per lone-pair and donate one H-bond per hydrogen.

Generally, H-bonding has rather complex implications when considering a dense liquid system consisting of many interacting molecules. In such a network-like arrangement the molecules cannot rotate freely, resulting in libration modes. The charge re-distribution taking place upon H-bonding also gives rise to a cooperativity effect, i.e. the strength of an H-bond depends on the surrounding H-bond situation and is thus non-additive $[14–16]$. Furthermore, it has been shown recently that relatively strong H-bonds are further strengthened by nuclear quantum effects while weaker ones are further weakened $[17]$.

The structure of water in a tetrahedral, H-bonded configuration is enthalpically favorable, but entropically unfavorable at the same time. The anomalous behavior of water can be understood considering a delicate interplay between a local enthalpy-favored tetrahedrally coordinated, and an entropy-favored, less constrained molecular arrangement. The local tetrahedral structure is less dense than the entropy-favored structure with broken hydrogen-bonds $[18]$.

Thus, H-bonding has fundamental consequences on the thermodynamic properties of water, such as high melting and boiling temperatures, large enthalpy of vaporization, strong surface tension, when compared to homologous compounds $H_2S$, $H_2Se$ and $H_2Te$ $[19]$. 
1.2 Theories of water

1.2.1 Models of the structure of liquid water

There have been numerous hypotheses about the molecular structure of the liquid which we briefly want to review here. This brief historical review can only fail to be complete, it is rather intended to point out different aspects of the problem and the different attempts to resolve the most fundamental questions about water. More complete reviews concerning this matter can, e. g., be found in the monograph by Eisenberg and Kauzmann [12] and the chapter of H. S. Frank in [20], an older review of early water models by Chadwell [21] and a more recent review by Ludwig [22]. The first models arose from attempts to explain the most obvious challenges, namely the density anomaly at 4°C and properties of aqueous solutions; more recent models were designed to connect experimental scattering data with molecular real-space structures and rationalize other experimental observations, such as the behavior of water in metastable states.

Mixture models have the longest history among the molecular structure models of water. H. Whiting, presenting a theory of cohesion for different liquids and solids in 1883, was one of the first authors to note [23]:

“Conspicuous amongst all liquids in this respect stands water, which expands greatly on solidifying. In all such liquids, the continual formation of solid particles, be it only for an instant, must tend to increase the volume, and the colder the liquid becomes, the greater will be the proportion of solid particles at any instant; so that, other things being equal, the liquid will expand by cooling.”

Whiting also stated some rough ratios of how many molecules would be “solid particles” up to the boiling point, according to his theory. W. C. Röntgen described this model of liquid water in more detail in his seminal work of 1892 [24]. Postulating “two kinds of differently constituted molecules”, such that he calls “ice-molecules” that, upon heating, reversibly interconvert into “molecules of the second kind” that occupy a smaller volume, he explained the temperature and pressure dependence of water observed in experiments. Némethy and Scheraga presented a more detailed mixture model of compact clusters of molecules with intact H-bonds that are in dynamic equilibrium with surrounding molecules with gradually less intact bonds towards the edge of the cluster regions [25]. These ideas have been taken up and further refined. A recent theoretical effort was made by Anisimov and co-workers to establish an equation of state that quantitatively models experimental data and assumes the existence of a second critical point at supercooled conditions [26–28]. They suggest a physical interpretation of the model in terms of water as a mixture.
1. General introduction

of two states of the same molecular species that could represent different local hydrogen bond arrangements and have different local densities [27]. Russo and Tanaka describe the behavior of water in simulations with a similar two-state model, introducing an order parameter for the translational order of the second coordination shell [29]. A more general picture has been developed from interpretations of a wide spectrum of experimental results in combination with molecular simulations by Pettersson, Nilsson and co-workers [18; 30; 31] which is described below in more detail.

**Continuum models.** In their 1933 article, Bernal and Fowler presented a different model of water that they derived by comparing x-ray diffraction data of the liquid with that of theoretical scattering patterns to conclude that there is a continuous transformation of the average structure from more tridymite-ice-like below 4°C, to quartz-like at ambient, to a close packed, ideal liquid structure at higher temperatures. They emphasized that the liquid is homogeneous but the average structure would more or less resemble these three structural arrangements, depending on temperature [32]. Pople further developed this idea in a detailed statistical mechanics analysis and suggested that the structure of liquid water could be tetrahedral, similar to the molecular arrangement in ice, but with the hydrogen bonds between the molecules gradually distorted to different extents depending on temperature and pressure [33]. The H-bonds in the liquid would bend, to a good approximation, independently in the liquid, which would also be the essential difference between the liquid and the crystal.

**Other models.** There have been many more structural models of water suggested. The hypothesis of the interstitials can be thought of as the liquid being an open, ice-like structure with defects and a fraction of the molecules diffusing between the cavities. On melting of ice Ih, water molecules would break their H-bonds and move into the cavities that the ice structure offers. Danford and Levy used this model to fit the radial distribution function of water obtained from x-ray diffraction to very high accuracy [34]. They also proved Pauling’s water hydrate model to be quantitatively inconsistent with experimental data. The interstitial water model can be useful if we think of a water molecule, its first coordination shell and a molecule penetrating into this first shell, e.g. for the liquid under pressure.

A random network model has been put forward by Bernal in his 1964 Bakerian lecture, where he described a molecular H-bond network of ring structures resulting in a complex response to temperature and pressure changes [35].
1.2 Theories of water

1.2.2 Water at supercooled conditions

Water exhibits many anomalies when compared to simple liquids, which is a consequence of its intermolecular hydrogen-bond network as mentioned above. Prominent properties are the density and the thermodynamic response functions: the isothermal compressibility $\kappa_T$, the isobaric heat capacity $C_P$ and the isobaric thermal expansion coefficient $\alpha_P$. Their temperature dependencies are shown in fig. 1.1 and have been discussed in detail in, e.g., a review by Angell [36].

Water can be supercooled, i.e. it can be cooled far below its melting point and exist in a metastable state on rather long time scales, depending on temperature and provided that there are no structural or dynamical perturbations causing nucleation events. Upon supercooling, the thermodynamic response functions, $\kappa_T$, $C_P$ and $\alpha_P$, change dramatically and seem to diverge towards temperatures of 228 K ($\kappa_T$) [9], and 226 K ($C_P$) [10]. The thermodynamic response functions are associated with fluctuations in entropy and density [41], indicating that these fluctuations sharply increase in water upon supercooling. Three major theories have been developed to explain this behavior and are currently under debate: The stability-limit conjecture, the singularity-free scenario and the liquid-liquid critical point hypothesis [11, 42].

The stability-limit conjecture explains the anomalous increase of response functions through a spinodal line possibly retracing back to positive pressures in the supercooled liquid regime, thus causing a mechanical instability due to diverging density and entropy fluctuations at the spinodal [43].

The singularity-free scenario suggests the presence of a line described by the pressure dependence of the temperature of maximum density having a negative slope in the T-P phase diagram and thus giving rise to pressure dependent extrema of $\kappa_T$ and $\alpha_P$ [44]. The isobaric heat capacity $C_P$ would be pressure independent and not exhibit any singularity.

The liquid-liquid critical point (LLCP) hypothesis [45] is based on the possible existence of a second critical point in “no-man’s land”, the temperature regime between the homogeneous nucleation and the spontaneous crystallization temperatures in the P–T plane. It furthermore hypothesizes the existence of a coexistence line between two distinct phases of a low-density liquid (LDL) and a high-density liquid (HDL) extending the coexistence line between the vitreous low- and high-density amorphous ices (LDA and HDA, respectively) [46], terminating in a critical point in the metastable region, the LLCP.

The aforementioned models by Anisimov and Pettersson and Nilsson both aim to unify the structural models of water under ambient and the supercooled conditions and naturally connect to the LLCP hypothesis for the supercooled,

5
Figure 1.1: Experimental data for the response functions of water: (a) isobaric heat capacity $C_p$, (b) isothermal compressibility $\kappa_T$, (c) isobaric thermal expansion coefficient $\alpha_P$. Note the minima in $C_p$ (309K) and $\kappa_T$ (319K) and the change of sign for $\alpha_P$ at the temperature of maximum density (277K).
metastable state.

1.2.3 A working hypothesis

All of the models discussed above were developed to explain certain aspects of water’s anomalous behavior. They seem to emphasize different, complementary perspectives on water and do not necessarily exclude each other.

The working hypothesis adapted in this thesis, as put forward in ref. [48], is based on the existence of LDL- and HDL-like instantaneous molecular environments. These are pictured to be structural fluctuations due to the in-

**Figure 1.2:** Schematic phase diagram of water with metastable regions. The first order transition line separating the LDA and HDA states is shown, terminating in the hypothetical liquid-liquid critical point. The Widom line emanating from the critical point divides the supercritical region into LDL- and HDL-like regions. The melting temperature, \( T_M \), the temperature of homogeneous ice nucleation, \( T_H \), and the temperature of spontaneous crystallization, \( T_X \), are indicated. The region between \( T_H \) and \( T_X \) left white has been termed “no man’s land” due to experimental difficulties to probe it. Reproduced from ref. [47] with modifications.
terplay between enthalpy-favored LDL-structures and entropy-favored HDL-structures, where LDL-structures would be tetrahedrally H-bonded molecules, while the HDL-structures are pictured as molecules with broken or distorted H-bonds. This hypothesis is appealing not least because it seamlessly connects to the LLCP hypothesis that can explain the behavior of water under supercooled conditions. On supercooling at ambient pressure, structural fluctuations would gradually favor local LDL-like structures [49]. In the LLCP scenario, this behavior is explained in terms of a hypothetical second critical point in metastable liquid water. A P–T phase diagram is schematically depicted in fig. 1.2 and shows the metastable state regions. The supercooled liquid state and the high- and low-density amorphous (HDA/LDA) states can be observed experimentally, limited by fast ice nucleation or crystallization. It has been shown that the transition between HDA and LDA is of first order [50, 51]. This first order transition line has been hypothesized to extend further up to higher temperatures and lower pressures terminating in a liquid-liquid critical point in the metastable region. The amorphous phases would have metastable liquid counterparts, HDL and LDL.

It has been shown that the supercritical fluid phase beyond a liquid-gas critical point is actually divided into a liquid-like and a gas-like region as a remnant of the subcritical domain, for argon [52], and for the gas-liquid critical point of water [53]. The dividing line, emanating from the critical point, has been termed Widom line and marks the locus of maximum correlation length that decays with growing distance to the critical point, as described in ref. [53]. In the supercooled region, there would be such a Widom line emanating from the LLCP and the thermodynamic response functions would be expected to exhibit maxima, coinciding with the maximum correlation length in the close vicinity of the critical point. The hypothetical existence of a LLCP in the metastable region could thus explain the anomalous behavior of water, even up to ambient conditions. The LLCP hypothesis for water is supported by theoretical investigations of water-like models [54–56] and by experimental evidence of liquid-liquid transitions in other tetrahedral liquids, e.g. silicon [57].
1.3 Overview over this work

This thesis summarises six different projects which have been grouped into three different chapters:

Chapter 3 deals with the evaporation of water, in particular the associated cooling process. We studied evaporative cooling of microscopic water droplets in vacuum using molecular dynamics simulations, Paper I. This theoretical investigation has been motivated by an experimental effort to supercool water droplets evaporatively to below the temperature of homogeneous ice nucleation. The structure of water was determined at these extremely low temperatures for the first time in Paper II.

The projects described in chapter 4 address molecular correlations in liquid water. Paper III is the result of a project which aimed at the determination of the radial distribution function (RDF) of water to high precision. A new oxygen-oxygen RDF was established as a structural standard for liquid water at ambient conditions that can be used as a benchmark in the development and improvement of interaction potentials for simulations. Recent x-ray scattering data by Skinner et al. [58] reveal intermediate range correlations in liquid water and were re-analyzed with focus on their temperature dependence. The intermediate range correlations were shown to be present in simulations of the TIP4P/2005 model of water and compared to the experimental data. The results of this project are summarised in Paper IV. The last section in chapter 4 is devoted to the investigation of the structure of water at the interface to a barium fluoride (111) crystal surface, Paper V.

The final chapter is focussed on molecular dynamics in the terahertz region. In the physics of disordered materials, an excess in the vibrational density of states (VDOS) over the Debye model is known as Boson peak (BP). In the VDOS calculated from simulations of bulk supercooled TIP4P/2005 water we investigate a similar feature. The findings have been presented in Paper VI.
1. General introduction
2. Theory and simulation techniques

In this chapter, the theoretical background will be briefly discussed which is the technical basis for simulations and analysis in projects described below. The first section deals with distribution functions and particularly the pair-distribution function and its relation to the experimentally observable structure factor. We then discuss the basics of simulation techniques that have been used in this work, Reverse Monte Carlo (RMC) and Molecular Dynamics (MD) simulations.

2.1 Theory of distribution functions

The structure of liquids, and disordered materials in general, characterized through a lack of long-range order, can be quantified by the probability distributions for finding constituents (i.e. atoms or molecules) in a certain configuration relative to each other. In the present section, a short general overview over distribution function theory is given following [41, 59]. This serves as the basis to develop the theory of the pair-distribution function (PDF). The PDF is then associated with the structure factor, which makes it a powerful link between the microscopic atomic or molecular structure and the observable scattering pattern in x-ray diffraction experiments.

2.1.1 General theory of distribution functions

Let us consider a canonical ensemble of $N$ particles in a volume $V$ at a temperature $T$ and assume an interaction potential $U(\vec{r}_1 \ldots \vec{r}_N)$ between the particles. The probability density of finding $n$ particles in a certain configuration is given by

$$P^{(n)}(\vec{r}_1, \ldots, \vec{r}_n) d\vec{r}_1 \ldots d\vec{r}_n = \frac{e^{-\beta U(\vec{r}_1 \ldots \vec{r}_N)}}{Z_N} d\vec{r}_{n+1} \ldots d\vec{r}_N,$$  \hspace{1cm} (2.1)

where $\beta = 1/k_B T$, with $k_B$ the Boltzmann factor, and the configurational partition function is defined as

$$Z_N = \int e^{-\beta U(\vec{r}_1 \ldots \vec{r}_N)} d\vec{r}_1 \ldots d\vec{r}_N.$$  \hspace{1cm} (2.2)
If we assume that the particles are identical, we have to introduce a combinatorial factor, that takes care of all the possible permutations of the \( n \) particles. The \( n \)-particle density distribution can thus be written as

\[
\rho^{(n)}(\vec{r}_1, \ldots, \vec{r}_n) = \frac{N!}{(N-n)!} \frac{1}{Z_N} \int e^{-\beta(U(\vec{r}_1) + \ldots + \vec{r}_N)} d\vec{r}_{n+1} \ldots d\vec{r}_N. \tag{2.3}
\]

The two-point density distribution can now be expressed as

\[
\rho^{(2)}(\vec{r}_1, \vec{r}_2) = N(N-1) \frac{1}{Z_N} \int e^{-\beta(U(\vec{r}_1) + \ldots + \vec{r}_N)} d\vec{r}_3 \ldots d\vec{r}_N. \tag{2.4}
\]

Consider now a decomposition of the probability distribution into a product of two one-particle probability distributions: one that describes the conditional probability of finding a particle in \( \vec{r}_1 \) under the condition that there is a particle in \( \vec{r}_2 \) and one describing the actual probability of finding a particle in \( \vec{r}_2 \)

\[
P^{(2)}(\vec{r}_1, \vec{r}_2) d\vec{r}_1 d\vec{r}_2 = \mathcal{P}^{(1)}(\vec{r}_1 | \vec{r}_2) d\vec{r}_1 \times \mathcal{P}^{(1)}(\vec{r}_2) d\vec{r}_2. \tag{2.5}
\]

From this, it follows directly that

\[
\rho^{(2)}(\vec{r}_1, \vec{r}_2) = N(N-1) \mathcal{P}^{(2)}(\vec{r}_1, \vec{r}_2)
\]

\[
= (N-1) \mathcal{P}^{(1)}(\vec{r}_1 | \vec{r}_2) \times N \mathcal{P}^{(1)}(\vec{r}_2)
\]

\[
= \rho^{(1)}(\vec{r}_1 | \vec{r}_2) \rho^{(1)}(\vec{r}_2)
\]

\[
\equiv g^{(2)}(\vec{r}_1, \vec{r}_2) \rho^{(1)}(\vec{r}_1) \rho^{(1)}(\vec{r}_2) \tag{2.6}
\]

where we have used the fact that for large distances \( |\vec{r}_1 - \vec{r}_2| \to \infty \), the effect of the local density at \( \vec{r}_2 \) becomes negligible in \( \vec{r}_1 \). In the last line of eq. (2.6), we have thus defined the pair-distribution function

\[
g(\vec{r}_1, \vec{r}_2) \equiv \frac{\rho^{(1)}(\vec{r}_1 | \vec{r}_2)}{\rho^{(1)}(\vec{r}_1)}. \tag{2.7}
\]

### 2.1.2 The pair-distribution function

For homogeneous, uniform and isotropic liquids, the pair-distribution function in eq. (2.7) becomes a radial distribution function due to spherical symmetry and depends only on the radial distance. With the definition of the density in eq. (2.3), we get

\[
\int_V \rho^{(1)}(\vec{r}) d\vec{r} = N \quad \Rightarrow \quad \rho^{(1)} = \frac{N}{V} \equiv \rho, \tag{2.8}
\]

\( \rho \) being the average density in volume \( V \). The relation between the pair-distribution function and the density pair-distribution defined in eq. (2.6) becomes

\[
\rho^{(2)}(\vec{r}_1, \vec{r}_2) = \rho^2 g^{(2)}(\vec{r}_1, \vec{r}_2). \tag{2.9}
\]
2.2 Reverse Monte Carlo simulations

We can further define \( \vec{r} \equiv \vec{r}_2 - \vec{r}_1 \), integrate over all possible \( \vec{r}_2 \) and, assuming spherical symmetry, arrive at a relation between the local density and the radial distribution function \[41]\n
\[
\rho(r) = \rho \cdot g(r). \tag{2.10}
\]

The actual calculation of the radial distribution function defined above is usually done by measuring the distances between the atoms, sorting the distances into discrete bins and normalizing appropriately [60]. Throughout the thesis, the term radial distribution function (RDF) is used in situations of spherical symmetry, while it is called a pair-distribution function (PDF) otherwise.

2.1.3 Relation to the structure factor

The x-ray scattering amplitude of a molecular structure can be calculated as the Fourier transform of the scattering potential given through its electron density. This can be shown within the first Born approximation to the Lippmann-Schwinger equation [61; 62].

Expressing the density-density correlations within the density distribution in terms of the two-point correlation function \( h^{(2)}(r) \equiv g(r) - 1 \), the spherically symmetric Fourier transform becomes

\[
S(q) = 1 + 4\pi\rho \int_0^{\infty} (g(r) - 1) r^2 \frac{\sin(qr)}{qr} \, dr, \tag{2.11}
\]

which is called the structure factor. It is closely related to the coherent differential x-ray scattering cross section as will be explained in section 4.1.1 in more detail where the radial distribution function is extracted from scattering data. The inverse transform

\[
g(r) = 1 + \frac{1}{2\pi\rho} \int_0^{\infty} (S(q) - 1) q^2 \frac{\sin(qr)}{qr} \, dq. \tag{2.12}
\]

is employed there to calculate the radial distribution function from the scattering data. In praxis, the integration in (2.12) always has a finite upper bound since the \( q \)-values have experimental limits. This introduces significant artifacts that are usually minimized by the application of a window function to dampen oscillations stemming from the finite \( q \)-range as demonstrated in Paper III.

2.2 Reverse Monte Carlo simulations

The radial distribution function introduced above can be calculated from molecular simulations. Here we describe the Monte Carlo and the molecular dynamics simulation methods. A certain variant of the Monte Carlo method, called
2. Theory and simulation techniques

Reverse Monte Carlo, is described below and has been applied to obtain results included in Paper III.

Generally, Monte Carlo (MC) techniques are used to integrate high-dimensional integrals as those encountered in, e.g., statistical physics by random sampling of the integrand. Integrating the high-dimensional equations of motion is one of its applications. The random sampling of phase space is one of the most efficient ways for high-dimensional integrations as the calculation of expectation values etc.

2.2.1 The Metropolis Monte Carlo method

In the canonical ensemble, the expectation value of a thermodynamic quantity $A$ is defined as

$$
\langle A \rangle = \frac{\int A(\{\vec{r}\}) e^{-\beta E(\{\vec{r}\})} d^{3N} \vec{r}}{\int e^{-\beta E(\{\vec{r}\})} d^{3N} \vec{r}} ,
$$

where $\beta = \frac{1}{k_B T}$, $E(\{\vec{r}\})$ denotes the energy of the configuration $\{\vec{r}\}$ of $N$ particles and the integrals run over all configurational space.

In order to integrate these $3N$-dimensional integrals, the configurations are generated randomly and the more configurations are sampled, the more accurate the values of the integrals become. The MC algorithm generally generates a Markov chain, i.e. a sequence of configurations, where a particular configuration depends on the previous configuration only through a random step.

The MC method depends on a configurational energy that is calculated for each random step. This energy is, e.g., calculated from pair-potentials between the constituents of the system, like Coulomb and Lennard-Jones interactions between molecules. Through a comparison of the energy of the previous and the new configuration it is decided whether or at what probability the new configuration is accepted. The Metropolis-Hastings algorithm generally iterates the following steps:

1) set initial configuration $\{\vec{r}\}_0$,

2) calculate the energy $E(\{\vec{r}\}_0)$ of $\{\vec{r}\}_0$,

3) generate a new configuration through a random propagation $\{\vec{r}\}_{i+1} = \{\vec{r}\}_i + \Delta \{\vec{r}\}$,

4) calculate the energy difference between the former and the new configuration

$$
\Delta E_i \equiv E(\{\vec{r}\}_{i+1}) - E(\{\vec{r}\}_i) ,
$$

5) if the energy is lowered, i.e. $\Delta E_i < 0$, the new configuration is accepted. Otherwise, calculate the probability $p(\Delta E_i)$ for acceptance, and employ
2.2 Reverse Monte Carlo simulations

A random number \(a \in [0, 1]\) to decide whether the new configuration is accepted, for example via the Boltzmann factor to generate a canonical ensemble

\[
p(\Delta E_i) = e^{-\beta \Delta E_i} \begin{cases} < a & \Rightarrow \text{reject new configuration} \\ \geq a & \Rightarrow \text{accept new configuration} \end{cases}
\]

where steps 3–5 are iterated. There are many details which are not considered here, as e. g., biased sampling techniques in order to make the algorithm more efficient.

The configurations generated by this algorithm will mirror the molecular structures of the real liquid depending on how well its energy landscape is represented by the potential function defined in the simulation rules (force field).

2.2.2 The Reverse Monte Carlo method

The Reverse Monte Carlo method has been developed by McGreevy and Pusztai [63] in order to solve the so-called inverse problem in scattering theory.

**The Inverse Scattering Problem.** Generally, the term *inverse problem* refers to a whole class of problems in different contexts of natural sciences and sociology, where information about the cause is extracted from the effect that is observed, i.e. it is the inverse of a model predicting an observation. There can be severe uniqueness problems, for different causes can lead to the same effect. Measurements, furthermore, often project out certain degrees of freedom, thus the information obtained is not complete and cannot uniquely determine a cause – model relationship.

In a x-ray scattering experiment, the incoming photons are scattered off a structured electron density causing a certain scattering pattern on the detector. The scattering pattern is connected to the structure factor as discussed in section 4.1.1. In order to extract the real-space structure from the measured data, solutions to the inverse problem have to be approximated. The RMC method is a powerful tool to accomplish this.

**The RMC algorithm.** The algorithm described in ref. [63] is used to find molecular structures that are compatible with experimental scattering data. Here, in contrast to the usual Monte Carlo (MC) simulations, it is not the change of configurational energy that is used in the acceptance criterion for a propagation step but rather the “distance” between the calculated and the experimental quantity that is fitted to, quantified using an error function \(\chi^2\). If an experimental structure factor \(S^{\text{exp}}(q)\) is given, the structure factor \(S^{\text{calc}}(q)\)
2. Theory and simulation techniques

is calculated from the theoretical radial distribution function (RDF) through a Fourier transform (eq. 2.11).

The theoretical structure factor $S^{\text{calc}}(q)$ is then compared to the experimental one, $S^{\text{exp}}(q)$ through the error function

$$
\chi^2_i \equiv \chi^2(\{q\}_i) = \sum_{j=1}^{N} \left( \frac{S^{\text{exp}}(q_j) - S^{\text{calc}}(q_j)}{\sigma(q_j)} \right)^2 ,$$

(2.14)

where $N$ is the number of discrete steps in the momentum-space coordinate $q$ and $\sigma$ denotes the standard deviation of experimental data at a certain $q$ and quantifies how tight the simulation is fitted to the data. Formally, the Metropolis-Hastings algorithm is employed, but the acceptance criterion is changed from energy-based to a $\chi^2$-based criterion (i.e. $\Delta \chi^2_i$ is substituted for $\Delta E_i$ in the above Metropolis-Hastings scheme) in order to reproduce the experimental data within their uncertainty. From the mathematical aspect, this doesn’t make a difference. It has, however, a completely different meaning when looked at from the physical point of view: The energy criterion requires a potential function to be evaluated for each configuration. This potential is not known exactly and commonly based on empirical force fields. The fit of observables to experimental data is a much more direct determination of the possible structures causing the diffraction pattern and can be seen as an iterative fitting procedure of the model structure to the real scattering structure.

There are, however, problems concerning the uniqueness of the fits. In the case of water there are three different relevant correlations, i.e. oxygen-oxygen, oxygen-hydrogen and hydrogen-hydrogen, and it is thus necessary to fit to at least three different data sets with complementary information, as x-ray (XRD) and neutron diffraction (ND) data. In neutron diffraction, isotope substitution at different concentrations is often used to disentangle these correlations.

It is necessary to impose further constraints on the model structures to avoid unphysical situations, e.g. keep the molecules intact by enforcing certain bond length and angle distributions as described in the supplementary material of [64]. Even then, it has been shown that a large variety of local structures are compatible with experimental data [64] [65].

It should be noted that another method, Empirical Potential Structure Refinement (EPSR), is used extensively as an alternative way of solving the inverse problem. This method employs empirical force field simulations. The difference between simulated and experimental data is used to modify force field (or “potential”) parameters to drive the simulated structure factor to reproduce the experimental one as close as possible [66].
2.3 Molecular dynamics simulations

The classical molecular dynamics (MD) method is based on Newtonian mechanics and is widely used to describe many-particle structures and dynamics on a molecular level using effective descriptions of the interactions between atoms. For every particle \( i \), with position \( \mathbf{r}_i \) and mass \( m_i \), the equation of motion reads

\[
\frac{d^2 \mathbf{r}_i}{dt^2} = -\frac{1}{m_i} \nabla_i \sum_{j \neq i}^N U(\mathbf{r}_i - \mathbf{r}_j),
\]

assuming a system of \( N \) particles that interact through a pair-potential \( U \). The set of equations of motion for all particles are integrated to obtain a trajectory \( \{\mathbf{r}\}(t) \) of the time evolution of the system. The simulation is propagated in time through an integration scheme which is iterated at small time steps of \( \Delta t \sim 0.1 - 2.0 \) fs. Different ensembles can be generated using barostat and / or thermostat algorithms to control the pressure and the temperature, respectively. Detailed introductions to MD simulations can be found in refs. [67, 68].

2.3.1 Force fields

The results presented in this thesis were obtained mostly from classical MD simulations with effective inter-atomic potentials from which the forces are calculated (eq. 2.15). The functional form of the effective potential together with parameters for different atom types is called the force field. The effective potential typically includes terms describing the non-bonded and bonded interactions. The non-bonded interactions, on their part, include Coulomb and Lennard-Jones-type dispersion interactions. The bonded interactions describe bonds, angles and dihedral potentials, often represented by polynomial expansions and associated force constants.

For simulations of bulk liquid water, we generically use the TIP4P/2005 model, a re-parametrization of the four-point transferable interaction potential [69]. It is currently one of the best effective descriptions of water-water interactions in that it represents the phase diagram qualitatively. The density maximum for this model is in near-quantitative agreement with the experimental value, while melting and boiling points are shifted by about 20 K towards lower temperature and 30 K towards higher temperatures, respectively. The model underestimates the rise of the isothermal compressibility towards lower temperatures while overestimating it towards high temperatures, which has been explained by an imbalance between structural and thermal fluctuations [18].
2. Theory and simulation techniques
3. Evaporative supercooling of water droplets

This chapter is devoted to the fundamental process of evaporative cooling. Evaporative cooling is an efficient way of energy conversion. It is important in atmospheric processes and widely utilized in nature by humans, animals and plants for cooling through transpiration and in technological applications such as cooling of power plants and evaporative coolers for air conditioning. In atomic physics, evaporative cooling has been applied successfully to achieve Bose-Einstein condensation at extremely low temperatures [70].

The present investigation was motivated by an experimental effort to supercool microscopic water droplets to below the homogeneous nucleation temperature of water and probe the structure of the bulk, supercooled liquid. Extensive molecular dynamics simulations have been performed in order to validate the Knudsen theory of evaporation that was used to calibrate the droplet temperature.

The theory is introduced first; MD simulations and results are discussed below and compared to the theoretical predictions for the TIP4P/2005 model of water. The experiment and its results for the structure of water below the homogeneous nucleation temperature are discussed in the end of this chapter. Parts of this chapter have been presented in the licentiate thesis Aspects of the local structure and dynamics of water, Daniel Schlesinger, Department of Physics, Stockholm University (2013).

3.1 Kinetic theory of evaporative cooling of water droplets

Kinetic theory provides the framework for the description of evaporation and thus we briefly want to review the basics generically applied in literature [71-75].

Starting with a general expression for the evaporation rate, the focus will be on evaporative cooling of spherical droplets and we aim for a quantitative description of the time dependent temperature of the droplet upon evaporation in vacuum.
3.1.1 Derivation of the Hertz–Knudsen evaporation rate

A mass flux is proportional to the (average) velocity and the mass density of the particles

\[ J_m(T) = \bar{v}(T) \rho(T), \]  

both of which depend on the temperature \( T \). The molecules are assumed to follow a Maxwellian velocity distribution

\[ f(\vec{v}) = \left( \frac{m}{2\pi k_B T} \right)^{3/2} e^{-\frac{m|\vec{v}|^2}{2k_BT}}, \]  

where \( m \) is the mass and \( \bar{v} \) the velocity of the particles. The expectation value of the velocity in a certain direction, say along the positive surface normal, evaluates to

\[ \langle v_\perp \rangle = \sqrt{\frac{k_BT}{2\pi m}}. \]  

The gas phase mass density can be approximated using the equation of state for an ideal gas \( \rho(T) = P_0(T)m/k_BT \), where \( P_0 \) denotes the vapor pressure. Thus, substituting the terms for the average velocity (3.3) and the density into equation (3.1), we obtain the mass flux

\[ J_m(T) = P_0(T) \sqrt{\frac{m}{2\pi k_BT}}. \]  

Dividing the mass flux by the particle mass \( m \) and multiplying with the (generally time-dependent) surface area \( A(t) \) from which the molecules evaporate gives the Hertz–Knudsen evaporation rate

\[ \Gamma(T) = \frac{P_0(T)}{\sqrt{2\pi mk_BT}} A(t). \]  

The evaporation rate derived here is a theoretical maximum rate under ideal conditions and does not take into account possible barriers to evaporation.

3.1.2 Evaporation coefficient

The ratio between the experimentally measured evaporation rate and the theoretical maximum rate is a material constant called \( \alpha \) and accounts for barriers to evaporation. For a perfect molecular description, this factor should equal unity. The literature value of the evaporation coefficient for water varies over a wide range [72, 75, 76].

The strong variation of the value for \( \alpha \) is not only a problem in experiments: In different molecular simulation studies different values have been
3.1 Kinetic theory of evaporative cooling of water droplets

reported. Recently, *Musolino and Trout*, using the finite temperature string method, found a theoretical value of $\alpha = 0.25$ [77], while *Varilly and Chandler* report a value of $\alpha \approx 1$ from a transition path sampling study and find that the evaporation event is well described by a ballistic escape from a deep well without additional barrier [78].

3.1.3 Cooling rate

The evolution of the surface temperature of a droplet can be described using the Hertz–Knudsen evaporation rate (3.5). A single molecular evaporation event will result in a loss of energy and a fast distribution of this energy loss onto all the accessible degrees of freedom, described by the heat equation. Thus, the time dependent-temperature for the evaporative cooling process can be expressed as

$$\frac{dT}{dt} = -\Gamma(T) \frac{\Delta H(T)}{MC_P(T)}$$

$$= -\frac{P_0(T)}{\sqrt{2\pi mk_BT}} A(t)\frac{\Delta H(T)}{MC_P(T)}$$

$$= -\frac{P_0(T)}{\sqrt{2\pi mk_BT}} \frac{A(t)}{\Delta V(t)} \frac{\Delta H(T)}{\rho(T) CP(T)} ,$$

where the ratio of the specific enthalpy of vaporization $\Delta H(T)$ per molecule and the heat capacity $C_P(T) \cdot M$ is the temperature change per evaporation event in the evaporation layer of mass $M$. The evaporation layer has a volume $\Delta V$ and its mass is thus $M = \Delta V \rho$. Note, that the heat capacity, the enthalpy of vaporization, the density and the vapor pressure are temperature dependent and the surface area of a droplet changes due to loss of matter during evaporation.

3.1.4 Heat conduction within a droplet

The theory above describes the evaporation from the surface of the droplet only. With increasing droplet size, the volume to surface area ratio increases. Thus, heat conduction within the droplet becomes increasingly important and eventually the limiting factor for cooling and has to be taken into account. Heat conduction is described by the heat equation

$$\frac{\partial T(\vec{r},t)}{\partial t} = \kappa \vec{\nabla}^2 T(\vec{r},t) ,$$

with the temperature field $T(\vec{r},t)$ at position $\vec{r}$ and time $t$, and the thermal diffusivity $\kappa$. This can be solved under the assumption that the solution is separable. Further, we assume spherical symmetry and apply the boundary
condition $T(r = r_0, t) = T_{surf}$ and the initial condition $T(r, t = 0) = T_0$. The solution becomes

$$T(r, t) = T_{surf} + 2 \left( T_0 - T_{surf} \right) \sum_{n=1}^{\infty} (-1)^{n+1} j_0 \left( \frac{n \pi r}{r_0} \right) e^{-\kappa \left( \frac{n \pi}{r_0} \right)^2 t}, \quad (3.8)$$

where $j_0(\cdot)$ denotes the spherical Bessel function of first kind. If the heat conduction within the droplet is fast enough (or the radius is very small), we can make the adiabatic approximation that the droplet is in equilibrium for each evaporation event, i.e. fast heat conduction guarantees a homogeneous droplet temperature. To approximate the rate of temperature change, consider the time derivative of the solution (3.8). The slowest decay ($n = 1$ term) takes place on a characteristic time scale of $\tau \equiv \frac{r_0^2}{\pi^2 \kappa}$. The temperature change rate for the slowest decaying term ($n = 1$) in the center of a droplet ($r = 0$) is approximated to

$$\left| \frac{\partial T(r = 0, t)}{\partial t} \right|_{t = \tau, n = 1} \approx \frac{2 \pi^2 (T_0 - T_{surf}) \kappa}{r_0^2 e}. \quad (3.9)$$

In table 3.1 the temperature change rates from conduction and evaporation for droplet sizes corresponding to those in the simulations and two different experimental techniques are compared to each other. As a result of this estimate,

<table>
<thead>
<tr>
<th>Droplet radius</th>
<th>T-change rate [K/s] (conduction)</th>
<th>T-change rate [K/s] (evaporation)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$r_0 = 3, \text{nm}$</td>
<td>$3.4 \cdot 10^{13}$</td>
<td>$2.0 \cdot 10^9$</td>
</tr>
<tr>
<td>$r_0 = 5, \mu m$</td>
<td>$1.2 \cdot 10^7$</td>
<td>$1.2 \cdot 10^6$</td>
</tr>
<tr>
<td>$r_0 = 25, \mu m$</td>
<td>$4.9 \cdot 10^5$</td>
<td>$2.4 \cdot 10^5$</td>
</tr>
</tbody>
</table>

Table 3.1: Comparison of the temperature change rates due to heat transport through conduction and evaporation, for different droplet sizes at 298K. The thermal diffusivity of water $\kappa \approx 1.43 \cdot 10^{-7} \text{m}^2/\text{s}$ was used for heat conduction, the evaporation rate was calculated for the whole droplet as heat reservoir.

a crossover is expected for the heat transport limiting process from evaporation limited for small droplets to conduction limited for larger droplets. The crossover is approximated to occur at about $75\, \mu m$ droplet radius. Thus, for simulations as well as for small droplet realizations in the experiment, heat conduction is much faster than evaporative heat transport. For larger droplets, heat conduction is expected to play a role and take over the limitation of cooling with increasing droplet radius.
3.1 Kinetic theory of evaporative cooling of water droplets

3.1.5 Geometrical effects

**Surface curvature:** In this project, the focus is on evaporative cooling of small droplets with spherical geometry. This is an approximation, because the surface can fluctuate locally, in particular for small droplet sizes as those considered in the simulations.

Water has a very high surface tension due to its hydrogen bond network at the interface. The surface tension $\gamma$ causes an enhanced pressure inside small droplets depending on their radius $r$, which is described by the Young–Laplace equation

$$\Delta P = \gamma \frac{2}{r}, \quad (3.10)$$

giving around 450 bar enhanced pressure inside a droplet of $r = 3$ nm and about 0.3 bar for $r = 5 \mu$m and is thus not expected to be important for experimental dimensions. The variation of the term $\Delta H(T) / p(T)\rho(T)C_p(T)$ due to the additional Young–Laplace pressure inside the droplet was found to be very small and maximally 2% in the relevant temperature range and thus considered insignificant.

More importantly, the vapor pressure is enhanced due to surface tension. The actual vapor pressure $P'_0$ can be calculated using the Kelvin equation

$$P'_0(T) = P_0(T) e^{2\gammaVm / rRT}, \quad (3.11)$$

where $V_m$ is the molar volume, $P_0$ the vapor pressure at a plane interface and $R$ the universal gas constant. It is important to note that the surface tension is a function of the length scale and temperature. The temperature dependent surface tension used below is a parametrization of the Guggenheim–Katayama relation [79] and the length scale correction was performed using the Tolman equation [80]. A lower size-limit for the applicability of the Kelvin equation with Tolman-corrected surface tension has recently been shown to lie below 1 nm in MD simulations of the mW model of water [81].

The exponential correction factor in eq. (3.11) for a droplet of $r = 1$ nm as in a typical MD simulation evaluates to about 3.1, while for droplet dimensions of $r = 5 \mu$m it is 1.0002 at $T = 298$ K. The correction thus plays a role on a sub-micrometer length scale and becomes significant only below 10 nm. Note, that the above discussion is valid for an ideal spherical droplet and is just an approximation here. In the simulations, the surface curvature varies locally due to fluctuations around the spherical geometry.

**Decrease of the droplet radius with particle evaporation:** An additional effect occurring during evaporative cooling of a droplet is the loss of mass and therefore a time-dependent decrease in the radius of the droplet and thus its
3. Evaporative supercooling of water droplets

Surface area, which in turn influences the evaporation rate. The time dependent radius can be expressed as

\[ r(t) = \sqrt[3]{\frac{3mN(t)}{4\pi \rho}}, \quad (3.12) \]

where \( N(t) \) is the total number of molecules in the droplet after interaction time \( t \). The particle loss is just the evaporation rate \( (3.5) \) integrated over time, by which the total number of molecules is decreased and the number of molecules can therefore be written as

\[ N(t) = N_0 - \Delta N(t) = N_0 - \int_0^t \Gamma(t')dt'. \quad (3.13) \]

The time dependent radius thus becomes

\[ r(t) = \left( r_0^3 - \frac{3m}{4\pi \rho(T(t))} \int_0^t \Gamma(t')dt' \right)^{1/3} \quad (3.14) \]

with the initial condition \( r(t=0) = r_0 \). Thus, surface area and droplet volume have to be calculated together with the evaporation rate and heat conduction.

3.1.6 Implementation of the Knudsen theory

As described above, there are several effects that have to be taken into account for a quantitative description of the evaporative cooling process of a droplet. We implemented a program to calculate the time-dependent temperature of an evaporating droplet including all the previously discussed influences, briefly described below.

**Evaporation.** The cooling rate \( (3.6) \) is calculated from the Knudsen evaporation rate \( (3.5) \) derived above. In the numerical calculation, the droplet with initial radius \( r_0 \) is divided into \( N \) spherical shells of width \( \Delta r \equiv r_0/N \) and evaporation changes the temperature in the outermost spherical shell of the droplet.

**Heat conduction.** A loss of heat in the outermost shell causes a temperature gradient \( \Delta T/\Delta r \) towards the next inner shell of the droplet. Driven by this gradient, a heat flux is established. Thus, heat is successively re-distributed from the center outwards to the droplet surface. The heat flux is described by Fourier’s law which, in the discrete case and for spherical symmetry, takes the form

\[ \frac{\Delta Q}{\Delta t} = -4\pi r^2 \kappa \frac{\Delta T}{\Delta r}, \quad (3.15) \]
where $\Delta Q$ is the heat change in the time interval $\Delta t$ and $\kappa$ denotes the thermal conductivity. For each shell, the difference between the heat flux into and out of the shell is calculated while the temperature change in the shell is given by

$$\Delta T = \frac{\Delta Q}{C_p \cdot \Delta V \cdot \rho},$$

(3.16)

with the specific heat capacity $C_p$, the volume of the shell $\Delta V$ and the density $\rho$. There are two special cases: For the innermost shell, which is in fact a sphere, the heat flux has to be calculated at one surface, only. The outermost shell, on the other hand, loses heat only through evaporation while gaining heat from the next inner shell through heat conduction.

The estimation for the rate of temperature changes in table 3.1 shows that, for small droplets as in the simulations and the small experimental droplet realization, temperature equilibration due to heat conduction within the droplet is a much faster process than temperature change via evaporation.
3. Evaporative supercooling of water droplets

3.2 MD simulations of TIP4P/2005 water droplets in vacuum

We performed MD simulations of droplets of TIP4P/2005 water \[69\] in vacuum to investigate the temperature change caused by evaporation and compare to the predictions of the kinetic theory. Four different droplet sizes were simulated, \(r_0 = 1\) nm, \(r_0 = 2\) nm, \(r_0 = 3\) nm, and \(r_0 = 4\) nm, for 100 ns total simulation time. The following simulation protocol was applied:

1. Spherical droplet from a simulation box with bulk TIP4P/2005 water, based on distances of oxygens to an arbitrary point;
2. NVT simulation for 50 ps to obtain homogeneous temperature distribution throughout the droplet and relax the surface (evaporation starts);
3. Vacuum simulation (NVE) for the desired simulation time, time step \(\Delta t = 1\) fs using the leap-frog integrator; Coulomb and Lennard-Jones forces are calculated between all atom pairs without cutoff.
4. Control energy conservation, measure temperature within the droplet, number of molecules in the droplet for each time step or averages over small time intervals.

3.2.1 Temperature dependence of relevant thermodynamic properties of the TIP4P/2005 water model

To assess the theoretical description of evaporative cooling, we compare the results from kinetic theory calculations to those from MD simulations. Therefore, the temperature dependencies of thermodynamic quantities of the TIP4P/2005 model involved in the kinetic theory description were determined. The temperature dependence of the density, the enthalpy of vaporization and the isobaric heat capacity were obtained as fits to bulk TIP4P/2005 simulation data while the saturation vapor pressure, the surface tension and the thermal conductivity were taken from the literature as indicated. The surface area was measured directly along the simulation trajectories. Vega et al. \[82\] interpolate the saturation vapor pressure for TIP4P/2005 and obtain (fig. 3.1a)

\[
P_s(T) = e^{12.4612 - 4476.552/(T-41.4984)} \text{ bar}.
\]  (3.17)

For the density of TIP4P/2005 we obtain (fig. 3.1b)

\[
\rho(T) \approx 199154.0 - 4798.08 T + 49.2902 T^2 - 0.278943 T^3 \\
+ 0.000940308 T^4 - 1.88965 \cdot 10^{-6} T^5 \\
+ 2.09734 \cdot 10^{-9} T^6 - 9.92214 \cdot 10^{-13} T^7 \text{ kg/m}^3
\]  (3.18)
Figure 3.1: Temperature dependencies of properties of the TIP4P/2005 water model: (a) saturation vapor pressure; (b) density; (c) isobaric heat capacity; (d) enthalpy of vaporization. The properties (b), (c) and (d) were obtained from own simulations; (a) was taken from ref. [82].

The isobaric heat capacity is obtained as (fig. 3.1c)

\[ C_p(T) \approx -450457.85 + 11650.27T - 130.82T^2 + 0.83T^3 - 0.0033T^4 + 8.27 \cdot 10^{-6}T^5 - 1.296 \cdot 10^{-8}T^6 + 1.15 \cdot 10^{-11}T^7 - 4.43 \cdot 10^{-15}T^8 \text{ J/mol/K}. \] (3.19)

For the enthalpy of vaporization, the fit to simulation results provides (fig. 3.1d)

\[ \Delta H_{vap}(T) \approx -187.44 + 4.70T - 0.034769T^2 + 0.00012385T^3 - 2.1674 \cdot 10^{-7}T^4 + 1.4959 \cdot 10^{-10}T^5 \text{ kJ/mol}. \] (3.20)

The surface tension for the TIP4P/2005 water model was parametrized by Vega et al. [79] as a modified Guggenheim-Katayama relation

\[ \gamma(T) = 0.22786 \left(1 - \frac{T}{641.4}\right)^{11/9} \left(1 - 0.6413 \left(1 - \frac{T}{641.4}\right)\right) \text{ N/m}. \] (3.21)
The surface area of the simulated droplets was found to vary due to changes of the droplet shape. The evaporation rate is directly proportional to the time-dependent surface area and is hence an important ingredient in the kinetic theory. Therefore, it was measured along the simulation trajectories through numerical integration of the instantaneous liquid interface \[83\]. Finally, the same thermal conductivity was used as for real water, since data for the TIP4P/2005 model are not available in the supercooled regime yet while it is known at higher temperatures of 300K and higher and was shown to overestimate the thermal conductivity under ambient conditions \[84\]. Note, however, that heat transport is very fast for the length scales considered and for the simulations, the temperature decrease is evaporation-limited as expected from the earlier estimation in table 3.1.

### 3.2.2 Results from simulations and comparison with theory

From the MD simulations performed by applying the protocol described above, we obtain the droplet temperature depending on the interaction time with vacuum, see fig. 3.2.

![Figure 3.2](image)

**Figure 3.2:** Results for the evaporative cooling of TIP4P/2005 water from non-equilibrium MD simulations (see protocol in the text). Comparison of the results for different droplet sizes as indicated, initial temperature 380K. Initially, there were 141 \((r = 1\text{ nm})\), 1120 \((r = 2\text{ nm})\), 3767 \((r = 3\text{ nm})\), 8985 \((r = 4\text{ nm})\) molecules in the droplets.
The size dependence of the temperature evolution was expected since the surface area-to-volume ratio of the droplets decreases with increasing droplet radius. While the evaporation rate per unit area does not change, the heat is redistributed onto a larger volume. Furthermore, the temperature fluctuations decrease with increasing number of molecules in the droplet.

The MD simulation results are compared to kinetic theory calculations that account for evaporation, heat conduction, mass loss and the modification of the vapor pressure due to surface tension. For the smallest droplet \( r_0 = 1 \text{nm} \), individual evaporation events can be identified to cause temperature jumps while the statistics is poor due to the small number of molecules (141 initially), cf. fig. 3.3.

Furthermore, in the derivation of the evaporation rate a Maxwellian velocity distribution has been assumed. The velocity distribution calculated from simulations inside a droplet is Maxwellian indicating that the droplet is in thermal equilibrium. For the droplet of \( r_0 = 4 \text{nm} \), the Maxwellian distribution averaged over the time window of \( 99.5 - 100\text{ns} \) corresponds to an average temperature of \( \sim 278 \text{K} \), see fig. 3.4. The velocity distribution of already evaporated water molecules accumulated in the gas phase from the beginning of evaporation process gradually shifts to lower temperatures and thus extends over a wider velocity range.
3. Evaporative supercooling of water droplets

Figure 3.4: Velocity distribution of a 4 nm droplet and the gas phase molecules averaged over the time window of 99.5 $\text{–} 100 \text{ns}$

It is concluded that the theoretical results calculated using the kinetic theory of evaporation and those from direct atomistic simulations are in very good agreement.
3.3 Evaporative supercooling of microscopic water droplets

This work was part of an experimental effort to shed light onto the structure of bulk water at extreme supercooled conditions. As discussed in the introduction, it is well known that the thermodynamic response functions of water such as isothermal compressibility $\kappa_T$ and the isobaric heat capacity $C_P$ change dramatically upon supercooling and seem to diverge at a temperature of about 228 K and 226 K, respectively, well below the homogeneous nucleation temperature of about 232 – 233 K [85, 86]. It has been under debate whether the response functions really diverge or rather exhibit a maximum, the latter being consistent with maximum fluctuations at the Widom line in the LLCP hypothesis.

There is an ongoing debate about the theoretical explanation of the enhanced fluctuations and different models were developed to explain the anomalous behavior of water, the most prominent being the stability limit conjecture, the singularity-free scenario and the liquid-liquid critical point hypothesis as described in the introduction. The liquid-liquid critical point scenario and the singularity-free scenario are both consistent with the experimental observations presented in Paper II.

In this project, the first experimental results were presented for the structure of bulk water in the so-called “no-man’s land”, the temperature region below the homogeneous nucleation temperature and above the temperature of spontaneous crystallization of about 150 K (see, e.g. Fuentes-Landete et al. in [8]) at ambient pressure. In this temperature range, ice nucleation takes place on short time scales that are too fast for conventional techniques. So far, measurements on deeply supercooled water have therefore been performed in nano-confined water [87, 88], where ice nucleation is strongly suppressed. This practice has been criticized due to the confinement potentially altering the thermodynamic properties of water [89]. The experimental results presented in Paper II have been obtained for bulk water in micrometer-sized droplets to avoid confinement effects.

In this section, we focus on the temperature calibration of evaporatively cooled water droplets. We calculated the time evolution of the droplet temperature based on the kinetic theory model described above. The temperature evolution for experimental dimensions and time scales was described using the same procedure, while the properties of the TIP4P/2005 water model were replaced by those of real water. Results on the structure of supercooled water and its analysis are discussed at the end of this section.
3.3.1 Experimental perspective

The experimental investigation has been carried out in the supercooled temperature regime, with the objective to measure the bulk water structure factor at extremely supercooled temperatures in “no-man’s land”. The focus was on three main aspects:

- deeply supercooled droplet temperatures
- non-confined water sample
- coherent and intense x-ray pulses to obtain the diffraction pattern from single droplets
- ultrafast measurement of the structure before crystallization

The requirements on the experiment were met by the use of droplet injection into a vacuum chamber, where the droplets were probed by x-ray laser pulses. The droplet injection was realized in two different ways: the Drop-on-Demand (DoD) method and the Gas Dynamic Virtual Nozzle (GDVN) setup [90], resulting in two different droplet diameters of 34 and 37 µm, and 9 and 12 µm, respectively.

The experiment was carried out at the Linac Coherent Light Source (LCLS) / Stanford Linear Accelerator Center (SLAC), a x-ray free electron laser (XFEL). In XFELs, electrons are accelerated to high energies of several GeV in a linear accelerator (LINAC) and injected into a so-called undulator, the heart of a XFEL. The undulator consists of an array of many magnets poled in alternating direction, perpendicular to the electron beam. Electrons in bunches traveling through this setup are forced onto an oscillatory trajectory by the Lorentz force and therefore emit energy in form of electromagnetic radiation. At high intensities of the electromagnetic field, the electrons can interact with the field originating from their own motion and become organized into sub-structures of the bunch, called micro-bunches. These micro-bunches of electrons emit coherently, i.e. in a collective fashion, and give rise to extremely high intensity and the laser properties of the emitted x-rays [91].

Fig. 3.5a shows the essential part of the experimental setup. The droplets fall into vacuum and cool down rapidly through evaporation. Thus, the droplet temperature decreases with increasing distance to the injection point. X-ray laser pulses probe the freely falling droplet at the interaction point and cause a diffraction pattern of individual droplets on the detector.

The diffraction patterns, called “shots”, were classified into two different kinds: Those that showed the characteristic water ring (“water shots”) and such that contained Bragg peaks indicating ice formation (“ice shots”), see fig. 3.5b.
3.3 Evaporative supercooling of microscopic water droplets

Figure 3.5: (a) Schematic picture of the experimental setup with the droplets falling into vacuum, the x-ray free electron laser probing the structure manifested in the scattering pattern on the detector; (b) typical water shot diffraction pattern; (c) typical ice shot, containing Bragg peaks. Reprinted from Paper II with permission.

and 3.5c. They were sorted and the water diffraction pattern was analyzed further to shed light on the structure of the supercooled water droplets.

3.3.2 Droplet temperature in the experiment

The evaporation kinetics depend on a number of thermodynamic properties of the evaporating material under consideration, as can be seen from the derivation of the evaporation rate, eq. 3.5. A major challenge consisted in obtaining these properties for water in the supercooled region. Thus far, experiments have provided data above or down to the homogeneous nucleation temperature. Therefore, for temperatures below the homogeneous nucleation temperature, extrapolations based on different functional forms were tested, suggested in literature and supported by simulations, as described in the supplementary information of Paper II. The droplet temperature evolution in the experiment was calculated using the same implementation of the Knudsen theory as has been described in section 3.1.6 and using the properties for water. An additional temperature calibration was provided by the fact that the temperature had been
measured directly in experiments on static water samples at the Stanford Synchrotron Radiation Laboratory (SSRL) down to a temperature of 251 K. The temperature dependence of the structure factor of the water droplets at moderately supercooled conditions have to overlap with and continue the trend of the SSRL data, see fig.3.7. Reprinted from Paper II with permission.

A rapidly increasing number of ice shots was observed with decreasing temperature. The ice shot fraction is shown in fig. 3.6 together with the temperature evolution. The data points taken at the lowest temperatures contained mostly ice shots, while a small fraction of the droplets was still found to be liquid at a temperature of $227^{+2}_{-1}$ K, well below the temperature of homogeneous ice nucleation $T_H \approx 232$ K.
3.3 Evaporative supercooling of microscopic water droplets

3.3.3 The structure of supercooled water

The structure factor was extracted from the water shot data. Since the accessible $q$-range was too small ($0.5 \, \text{Å}^{-1} \leq q \leq 3.2 \, \text{Å}^{-1}$), the structure factor could not be Fourier transformed directly to obtain a RDF. To draw conclusions about the real-space structure, MD simulations were employed.

**Figure 3.7:** The structure factor of water for a wide temperature range (a): $q$-positions of peaks $S_1$ and $S_2$ as a function of temperature (b), note the overlap between data obtained in static experiments with direct temperature measurement and the droplet data. Reprinted from Paper II with permission.

The height of the second peak, denoted as $g_2$, in the RDF has been found to correlate with the tetrahedrality of the liquid. Using the TIP4P/2005 water model, the dependence of the split between the first diffraction peaks in the structure factor $S_1$ and $S_2$, $\Delta q$, on $g_2$ was established as shown in fig. 3.8a. This correlation curve was used to translate the peak split $\Delta q$ to a $g_2$-value for the experimental data, fig. 3.8b. The data show a much stronger continuous increase of $g_2$ with decreasing temperature than the water models, SPC/E and TIP4P/2005 and tend towards the value of the low-density amorphous (LDA) state, which had been determined in neutron diffraction experiments [22]. This is illustrated in the comparison of a RDF from simulations with a $g_2$ value corresponding to the lowest temperature data and experimental data for the RDF of LDA and liquid water at ambient conditions in fig. 3.8c.

We interpret the findings in terms of a continuous and accelerated transition
3. Evaporative supercooling of water droplets

Figure 3.8: (a) The peak split $\Delta q$ in the structure factor can be correlated with the peak height of the second coordination shell, $g_2$, in the RDF using MD simulations. (b) The correlation curve from simulations can be used to translate the experimentally determined $\Delta q$ into a $g_2$-value, which can then be used to (c) find a corresponding $g_{OO}(r)$ from simulations. Reprinted from Paper II with permission and modifications.

of the water structure towards an average LDL-like arrangement. This can be understood within the LLCP hypothesis, where isobaric supercooling of a water sample would be pictured to first cool it below the melting line $T_m$ and then, at the extreme supercooling achieved in this investigation, below the
3.3 Evaporative supercooling of microscopic water droplets

temperature of homogeneous ice nucleation $T_H$, see fig. [1.2]. Below $T_H$, the metastable state would approach the Widom line $T_W$ from above, that would extend from the hypothetical LLCP to lower pressures and higher temperatures and would cause the accelerated structural transition towards LDL, and thus the increase of $g_2$ upon cooling.
3. Evaporative supercooling of water droplets
4. Molecular correlations in liquid water

The structural arrangement of molecules in disordered materials and liquids is most commonly described by spatial correlation functions, particularly radial distribution functions in the case of isotropic liquids. The molecular structure is the basis to understanding the behavior of the liquid in different situations.

4.1 The oxygen-oxygen radial distribution function of water

In the history of x-ray scattering there have been numerous experiments on water, the pioneering one conducted by Bernal and Fowler in 1933 [32]. A RDF published by Narten and Levy in 1971 [93] has for a long time been considered a structural standard for liquid water. In the meantime, much effort has been made to improve the measurement techniques, overcome difficulties and obtain higher precision data.

The result of the project presented here is a new state-of-the-art RDF of liquid water at ambient conditions that can be used as a benchmark for simulations. It has been published in Paper III. This chapter has to a large extent been presented in the licentiate thesis Aspects of the local structure and dynamics of water, Daniel Schlesinger, Department of Physics, Stockholm University (2013).

4.1.1 Analysis of scattering data

In x-ray scattering experiments the differential scattering cross-section \( I(q) \) is observed, which, in the first Born approximation, is proportional to the square of the Fourier-transformed scattering potential. In order to extract the RDF as the structural quantity of interest, some further processing is necessary.

The scattering cross-section can be decomposed into different contributions

\[
I(q) = I^{\text{self}}(q) + I^{\text{dist}}(q),
\]  

(4.1)
where the first term is called the *self*-scattering part and the second one the *distinct* scattering part. The distinct scattering term provides information about the interatomic structure which is to be extracted. The distinct scattering term can again be subdivided into an intramolecular and an intermolecular part

\[ I(q) = I^{self}(q) + I^{intra}(q) + I^{inter}(q). \] (4.2)

The self-scattering and the intramolecular part have to be subtracted in order to extract the intermolecular correlations. This can be achieved in two different ways using either an atomic or a molecular scheme.

In the **molecular normalization scheme**, the molecular form factor is defined as

\[ I^{mol}(q) = I^{self}(q) + I^{intra}(q) \] (4.3)

and the structure factor can be written as

\[ S^{mol}(q) = 1 + \frac{I(q) - I^{mol}(q)}{\omega(q)}, \] (4.4)

with the weighting factor \( \omega(q) = (\sum_i c_i f_i(q))^2 \) and \( c_i \) being the number concentration of atom type \( i \) and \( f_i(q) \) its atomic form factor. The molecular form factor for water contains contributions to the self-scattering and the intramolecular scattering

\[ I^{mol}(q) = f_O^2(q) + 2f_H^2(q) + 4f_O(q)f_H(q) \frac{\sin(qr_{OH})}{qr_{OH}} e^{-\frac{1}{2}\sigma_{OH}^2 q^2} + 4f_H^2(q) \frac{\sin(qr_{HH})}{qr_{HH}} e^{-\frac{1}{2}\sigma_{HH}^2 q^2}, \] (4.5)

where \( r_{OH} \) and \( r_{HH} \) are the intramolecular distances between the atoms indicated by the indices and \( \sigma_{OH} \) and \( \sigma_{HH} \) the corresponding standard deviations. The molecular form factor of water has been determined in quantum chemical calculations by Wang et al. [94] and was employed in Paper III.

In the **atomic normalization scheme**, an independent atom approximation is adopted. Molecular form factors are often unknown or hard to determine while the atomic form factors are listed for numerous elements and can be used in an independent atom approximation. The structure factor is then obtained by subtracting the atomic self-scattering contribution \( I^{atom}(q) = \sum_i c_i f_i^2(q) \) from the scattering cross sections and is written as

\[ S^{atom}(q) = 1 + \frac{I(q) - I^{atom}(q)}{\omega(q)}. \] (4.6)
4.1 The oxygen-oxygen radial distribution function of water

![Graph of oxygen-oxygen radial distribution function](image)

**Figure 4.1:** The coherent differential scattering cross section and the corresponding oxygen-oxygen structure factor (inset) from experiment. The theoretical molecular form factor (red dashed curve) by Wang et al. [94] was used to subtract self- and intramolecular contributions from \( I(q) \). Furthermore, the intermolecular O-H contribution obtained from neutron diffraction measurements [95] was subtracted to determine the O-O correlations (see [Paper III] for further details). The data analysis is summarized in the text. The data presented are available in the supplementary material of [Paper III].

This scheme was improved by Sorensen et al. [96], who introduced the modified atomic form factor (MAFF)

\[
f_{i}^{\text{mod}}(q) = \left( 1 - \frac{a_i}{z_i} e^{-\frac{q^2 z_i^2}{\delta^2}} \right) f_i(q) \tag{4.7}
\]

to account for electron redistribution in the molecular environment. The constant \( a_i/z_i \) is the ratio between the charge transfer due to the bond and the number of electrons on the free atom; \( \delta \) broadens the charge distribution in reciprocal space. This normalization scheme is used in Reverse Monte Carlo (RMC) simulations to calculate the structure factor from the radial distribution function, while the simulation is performed via single atom moves and constraints [64]. Since we focus on intermolecular oxygen-oxygen correlations, the contributions stemming from intermolecular O-H and H-H correlations have to be subtracted from the total intermolecular structure factor. The contribution from H-H correlations is shown to be negligible in this context.
Figure 4.2: The O-H contribution to the RDF and the structure factor from ND experiments [95], MD and RMC simulations. Reproduced with permission from Paper III. Copyright 2013, AIP Publishing LLC.

Due to the small magnitude of the weighting factor. Thus, to a very good approximation, the oxygen-oxygen structure factor can be expressed as

$$S_{OO}(q) \approx \frac{S_{mol}^{mol}(q) - \omega_{OH}S_{OH}(q)}{\omega_{OO}},$$

with the weighting factors $\omega_{OO} = f_O^2(q)/\omega(q)$ and $\omega_{OH} = 4f_O(q)f_H(q)/\omega(q)$. The O-H contributions obtained from neutron diffraction experiments and RMC and MD simulations are compared in fig. 4.2. There are significant differences between the RMC, MD and ND data, particularly in the first peak in $g_{\text{inter}}(r)$ around $r \approx 2$ Å. Using the three datasets, it has been shown that the uncertainty introduced to O-O RDF is small and significant only in the region of the first O-H peak, below 2.5 Å.
4.1 The oxygen-oxygen radial distribution function of water

4.1.2 The oxygen-oxygen radial distribution function

With the considerations above and the relationship between radial distribution function and structure factor (2.12), the oxygen-oxygen radial distribution function can be calculated via a Fourier transformation

\[
g(r) = 1 + \frac{1}{2 \pi \rho} \int_{0}^{q_{\text{max}}} M(q, \Delta(r))(S(q) - 1) q^2 \frac{\sin(qr)}{qr} dq,
\]

where the upper integral bound is identical to the maximum \(q\)-value of the data set under consideration and the modified Lorch-function \(M(q, \Delta(r)) = \sin(q \Delta(r))/q \Delta(r)\) was used with \(\Delta(r) = (1 - e^{-|r-a|/b}) \pi / q_{\text{max}}\) (\(a\) and \(b\) parameters). The result of the transformation is shown in fig. 4.3. Two aspects are particularly important to emphasize: The x-ray diffraction data sets used in this study were measured to very large \(q\)-values (particularly the data set by L. Skinner obtained at the Advanced Photon Source (APS)) and a modified window function was used to remove truncation artifacts. The length of the \(q\)-range clearly affects the nearest neighbor peak, both in position and height. We show that the peak coordinates converge for large \(q\)-ranges above \(q \sim 20\,\text{Å}\). In the Fourier transform, a Lorch function is used that both depends on \(q\) and on \(r\). This particular window function is chosen to leave the region of the nearest neighbor peak unchanged to determine its coordinates to a high precision.
4. Molecular correlations in liquid water

4.2 Intermediate range correlations in liquid water

In a recent study, Skinner et al. [58] presented high-quality x-ray diffraction data of water in a wide range of temperatures of roughly 250 – 340 K. This temperature range was chosen as to include the compressibility minimum at about 319 K and to investigate the associated structural changes in the liquid. In this current section we re-analyze the data for the oxygen-oxygen RDFs by Skinner et al. for correlations in the intermediate range, particularly the features found at distances \( r > 10 \text{ Å} \). We then compare the experimental RDFs to simulation data obtained from large scale simulations of the TIP4P/2005 model with 45,000 molecules [97] and investigate structural changes with temperature. The results of this analysis are summarized in Paper IV.

The RDFs by Skinner et al. were first smoothened to reduce the noise level and oscillations introduced by the Fourier transform of the structure factor. We use the Gaussian filter [98], i.e. every data point in the smooth RDF is calculated as the average over data points in the neighborhood of the original data point, weighted by a Gaussian function. The width of the normalized Gaussian weighting function, \( d \), can be adjusted. This procedure dampens sharp features, as fast oscillations, but diminishes the height of all varying features at the same time. We tested different widths of the Gaussian weighting function. The original spacing in the distance coordinate \( r \) of the experimental data is \( \Delta r = 0.01 \text{ Å} \), while the RDFs from simulations have been calculated at double this step size. To obtain comparable data sets, we use a Gaussian width of \( d \approx 1.5 \text{ Å} \), i.e. average over 74 data points for the simulation and 150 data points for the experimental data, respectively. A smoothing of simulation and experimental data at a width of \( d = 0.6 \text{ Å} \) does not qualitatively change the results presented below.

The smooth RDFs are presented in fig. 4.4 for the intermediate distance range of 8 – 20 Å and the insets show the range between 14 – 20 Å magnified. The excellent agreement of the simulation data with the experimental results rules out that the features investigated here are artifacts of the Fourier transform or due to noise. All features found in the experimental data are present in the simulation data with comparable intensity. Clearly, the temperature dependence is shifted when comparing experiment and simulations, which is in agreement with the phase diagram of TIP4P/2005 being shifted in temperature: its melting point has been reported to be at about \( T_m = 252 \text{ K} \) [69] and the boiling point is found at \( T_b = 401 \text{ K} \) [82], while the model reproduces the temperature of maximum density near-quantitatively at \( T_{\text{max}} = 278 \text{ K} \) [69].

We now turn to characterize the intermediate range features. The temperature...
Figure 4.4: Oxygen-oxygen radial distribution functions in the intermediate range for different temperatures from experiment (a) and simulations of the TIP4P/2005 model (b). The long-range features are shown enlarged in the insets.
dependence is investigated first, where we choose to measure the height of the features as a function of temperature. We then decompose the RDFs in simulations in terms of an order parameter into high-density liquid (HDL) and low-density liquid (LDL)-like contributions.

4.2.1 Temperature dependence

In the present investigation we analyze three different features, at about $r_5 \approx 11 \, \text{Å}$, $r_6 \approx 13 \, \text{Å}$, and $r_8 \approx 17 \, \text{Å}$ and define their heights as $g_5 \equiv g(r_5)$, $g_6 \equiv g(r_6)$, and $g_8 \equiv g(r_8)$, respectively. It must be mentioned that at higher temperature and for larger distance the features naturally become harder to identify and uncertainties increase. We also emphasize that the exact heights depend on how the data have been smoothened. Nevertheless, the features are robust and show a very similar behavior in the experimental and simulation data.

Figure 4.5 shows the temperature dependence of $g_5$, $g_6$, and $g_8$. The fifth shell peak $g_5$ increases sharply upon cooling and experiment and simulation results are in excellent agreement. The rise of $g_5$ in the experimental data can be seen to accelerate upon cooling, and more so than in the simulation data. This feature has been investigated to great detail in an earlier study by Huang et al. [97] and was found to be associated with the emergence of LDL-like arrangements in the liquid at ambient temperatures.

Interestingly, the sixth shell feature, $g_6$, is found to first grow upon cooling to then exhibit a maximum and decrease quickly upon further cooling. A similar behavior is observed for the density of water and we therefore compare the experimental data of $g_6$ to the mass density in fig. 4.6. There is a slight shift in temperature between the maxima of about 5 K. The underlying molecular structures causing this behavior can be understood within the two-state picture of water discussed below in more detail.

We further observe a feature between about 16 – 17.5 Å denoted as $g_8$. It shifts to higher distances upon cooling. The temperature dependence of $g_8$ is weak and can mainly be observed in the simulations while the scattering in the experimental data starts to cover the signal.

4.2.2 Structural analysis

In this section we make an attempt to characterize the underlying molecular structures contributing to the intermediate range features discussed above. The features between about 8.5 – 11 Å show a strong temperature dependence and
Figure 4.5: Temperature dependence of the intermediate range features. Comparison of experimental and simulation data for $g_5(T)$, $g_6(T)$ and $g_8(T)$.

have previously been analyzed in terms of a structural order parameter, the local structure index (LSI) \cite{97}. The LSI value, which has been introduced by Shiratani and Sasai \cite{100}, is defined for each molecule $i$ as

$$I(i) = \frac{1}{n(i)} \sum_{j=1}^{n(i)} (\Delta(j,i) - \bar{\Delta}(i))^2,$$  \hspace{1cm} (4.10)

where $n(i)$ is the number of neighbor molecules within a oxygen-oxygen distance of 3.7 Å; the neighbors are ordered according to their distances to the oxygen of the central molecule $i$, $r_1 < r_2 < \ldots < 3.7 \text{ Å} < r_{n(i)+1}$, such that $\Delta(j,i) = r_{j+1} - r_j$ with the average $\bar{\Delta}(i)$ can be defined. The LSI takes rela-
4. Molecular correlations in liquid water

**Figure 4.6:** The feature $g_6$ and the mass density as functions of temperature in comparison. Density data taken from [40, 99].

relatively high values for ordered molecular arrangements and low values for more disordered structures [100].

In the present study we divide the molecules into two groups, with LSI values above and below the average LSI, respectively. The RDFs are calculated for each of the groups separately. This decomposition is performed for simulations at two different temperatures of $T = 253$ K and $T = 298$ K and the results are shown in fig. 4.7. The average LSI values used for the subdivision were found to be $\bar{I} = 0.0550 \text{ Å}^2$ at $T = 253$ K and $\bar{I} = 0.0381 \text{ Å}^2$ at $T = 298$ K.

It should be noted that, in the present investigation, we calculated the LSI values in the direct, instantaneous structure, not the inherent structure [97, 100]. The region between $8 - 12$ Å has been analyzed in detail in a previous study by Huang et al. [97]. The analysis in terms of the LSI showed that the feature $g_5$ is mainly due to molecules with high LSI values indicative of a LDL-like molecular arrangement at higher temperatures.

At the position of $g_6$ we observe that the contributions from both, low and high LSI RDFs almost coincide. The change of the density with temperature, found to be similar to the changes in $g_6$, can be understood in terms of different local favorable structures: Upon cooling, thermal fluctuations decrease and normal thermal contraction cause the liquid to become denser. Upon further cooling, structural fluctuations into local LDL-like molecular arrangements increase, thus causing the density to exhibit a maximum and to expand below the temperature of 277 K. On the macroscopic level, one would observe the average behavior of HDL- and LDL-like contributions. The LSI analysis in fig. 4.7 shows that an inward shift of the high-LSI correlation causes $g_6$ to exhibit a
4.2 Intermediate range correlations in liquid water

maximum and shrink upon cooling. We further notice a redistribution of intensity to a feature emerging at 15 Å, which is found in the experimental data at the lowest temperature. According to the decomposition in fig. 4.7, this latter feature stems from a redistribution from HDL- to LDL-like arrangements, similar to what is observed for \( g_4 \). For the largest distances investigated we can state that the shift of \( g_8 \) in position seems to be due to a redistribution of LDL-like structures to larger distances upon cooling.

![RDFs calculated for molecules with LSI above and below the average value from simulations at \( T = 253 \) K and \( T = 298 \) K.]

In summary, we have investigated intermediate range correlations in liquid bulk water. The RDFs extracted from experiment and simulations of the TIP4P/2005 water model are in excellent agreement. The temperature dependence of the intermediate range features have been analyzed and the behavior of \( g_6 \) was found to exhibit similarities with that of the density. The underlying structural changes were further analyzed using a decomposition into high-LSI and low-LSI contributions to the RDFs from simulations. The structural analysis strongly suggests that there are rather pronounced structural change with temperature, which can even be observed around ambient conditions. These structural changes can be understood in terms of different molecular arrangements with a redistribution between highly ordered, LDL-like, and more disordered HDL-like local molecular arrangements. Furthermore, the results obtained here are consistent with the conclusion drawn from small-angle x-ray scatter-
ing of water at ambient conditions that water is inhomogeneous to a length scale of about 1 nm [101].
4.3 The structure of water on a Barium fluoride (111) surface

This project has been a joint effort of experimental work and MD simulations. In a x-ray absorption study of water on a BaF$_2$(111) surface it was found that the water adapts an HDL-like structure. We performed MD simulations in order to shed light on the molecular structure and the results were found to be consistent with the experimental findings.

The BaF$_2$(111) surface has been suggested to be a template for ice formation due to its lattice constant being close to that of hexagonal ice $I_h$. This hypothesis has been subject of earlier experimental investigations by Sadtchenko et al. \cite{102}. In the present investigation, the template effect was not confirmed and the surface was rather found to locally disturb the structure of water severely, in agreement with the results by Sadtchenko et al.

The results of this project were published in Paper V. This chapter has to a large extent been presented in the licentiate thesis Aspects of the local structure and dynamics of water, Daniel Schlesinger, Department of Physics, Stockholm University (2013).

4.3.1 Experimental results

The oxygen K-edge x-ray absorption spectrum (XAS) has been established as a probe for the local structure of liquid water \cite{103,104}. Certain features in the XAS have been interpreted to be related to the local H-bond situation in liquid water, the pre- and main-edge ($\sim 535$eV) mainly to weakened, asymmetric H-bonds, the post-edge ($\sim 540 – 542$eV) mainly to strong H-bonds in a local tetrahedral structure.

The XAS of liquid thin-film water on BaF$_2$, shown in fig. 4.8, exhibits a strong resemblance to that of the high-density liquid (HDL), where the large main/post-edge ratio indicates a high density \cite{105}. The XAS of ice $I_h$, fig. 4.11 (a, i), clearly shows a strong post-edge, whereas the pre-edge has almost vanished, consistent with the interpretation above. Fig. 4.11(b) shows the resemblance of water on BaF$_2$(111) and an aqueous NaCl solution, with a more disordered average local structure, a strong pre-edge feature and decreased post-edge intensity. The structural changes of water due to NaCl have been characterized more recently \cite{107}. The suppression of fluctuations into local LDL-like structures in the vicinity of ions has been interpreted to push the LDL/HDL ratio to favor a more disordered, HDL-like environment on the average.

From these findings, it was concluded that the local structure of water on a BaF$_2$(111) crystal surface is locally disturbed with broken or asymmetrical
4. Molecular correlations in liquid water

Figure 4.8: a) Comparison of XAS of (i) bulk ice $I_h$ (dashed), ice VII (solid) \[105\] with the spectra of (ii) 2 monolayers crystalline ice and (iii) supercooled water on BaF$_2$(111) at 1.5 Torr at 259 K (90% relative humidity). (b) Comparison of XAS spectra of (i) supercooled water on BaF$_2$(111) at 1.5 Torr at 259 K (90% relative humidity) with (ii, solid) liquid water, and (ii, dashed) 6M NaCl solution measured at room temperature \[106\]. The shaded area represents the difference between bulk ambient liquid and thin-film water. Figure taken from Paper V, reprinted with permission.

H-bonds between the water molecules.

4.3.2 MD simulations of water on a BaF$_2$(111) surface

We performed MD simulations to investigate the molecular structure of water on the BaF$_2$(111) surface which was experimentally found to resemble an HDL-like structure as described above. The water structure was characterized by calculating the oxygen-oxygen pair-distribution functions from the simulations. Different force-fields, charge-pairs for the crystal ions and adsorption energies were compared to ensure independence of the findings on these properties.

The MD simulations were performed to model the behavior of H$_2$O on a fluorine-terminated BaF$_2$(111) surface with 256 BaF$_2$, and 500 H$_2$O molecules, corresponding to about 2.5 monolayers water on the crystal surface. We used
the GROMACS package ver. 4.5.3 \cite{108}, the OPLS-AA force field \cite{109}, and
the TIP4P/2005 water model \cite{69}. Each simulation was equilibrated for at
least 5 ns, generic thermodynamic properties were monitored to ensure equili-
bration. The production runs were performed in the NPT ensemble for 20 ns
at a time step of 1 fs using velocity rescaling \cite{110} to set the temperature; the
Berendsen barostat \cite{111} was applied for the pressure control. All simula-
tion results shown here were obtained at $P = 1 \text{bar}$ and $T = 290 \text{K}$ or $260 \text{K}$,
respectively.

Pair-distribution functions were calculated in layers oriented parallel to
the surface in order to investigate the structure of water close to the BaF$_2$(111)
surface. We use a cylindrical normalization which we want to discuss briefly.

A general definition of the pair-distribution function reads \cite{60}

$$g(r) = \frac{V}{N^2} \left\langle \sum_i \sum_{j \neq i} \delta(\vec{r} - \vec{r}_{ij}) \right\rangle,$$  \hspace{1cm} (4.11)

where $r \equiv |\vec{r}|$, $\vec{r}_{ij}$ is the distance vector between atom $i$ and $j$, and $V$ and $N$
denote the total volume and the total number of molecules included in the
calculation, respectively. In practice, we evaluate eq. (4.11) here for oxygen
atoms, by counting the oxygen-oxygen distances in small intervals $[r; r + \delta r]$.
The histogram obtained has to be normalized by the total number of molecules
$N$ and the average number of oxygen-oxygen distances in each bin is divided
by the number of atoms of an ideal gas at the same density in the volume
associated with the distance bin.

This procedure is further adapted to the cylindrical symmetry of the prob-
lem considered here. The total volume is taken to be a flat, cylindrical disk
with the symmetry axis perpendicular to the plane, and the constant factor thus
becomes

$$\frac{V}{N^2} = \pi h \frac{R^2}{N^2},$$  \hspace{1cm} (4.12)

where the thickness of the disk and the maximum radius were set to $h = 1 \text{Å}$
and $R \approx 40 \text{Å}$, respectively. The number of oxygen atoms within this layer and
the distance bin $[r; r + \delta r]$ is divided by the associated volume of a cylindrical
shell

$$v(r) = \pi h \left((r + \delta r)^2 - r^2\right),$$  \hspace{1cm} (4.13)

so that the pair-distribution function, with the above definition of the constant
$V/N^2$, converges to unity for large radii.
4. Molecular correlations in liquid water

4.3.3 Results for the molecular structure of water on BaF$_2$(111) from MD simulations

In the simulations we observe a pronounced layering of TIP4P/2005 water molecules along the surface, quantified in the inset of fig. 4.9. The density profile along the surface normal shows a sharp first peak indicating a strong localization of the contact layer of molecules on the surface. A second and incomplete third layer can be identified that are broader in shape. We investigate the structure of water within the layers by calculating oxygen-oxygen PDFs with the cylindrical normalization introduced above. The layers were defined as cylindrical volumes extending parallel to the surface with 1 Å in height. The results are shown in fig. 4.9. The structure of the contact layer is dramatically changed when compared to the bulk: the second and the third coordination shells collapse to about 3.3 Å and 6 Å while the first peak is significantly decreased.

The structures found for the contact and the second layer are compared to the structure of the bulk liquid from simulations, bulk water under pressure [112] and of a NaCl solution, where the latter was observed to exhibit a similar structure as the compressed liquid [113, 114]. The interaction with alkali halide solutions has been studied in more detail recently using transmission mode XAS [107]. It was concluded that the local H-bond configuration becomes locked into an HDL-like structure at least in the first hydration shell of the ions, thus shifting the LDL/HDL ratio towards more disordered HDL-like average configurations. Recent simulations of potassium halide solutions show similar effects, with particularly the fluoride anion affecting the local structure [115].

From the simulations, a very high local density of 1.23 g/cm$^3$ was found within the first layer, integrated from a distance of 1.3 Å from the crystal to the minimum in the density profile (cf. inset in fig 4.9). For $T = 260$ K, the structure is slightly better defined than for $T = 290$ K, but does not change qualitatively.

The collapse of the second coordination shell is mainly due to two water molecules H-bonding to the same fluoride ion on the surface, causing the oxygen atoms to be closer together than they would be in the bulk. This is illustrated in fig. 4.10 with a histogram of oxygen-oxygen distances between molecules simultaneously H-bonding to the same fluorine ion at the surface.

The findings from simulations are in qualitative agreement with the results from the XAS experiments, where the spectra indicate a HDL-like structure. In the experiment, the conclusions even hold for supercooled water at a temperature 259 K.
4.3 The structure of water on a Barium fluoride (111) surface

Figure 4.9: Oxygen-oxygen pair-distribution functions of (a) the first layer H$_2$O on BaF$_2$(111) from simulations, full line $T = 260$ K, dotted line $T = 290$ K; (b) HDL, taken from reference [112]; (c) NaCl solution, mole ratio 1:10 taken from reference [113]; (d) bulk H$_2$O at $T = 260$ K from simulations, calculated with the same anisotropic normalization as (a) and (e) for comparison; (e) second layer H$_2$O on BaF$_2$(111) from simulations, full line $T = 260$ K, dotted line $T = 290$ K

Inset: Histogram of distances between the oxygen atoms of H$_2$O and surface atoms. Reprinted from Paper V with permission.
Generally, simulations can give valuable insights into structure and dynamics on the molecular level and complement experimental results. But it is important to keep in mind that simulations are performed using models and the results might not always represent what happens in reality. In order to test how robust the simulation results were we repeated the simulations using different force fields, varied the effective charges of the ions in empirical force field simulations and compared the adsorption energies obtained with empirical force fields with results from density functional theory (DFT).

**Test of different water models.** We performed simulations with four different water models: the three-point models SPC/E and TIP3P and the four-point models TIP4P and TIP4P/2005. All four tested water models exhibit a similar PDF within the first layer at the interface, see fig. [4.11](#). Interestingly, the shell structure is less pronounced for the three–point models TIP3P and SPC/E as also found in simulations of the bulk. Nevertheless, all models predict high-density structures of the first-layer water on the BaF$_2$(111) surface, with a strongly diminished first peak and the inward collapse of the second and third coordination shell, when compared to the bulk structure.
4.3 The structure of water on a Barium fluoride (111) surface

Figure 4.11: Comparison of the O-O pair-distribution functions in the first layer of H$_2$O on BaF$_2$(111) obtained with different water models. The crystal was described with the OPLS force field in all cases.

Effective charges of the crystal ion pairs. Coulomb interaction between partial charges within the water molecule and the ionic charges of the surface ions provides the dominant interaction in the system under consideration. Thus, the effective charges of the surface ions were expected to play a prominent role for the structure observed. MD simulations were performed with three different charge-pairs for ions in the BaF$_2$(111) slab to investigate the influence on the O-O pair-distribution function (PDF) of water on the surface. The results are shown in fig. 4.12. There is a clear effect of the changes in charge on the PDF. However, comparison to the bulk water O-O PDF calculated with the same method clearly shows that even an unrealistically weak charge-pair ($q_F = -0.5e$, $q_{Ba} = +1.0e$) still results in an HDL-like PDF.

Adsorption energies from MD and DFT. In order to benchmark the empirical force fields used in the MD simulations, we compared the adsorption energies of an isolated water molecule on a (3×3) four-layered BaF$_2$(111) slab. The adsorption energies were calculated from energy-minimized simulation boxes using empirical force fields and from density functional theory (DFT) using different functionals for comparison and shown in tables 4.1 and 4.2. The real-space-grid based GPAW [116] code was used with a grid-spacing of
Figure 4.12: Comparison of first-layer O-O pair-distribution functions for water on BaF$_2$(111) with different effective ionic charges, as indicated. A bulk water O-O pair-distribution function obtained from a 1 Å thick slab through the simulation box (i.e. the same conditions and normalization as for the surface layer, $T = 260$ K) is plotted for comparison.

0.2 Å.

<table>
<thead>
<tr>
<th>Water model (BaF$_2$ described by OPLS for all cases)</th>
<th>Adsorption energy [kJ/mol], charge-pair (-1.0e, +2.0e)</th>
<th>Adsorption energy [kJ/mol], charge-pair (-0.87e, +1.74e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TIP4P/2005</td>
<td>−41.2</td>
<td>−34.6</td>
</tr>
<tr>
<td>TIP4P (OPLS)</td>
<td>−37.1</td>
<td>−30.7</td>
</tr>
<tr>
<td>SPC/E (OPLS)</td>
<td>−33.5</td>
<td>−26.9</td>
</tr>
<tr>
<td>TIP3P (OPLS)</td>
<td>−27.0</td>
<td>−21.5</td>
</tr>
</tbody>
</table>

Table 4.1: Adsorption energies obtained with the MD force fields for two different ion charge-pairs. The structures were energy-minimized, they are the same as obtained from DFT calculations. Reproduced from Paper V with permission.

It is clear that the different force-fields give values for the adsorption energies in good comparison to those obtained with DFT, in particular for the PBE and BEEF functionals, where the latter includes also non-local correlations describing van der Waals interactions. In quantum chemical calculations of ionic systems one typically finds lower charges than the nominal ones; in fact, using the intermediate charge-pair brings the force-field values into even...
4.3 The structure of water on a Barium fluoride (111) surface

<table>
<thead>
<tr>
<th>DFT functional</th>
<th>Adsorption energy [kJ/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>BEEF-vdW</td>
<td>−33.1</td>
</tr>
<tr>
<td>PBE</td>
<td>−30.7</td>
</tr>
<tr>
<td>RPBE</td>
<td>−14.0</td>
</tr>
</tbody>
</table>

**Table 4.2:** Adsorption energies obtained with different DFT functionals for comparison with the MD results in table 4.1. Reproduced from Paper V with permission.

better agreement with the DFT values. Note, however, that the conclusions on a highly compressed contact layer are independent of force-field and charge-pair.
4. Molecular correlations in liquid water
5. Molecular dynamics in liquid water

This chapter is devoted to the molecular dynamics of water. After a general overview over the time scales of different dynamical processes, the focus will be on a particular phenomenon called the Boson peak and the observation of a similar feature in simulations of supercooled bulk water.

5.1 Dynamics in liquid water

The dynamics in liquid water is a very wide field and can be subdivided into the dynamics on different time scales: The fastest possible processes are electronic excitations and relaxations that take place on a time scale of up to a few femtoseconds and are relevant for interactions of photons with water molecules, as in x-ray spectroscopies. Intramolecular vibrations appear just below 10 fs and librations around 50 fs. They are probed using infrared (IR) spectroscopies. In MD simulations at ambient temperature, the averaged velocity autocorrelation function of water decays on a time scale of a few hundred femtoseconds, indicating that oscillations about an instantaneous position are dampened out on this time scale. On a time scale of several hundred femtoseconds to picoseconds, proton transfer reactions take place. It is also in this range that intermolecular and collective vibrations start playing a role which will be discussed in detail below. On longer time scales, phonon excitation and hydrodynamic motions become dominant.

5.2 The Boson peak

Generally, the low frequency acoustic phonon spectrum of a harmonic crystal can be described by the Debye model. It is based on the assumption of a linear dispersion relation, which is justified for acoustic modes at small frequencies. For a linear dispersion relation

\[ \omega = c k, \]  

(5.1)
5. Molecular dynamics in liquid water

with frequency $\omega$, sound velocity $c$ and wave vector $k$, the Debye approximation for the vibrational density of states (VDOS) evaluates to

$$g_D(\omega) = \frac{3}{2\pi^2} \frac{\omega^2}{c^3}$$

thus predicting an $\omega^2$-dependence of the density of phonon states, $g_D(\omega)$ on the frequency $\omega$ \[117,118\]. The Boson peak (BP) is an excess over the density of states predicted by the Debye approximation and is observed to be a universal phenomenon in disordered materials exhibiting a glass transition and occurs at frequencies of about $0.5 - 2.5 \text{ THz}$ (corresponding to ca. $16 - 80 \text{ cm}^{-1}$ or $2 - 10 \text{ meV}$). The BP can be observed experimentally in inelastic neutron scattering (INS) \[119\] and inelastic x-ray scattering (IXS) \[120,121\] for most glasses and supercooled liquids.

There is no general agreement on the origin of the BP, but there are two major hypotheses. One explains the BP in terms of collective dynamics and propagating modes while the second one associates it with local or quasi-local molecular motions \[122\].

An interpretation was given by Sokolov et al. \[123\] in terms of glass transition dynamics in fragile and strong systems and in a mode-coupling theory (MCT) picture. For fragile systems, i.e. such that follow a non-Arrhenius behavior, the collective motion would be structural relaxation, corresponding to fast $\beta$-relaxation. For strong systems, i.e. such that show an Arrhenius-type temperature dependence of the relaxation time, on the other hand, the collective motions would be “frozen in” into vibrations. Sokolov et al. also reported the observation of an excess density of vibrational states in Raman spectra with the quasi-localized collective atomic vibrations involving about $30 - 100$ atoms \[123\].

The explanation in terms of a quasi-localized nature of the BP was opposed by Marruzzo et al. \[124\] who identified the BP related vibrations to be mainly associated with spatially fluctuating shear stresses. This interpretation was developed further as presented by Chumakov et al. \[125\], with the BP as a remnant of the transverse acoustic van Hove singularity in the parent crystal. This correspondence would then suggest that the BP originates from the piling up of the acoustic states near the boundary of the pseudo-Brillouin-zone \[125\]. This latter interpretation, however, has been challenged by theory. Schirmacher showed in his textbook \[126\] that the BP marks the crossover from wave-type vibrational excitations to disorder-dominated vibrations that would be characterized by a random Hamiltonian. He emphasizes explicitly, that the BP would not be connected to a van Hove singularity whatsoever.

It becomes clear that the origin of the BP remains puzzling and that it has
yet to be explained conclusively.

5.2.1 Low-frequency vibrational dynamics of bulk supercooled water

In INS experiments a BP has been reported for protein hydration water \[127\] and for supercooled water in confinement [88]. We performed extensive MD simulations of the TIP4P/2005 water model to investigate the VDOS of the bulk supercooled liquid. We ran a series of simulations at temperatures of \(T = 210 - 260\) K at ambient pressure. The simulations were first equilibrated in the \(NPT\) ensemble using the Nosé-Hoover thermostat and the Parrinello-Rahman barostat. We then switched to the \(NVT\) ensemble for further structural relaxation. In the supercooled temperature region, the equilibration time starts to rise sharply. The structural relaxation time \(\tau_\alpha\) can be found from the relaxation of the incoherent intermediate scattering function defined below. Since \(\tau_\alpha \approx 20\) ns at \(T = 210\) K, these equilibrations were run for up to 100 ns. We finally switched to the microcanonical ensemble \((NVE)\) in which we performed the production runs for the calculations of dynamic quantities. The simulations were run at integration time steps of 0.2 – 1.0 fs in double precision mode.

The velocity autocorrelation function

\[
C(t) = \left\langle \frac{1}{N} \sum_i \vec{v}_i(t) \vec{v}_i(0) \right\rangle
\]

was computed from MD simulations for different temperatures and system sizes and Fourier transformed

\[
g(\omega) = \int C(t) e^{i\omega t} dt
\]

to obtain the VDOS \(g(\omega)\), shown in fig. 5.1.

In the low frequency end of the phonon spectrum, we identified peaks that are due to finite size effects as has been discussed in the literature [128]. By scaling the system size, they were shown to extrapolate to zero frequency for infinite system size as shown in fig. 5.1b. These finite-size peaks are connected to the transverse current spectrum \(C_T(k, \omega)\) at the smallest wave vectors \(k\) possible in the simulation box which is shown in fig. 5.1 together with the VDOS.

The BP is most easily identified by removing the Debye-predicted dependence in the reduced VDOS \((g(\omega) - g(0))/\omega^2\) as shown in fig. 5.2. We find a broad feature around \(37\) cm\(^{-1}\), unaffected by system size scaling. In comparison, the BPs reported for protein hydration water and supercooled confined water are located at about \(30\) cm\(^{-1}\) [127] and \(45\) cm\(^{-1}\) [88], respectively, in
5. Molecular dynamics in liquid water

Figure 5.1: (a) Vibrational density of states (VDOS) together with the transverse current spectrum $C_T(k, \omega)$ which for low values of $k$ is identified to cause the finite size peaks in the VDOS. (b) The peak positions of the first sharp peaks found in the VDOS are shown to extrapolate to $\omega = 0$ for infinite system size $L$.

good agreement with our result. This is the first time that a similar feature could be shown to emerge in bulk supercooled water. The BP is often observed in experimental data for the dynamic structure factor. To connect the results found in simulations to this quantity we calculated the incoherent intermediate scattering function

$$F_S(k, t) = \left\langle \frac{1}{N} \sum_i e^{-i\mathbf{k} \cdot \mathbf{\tilde{r}}_i(t) - \mathbf{\tilde{r}}_i(0)} \right\rangle,$$

(5.5)
5.2 The Boson peak

Figure 5.2: Reduced VDOS at low temperatures. The broad feature is present in the supercooled liquid, and blue-shifted in the amorphous LDA states and the ice Ih crystal. The simulations quenched into amorphous LDA states at $T = 150K$ and $T = 100K$ tend towards the excess in the VDOS of hexagonal ice Ih with decreasing temperature.

That is then Fourier transformed to give the dynamic structure factor

$$S_S(k, \omega) = \int F_S(k, t) e^{i\omega t} dt.$$  \hspace{1cm} (5.6)

The incoherent intermediate scattering function $F_S(k, t)$ and the dynamic structure factor $S_S(k, \omega)$ calculated from our simulations are shown in fig. 5.3. $F_S(k, t)$ shows the emergence of a time scale-separation upon supercooling. The two relaxation processes are called $\alpha$- and $\beta$-relaxation, i.e. slow relaxation at longer times and a faster relaxation at smaller time scales, respectively, leading to the plateau-like structure [41, 129]. The intermediate scattering function has been investigated in detail in simulations of the TIP4P water model and compared to predictions from MCT, indicating a fragile-to-strong crossover of the liquid at the Widom line [130].

$S_S(k, \omega)$, that is observable in experiments, clearly shows a BP-like feature in the liquid. When the liquid simulation is quenched to 150K and 100K into LDA states at a cooling rate of $2 \cdot 10^{10} K/s$, this feature persists and is shifted towards higher frequency with decreasing temperature and observed to shift towards the position of a similar feature in simulations of hexagonal ice.

We conclude that we found a BP-like feature in simulations of supercooled bulk water and its onset to coincide with crossing the Widom temperature $T_W$
5. Molecular dynamics in liquid water

Figure 5.3: (a) Incoherent intermediate scattering function $F_S(k,t)$ and (b) its temporal Fourier transform, the incoherent dynamic structure factor, $S_S(k,\omega)$. $F_S(k,t)$ clearly shows the emergence of relaxation processes on two separate time scales of $\alpha$- and $\beta$-relaxation. $S_S(k,\omega)$ can be measured in INS experiments. It shows the emergence of the BP-like feature upon decreasing temperature between $T = 240$ and $230 \text{K}$. Of the water model. This feature is thus associated with the structural crossover to a stiffer LDL-like liquid. A similar feature has been observed in the VDOS of LDA states and ice, where it is shifted to higher frequencies. Our observations thus support an interpretation similar to that by Chumakov et al. [125], that the low-frequency vibrational dynamics in the deeply supercooled liquid starts to resemble that of the related crystalline ice Ih.
Summary and Outlook

This thesis has been focused on water, its properties and their relation to the structure and dynamics on the molecular level.

Molecular dynamics simulations of the evaporative cooling process for nanometer sized droplets were compared to calculations using the Knudsen theory of evaporation. The results were found to be in very good agreement and we concluded that the generically used evaporation coefficient is unity provided that the thermodynamic properties of the evaporating material are known. The results could thus be of use for other liquids than water. An interesting perspective would be the application to cloud-microphysics with evaporation and condensation processes of tiny droplets. In simulations, the droplets could furthermore be doped with ions to investigate the effect on their evaporation kinetics.

The Knudsen theory of evaporation was further used to calibrate the temperature in an experiment in which the evaporative cooling technique was applied to supercool water droplets to unprecedentedly low temperatures below the previously accepted temperature of homogeneous ice nucleation. The liquid structure probed with high intensity x-ray pulses from the free electron x-ray laser LCLS was found to change continuously and in an accelerated fashion towards a low-density amorphous structure and can thus be regarded as low-density liquid-like, in agreement with predictions by the liquid-liquid critical point hypothesis. This experiment might be the key to probe water even deeper down into “no-man’s land” from above, possibly also at higher pressures, so as to further test the liquid-liquid critical point hypothesis and alternative explanations of water’s anomalous behavior.

We further investigated the dynamics of the bulk liquid upon deep supercooling in simulations. The low-frequency vibrational spectrum was found to exhibit an excess over the intensity predicted by the Debye approximation, similar to the Boson peak, which is a universal feature of amorphous materials. This Boson-like peak was observed to emerge upon crossing the Widom line of the TIP4P/2005 model where the liquid transforms into a low density liquid that is tetrahedrally ordered and starts to stiffen.

The structure of water on a molecular level is highly adaptable to various situations, a property that makes water an outstanding solvent and versatile medium. Recent high-quality x-ray diffraction data of bulk water at ambi-
ent conditions provided the radial distribution function of water to very high precision. Simulations were employed to determine the O-H contribution to the radial distribution function and to estimate uncertainties caused by the subtraction of this contribution obtained from neutron scattering experiments. The oxygen-oxygen radial distribution function is key to many properties and the structural data presented can be considered the current standard.

Even more recent experimental data show delicate molecular correlations to distances of up to 17 Å. These intermediate range correlations were found to be present in simulations of the TIP4P/2005 model and there is a striking qualitative agreement between experimental and simulation data. The temperature dependence of the intermediate range features is non-trivial and might lead to a deeper understanding of neat water at ambient conditions on mesoscopic length scales. The structural analysis of the intermediate range feature observed showed that the liquid can be understood within the two-state model in terms of low-density liquid and high-density liquid-like molecular arrangements with a shift of the fluctuations between these structural motifs upon temperature changes in favor of one or the other.

The structure of water at interfaces is of crucial importance since interfacial water is the most common form of water in nature and might be helpful in future applications. In contrast to the structure at extreme supercooled conditions, the molecular arrangement in the liquid at a barium fluoride (111) surface resembles much more that of water under high pressure and was thus concluded to be high-density liquid-like. Our findings confirm that the barium fluoride (111) surface does not promote ice formation but instead strongly suppresses structural fluctuations into low-density liquid arrangements at the interface.

All the different aspects of water’s properties and behavior discussed above can be understood in terms of the liquid-liquid critical point hypothesis with competing structural and thermal fluctuations between the extremes of low- and high-density liquid-like molecular arrangements.
Sammanfattning

Vatten är en fascinerande substans som ännu inte är fullständigt förstådd på en fundamental nivå. Den föreliggande avhandlingen handlar om olika aspekter av vätskan vars egenskaper uppvisar många anomalier jämfört med enkla vätskor som t. ex. argon. Här undersöker vi egenskaper av rent vatten, speciellt den molekylära strukturen och dynamiken med hjälp av molekylära simuleringar.


För vätskan i vanliga temperaturområdet etablerade vi en ny standard för syre-syre parfördelningsfunktionen och undersökte det icke-triviale temperaturberöendet av svaga korrelationer så långt ut som 17 Å. Vi undersökte dessutom vattens struktur vid ytan av en barium flourid (111) kristall, där det visade sig att vattens struktur liknar den av vatten vid högtemperatur.

Vi kunde också visa i molekylära simuleringar av underkylt vatten att lågfrekvens vibrationsspektrummet uppvisar en topp som anknyter till en liknande topp i spektrumet av amorfa material. Toppen uppstår när vatten kyls ner och ändra sin struktur till en mer ordnad vätska med låg densitet.
I would like to express my deep gratitude to my supervisor Lars G. M. Petersson and my co-supervisor Anders Nilsson. Lars, thank you for your constant guidance and for always being available for discussions, for your strong support and patience. Our research was to a large extent directed by the experimental activities and I’m grateful for this guidance and the greater vision, Anders. It was a privilege to work in this group and I’m grateful for all I’ve learned about water, simulation and experimental techniques. I’d like to thank you in particular for the numerous opportunities to go to schools, conferences, beam-times and collaborations.

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The work in close collaboration with experimentalists has been a great experience, mainly due to Jonas (Nature guy), Fivos (man with blue glasses and a beer in a massage chair), Simon (presentation trainer and after-work connection), Katrin and Peter (bbq masters), Harshad (room mate in Japan) and Stefano (THz). I also want to thank Lawrie, Sarp, Congcong and Hirohito for collaborations and all I’ve learned from you about experiments; Jerry, well, for the experiments concerning certain solutions and a lot of insights into life.

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Imagine, how incredibly lucky I was to go to Göteborg to learn statisti-
5. Acknowledgement

cal mechanics of liquids and to get correlated with these “particles”: Joakim, Sasha and Aymeric. It has been a great pleasure to study with you. Sasha and Joakim, I’m not only grateful for all the discussions about MD simulations but also for an uncountable number of badminton matches. Joakim, your intellect is much appreciated but your moral is concerning, we have to talk. Your pragmatic approach to life, Sasha, is admirable and will be missed, don’t forget the spot in Bergianska trädgården. Aleks and Zoltan, thank you for numerous discussions about science and free will.

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Stockholm, September 2015
Daniel Schlesinger
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