Liquid-Liquid Critical Point in ST2 Water

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Zusammenfassung


In der vorliegenden Arbeit wurden eben solche Molekulardynamik Simulationen verwendet, um den flüssig-flüssig kritischen Punkt zu untersuchen. Im NVT Ensemble, in welchem die Teilchenzahl, das Volumen und die Temperatur konstant gehalten werden, konnten die beiden Phasen in Koexistenz gefunden werden. Im NPT Ensemble, in welchem die Teilchenzahl, der Druck und die Temperatur konstant gehalten werden), wurden Fluktuationen zwischen den beiden Phasen beobachtet. Mithilfe von “Finite Size Scaling” des Challa-Landau-Binder Parameters konnte
Summary

Liquid water is both: a very important liquid for Earth, animals, humans and human culture, but also a liquid with a lot of still not fully understood anomalies. Upon cooling the response functions as the specific heat and the compressibility increase and the thermal expansion coefficient decreases for liquid water. By cooling liquid water below the freezing temperature the mentioned quantities seem to diverge at about $-45^\circ C$ at ambient pressure. This gave rise to the hypothesis of the existence of a liquid-liquid phase transition ending in a liquid-liquid critical point (LLCP) in the deeply supercooled region of water. This hypothesis is very hard to prove experimentally as the liquid-liquid critical point lies deep in the so called “no mans land”, a region in which liquid water is not accessible but freezes. In molecular dynamic simulations however crystallization events pose less problems, as the system sizes are smaller and the liquid contains no impurities i.e. crystallization cores, therefore crystallization takes place less frequent.

In this work molecular dynamics is used to investigate the liquid-liquid phase transition and the liquid-liquid critical point. In the constant volume ensemble the two phases have been observed at coexistence and the phase transition therefore verified. In the constant pressure ensemble the two different phases have been observed and the system flipping between them. Using finite size scaling of the Challa-Landau-Binder parameter the critical point has been located. The position is confirmed using the order parameter distribution function, assuming that the universality class of the LLCP is the same as the one of the three dimensional Ising model and the liquid-vapor critical point. The finite size scaling of the amplitude of
the order parameter distribution function confirms the compatibility with this universality class. The intermediate scattering function and the oxygen-oxygen radial distribution function have been analyzed. By applying several different structural order parameters, the structure of the low density liquid phase has carefully been analyzed in order to distinguish it from crystals. As a result growing crystallites have been observed which melt again. Few simulations where the whole system crystallizes have also been observed. Excluding these few crystallized simulations, the systems could be thermalized well in the 1000 ns long simulations.
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Introduction

1.1 Water, an Important but Complex Liquid

On one hand water is a liquid with a complex phase diagram and many anomalies, on the other hand it is hard to underestimate the importance of water for human beings. Our planet’s surface is covered by two thirds with oceans, our landscapes are formed by rain and ice, but more importantly we need water to grow our food and our body consists by four fifths of water. This importance of water is proven by the fact that ancient cultures as the Mesopotamians and Egyptians lived near to the water at the rivers of Euphrates, Tigris and Nile. The combination of abnormal behavior and the importance of the substance makes it very interesting to study all properties of water, even if they are hidden and at non ambient conditions in the phase diagram. In this thesis I am using molecular dynamics to investigate the deeply supercooled region in the phase space and test the hypothesis which claims that water separates in two liquid phases at very low temperatures.

In this first chapter I will start with the experimentally known part of the phase space. Then I will discuss the nature of some important anomalies of water at ambient and supercooled conditions. I will continue with the three most common hypotheses which explain these anomalies. One of them, the liquid-liquid phase-transition hypothesis, is the hypothesis investigated in this thesis. I will proceed
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with a discussion of other materials and toy models which show similar anomalies as water or show a liquid-liquid phase transition. During my thesis I have been attempting of using ab-initio methods to investigate the liquid-liquid critical point in supercooled water, sadly this attempt ends in a brief discussion why this has not been possible. The chapter will end with an overview on the thesis.

1.1.1 The Phase Diagram of Steam, Water, Ice and Amorphous Ice

The phase diagram of the different ice phases of water is very rich: eleven different crystal phases are known as shown in figure 1.1. Roughly they can be classified in three different groups according to their density. The commonly known ice from drinks and frozen lakes is the hexagonal ice. Together with the cubic ice and ice XI they form the group of the low density ices. High density ices can be found for high pressures, where they exist even for temperatures up to 1000K. Between the low density ices and the high density ices some ices with intermediate densities exist. Burton and Oliver showed in 1935 [19] that water, if frozen fast enough, it forms a solid without long range order, hence a form of amorphous ice. This amorphous ice has a density of around 0.94 g/cm$^3$. In 1985 Mishima, Calvert and Whalley [63] found a phase transition between two amorphous ices with different densities called low density amorphous ice (LDA) and high density amorphous ice (HDA). The LDA phase is the same phase as discovered by Burton and Oliver. The HDA phase is a new phase with a density of about 1.17 g/cm$^3$. An amorphous ice with even higher density of 1.269 g/cm$^3$ has been found again by Mishima in 1996 [60], but only regarded as a new phase in 2001 by Loerting [54].

Water can be superheated over its boiling temperature of 100°C at ambient condition. In the other direction pure water, with few condensation cores, can be supercooled at lower temperatures than the normal freezing temperature of 0°C. Supercooling of water at ambient pressure is possible down to temperatures of $\approx -38^\circ$C [91]. Below this temperature supercooled water will crystallize immedi-
1.1. Water, an Important but Complex Liquid

Fig. 1.1: Phase diagram of water as presented by Chaplin [21]. It shows the well known liquid and vapor phases with their shared first order phase transition ending in the critical point and followed by the Widom line, i.e. the continuation of the phase transition line defined as the line of maximum correlation length. At this line water and steam are in principle indistinguishable. The phase diagram shows also the different phases of ice. The hexagonal ice (ice Ih) is the best known phase of ice. Together with cubic ice and ice IX they form the low density ices. At high pressures ice VII, ice VIII and Ice X can be formed. For pressures in between ice phases with intermediate densities exist.

ately. The line where this crystallization happens, depending on the pressure $P$, is called homogeneous crystallization line $T_h(P)$. The above mentioned amorphous phases exist at much lower temperatures and are crystallizing at temperatures higher than $\approx -120^\circ C$, because only at higher temperatures the diffusion is big enough to lead to crystallization in a reasonable time scale. The line where this crystallization happens depending on the pressure $P$ is called crystallization curve.
Fig. 1.2: Different states of liquid water at ambient pressure. Data are from Mishima et al. 1998 [64]. There exists a region in the phase diagram, where liquid water can not be found experimentally. This region is called “No mans land”. 

\[ T_{x}(P) \]. The area in the phase diagram between these two lines \( T_{h}(P) \) and \( T_{x}(P) \) is called “no mans land” since liquid bulk water in this area is not accessible by experiments.

### 1.1.2 Anomalies of Water

Since water is the best known fluid for most people, it is thought as a very typical fluid. But the opposite is true, often water behaves in the opposite way than normal fluids. Moreover, water has many anomalies, more than 62 are known [21]. In this section some of the most important anomalies of water are presented.

Widely known is that ice is less dense than water and therefore swimming on its top. Also the existence of a density maximum in water at about 4°C at atmospheric pressure and that therefore the bottom of a lake has a temperature of around 4°C is well known. The fact that water becomes less dense with cooling and the existence of a line of temperature with maximal density (TMD) it is called density anomaly. The density anomaly is located in a cascade with two other anomalies: the diffusion
1.1. Water, an Important but Complex Liquid

Fig. 1.3: Sketch of the cascade of the density, diffusion and structural anomaly as found by Errington et al. in 2001 [23]. Inside the region of the density anomaly the density increases with increasing temperature at constant pressure. Inside the region of the self diffusion anomaly the diffusion becomes bigger for increasing density. And in the region of structural anomaly water becomes more disordered when compressed. The ordering is measured using the structural order parameter $q$ shown in equation 1.1.
measure the degree of order [23]:

\[
q = 1 - \frac{3}{8} \sum_{j=1}^{3} \sum_{k=j+1}^{4} \left( \cos \psi_{jk} + \frac{1}{3} \right)^2
\]

(1.1)

where \( \psi_{jk} \) is the polar angle of the relative vector \( r_{jk} = r_j - r_k \), see Figure 2.6.

Another interesting fact about water is its big heat capacity, or specific heat \( C_p = \frac{\partial U}{\partial T} \bigg|_P \). It has an effect on every day’s life, since it is the reason why oceans are cooler than continents in summer and warmer in winter. It is why there is a big difference between the climate at the coast and the continental climate. The specific heat is not only high at ambient condition, but unlike in most other fluids where the specific heat is decreasing with decreasing temperature, the specific heat in water is increasing as the temperature is lowered. The same is true for other response functions as the isothermal compressibility \( \kappa_T \) and the thermal expansion coefficient \( \alpha \). This has been reported for the first time in 1851 by Grassi for the isothermal compressibility. More than 125 years later Speedy and Angell [9, 10, 91, 92] measured all the response functions in water from ambient temperatures down into the deeply supercooled region nearly to the homogeneous nucleation temperature. They found the response function monotonously increasing with temperature. A fit to their results suggests a divergence of all the response functions at \( \approx -45^\circ \text{C} \) in the inaccessible “no mans land”.

1.2 Hypothesis to Explain the Increase and Divergence of the Response Functions

This subsection introduces the three most common hypothesis explaining the diverging response functions. Each of this scenarios appears in existing models.
1.2. Hypothesis to Explain the Increase and Divergence of the Response Functions

Stokely et al. [97] presented models which show all of these scenarios depending on the model parameter. The question however remains which of them is the right description for water.

1.2.1 Stability Limit Hypothesis

In 1982 Speedy [91] introduced the stability limit hypothesis. It postulates the existence of a line \( p_s(T) \) where water is super compressible \( (\frac{\partial p}{\partial V})_T \to 0 \) as \( p \to p_s(T) \). This line \( P_s(T) \) stretches from the liquid-gas critical point to negative pressures and back to positive pressures, see figure 1.4. The divergence of the compressibility upon cooling is therefore straightforward, as \( \kappa_T \) diverges at \( p_s(T) \), also the other response functions diverge because of their relations to the compressibility.

The stability limit hypothesis also explains the existence of the density anomaly: Since the slope of the line \( p_s(T) \) is connected with the thermal expansion coefficient, the thermal expansion coefficient is changing sign as \( p_s(T) \) changes sign. It follows that a line with \( \alpha = 0 \) i.e. extremal in the density exists. It is clear that the slope of the spinodal has to change if it intersects with the TMD line. The TMD line is negatively curved in the pressure–temperature plane and seems therefore to intersect the spinodal. [90]. Experimental verification is difficult since nucleation of ice prevents measurements (“no mans land”). However molecular dynamic simulations show a bent TMD line which doesn’t favor the stability limit hypothesis.

1.2.2 Liquid-Liquid Phase-Transition Hypothesis

In 1992 Poole et al. [77] came up with another hypothesis for the explanation for the increasing response functions: In molecular dynamic simulations using the ST2 [96] atomic water potential they found indications for a phase transition between two liquid phases called low density liquid (LDL) and high density liquid (HDL) ending in a critical point. These two liquid phases fit as successors of the high and low density amorphous ices mentioned in section 1.1.1. This liquid-liquid phase transition has not been observed in experiments, since it would be located in the
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Fig. 1.4: Schematic phase diagram predicted by the stability limit hypothesis introduced by Speedy in 1982 [91]. The spinodal line starting at the liquid gas critical point changes slope at negative pressure and comes back into the positive pressure. Since the thermal expansion coefficient is proportional to the slope of the spinodal, it changes sign and therefore we find the line of maximal density TMD. Since \((\frac{\partial p}{\partial V})_T \to 0\) as \(p \to p_s(T)\), the response functions diverge at the spinodal being the explanation for their strong increase upon supercooling water.

experimentally unreachable “no mans land”. The critical point explains the strongly growing response functions, since according to the theory of critical phenomena, they have to diverge at the critical point, and strongly increase approaching the Widom line. A sketch of the phase diagram between these two liquids is shown in figure 1.5. A first order phase transition separates the LDL from the HDL phase at high pressures. This first order phase transition ends with a (liquid-liquid) critical point (LLCP). For pressures below the critical pressure \((P_c)\), the region is called supercritical and LDL and HDL change without phase transition. This is different
1.2. Hypothesis to Explain the Increase and Divergence of the Response Functions
to the liquid gas critical point where the supercritical region has higher pressure than the critical pressure. The question how the TMD line is related with a critical point is not discussed in the mentioned papers. However, since artificial potentials are known for which a LLCP exists with no density anomaly, it is known that the density anomaly is not a necessary consequence of a LLCP.

The hypothesis has further been studied in more detail for different atomic water potentials. Table 4.4 gives an overview on the several molecular dynamic studies. The first entry is the paper of Poole et al. 1992 [77] where the idea of a liquid-liquid critical point in supercooled water has been brought up for the first time. Soon after, the LLCP has been located by looking at the maximum of the isothermal compressibility $\kappa_T$ in simulations in the constant temperature, constant volume ensemble simulated using molecular dynamics by Harrington et al. 1997 and in the same year by Sciortino et al. [33, 88] for the ST2 and the SPC/E atomic water potential. In the year 2002 Yamada et al. [106] performed molecular dynamic simulations in the $NVT$ ensemble and located the critical point using van der Waals loops. In 2005 Poole et al. [76] investigated again the ST2 potential in the $NVT$ ensemble using systems with 1728 molecules a huge part of the phase space

<table>
<thead>
<tr>
<th>Potential</th>
<th>$P_c$</th>
<th>$T_c$</th>
<th>$\rho_c$</th>
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<td>ST2 [77]</td>
<td>200MPa</td>
<td>235K</td>
<td>1g/cm$^3$</td>
</tr>
<tr>
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</tr>
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<td>235K</td>
<td>1g/cm$^3$</td>
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<tr>
<td>TIP5P [106]</td>
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<td>217 ± 3K</td>
<td>1.13 ± 0.04g/cm$^3$</td>
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<td>TIP4P2005: [4]</td>
<td>135MPa</td>
<td>193K</td>
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Table 1.1: Several results of simulations using different water potentials and estimations of their liquid-liquid critical point.
Fig. 1.5: Sketch of the phase diagram of LDL, HDL and the liquid-liquid critical point. The liquid-liquid phase transition line arises with negative slope and curvature out of the glassy region and ends in a liquid-liquid critical point. Unlike in the case of the liquid-gas critical point, the supercritical region has a lower pressure than the LLCP.
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Fig. 1.6: Overview of the different places where the critical point has been placed by the different simulations shown in table 4.4. It becomes obvious how different the estimations are when using different atomistic water models. The different estimations for the ST2 models are shown in different green circles, the estimation of their critical points lie close together.


Also experimental evidences for the liquid-liquid phase transition hypothesis have been found. For example by Bellissent-Funel in 1998 [12], he saw two liquid structures in water from neutron diffraction. He investigated water for different pressures and found two different structure functions, similar to LDA and HDA what he interpreted as finding evidences of LDL and HDL similar liquids in water. Hard experimental evidences for the liquid-liquid phase-transition hypothesis are very difficult to reach since the hypothetical phase transition is located deeply in the “no mans land”. By confining water in one dimensional nano pores, however water can be prevented from freezing and the “no mans land” disappears.
This method was applied, using nano porous silica matrices, in 2006 by Liu et al. [52], where the water has been studied using quasi elastic and inelastic neutron scattering to measure the self diffusion. Also Mallamace et al. 2008 [58] confined water to suppress crystallization. They used NMR methods to measure the proton chemical shift $\delta$. In the temperature dependence of this proton chemical shift, they observe a change of slope upon crossing the locus of maximum correlation length (i.e. the Widom line) and explain it with the a change of the phase (LDL-HDL). In 2011 Zhang et al. [108] measured the density in confined water using neutron scattering in heavy water. They measured the density-temperature curve for different pressures and upon cooling and warming. For a pressure below 1kBar the difference between the warming and the cooling experiment was very small, but for higher pressures the two curves differ and show a hysteresis compatible with the liquid-liquid phase-transition hypothesis.

In 2002 Kiselev and Ely [48] estimated a crossover equation of state for water. This equation of states shows an existence of a second critical point, which is below the homogeneous nucleation temperature and therefore hidden in the “no mans land”. Similar did Fuentevilla and Anisimov in 2006 [28] where also they found a liquid-liquid critical point and they postulate the theoretical scaling fields.

In 1998 Mishima and Stanley [65] investigated the melting curve of ice IV. They showed that this melting curve undergoes a discontinuity at the location, where the liquid-liquid phase transition is proposed. In 2000 Mishima published a paper [61], where he investigated further the ice melting lines which are all consistent with the liquid-liquid phase transition hypothesis.

### 1.2.3 Singularity Free Hypothesis

Sastry et al. showed in 1996 [85] that independent of the two other introduced scenarios, the increase of the isothermal compressibility $\kappa_T$ on cooling below the negative sloped TMD line is a requirement of thermodynamics. They conclude that the increase in $\kappa_T$ on cooling is consistent with both proposed scenarios, but cannot
be used as a support neither for the stability limit, nor for the liquid-liquid critical point scenario.

1.3 Other Materials and Water like Models

1.3.1 Other Materials with a Liquid-Liquid Critical Point

**Carbon** In 1979 Ferraz and March [24] proposed two liquid phases in carbon, a metallic phase and a non metallic phase. In 1993 Van Thiel and Ree [100] investigated this problem further and introduced a macroscopic multiphase model of carbon with which it is possible to compute the equation of state of liquid carbon and its phase space, which shows a liquid-liquid phase transition. Using flash heating Togaya investigated in 1997 [99] the slope of the melting line in carbon and found therein a discontinuous change consistent with a liquid liquid phase transition in carbon. Using atomistic simulation methods Glosli and Ree [30] in 1999 seemed to have found a phase transition in the liquid carbon phase, ending in a critical point. Wu, Glosli, Galli and Ree in 2002 [105] however used first-principles molecular dynamics simulations which showed no evidence of a liquid-liquid phase transition in carbon. This absence of a liquid-liquid phase transition has been confirmed by Wang et al. 2005 [103] using first-principles electronic structure theory. This story teaches us to be careful with the claim of the existence of a liquid-liquid critical point and that results from ab-inito methods can differ qualitatively from standard molecular dynamics simulations.

**Silicon** In 2003 Sastry and Angell [84] found a liquid-liquid phase transition in supercooled liquid silicon using the empirical Stillinger-Weber potential. Four years later Jackse and Pasturel [43] confirmed these results using first principles simulations. The structural quantities of these ab initio simulations however were quite different to the ones originating from the empirical potential. However in both cases two liquid structures were found. In 2010 Beye et al. [15] could prove the
1. Introduction

existence of this phase transition by experimental results. The electronic structure of the two phases are easily distinguishable and latent heat has been observed during the transition. The debate of a critical point at the end of this phase transition has been ended in 2011 by Vasisht et al. [102] where the critical point has been found at negative pressure of about $-0.60 \pm 0.15$GPa using again the empirical Stillinger-Weber potential.

In 2000 Katayama et al. [46] found strong experimental evidences for a liquid-liquid phase transition in phosphorus using X-ray diffraction observations. Further materials such as Te, Se, Bi, Cs and S as well as network forming fluids like SiO2 and GeO2 show liquid-liquid phase transitions [80].

1.3.2 Jagla Potentials, a Family of Toy Models for Water

It is interesting to see what kind of thermodynamic scenarios can be produced with different potentials and how these scenarios change by manipulating these potentials. It can also be tested whether different anomalies arise always together, and whether the existence of a liquid–liquid critical point is needed for some of the anomalies. In 1999 Jagla [42] found that a simple potential, a spheric symmetric potential $U(r)$ as sketched in figure 1.7 b), shows similar anomalies as water (density anomaly and LLCP), with very few parameters. This motivated several other people to study these types of systems, see different potentials in figure 1.7. We will explain the most important things that have been learned: A comparison between TIP5P water and a similarly parameterized ramp potential has given good agreement as shown by Yan in 2008 [107]. The singularity free hypothesis introduced in section 1.2.3 shows that the density anomaly can exist without liquid-liquid critical point. In 2001 Franzese et al. [27] found a potential which shows a liquid-liquid critical point, but no density anomaly. Therefore the concept of liquid-liquid phase transition is independent of the density anomaly, however they are observed together quite often. In 2003 Buldyrev et al. showed [18] that for every step added to potential c) in figure 1.7 a further liquid-liquid critical point comes to existence.
1.4 Why Not to use Ab-initio Methods to Probe the Liquid-Liquid Critical Point in Water?

This gives the taste on what is important to create liquid-liquid critical points. Some differences between these Jagla models and water still remain: For example is the slope of the transition positive in the case of the Jagla potential and negative in the case of water.

1.4 Why Not to use Ab-initio Methods to Probe the Liquid-Liquid Critical Point in Water?

Ab-initio Methods calculate the forces between the atoms by calculating the electronic structure using quantum mechanics. Where standard molecular dynamics needs artificially constructed potentials (as the different water potentials named in table 1.1), ab-initio methods are in principle able to build everything based on first principles. As briefly discussed: differences between ab-initio simulations and standard molecular dynamics simulations can show qualitative effects.

To model the electronic structure ab-initio methods have to calculate the electron wave functions. To do this in a reasonable amount of time, only single electron wave functions are considered. This simplification has two effects: first the antisymmetrisation of the electronic wave function is not considered and second the correlation between the electrons are simplified. Both of these effects are too strong to be neglected and have to be corrected using the local density approximation.

The different locations for a liquid-liquid critical point of the different water potentials shown in 1.6 make it clear that simulations of water using ab-initio methods would be a great progress. Furthermore in subsection 1.3.1 I mentioned that ab-initio methods were used for the proposed liquid-liquid phase transition in both: carbon and silicon. So why should ab-initio methods not be also used for water?

Comparing simulations of ab-initio water with experiments shows that the radial distribution function $g(r)$ is over-structured for ab-initio water as Grossman et al. showed in 2004 [31]. Moreover different approximations to correct the missing anti-symmetrisation and the missing correlation give different structures and even
1. Introduction

Fig. 1.7: Sketches of the different spherical symmetric core softened hard core potentials. The potential a) has been introduced by Hemmer and Stell in 1970 [34]. It has also been used 2008 by Yan et al. [107] to compare with the effective potential of the first two shells in TIP5P water. The potential sketched in b) is the original “Jagla” potential, published in 1999 by Jagla [42] where he found water like anomalies in this simple spheric symmetric hard core potential. The potential c) shows also water like properties as shown by Franzese in 2001 [27] and later by Skibinsky et al. [89] and Malescio et al. [57]. In 2003 Buldyrev et al. showed [18] that for every step added to potential c) a further liquid-liquid critical point comes to existence.
different densities for water at ambient conditions, seen Schmidt et al. 2009 [87]. For 128 molecules one time step needs about 100s [101] computation time, where the time step is typically smaller than 1fs. With these times it is impossible to reach the 1ms needed to sufficiently thermalize the LDL phase. Ab-initio simulations involving 128 molecules simulated over 25ps as done by Kühne et al. in 2009 [49] for ambient temperature belong to the longest ab-inito water runs done up to now and show how large the gap is to the 1ms needed for water in the supercooled region.

Concluding the use of ab-initio techniques for probing the LLCP of water are neither possible (needed computer time), nor do they give confident water structures. Therefore in this thesis the liquid-liquid critical point of water is probed using standard molecular dynamics. As potential the well understood ST2 potential is used.

### 1.5 Overview over the Thesis

In this first chapter an overview on the known phase diagram of water given. Some important anomalies of water were presented and three different hypothesis to explain these anomalies were introduced. One of these hypotheses, the liquid-liquid phase transition hypothesis is the most promising. This hypothesis will be investigated in this thesis. The important literature about the liquid-liquid phase transition hypothesis has been discussed.

Chapter 2 is an introduction into phase transitions and critical phenomena. Phase transitions are discussed and the concept of universality classes and critical exponents are introduced. The order parameter distribution function is introduced and the difference between fluids and lattice models are discussed. Later several structural order parameters are defined to distinguish not only between LDL and HDL, but also between LDL and crystals. A brief discussion of two structural functions, the radial distribution function $g(r)$ and the intermediate scattering function $S(k)$ are introduced. The chapter ends with a list of how different people located the
1. Introduction

critical point in the literature.
In the third chapter the used and some related techniques of the molecular dynamics methodology are briefly discussed. Furthermore several different water Models are introduced.
“Investigation of supercooled ST2 water” is the title of the fifth chapter where I show what I did during this thesis.
The thesis ends with a discussion and outlook in chapter five.
Phase Transitions and Critical Phenomena

2.1 What is a Phase Transition

Phase transitions are defined in the thermodynamic limit, i.e. a system with infinite volume $V$ and infinite number of particles $N$ but finite density $\rho = N/V$, and in equilibrium, i.e. being with its environment in balance and at constant pressure, density and temperature. Of course such systems are only theoretical but they are a good approximation for bulk systems in nature where the system’s surface is negligible in respect to the systems volume. We will see later that we have to go away from this concept of the thermodynamic limit, as some metastable states, as discussed in this thesis, do not exist in the thermodynamic limit. According to Landau and Lifschitz [50] a system in a given thermodynamic state point is defined by two of the three thermodynamic quantities pressure, temperature and density. Such a system does not have to be homogeneous, but can consist of two or more homogeneous parts. These different parts are called phases and a system consisting of more than one phase is called a system at phase equilibrium. An example is a glass filled with a mix of ice and water at $0^\circ$C and 1atm in a environment screened from electromagnetic radiation. By changing the thermodynamic quantities of a
system in phase $A$ to the ones of phase $B$, one forces the system to undergo a phase transition to phase $B$. A parameter able to distinguish between the phases $A$ and $B$ is called an order parameter. An example of an order parameter is the density at the phase transition between water and steam. For the transition between water and ice, or between different ice phases, one needs order parameters that differentiate between the orientation of the ice and the liquid structure (see section 2.3.2).

A phase transition takes place along a line in the plane of the two chosen thermodynamic quantities to describe the system. If such a line of phase transitions ends, the endpoint is called critical point. Behind this critical point no difference between the two old phases exists anymore. It is then possible to bring phase $A$ to phase $B$ without any phase transition. A phase transition between a crystal and an amorphous state can not show any critical point since a crystal is distinguished by discrete symmetries which can not be broken in a continuous way [50].

Phase transitions were classified by Paul Ehrenfest by the lowest derivative of the Gibbs potential $g$ relative to the two other thermodynamic variables ($P$ and $T$), which is discontinuous. So a phase transition between phase $A$ and $B$ is called of $n$-th-order if

$$\frac{\partial^n g_A}{\partial T^n} \neq \frac{\partial^n g_B}{\partial T^n} \quad \text{and} \quad \frac{\partial^n g_A}{\partial p^n} \neq \frac{\partial^n g_B}{\partial p^n}.$$ 

It is common to distinguished only between first and second order. Where all the phase transitions higher than first order are called second order. In experiments first order phase transitions are easily detected by the occurrence of latent heat, i.e. the discontinue change of the specific heat.

Important quantities to study are the response functions. They describe the response of a thermodynamic variable. Examples are the specific heat: $c_p = \frac{\partial U}{\partial T} |_p$, the compressibility $\kappa_T = -\frac{1}{V} \frac{\partial V}{\partial p} |_T$ and the thermal expansion coefficient $\alpha_p = \frac{1}{V} \frac{\partial V}{\partial T} |_p$.

They can also be calculated using the fluctuations [7]:

$$\langle \delta V^2 \rangle_{\text{NPT}} = V k_B T \kappa_T$$  \hspace{1cm} (2.1)

$$\langle \delta (\mathcal{H} + PV)^2 \rangle_{\text{NPT}} = k_B T^2 C_P$$  \hspace{1cm} (2.2)

$$\langle \delta V \delta (\mathcal{H} + PV) \rangle_{\text{NPT}} = k_B T^2 V \alpha_P$$  \hspace{1cm} (2.3)
2.1. What is a Phase Transition

Here $\mathcal{H}$ stands for the Hamiltonian (energy) of the system and $\delta$ means the fluctuations: $\delta X = \langle X^2 \rangle - \langle X \rangle^2$. At the critical point the fluctuations diverge and therefore also the response functions diverge. Also the so-called correlation length $\xi$, a quantity to measure the typical distance over which two particles are correlated, diverges. As mentioned above the critical point is located at the end of the line of first order phase transition. This line however is continued by a line of the loci of maximum correlation length, or for practical reasons the loci of maximal response functions. This line continuing the first order phase transition is called Widom line.

![Fig. 2.1: Simplified phase diagram of water. The first order phase transition line between water and gas ends in the critical point. The line of first order phase transition however has a successor: the Widom line, i.e. the line of maximal correlation length. The response functions therefore show maxima as the Widom line is approached. The Widom line however does not separate two different phases, on the Widom line one can go from one state to another without any phase transition.](image)

In the thermodynamic limit a system undergoes a phase transition exactly at the same pressure and temperature, but for finite systems, superheating or supercooling
can be observed. This means a phase with thermodynamic quantities in phase $A$ can stay in phase $B$ for some time, see figure 2.2. In the example of water, a system at 1atm can be heated up over 100°C (overheating) or can remain liquid at negative temperatures if it is very pure and no perturbations are performed (supercooling). The line up to which a phase can maximally be supercooled or overheated is called spinodal.

### 2.2 Universality Classes and the Critical Exponents

If the phase diagram of figure 2.2 is projected to the $\rho – T$ plane a phase diagram as shown in figure 2.3 results. It shows the two areas $A$ and $B$ where systems exhibit pure phases. Furthermore it shows the phase transition line ending in the critical point. Between the region of the two pure phases exists an area where a system splits into the two pure phases.

It has been shown that the behaviour of this phase transition is the same for several gases, like $Ne$, $Ar$, $Kr$, $N_2$, $O_2$, $CO$ and $CH_4$ if the density is normalized by the critical density and the temperature by the critical temperature [32]. The form fits the power law: $\rho - \rho_c \sim \left( \frac{T - T_c}{T_c} \right)^\beta$ for $\beta$ near to $1/3$. Also the specific heat and the compressibility show the same behavior for different materials near the critical point. Their temperature dependence follows a power law as well. The corresponding exponents are called critical exponents. Different systems showing critical points with different exponents have been found, one example is the Ising model introduced in section 2.2.1. This gave rise to the idea that there are so-called universality classes, where different systems are assigned to the same universality class if they have the same critical exponents, the same shape of $\rho(T)$ and the order parameter distribution function see section 2.3.1.
2.2. Universality Classes and the Critical Exponents

Fig. 2.2: Phase diagram including overheating or supercooling. For a system with finite size metastable states can exist. These metastable phases can only exist up to the so-called spinodal lines. For a system in the thermodynamic limit no metastable states exist and the phase transition takes place as soon as the pressure of the phase transition $P_t$ is reached (pink dotted line). For smaller system sizes however the location of the phase transition is history dependent. Upon decreasing the pressure (cyan slashed line) the system is still in the phase with higher density although the pressure of the phase transition is already crossed. It only changes the phase at the spinodal (dotted black line). Upon decreasing the pressure the same hysteresis effect exists (orange line).

2.2.1 Ising Model as Prototype of a Second-Order Phase Transition

The most often studied model with a second-order phase transition is the Ising model, introduced in the twenties by Ernst Ising [41]. It has been solved in the case
Fig. 2.3: Sketch of a phase transition ending in a critical point in the T-\(\rho\) - plane. At temperatures above the critical temperature \(T_c\) the system is homogeneous for all densities. Below \(T_c\) the system shows phase segregation as the density is changed from \(\rho_A\) to \(\rho_B\) in the shaded region, one part having a density \(\rho_A\) the other a density of \(\rho_B\).

of the two dimensional square lattice by Onsager in the forties [72]. This model became a drosophila for critical systems and is discussed here to introduce some concepts and later as a reference to a simple system. The model consists of spins on a lattice, able to point up or down (represented as +1 or −1). The total energy is defined as (see [39]):

\[
E = \sum_{(i,j)} s_i s_j + H \sum_i s_i
\]

where \(H\) is an external field and \(\langle i, j \rangle\) means the sum over the nearest neighbors. The system shows a second-order phase transition for a square lattice in two and three dimensions. An important symmetry of the system is: \(s \rightarrow -s\) and \(H \rightarrow -H\),
called “particle-hole” symmetry. Therefore also the phase diagram has this same symmetry and the critical point is located at \( H = 0 \). The order parameter is the spontaneous magnetization \( m = \lim_{H \to 0} \sum_i s_i \). The symmetry implies that the fluctuations in \( E \) and in \( m \) are statistically independent.

The correlation length \( \xi \) is defined using the correlation function: \( \Gamma(r) = \langle m(r)m(0) \rangle - \langle m(r) \rangle \langle m(0) \rangle \). The correlation function behaves like \( \Gamma(r) = \frac{e^{-r/\xi}}{r} \) where \( \xi \) is called the correlation length. It is a measure for the spatial memory and diverges at the critical point. This means that the correlation function takes the form: \( \Gamma = \frac{1}{r} \) with no characteristic length scale [39].

As mentioned above, the correlation length \( \xi \) diverges at the critical point. This means that for any size, simulated or measured, the correlation length is bigger than the system size and hence the correlation length is cutoff at the system size. Therefore the system has finite size effects. This can be considered in the scaling.

At critical external field \( H_c = 0 \) the system is characterized by the way the response functions diverge: define \( t = \frac{T - T_c}{T_c} \) then [25]:

\[
C_P \sim |t|^{-\alpha} \tag{2.4}
\]
\[
m \sim |t|^{-\beta}, t \to T_c^- \tag{2.5}
\]
\[
\kappa_T \sim |t|^{-\gamma} \tag{2.6}
\]
\[
\xi \sim |t|^{-\nu} \tag{2.7}
\]

the exponents \( \alpha, \beta, \gamma \) and \( \nu \) are called critical exponents. These critical exponents are constant within a given universality class. Not every combination of these critical exponents is possible, but they have to satisfy the so-called hyper scaling laws [39, 93]:

\[
\gamma = \nu (2 - \eta) \tag{2.8}
\]
\[
\alpha + 2\beta + \gamma = 2 \tag{2.9}
\]
\[
\gamma = \beta (\delta - 1) \tag{2.10}
\]
\[ \nu d = 2 - \alpha \] (2.11)

where \( d \) is the dimensionality of the space.

2.3 Order Parameters and How to Distinguish LDL and HDL?

An order parameter is a quantity able to discriminate between two phases, and often 0 in the disordered phase. In a magnetic system, for example the above introduced Ising model, the absolute value of the magnetization \( M \) serves as an order parameter. It has the value of the total below and 0 above the critical point. In fluids the density is often used to discriminate between the phases. Structural order parameters are typically created to discriminate between phases of crystals with different lattices or between crystals and liquids.

In the first subsection 2.3.1 we discuss that a mixture of energy and density should be taken as order parameter and how the distribution of this order parameter behaves. In subsection 2.3.2 different structural order parameters are discussed. They will mainly be used to find crystallization events.

2.3.1 Order Parameter Distribution Function

2.3.1.1 The Case in the Ising Model

The order parameter distribution function of a system at the critical point is a universal quantity and is therefore the same for all the systems in the same universality class. For different universality classes the order parameter distribution functions are different. The difference between the two and three dimensional Ising universality class is mainly in the height of the central minimum with respect to the two peaks as shown in Fig. 2.4. The distribution function \( p_L(M, E) \) scales for different system sizes as [104]:

\[ p_L(M, E) \sim \Lambda_M^+ \Lambda_E^+ p_{M,E}(\Lambda_M^+ \delta M, \Lambda_E^+ \delta E) \] (2.12)
2.3. Order Parameters and How to Distinguish LDL and HDL?

where \( \Lambda_E = a_E L^{1/\nu} \), \( \Lambda_M = a_M L^{(d-\beta)/\nu} \) and \( \Lambda_M \Lambda_M^+ = \Lambda_E \Lambda_M^+ = L^d \) and \( \delta M = M - \langle M \rangle_c \) and \( \delta E = E - \langle E \rangle_c \). \( E \) stands for the energy, \( \langle E \rangle_c \) the energy at criticality and \( M \), respectively \( \langle M \rangle_c \) stand for the magnetization respectively the magnetization at criticality. This results in:

\[
p_L(M) \sim a_M^{-1} L^{\beta/\nu} \tilde{p}_M(a^{-1} L^{\beta/\nu} \delta M)
\]

if only the magnetization \( M \) is considered.

Fig. 2.4: Distribution functions of the order parameter for the two and three dimensional Ising model at criticality. The distribution function of the two dimensional Ising model [17] (left) has a lower minimum than the one of the three dimensional (right) Ising model [53]. The parameter \( M_c \) has to be chosen such that the mean value of \( M \) is zero, the parameter \( A \) such that the variance is unity.

2.3.1.2 Mixing Fields

For the Ising model exists a “particle-hole” symmetry: the transformation \( s \rightarrow -s \) and \( H \rightarrow -H \) will not change the energy of the system. The fluctuations in energy
δu = u − uc and in the magnetization δm = m − mc are independent: ⟨δuδm⟩ = 0 and the magnetization is and serves as an order parameter.

Fig. 2.5: Contour plot of a two dimensional histogram of density and energy shows two peaks for the two phases at the liquid-liquid phase transition in ST2 water. The distribution is clearly bimodal. Also the energy distribution shows bimodality as shown for the red distribution marked with a. The same is true for the density distribution in b. However for both distributions (a and b) the two peaks have different height: at low density is sampled more often, in b the high density shows a higher peak. Therefore they disagree on which phase the system is located. Only for the distribution of \( M = \rho + sE \), shown in c the two peaks have the same size. \( M \) is called the “ordering operator” [35], its analog in the Ising model is the spontaneous magnetization. The distribution \( E = \rho - sE \) on the other side shows only a Gaussian peak. It does not allow to distinguish between the phases and is therefore in analogy to the Ising model called “energy-like operator”.

In a phase transition of a fluid however the fluctuations of the energy and the density are correlated and the energy changes if the system undergoes a phase transition and both: energy and density could serve as an order parameter.
2.3. Order Parameters and How to Distinguish LDL and HDL?

2.5 shows this behavior in the contour plot and in the energy (a) and density (b) histograms. At this state at the phase transition near to the critical point, the energy histogram (a) suggests that the state is slightly in the LDL phase, whereas the density histogram (b) suggests the opposite. By mixing energy and density a new order parameter, called “ordering operator”, \( \mathcal{M} = \rho + sE \) is created for which the two maxima have the same height at the phase transition (c) in figure 2.5. The value of the parameter \( s \) is roughly such that a line with slope \( s \) goes through the two maxima in the contour plot. A more precise slope is the result of using \( s \) as a fitting parameter for the order parameter distribution function. With \( \mathcal{E} = \rho - sE \) an other quantity, the “energy-like operator” results (d), as the energy in the Ising model, also the “energy-like operator” is independent of the phase.

This field mixing is not only important for the order parameter distribution function, but it also affects the scaling of the specific heat for fluids. It does not behave as in the Ising model:

\[
C_p = L^d \left( \langle E^2 \rangle - \langle E \rangle^2 \right) / k_B T^2 \sim L^{\alpha/\nu} \quad (2.13)
\]

but as:

\[
C_p = L^d \left( \langle E^2 \rangle - \langle E \rangle^2 \right) / k_B T^2 \sim L^{\gamma/\nu} \quad (2.14)
\]

since not only the “energy-like” fluctuations are considered, but also some parts of the “ordering operator” like fluctuations which have the bigger exponent \( \gamma \) hiding the increase of the energy fluctuations with the smaller exponent \( \alpha \). Using the “energy-like operator” \( \mathcal{E} \) instead, gives back the correct exponent \( \alpha \):

\[
C_p = L^d \left( \langle \mathcal{E}^2 \rangle - \langle \mathcal{E} \rangle^2 \right) / k_B T^2 \sim L^{\alpha/\nu} \quad (2.15)
\]

2.3.2 Structural Order Parameter

In the following we show the definition of different structural order parameters. They are designed to distinguish between different phases by analyzing the geometrical structure. They serve especially well to distinguish between liquid and
crystalline structures. For simplicity, only the structure of the oxygen atoms, of the water molecules studied in this thesis, are considered. The structural order parameter can be defined on the bonds between two atoms or on the atoms themselves. There are also different ways on how the neighbors are chosen. Two definitions of neighbors are used: the first coordination shell consists of the four nearest neighbors. The second coordination shell is defined as the fifth to sixteenth nearest neighbor. For some structural order parameters the neighbors in the second coordination shell are better in distinguishing between HDL, LDL and ice than the first.

The structural order parameters typically are constructed evaluating the spherical harmonics for a given $l$ of the relative direction between two oxygen atoms. Different $l$’s are sensitive to different symmetries. The spherical harmonics for $l = 3$ for example are sensitive to the diamond structure, for $l = 6$ they are sensitive to the hexagonal closest package (hcp) structure. Since the crystalline structures are expected to be in hcp, diamond or a mix of these structures, these two values for $l$ are used. The definitions of $\theta_{ij}$ and $\varphi_{ij}$ are shown in Fig. 2.6.

### 2.3.2.1 $Q_6$

The order parameter $Q_6$ as defined by Steinhardt in 1983 [94] will be used to show that LDL scales like a liquid. This first needs the definition:

$$q_{i,m}^l = \frac{1}{4} \sum_{j \in n_i} Y_m^l(\vec{r}_{ij}), \quad -l \leq m \leq l$$

where $n_i$ are either the first or the second coordination shell neighbors and $\vec{r}_{ij} = \vec{r}_j - \vec{r}_i$ is the vector between particle $i$ and $j$ in some arbitrary coordination system, the quantity $q_{i,m}^l$ depends on this choice of the coordinate system. Averaging the quantities over all the particles $Q_{l,m} = \sum_{i=1}^{N} q_{i,m}^l$, and summing over all $m$:

$$Q_l = \frac{1}{N} \left( \sum_{m=-l}^{l} Q_{l,m} Q_{l,m}^* \right)^{1/2}$$

(2.16)
2.3. Order Parameters and How to Distinguish LDL and HDL?

Fig. 2.6: Definition of $\theta_{ij}$ and $\varphi_{ij}$ relative to the coordinate system. The quantities $Y_i^m(\theta_{ij}, \varphi_{ij})$ are dependent on how the coordinate system is chosen. The quantities $Y_i^m(\theta_{ij}, \varphi_{ij})Y_i^m(\theta_{ij}, \varphi_{ij})^*$ where $^*$ means the complex conjugated are independent of the definition of the coordinate system.

results in a quantity independent on the choice of the coordinate system. We used $Q_l$ for $l = 3$ and $l = 6$.

2.3.2.2 $q_l$

The local structural order parameter $q_l$ is defined using the above definition of $q_{i,l,m}$, averaged over the particles $i$ and summed over all $m$:

$$q_l = \frac{1}{N} \sum_{i=1}^{N} \sum_{m=-l}^{l} q_{i,l,m}$$  \hspace{1cm} (2.17)

where $N$ is the number of particles. Using this definition, $q_3$ and $q_6$ have been used. It turned out that $q_l$ calculated on the second coordination shell can distinguish
better between LDL and crystals than $q_l$ calculated on the first coordination shell.

2.3.2.3 $d_3$

The order parameter $d_3$ as defined by Ghiringhelli et al. in 2008 [29] is a bond based parameter designed to distinguish between a fluid and a diamond structure. It uses the $Y_{3m}$ spherical harmonics to identify the tetragonal symmetry of the diamond structure. To define $d_3$ the property

$$q_{3,m}(i) = \frac{1}{4} \sum_{i \in n_i} Y_{3m}\left(\frac{\vec{r}_{ij}}{|\vec{r}_{ij}|}\right)$$  \hspace{1cm} (2.18)

is used, where $n_i$ is the set containing the four nearest neighbors. In the initial definition, Ghiringhelli et al. used all particles and a smooth cutoff function. Renormalizing this quantity results in:

$$q'_{3,m}(i) = \frac{q_{3,m}(i)}{\left(\sum_{m=-l}^{l} q_{3,m}(i)q^*_3,m(i)\right)^{1/2}}.$$  \hspace{1cm} (2.19)

where $q^*_3,m(i)$ is the complex conjugate of $q_{3,m}$. This normalized quantity is then used to define:

$$d_3(i,j) = \sum_{m=-l}^{l} q_{3,m}(i)q^*_3,m(j),$$  \hspace{1cm} (2.20)

for $i$ and $j$ nearest neighbors. This defines a quantity between $-1$ and $1$ where a perfect structure of both, diamond and graphite has a value of $-1$. This parameter is used to identify the largest crystal and calculate its size. A molecule is part of a crystal if three out of its four bonds with its nearest neighbors have a $d_3$ smaller than $d_c = -0.87$. This is the same cutoff as used by Ghiringhelli et al. in 2008 [29].

2.3.3 The Radial Distribution Function $g(r)$

The radial distribution function gives the probability of finding any particle $i$ at the distance $r = |\vec{r}_i - \vec{r}_j|$ away from a particle $j$, relative to the probability expected
from a purely random distribution at the same density [7]:

\[ g(\vec{r}) = \frac{V}{N^2} \left\langle \sum_i \sum_{i \neq j} \delta(r - r_{ij}) \right\rangle \]  

(2.21)

Since a fluid has no long range order, \( g(r) \to 1 \) for \( r \to \infty \). The quantity \( g(r) \) can be used to analyze the structure of a fluid or crystal. For this, \( g(r) \) can be split up into \( g(r) = \sum_{i=1}^{\infty} g_i(r) \) where \( g_i(r) \) is the contribution of the \( i \)-th nearest particle, as it is defined by Saika et al [82]. The radial distribution function \( g(r) \) can also be used to estimate the ensemble average of a quantity \( \mathcal{A} \) if the pair function of this quantity \( a(r) \), which describes the average amount of \( \mathcal{A} \) for two particles at distance \( r \), is known [7]:

\[ \langle \mathcal{A} \rangle = \left\langle \sum_i \sum_{i>j} a(r_{ij}) \right\rangle = \frac{1}{2} N \rho \int_0^{\infty} a(\vec{r}) g(\vec{r}) 4\pi r^2 dr \]  

(2.22)

The energy can then be written as:

\[ E = \frac{3}{2} N k_B T + 2 \pi N \rho \int_0^{\infty} r^2 v(r) g(r) dr \]  

(2.23)

and pressure times volume is:

\[ PV = N k_B T + \frac{2}{3} \pi N \rho \int_0^{\infty} r^2 w(r) g(r) dr \]  

(2.24)

### 2.3.4 Intermediate Scattering Function

In experiments the intermediate scattering function is a quantity easy to measure. It is the Fourier transformation of the density and can be written as [26]:

\[ S(\vec{r}, t) = \frac{1}{N} \left\langle \sum_{j,k} e^{i \vec{k} \cdot (\vec{r_j}(t) - \vec{r_k}(t))} \right\rangle \]  

(2.25)

where \( \langle . \rangle \) stands for the ensemble average, \( \vec{r}_l(t) \) is the position of particle \( l \) at time \( t \), \( \vec{k} \) the wave vector and \( k \) its magnitude \( |\vec{k}| \). \( S(\vec{k}, t) \) describes the time evolution

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2. Phase Transitions and Critical Phenomena

of the spatial correlation along the wave vector $\vec{k}$. The correlation time is also calculated using the intermediate scattering function:

$$C_{O\!O}(k, \tau) = \langle (S_{O\!O}(k, t) - \langle S_{O\!O}(k, t) \rangle_t) \times (S_{O\!O}(k, t + \tau) - \langle S_{O\!O}(k, t + \tau) \rangle_t) \rangle_t,$$

where $\langle . \rangle$ stands for the average over time $t$. As $k$ the first three maxima of $\langle S_{O\!O}(k, t) \rangle_t$ are investigated and the $k$ for which $C_{O\!O}(k, \tau)$ decays slowest is finally used. The correlation time is defined as the time after which this function falls below $1/e$ (Fig. 2.7).
2.4 How to Locate a Critical Point?

In different studies the critical point has been located using different techniques:

**Increase of Response Functions**  As the response functions $C_p$, $\kappa_T$ and $\alpha$ have a maximum at the Widom line and will diverge at the critical point, the Widom line can be found as the line where the response functions have their maximum for a given temperature or pressure and the critical point can then be estimated as the point on the Widom line where the response functions have a maximum. This strategy has been chosen for example by Abascal and Vega in 2010 [4].

**Van der Waals loops**  Another popular way of locating the critical point is to look at the van der Waals loops. At the first order phase transition line the isotherms are not monotonic in the $\rho - p$ diagram, but they show a small local minimum followed by a local maximum as shown in figure 2.8. The closer the temperature of the isothermal becomes, the bigger becomes the difference between the two local extrema. At the critical isothermal no extremum exists anymore, but only a saddle point. The critical point can be localized between the last isothermal with minimum and maximum and the first line with monotonic behavior. This has been done by Paschek [74], Brovchenko[16] and Cuthbertson [22].

The criterion of a saddle point can also be formalized: So the critical point should be located where $\frac{\partial \rho}{\partial P} = 0$ and $\frac{\partial^2 \rho}{\partial P^2} = 0$.

**Challa-Landau-Binder parameter**  In a simulation at constant pressure, the system can switch between the two phases LDL and HDL at the first order phase transition line and show therefore a bimodal density (or energy) histogram. The temperature of the phase transition for a given pressure can be estimated in this way what gives the first order phase transition line. The critical point can be located as the end of this phase transition, which can be detected as the end of bimodality, since a system at the Widom line is not changing between LDL and HDL but stays at a phase in between.
Fig. 2.8: Schematic figure of the van der Waals loop. The subcritical isotherms show a non monotonic behavior with a minimum and a maximum in the pressure. The supercritical isotherm shows a monotonic behavior and the critical isotherm shows a monotonic behavior with a saddle point at the critical point.

However for finite system sizes also systems at the Widom line show bimodal behavior. To be sure that also a system at the thermodynamic limit shows a bimodal density distribution, a scaling for the bimodality for infinite system has to be performed and therefore a measure for the bimodality is needed. Such a measure is the Challa-Landau-Binder parameter defined for the quantity $X$:

$$\Pi = 1 - \frac{\langle X \rangle^4}{3 \langle X^2 \rangle^2} \tag{2.26}$$

Where $X$ is either energy or density. The Challa-Landau-Binder parameter is $2/3$ for a monomodal distribution and smaller otherwise. The critical point is then located between two pressures for which the first shows a Challa-Landau-Binder parameter extrapolated for an infinite system size to $2/3$ and a the second shows
2.4. How to Locate a Critical Point?

A Challa-Landau-Binder parameter extrapolated for an infinite system size to less than \(2/3\). This method has been used for example by Strekalova et al [98].

**Order parameter distribution function** As we know from 2.3.1 the order parameter distribution function has a universal shape at the critical point. Its shape is therefore known if the universality class is known (namely the three dimensional universality class in the case of the LLCP). The critical values are chosen in such a way that the critical order parameter distribution function is best fitted by the order parameter distribution function obtained from direct simulation or histogram reweighting of results originating from simulations. This method has been used by Liu et al. [53].
2. Phase Transitions and Critical Phenomena
Molecular Dynamics

3.1 Introduction

Molecular dynamics is a technique to calculate dynamically interacting particles by numerical integration of the Newton equations. The first steps have been taken by Alder and Wainwright in 1957 [5, 6], by modeling perfect elastic collision. In 1964 Rahman took the next step and did the first simulation of Lennard-Jones particles [78]. It took another seven years until the first studies using water models were done by Rahman and Stillinger [78], which have been improved by Stillinger in 1974 [96].

The idea is to integrate Newton’s equations for a given potential energy function using numerical integration schemes.

\[ \vec{F} = m\ddot{\vec{x}} \]  
\[ \vec{F} = -\vec{\nabla}U \]  

The simplest and most often used potential function (and thereof derived force) is the Lennard Jones potential:

\[ U_{LJ}(\vec{r}_{ij}) = -4\varepsilon \left( \left( \frac{\varepsilon}{|\vec{r}_{ij}|} \right)^6 - \left( \frac{\varepsilon}{|\vec{r}_{ij}|} \right)^{12} \right) \]
3. Molecular Dynamics

Where $\vec{r}_{ij} = \vec{r}_i - \vec{r}_j$, where $\vec{x}_i$ is the position of the molecules $i$. Molecular dynamics simulations are chaotic in the way that two simulations with initial conditions having very small differences or two simulations starting at the same initial condition, but one integrating with very small errors, can lead to totally different particle positions after a reasonable time. Integration errors on computer however cannot be made infinitesimally small. In practice the integration step has to be chosen small enough, such that integration errors will not harm the simulation results, i.e. the thermodynamic averages.

As integration scheme the Velocity Verlet algorithm can be used:

$$\vec{x}(t + \Delta t) = \vec{x}(t) + \dot{\vec{x}}(t)\Delta t + \frac{1}{2} \ddot{\vec{x}}(t)\Delta t^2$$  \hspace{1cm} (3.4)

$$\dot{\vec{x}}(t + \Delta t) = \dot{\vec{x}}(t) + \frac{1}{2} \left( \ddot{\vec{x}}(t) + \ddot{\vec{x}}(t + \Delta t) \right) \Delta t$$  \hspace{1cm} (3.5)

The number of simulated particles is much smaller than in experiments. Therefore the fraction of boundary particles over the particles in the bulk is much bigger than in experiments and boundary effects are overestimated. To avoid this, periodic boundary conditions are introduced and forces have not only to be calculated with all other molecules but with all other molecules at positions $\pm n_i L_i$ for $n_i \in \mathbb{N}$ and $i \in \{x, y, z\}$. Using this trick, the number of particles becomes effectively infinity and as the potential not decaying to zero at finite length, an arbitrary cutoff is introduced, which has to be treated carefully.

As a result of a molecular dynamic simulation structural properties as introduced in section 2.3 are of interest. But first thermodynamic observables as the temperature $T$, the stress or pressure $P$, the density $\rho$ and the energy $U$ are important quantities of such simulations. The temperature is defined through the kinetic energy:

$$T = \frac{2}{3Nk_B} E_{kin} = \frac{1}{3Nk_B} \sum_{i=1}^{N} \dot{\vec{r}}_i^2 m_i.$$  \hspace{1cm} (3.6)

where $k_B$ is the Boltzmann constant, $N$ is the number of particles and the sum
runs over all the particles. The density is defined simply as:

\[ \rho = \sum_{i=1}^{N} m_i / V. \]  (3.7)

where \( V = L_x L_y L_z \) is the volume defined as the product of the length, height and depth of the simulation box. The energy is nothing else but the sum over all the inter particle energies:

\[ U = \frac{1}{2} \sum_{i=1}^{N} \sum_{j \neq i} U(\vec{r}_{ij}). \]  (3.8)

The pressure is calculated using the internal viral \( \mathcal{W} \):

\[ P = \frac{N k_B T + \mathcal{W}}{V} = \frac{N k_B T + \frac{1}{6} \sum_{i=1}^{N} \sum_{j \neq i} \vec{r}_{ij} \cdot \vec{f}_{ij}}{V}. \]  (3.9)

Note that for the case of periodic boundary conditions this is only true if pair-additive water models are used, see Ref. [55]. As mentioned earlier a cutoff is introduced for the Lennard Jones potential at distance \( r_c \). This cutoff however affects the total energy and the pressure. They can be corrected using the following approximation assuming \( g(r) = 1 \) in equation 2.23 for \( r > r_c \) see also [7], p. 65:

\[ E_{\text{full}} \approx E_c + E_{\text{LRC}} = E_c + 2\pi N \rho \int_{r_c}^{\infty} r^2 u(r) dr \]  (3.10)

where \( u(r) \) is the intermolecular potential function. The correction for the pressure can be done using equation 2.24.

\[ (PV)_{\text{full}} \approx (PV)_c + (PV)_{\text{LRC}} = (PV)_c + \frac{2}{3} \pi N \rho \int_{r_c}^{\infty} r^2 w(r) dr \]  (3.11)

where \( w(r) \) is the intermolecular pair viral function \( w(r) = r \frac{d \sigma(r)}{dr} \). Due to long range correlations near to a critical point the approximation \( g(r) = 1 \) for \( r > r_c \) may lead to worse results with correction than without. I therefore did not include these corrections.
3.2 Water Models

Over time many different water models have been proposed. There exist models with rigid and with flexible structure, models including polarization effects and models including three body forces (as the mW model by Molinero and Moore [66]). Here we discuss the very common rigid molecule potentials. They differ by the number of particles (atoms plus interaction sites) and their parameterization. In figure 3.1 different arrangements for the atoms and ghost sites are shown. For the parametrization some parameters are approximately known, for example the distance between the oxygen atom and hydrogen atom or the angle between the two hydrogen atoms. The other parameters are then carefully chosen in such a way that the properties such as phase transitions and density maxima take place at the correct pressure and temperature. In table 3.1 the values for different water models are shown.

In this thesis the ST2 water potential is investigated. It has often been used to study supercooled water. It has a higher self-diffusion near the liquid-liquid critical point than other water potentials, since the LLCP is outside the glassy region. The ST2 potential has a speciality: A modulation function is applied to the electric potential, this modulation function removes electronic interaction for nearly touching molecules:

\[
S = \begin{cases} 
0 & (0 \leq R_L), \\
\frac{(r_{ij} - R_L)^2(3R_U - 2r_{ij})}{(R_U - R_L)^2} & (R_L \leq r_{ij} \leq R_U) \\
1 & (R_U \leq r_{ij}). 
\end{cases}
\]

Where \( R_L = 2.0160\text{Å}, \) \( R_U = 3.1287\text{Å} \) and \( r_{ij} \) is the distance between the center particles (oxygen atoms) of the interacting molecules.
### 3.2. Water Models

<table>
<thead>
<tr>
<th>Model</th>
<th>$\sigma$/Å</th>
<th>$\varepsilon$/kJmol$^{-1}$</th>
<th>$r_1$/Å</th>
<th>$r_2$/Å</th>
<th>$q/e$</th>
<th>$\vartheta^\circ$</th>
<th>$\varphi^\circ$</th>
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<tbody>
<tr>
<td><strong>3 sites:</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SPC [14]</td>
<td>3.166</td>
<td>0.65</td>
<td>1</td>
<td>-</td>
<td>0.410</td>
<td>109.47</td>
<td>-</td>
</tr>
<tr>
<td>SPC/E [13]</td>
<td>3.166</td>
<td>0.65</td>
<td>1</td>
<td>-</td>
<td>0.4238</td>
<td>109.47</td>
<td>-</td>
</tr>
<tr>
<td>TIP3P [44]</td>
<td>3.15061</td>
<td>0.6364</td>
<td>0.9572</td>
<td>-</td>
<td>0.4170</td>
<td>104.52</td>
<td>-</td>
</tr>
<tr>
<td><strong>4 sites:</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TIP4P [44]</td>
<td>3.15365</td>
<td>0.6480</td>
<td>0.9572</td>
<td>0.15</td>
<td>0.52</td>
<td>104.52</td>
<td>52.26</td>
</tr>
<tr>
<td>TIP4P/EW [37]</td>
<td>3.15365</td>
<td>0.680946</td>
<td>0.9572</td>
<td>0.125</td>
<td>0.52422</td>
<td>104.52</td>
<td>52.26</td>
</tr>
<tr>
<td>TIP4P/Ice [3]</td>
<td>3.1668</td>
<td>0.8822</td>
<td>0.9572</td>
<td>0.1577</td>
<td>0.5897</td>
<td>104.52</td>
<td>52.26</td>
</tr>
<tr>
<td>TIP4P/2005 [1]</td>
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<td>0.7749</td>
<td>0.9572</td>
<td>0.1546</td>
<td>0.5564</td>
<td>104.52</td>
<td>52.26</td>
</tr>
<tr>
<td><strong>5 sites:</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>ST2 [95]</td>
<td>3.1</td>
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<td>1</td>
<td>0.8</td>
<td>0.24357</td>
<td>109.47</td>
<td>109.47</td>
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<tr>
<td>TIP5P [56]</td>
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<td>0.9572</td>
<td>0.7</td>
<td>0.2410</td>
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<td>109.47</td>
</tr>
<tr>
<td>TIP5P/EW [79]</td>
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<td>0.7</td>
<td>0.2410</td>
<td>104.52</td>
<td>109.47</td>
</tr>
</tbody>
</table>

Table 3.1: Different parameters for selected water models. The different geometries are shown in figure 3.1. $109.47^\circ$ is the angle in a perfect tetrahedral structure, $104.52^\circ$ is the value for water. The TIP4P potential has been reparameterized three times for different purposes. TIP4P/ice is a good model for the different phases of ice. TIP4P/2005 is the water model best fitting the water properties. The ST2 potential is an old but in the field of super cooled water often used water model, since its dynamics is faster than at the other water models and the simulation times therefore shorter.
3. Molecular Dynamics

3.3 Molecular Dynamic Techniques

3.3.1 Electrostatic Forces

As the electrostatic potential decays only with $1/r$ for $r$ being the distance from the charge, it should not be cut without taking the long range into account. The
probably most often used method is the Ewald summation method. It splits the
electric field in short range, where the field is highly oscillating, and and long range
where the electric field has oscillation frequencies. The short range part is calculated
in real space, the long range part is calculated in the Fourier space, which does not
need too many \( \vec{k} \) vectors because the high frequencies are dealt with in the real
space [7].

An other method is the reaction field method [11]. For every molecule \( i \) the reaction
field method consists of two parts: short-range contributions from molecules nearer
to molecule \( i \) than a cutoff \( r_c \), are treated normally. Molecules further away than
\( r_c \) are considered to act like a dielectric continuum responding to the “cavity” \( R_i \)
consisting of all the molecules inside a sphere with radius \( r_c \) around molecule \( i \).
The effect of this dielectricum on molecule \( i \) is:

\[
\vec{E} = \frac{2 (\varepsilon_s - 1)}{2\varepsilon_s + 1} \frac{1}{r_c} \sum_{j \in R_i} \vec{\mu}_j
\]

Where the summation runs over all the molecules in \( R_i \) including molecule \( i \) itself.

If a molecule moves from outside the cavity into the cavity and therefore reacting
now directly with molecule \( i \), the energy might change because the now new term
of the direct contribution has necessarily to be the same as that from the indirect
treatment coming from the reaction field. This is affecting the energy conservation
negatively. This is avoided by weakening the explicit interactions using a linear
interpolation function [7].

In order to be comparable with Poole et al. [77], I used the reaction field method.

### 3.3.2 How to Constrain the Atoms Inside the Molecules?

Molecules can be modeled by introducing springs between different atoms. In order
to hold the molecule together, such spring forces would need to be larger than the
forces of the force field and would therefore lead to smaller time steps than otherwise
needed. To avoid smaller time steps the atoms can be constrained inside a molecule.
For this work the Shake algorithm introduced by Ryckaert et al. in 1977 [81] has
been used to constrain the atoms inside the water molecules.

3.3.3 Thermostat

Basic molecular dynamics is just integrating Newton’s equations and therefore preserves the energy, so simulates the microcanonical ensemble. To compare simulations to experiments, it is better to choose the same ensemble, namely the one at constant temperature. Also for simulations investigating a phase transition, constant temperature ensembles are favored. Several methods have been proposed for this purpose and discussed in textbooks as for example Allen and Tildesley [7]. The simplest idea to bring the temperature to a given value is to rescale all the velocities to guarantee a given temperature, however this strategy doesn’t lead to a Maxwell-Boltzmann distribution of the velocities. Andersen [8] proposed to choose the velocities randomly from a Maxwell-Boltzmann distribution after a given time interval. This approach introduces some kind of randomness and is not the most desired way. In this work the Nosé-Hoover thermostat [36, 67–70] has been used. It is proven to provide a Maxwell-Boltzmann distribution of the velocities. However it can introduce non physical energy fluctuations [20], if the parameters are not chosen carefully.

The Nosé-Hoover thermostat introduces a velocity dependent force $\xi \vec{p}$ changing the velocity of a particle, see equation 3.14. $\xi$ itself evolves according to equation 3.15.

\[
\dot{\vec{r}} = \frac{\vec{p}}{m} \quad (3.13)
\]

\[
\dot{\vec{p}} = f - \xi \vec{p} \quad (3.14)
\]

\[
\dot{\xi} = \frac{f}{Q} (k_B T_{is} - k_B T_{shoud}) \quad (3.15)
\]

$f$ is the number of degrees of freedom and $Q$ is called “thermal inertia parameter” and is controlling how fast $\xi$ is responding to a wrong temperature,
3.3. Molecular Dynamic Techniques

3.3.4 Barostat

Since the two phases LDL and HDL differ mostly in their density it is interesting to see how the system is behaving at constant pressure. For the Berendsen barostat the coordinates and the box size are scaled every n-th time step according to eqn 3.16 - 3.18:

\[
\mu = \left( 1 - \frac{\Delta t}{\tau_P} (P - P_0) \right)^{1/3}
\] (3.16)

\[
\vec{r}_i \rightarrow \mu \vec{r}_i
\] (3.17)

\[
L \rightarrow \mu L
\] (3.18)

Where \( \tau_P/n \) is the decay time.

A more modern barostat has been proposed by Anderson [8, 59] and has been designed in a similar spirit as the Nosé-Hoover thermostat. New coordinates \( s \) are introduced:

\[
\ddot{s}_i = V^{-1/3} \ddot{r}
\] (3.19)

\[
\dot{s}_i = V^{-1/3} \dot{v}
\] (3.20)

\[
\ddot{s} = \frac{f}{mV^{1/3}} - \frac{2}{3} \frac{\dot{s}\dot{V}}{V}
\] (3.21)

\[
\ddot{V} = \frac{(P_{\text{is}} - P_{\text{should}})/Q}{Q}
\] (3.22)

\( Q \) is called mass with units \((\text{mass})(\text{length})^{-4}\). It has been suggested to use a value: \( Q\sigma^4/m = 0.0027 \) [8] if used together with a Lennard Jones potential. By testing different values of \( Q \), we found unphysically strong fluctuations in density for some values of \( Q \). As the measured decay time did not seem to depend monotonously on \( \tau_P \), we decided to use the Berendsen barostat, which is simpler to handle and not showing these unphysical effects.
Histogram reweighting is used to interpolate between the simulated state points. It reduces the amount of simulations and hence the computation time. Histogram reweighting has been initially introduced for Monte Carlo simulations by Salsburg et al. in 1959 [83]. The idea behind the technique is to add up the statistics of several simulations, reweighted with the correction to the Boltzmann weight $e^{\Delta E/k_B T}$, where $\Delta E$ is the difference in the energy between the two state points. For the theory and the algorithm itself we follow Panagiotopoulos work of the year 2000 [73] where he does the reweighting for the grand canonical ensemble. However, I work in the $NPT$ ensemble.

As we use the $NPT$ ensemble, the pressure $P$ and the temperature $T$ respectively the inverse temperature $\beta = 1/k_B T$ are held constant and serve therefore as external parameters. The variables $E$ (total energy) and $V$ (volume) fluctuate during the run and are the quantities of interest. For the histogram reweighting the probability distribution function $f(E,V)$ for these two variables is needed:

$$f(V,E) = \frac{\Omega(V,E) \exp(-\beta E - \beta V P)}{\Theta(V,\beta)}.$$  \hspace{1cm} (3.23)

where $\Omega(V,E)$ is the density of states and $\Theta(V,E)$ is the partition function for the $NPT$ ensemble. The distribution $f(V,E)$ can be measured from the simulation, but neither $\Omega(V,E)$, nor $\Theta(V,E)$ are known at this point. However $\Theta(V,E)$ is constant throughout a run and therefore we can rewrite eqn 3.23 as:

$$\Omega(V,E) = f(V,E) \exp(\beta E + \beta V P) c$$ \hspace{1cm} (3.24)

where $\Theta(V,\beta) = c$ is constant. From equation 3.24 the entropy is obtained:

$$S(N,V,E)/k_B = \ln \Omega(N,V,E) = \ln f(V,E) + \beta E + \beta PV + C,$$ \hspace{1cm} (3.25)

where $C = \ln c$. Since $C$ is a constant depending on the external parameters $\beta$ and $P$, this equation is not valid for different values of $\beta$ and $P$. But for two simulations
with different $\beta$ and $P$ which have an overlap in $E$ and $V$, the constants $C$ can be tuned in such a way, that the functions are identical in the region of overlap. The probability for a state with energy $E$, volume $V$, inverse temperature $\beta$ and pressure $P$ is then given as:

$$p(V, E, T, P) = \frac{\sum_{i=1}^{R} f_i(V, E) \exp \left[ -\beta E - \beta PV \right]}{\sum_{i=1}^{R} K_i \exp \left[ -\beta_i E - \beta_i PV - C_i \right]}$$  \hspace{1cm} (3.26)

where $K_i$ is the number of states observed in run $i$:

$$K_i = \sum_{V, E} f_i(V, E).$$  \hspace{1cm} (3.27)

The constants $C_i$ are called weights and are defined as:

$$\exp(C_i) = \sum_{E} \sum_{V} p(V, E, P_i, \beta_i).$$  \hspace{1cm} (3.28)

Equations 3.26 and 3.28 depend on each other. They are solved in a self-consistent way by iterating $C_i$ until convergence is achieved. The nominator and denominator of equation 3.26 can become quite big and double precision floating point data types have problems to handle them. It is therefore convenient to rewrite it as:

$$p(V, E, T, P) = \frac{\sum_{i=1}^{R} f_i(V, E)}{\sum_{i=1}^{R} K_i \exp \left[ -\beta_i E - (\beta_i P - \beta P)V - C_i \right]}$$  \hspace{1cm} (3.29)

The energy and density and volume at an intermediate state point is then easily calculated as:

$$\langle U \rangle_{P, \beta} = \sum_{E} \sum_{V} E p(V, E, P, \beta)$$

and

$$\langle \rho \rangle_{P, \beta} = m \sum_{E} \sum_{V} \frac{p(V, E, P, \beta)}{V}$$

$$\langle V \rangle_{P, \beta} = \sum_{E} \sum_{V} V p(V, E, P, \beta),$$
where $m$ is the mass of the simulated system.
Error bars are estimated by comparing data from real simulations with reweighted data. The differences are typically biggest near a phase transition since already the molecular dynamic simulations have more problems to collect good statistics at this points in the phase diagram. In figure 3.2, we show the extreme case of a first order phase transition at 240 K where we know that the system has problems to equilibrate the phase at lower density. It shows an error in the temperature of $\approx 0.25$ K, estimated by the temperature difference between the simulated histogram and the best fitting histogram achieved using histogram reweighting. This extreme case should show extreme error bars and we can assume that error bars are smaller in all other cases.
Fig. 3.2: Comparison of the density histogram based on simulation data and the density histogram based on histogram reweighting, in order to estimate the error bars. Lines in blue show the histograms for simulations at 234 K, 237 K and 240 K, which are used for the reweighting process. In red the histogram with data originating from a run at 238 K is shown. It serves as a control curve for the reweighted histogram. The curve originating from the histogram reweighting process is shown in green. In the upper panel it is shown for 238 K, the same temperature as the control run. In the lower panel for 237.75 K, which has been chosen to fit the red curve the best possible. This suggests an error in the temperature of 0.25 K and gives also error bars on the density distribution. For all the simulations in this figure, the number of molecules is 343 and the pressure is 240 MPa.
3. Molecular Dynamics
Investigation of Supercooled ST2 Water

This chapter shows the work that has been done for this thesis and mainly follows Ref. [47]. It starts with a section where the simulation code is validated and the “No mans land” is investigated in the constant volume ensemble. The next section deals with the simulation protocol in the constant pressure ensemble. Single simulations at constant pressure are investigated in the third section. Especially the interplay between the liquid phases, the correlation time and crystallization are considered. The next two sections are dealing with the localization of the critical point and its universality class. It is then shown that the LDL phase is liquid and not a crystalline phase as proposed in by Limmer and Chandler in [51]. The chapter ends with two sections concerning the different structures. The first analyzes LDL and HDL using the intermediate scattering function and the radial distribution function. The second is interested to find the best structural order parameter to distinguish between LDL and observed crystals.
4.1 Investigations in the NVT Ensemble

The code is validated in the NVT ensemble by simulating the same state points as published in Poole et al. [76] Fig. 1 b). The same density of 0.83g/cm³ and number of 216 (6x6x6) molecules are used. Averaging at each state point over ten simulations with different initial conditions allows to estimate the error bars. In Fig. 4.1 I compare our results with those of Poole et al. [76] and the agree well within the error bars. This gives confidence that the calculations are correct, respectively that the simulation code is free of bugs.

According to Landau and Lifschitz [50] two phases can only be distinguished if they are in contact and exist at the same time, i.e. a phase segregation. For such a phase segregation the system has to pay an energy penalty proportional to the surface of the phase boundary. To control the place of the phase boundary, simulations in the constant volume ensemble have been performed in a rectangular box where the length in z-dimension is twice the length of the other two dimensions. For the system it is energetically optimal to exhibit a phase boundary perpendicular to the z-direction. In Fig. 4.2 a snapshot at 60 ns of this simulation showing the oxygen atoms colored according their local $q_6^{(2)}$ orientation order parameter is presented. The phase segregation is obvious. To present time dependence, the mean density is projected on the z-axis and plotted versus the time using a contour plot. It clearly shows: the system is phase segregated during all time steps. The position of the two phases however is changing with time.

In the NVT ensemble the critical point can be located by checking the crossing point of the isochores. For this I have simulated 36 state points in the NVT ensemble during 100ns. The first 20ns of these 100ns were skipped as thermalization time and the following 80ns were used for the evaluation. For each state point two different simulations with different initial conditions served to estimate the error. The time step for all the simulations is 1fs. The cutoff is 7.8Å and the shake tolerance is $2 \cdot 10^5$Å. The thermal inertia parameter of the thermostat is $Q = 10$nm²g.

The temperature-pressure diagram for the different isochores is shown in Fig. 4.3.
Fig. 4.1: Comparison with Fig. 1 b) of Poole et al 2005 [76]. NVT simulation at 0.83g/cm$^3$ using $N = 216$ molecules. I estimated the error bars calculating the variance over 10 different simulations with different initial conditions for every state point. The same results as Poole et al. are found within the error bars.
Fig. 4.2: Constant volume simulation at $T = 240\text{K}$ and $\rho = 0.95\text{g/cm}^3$ in a rectangular box where the height is twice as long as the length and the depth. The system segregates perpendicular to height, see the snapshot at 60 ns where the oxygen atoms are shown and colored according to the local $q_{6}^{(2)}$ parameter. The contour plot shows the mean density projected on the z-axis, shown as percentage of the total height. They system shows a phase segregation for the entire time during the 100ns.

The critical point is estimated by the crossing of the isochores. This estimation leads to a critical temperature between 250K and 251K and a critical pressure between 180MPa and 190MPa. These temperatures are higher than Poole et al.
Fig. 4.3: Location of the critical point in the NVT ensemble. Using different isochores with 216 molecules for temperatures near the liquid-liquid-critical point the location of the critical point is estimated by the crossing of the isochores leading to a critical pressure between 180MPa and 190MPa and a critical temperature between 250K and 251K.

estimated [76], but probably inside their unspecified error bars. We will see that the calculation in the NPT ensemble with larger system sizes leads to a higher critical pressure and a lower critical temperature.

In conclusion the results of Poole et al. [76] have been validated in the constant
volume ensemble and furthermore constant segregation between the two phases have been found. In the next chapter we will investigate the constant pressure ensemble.
4.2 Simulation Protocol in the NPT Ensemble

Molecular dynamic simulations in the NPT ensemble for four different system sizes: 216, 343, 512 and 729 molecules and for many state points as shown in Fig. 4.4 have been performed. The simulated pressures reach from 190MPa (subcritical pressure), where the Widom line is crossed by changing from LDL to HDL, to 240MPa (supercritical pressure) where a first order phase transition takes place. LDL simulations at 240MPa however take much too long to equilibrate properly, therefore simulations at this pressure can only be used to determine the temperature of phase transition assuming there is a phase transition between LDL and HDL. As the other system sizes, the system size of 216 molecules shows phase transition behavior, but the position of the critical point strongly deviates from the ones of the larger system sizes. Therefore this system size has to be handled with a lot of care.

For the simulations I used the following protocol consisting of three steps: 1) For a chosen initial density a constant volume simulation is performed at 300K for 1ns (first pre-run). 2) The ensemble is then changed to NPT by adding a Berendsen barostat with $\tau_P = 6$ps and the temperature is changed down to 265K, where the system is going to the HDL phase for all our analyzed systems during 1ns of thermalization. 3) After this two pre simulations the system is quenched to the final pressure and temperature and the production simulations start, from which the first 100 – 200ns are cut as thermalization time. The length of the thermalization time will be discussed in the next section.

For several state points multiple simulations differing by the initial condition are performed. Changes in the initial densities of the first pre-run were responsible for the differences of the initial conditions. As the second pre-run brings them all to the same density again and its duration of 1ns is much longer than the correlation time in the HDL phase (see next section), no correlation with the initial density remains for any property, as for example the correlation time.
Fig. 4.4: Overview over the state points where simulations have been done. Different symbols show different system sizes. The background coloring indicates the phase. Blue: LDL, red: HDL, violet: at the phase transition or Widom line, where both liquids are sampled. The yellow line shows the border below which simulations could not be equilibrated.
4.3 Investigation on the Individual Simulations

Before analyzing averaged values, a look at individual time evolutions is taken to get an understanding of their behavior and to make sure no configuration is missed. I show this analysis to demonstrate how carefully the single simulations are analyzed in order to find all crystallization events. These events are interesting because it has been proposed that LDL is not a liquid, but a crystalline phase or at least is unstable against crystallization [51] and therefore crystallization events should happen very often.

To show how the individual simulations are analyzed let us consider 343 molecules at a pressure of $195\text{MPa} < P_c$ where the liquid is subcritical (i.e. at the Widom line and not at the first order phase transition) as we will see later. By changing the temperature the Widom line can be crossed. As the temperatures rise from 243K to 252K the system is changing from an LDL to a HDL state continuously without a phase transition, by crossing the Widom line. The correlation time for different pressures using the procedure presented in section 2.3.4 is studied.

Using the intermediate scattering function as defined in section 2.3.4 on the oxygen atoms $S_{OO}(k,t)$ the correlation of $S_{OO}(k_1,t)$ and $S_{OO}(k_1,t + \tau)$ is determined to obtain the time correlation function. The value $k_1$ is defined as the position of the first maximum in $\langle S_{OO}(k,t) \rangle_t$. The correlation time is defined as the time till the correlation function falls below $1/e$. The first 200ns have been skipped to thermalize and the remaining 800ns have been used for the evaluation. Fig. 4.5 shows this evaluation for several temperatures for the pressure and system size mentioned above. Apparently the HDL phase is evolving nearly four orders of magnitude faster than LDL. However LDL can be equilibrated during the time of simulation, as the simulation time is 10 times the correlation time of the system with the longest correlation time. The correlation becomes noisy for big correlation times because of the small of statistics.

In Fig. 4.6 this thermalization time is investigated for the simulation with the longest correlation time. For this purpose thermalization times of 200, 400, 600
4. Investigation of Supercooled ST2 Water

Fig. 4.5: Correlation times for different temperatures at the subcritical pressure of 195 MPa ($P_c \approx 206MPa, T_w(195MPa) \approx 249K$) for 343 molecules. The first 200 ns have been skipped as thermalization time, the other 800 ns have been used for the evaluation. The dotted line is at $1/e$, the correlation time is defined as the time it takes until the correlation has fallen below $1/e$. The point $t = 0$ is shown at 5ps as 0 is not visible on the logarithmic scale.

and 800 ns were tested and very similar behavior has been found. The spreading gives a measure for the error bar. To see how small the thermalization time can be made, thermalization times of 0-50 ns have been investigated (shown in Fig. 4.6 as thicker lines). For these thermalization times the correlation time drops and therefore these thermalization times are considered to be too small. The dashed-dotted line with a thermalization time of 100 ns gives a reasonable correlation time.
It is therefore assumed that thermalization times of 100 ns are enough, consistent with the fact that the correlation time is around 100 ns.

Fig. 4.6: Variation of the thermalization and evaluation time for the time correlation function for 195 MPa, \(T=243\) K, and 343 molecules. In order to determine how long the thermalization time has to be chosen and how big the error on the correlation time is. Since all curves with the exception of the green one (400-600 ns) have very similar correlation times, the error seems to be quite small. 200 ns as thermalization time seem to be enough. A thermalization time of 100 ns already seems to give a reliable correlation time, what of course is consistent with the correlation time of about 100 ns.

Next it is studied how the density behaves at 195 MPa. As the system changes from LDL to HDL when increasing the temperature, the density should increase.
In Fig. 4.7 the density versus time is plotted for the ten simulations investigated before. The simulations with the lowest two temperatures have a density below 0.90g/cm³. At a temperature of 245K, the density is still at this low value for most of the times, but has spikes increasing up to 0.95g/cm³. These spikes become more frequent and their width increases with increasing temperature, until 249K where the system is fluctuating heavily between 0.90g/cm³ and 1g/cm³ and can not decide in which phase it likes to stay. Increasing the temperature further the system stays more and more in the high-density phase and has some spikes into the LDL phase.

As this system at 195MPa has a pressure below \( P_c \) (subcritical) the change of the phase is not really a phase transition but a smooth crossing of the Widom line. As the fluctuations are largest for 249K the Widom temperature for this pressure can be located at \( T_W(195\text{MPa}) \approx 249\text{K} \). For some temperatures up to eleven samples with different initial conditions have been simulated.

For some temperatures I did not only simulate one sample, but up to eleven samples with different initial conditions. The samples differ in the initial density of the first step in the simulation protocol. Eleven different samples were simulated for example for the temperature of 246K and 195MPa. If the correlation times are checked for these samples as done in Fig. 4.8 we see some fluctuations for a correlation time around 3–30ns and two outliers, with an initial density of 0.88g/cm³ and 0.93g/cm³ respectively.

The time behavior of the density for these different simulations is checked, in order to understand why these two simulations are different, see Fig. 4.9. In these simulations the density is mostly below 0.85g/cm³ but has spikes to higher densities as discussed above. The two simulations with high correlation time have only few spikes and visit therefore the HDL phase, much less. It remains to know whether this correlation between the frequency of the spikes and the correlation time is valid also for the other simulations.
4.3. Investigation on the Individual Simulations

Fig. 4.7: Density change with increasing temperature and flipping at the Widom line. Density for runs at 195 MPa, 343 molecules and different temperatures. The “Widom-temperature” at this pressure is estimated as $T_W(195) \approx 249\text{K}$ because of the density behavior.
Fig. 4.8: Correlation times for simulations with different initial conditions at 246K and 195 MPa. 200 ns are skipped as thermalization time, for the evaluation the following 800 ns have been used (200ns -1000ns). Correlation times for the configurations starting with 0.88 and 0.93 are much longer than the others. The two outliers with initial densities 0.88g/cm³ and 0.93g/cm³ (blue and cyan line) spent much less time in the HDL phase than the other simulations, as visible in Fig. 4.9.
4.3. Investigation on the Individual Simulations

Fig. 4.9: Density for simulations at 195 MPa, T=246 K, 343 molecules and different initial conditions (different initial densities in the pre-runs). Most of the simulations show many spikes to high density, but not so the two simulations with starting density of 0.88 and 0.93 (both shown in blue). These two simulations have also a bigger correlation time than the other simulations as Fig. 4.8 shows. The low density in the beginning of the run with an initial condition of 0.95g/cm³ is not affecting the correlation time since the first 200ns are skipped. Fat black dashed lines are shown at 0.9g/cm³. Thin black dashed lines are shown at 1.05g/cm³.
Fig. 4.10: Correlation between the average density, energy and largest crystal size (thermalization time 100 ns) vs correlation time for systems at 195 MPa and 246 K (subcritical pressure and in the LDL phase). It is clear that the data are correlated between the density and the energy. For the largest crystal size this is debatable. The largest crystal size is probably affecting the correlation time only for very big crystals spreading through nearly the whole system.
4.3. Investigation on the Individual Simulations

As the number and the height of the spikes depends on the threshold used to define a spike, the correlation between the correlation time and the average density is investigated, removing for both the first 100 ns as thermalization time. The same has been done for the average potential energy and the average size of the largest crystal as defined in subsection 2.3.2.3. These three correlations are plotted in Fig. 4.10. The correlation between the average density and the average energy, which both can be used as order parameters between HDL and LDL, is clear. A correlation with the average largest crystal size for such small crystals is less evident.

The correlation time increases dramatically if crystals with sizes comparable to the system size appear, as found in simulations at 205MPa (very near to the estimated critical pressure of \( P_c \approx 206\text{MPa} \) and 246K what is within the error bar the critical temperature \( T_c \approx 246 \pm 1\text{K} \)). For eleven independent simulations at this state point seven simulations with correlation times of the order of 1ns, two of the order of 10ns and two between 100ns and 1000ns are found, see Fig. 4.11.

To find the reason for these two cases of very long correlation time the density evolution as presented in Fig. 4.12 has been shown. As the state point is very near to the critical point the simulations are expected to fluctuate between the two systems. The simulations with moderately higher correlation times had the initial density of 0.86g/cm\(^3\) and 0.88g/cm\(^3\). Apparently they spend more time in the LDL phase than the other simulations. The same is true for the simulation with the initial density of 0.91g/cm\(^3\), but a large part where it is in the LDL phase is during the first 200ns which are removed. The two outliers with strongly increased correlation times have the initial density of 0.90g/cm\(^3\) and 0.93g/cm\(^3\). The simulation with initial density of 0.90g/cm\(^3\) becomes nearly constant in density shortly before 400ns. Similar is true for the simulation with an initial density of 0.93g/cm\(^3\), but it has a density jump to a plateau of higher density at \( \approx 900\text{ns} \).

To understand this behavior the size of the largest crystal has been investigated for every simulation, using the \( d_3 \) structural order parameter as defined in section 2.3.2.3. In Fig. 4.13 the size of the largest crystal is shown for different initial densities. Obviously the largest crystal for the two simulations in question (initial
Fig. 4.11: Correlation times for simulations with different initial conditions at 246K, 205 MPa and 343 molecules. Seven of the eleven simulations with independent initial conditions have a correlation time of the order of 1ns, two of the order of 10ns and two between 100ns and 1000ns. The extreme outliers turned out to crystallize during the simulation. The thermalization time is 200ns, the evaluation time is 800ns.

densities: 0.90g/cm$^3$ and 0.93g/cm$^3$) is of the order of the system size, so the reason for the big correlation time is the crystallization of a substantial part of the system. The crystallization events can also be seen in the density especially the simulation with initial condition 0.93g/cm$^3$. In this event the density is increasing from about 0.88g/cm$^3$ to 0.92g/cm$^3$. In all investigated simulations four crystallization events could be found. All of them happened close to the phase transition respectively
the Widom line. This is consistent with the fact that the ice structure is much more similar to LDL than to HDL and therefore HDL nearly never crystalizes. On the other hand the self-diffusion of LDL is highest close to the HDL phase and the higher the self-diffusion, the higher is the probability of creating a nucleation crystal.

Crystallization needs a sufficiently large crystal nucleus to be initiated. In several systems small crystallites with up to 30 molecules could be found, which melted again, sometimes even after 700ns, see Fig. 4.14 for examples. It is therefore assumed that a nucleation crystal larger than about 40 molecules has to be formed in order to initialize a full crystallization process.

Consider the influence of the system size on the correlation time: The correlation function for the four different system sizes are compared for the lowest temperature at the supercritical pressure of 210MPa (LDA), see Fig. 4.15. The correlation functions are very similar and so are the correlation times. Furthermore there is no systematic dependence indicating a system size effect. The temperature of 243K is in the LDL phase and not too close to the critical point where critical slowing down should appear. In the LDL phase in fact the long correlation times stem from the small self-diffusion, not from the slowing down at criticality. Also other properties are similar for different system sizes: as for example the time dependence of the density or the largest crystals.

To conclude: Flipping between the two phases LDL and HDL has been observed in the subcritical region for the first time at the liquid-liquid critical point and can serve as an important evidence for the existence of the liquid-liquid critical point. Both phases LDL and HDL can be equilibrated, HDL in about 20 ps and LDL within 100 ns if no crystallization events take part and the evolution is not hindered by long living crystallites as in Fig. 4.14. However anti-correlation between the density and the correlation time and between the energy and the correlation time exists. Few non-reversible crystallization events have been found for the system size of 343 molecules and smaller, but none in the larger system sizes. Many small crystallites have been observed in all simulations in the LDL phase. These crystallites grew up
4. Investigation of Supercooled ST2 Water

to 40 molecules and melted again, giving rise to the idea of the existence of some kind of energy barrier against full crystallization.
4.3. Investigation on the Individual Simulations

Fig. 4.12: Density fluctuations for very long correlation times. Most of the simulations fluctuate between LDL and HDL except the ones with initial conditions of 0.90g/cm³ and 0.93g/cm³ (plotted in blue). These two exceptions stay at a constant density after some time. In Fig. 4.13 large crystals are found to explain this fact. All the simulations were made at a constant pressure of 205 MPa and at a temperature of $T = 246K$, with $N = 343$ molecules and different initial conditions. Fat black dashed lines are shown at 0.9g/cm³, thin black dashed lines are shown at 1.05g/cm³.
4. Investigation of Supercooled ST2 Water

Fig. 4.13: Size of the largest crystal for simulations at 205MPa, 246 K, 343 molecules and different initial conditions. The two simulations with initial densities of 0.90 and 0.93 are crystallizing (colored blue). For the other simulations the size of the largest crystal is smaller than 30 molecules during all the time but they are shown (red curves) ten times larger than they are in reality for better visualization.
4.3. Investigation on the Individual Simulations

Fig. 4.14: Size of the largest crystal for two systems at 195MPa, 246K and 343 molecules with different initial conditions. The upper figure shows a crystal growing to about 25 molecules and melting only after $\approx 700\text{ns}$. It proves that small crystallites can survive a long time. The lower figure shows a crystal growing as large as 40 molecules and melting again. Many similar crystallites growing and melting have been found for all investigated system sizes. This allows the conclusion that LDL is quite stable against crystallization.
Fig. 4.15: Correlation function for four systems with different sizes at 210MPa and $T = 243$K. The correlation functions and in particular the correlation times for all four system sizes are quite similar. Conclusion: the system size has negligible effect on the correlation time.
4.4 Localization of the Critical Point

In the former section simulations which flip between HDL and LDL have been found and have been seen as evidence that the state point of the simulation is located in the subcritical region. A second look at such a simulation with strong fluctuations is taken in Fig. 4.16. In panel a) the density fluctuations are shown. These fluctuations result in the density histogram shown in panel b) if the first 100 ns of the 1 µs time series are discarded. The histogram shows that two states are sampled. A high density state at about 1.02 g/cm³ and a low density state at about 0.88 g/cm³. Two snapshots of the system are shown where the displayed oxygen atoms are colored according to the structural order parameter $q_6$ on the second coordination shell for the LDL phase (c) and the HDL phase (d), see color scheme on the right.

The shape of the histogram can be used to judge where the critical point is located. It is however not the histogram of the $\rho$, but of the ordering operator $M = \rho + sE$ and we fit it with the order parameter distribution function as described in section 2.3.1. Histogram reweighting as described in section 3.4 has been used to interpolate between the simulated state points. The input data for the reweighting come from the simulations shown in Table 4.1 for 343 molecules. Simulations, which crystallized and formed a stable crystal have been removed. The liquid-liquid critical point is believed to fall into the same universality class as the liquid-gas critical point and the 3D Ising model, see also Refs. [38] [53].

The universal form of the order parameter distribution function of the 3d Ising has been fitted using temperature, pressure and the field mixing parameter $s$. The scaling parameter is $x = A(M - M_c)$, where $M = \rho + sE$. $M_c$ has been chosen such that the mean value of $M$ is zero and $A$ has been chosen such that the variance is unity. The mixing parameter $s$ serves as an additional fitting parameter. Fig. 4.17 shows the result for 343 molecules and how it changes for different densities: For 205MPa (blue squares) the minimum in the center of the order parameter distribution function is too high, hence we know this pressure is below $P_c$. For
Fig. 4.16: Density flipping between LDL and HDL at coexistence. The 1 µs time series (panel a) shows how frequently, at constant \( P = 215 \text{ MPa} \) and \( T = 244 \text{ K} \), \( N = 343 \) ST2-water molecules switch from LDL to HDL states. b) The histogram, of the sampled densities, in arbitrary units, after discarding the first 100 ns of the 1 µs time series. For LDL \( \rho = (0.89 \pm 0.01) \text{ g/cm}^3 \) and for HDL is \( \rho = (1.02 \pm 0.03) \text{ g/cm}^3 \) with a difference of 3% at this state point. Snapshot of the LDL c) and of the HDL d) state showing only oxygen atoms, colored according to their local \( q_6^{(2)} \) structural parameter (color codes on the right) with \( q_6^{(2)} = (0.3 \pm 0.06) \) for LDL and \( q_6^{(2)} = (0.2 \pm 0.05) \) for HDL.
Table 4.1: Numbers of simulations used for the histogram reweighting in order to obtain the order parameter distribution function for $N = 343$ molecules.

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210MPa (green circles) the minimum of the OPDF is too low what suggests that this pressure is above $P_c$. Our estimation of $P_c$ comes from the third pressure of $206 \pm 3$MPa (red triangles, error bar because of histogram reweighting between the pressures) where the OPDF fits best the one of the three dimensional Ising model shown in black, coming from Ref [53]. Histogram reweighting has been used to interpolate between the temperatures (and for the results for 206MPa also pressures) coming from NPT simulations.

The same procedure is executed for $N = 512$ and $N = 729$ molecules. The considered state points for the histogram reweighting can be found in Table 4.2 for $N = 512$ molecules and in Table 4.3 for $N = 729$ molecules. In Fig. 4.18 the critical order parameter distribution function for all three system sizes are shown. The critical temperatures and critical pressures coming from these fits can be found in Table 4.4. They are close to the estimation for the critical point obtained in other papers as shown in Table 4.5. As mentioned in the beginning the system size of $N = 216$ molecules suffers from strong finite size effects, it showed a critical point.
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<td>246K</td>
<td>1</td>
<td>2</td>
<td>6</td>
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<td>247K</td>
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<td>252K</td>
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Table 4.2: simulations used for the histogram reweighting to arrive to the order parameter distribution function for $N = 512$ molecules.

of $185 \pm 4$MPa.

To conclude: The critical point has been localized at $T_c = 246 \pm 1$K and $P_c = 208 \pm 3$MPa which fits best the critical 3d Ising order parameter distribution function. The same critical temperatures and critical pressures have been found within the error bars for three system sizes out of four. The smallest system size shows strong finite size effects and a critical pressure of $186 \pm 5$MPa which is consistent with the pressure estimated in the NVT ensemble using also 216 molecules.
Table 4.3: simulations used for the histogram reweighting in order to arrive to the order parameter distribution function for $N = 729$ molecules. Up to the simulations at 190MPa, 250K and 251K all simulations had a runtime of 1000ns.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>190MPa</th>
<th>200MPa</th>
<th>210MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>242K</td>
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<td>243K</td>
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<td>252K</td>
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</tbody>
</table>

Table 4.4: Critical temperatures and pressures of the LLCP, estimated through best fitting to the 3d Ising critical order parameter distribution function shown in Fig. 4.18. The amplitude $A$ originates from the scaling parameter $x$ and serves as a fitting parameter to $x = A (M - M_c)$.

<table>
<thead>
<tr>
<th>Ensemble</th>
<th>$T_c$</th>
<th>$P_c$</th>
<th>$\rho_c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$NVT^1$ [76]</td>
<td>$T_c = 246 \pm 1K$</td>
<td>$P_c = 206 \pm 3MPa$</td>
<td>$\rho_c = 0.94g/cm^3$</td>
</tr>
<tr>
<td>$N = 512$</td>
<td>$T_c = 246 \pm 1K$</td>
<td>$P_c = 208 \pm 3MPa$</td>
<td>$A = 0.0588(7)$</td>
</tr>
<tr>
<td>$N = 729$</td>
<td>$T_c = 246 \pm 1K$</td>
<td>$P_c = 208 \pm 3MPa$</td>
<td>$A = 0.0613(8)$</td>
</tr>
<tr>
<td>$\mu PT^2$ [53]</td>
<td>$T_c = 237 \pm 4K$</td>
<td>$P_c = 167 \pm 24MPa$</td>
<td>$\rho_c = 0.99 \pm 0.02g/cm^3$</td>
</tr>
</tbody>
</table>

Table 4.5: List of estimates of the liquid-liquid critical point in ST2 water. The critical points do not coincide because different ensembles, different sizes and different techniques have been used.

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4. Investigation of Supercooled ST2 Water

Fig. 4.17: Order parameter distribution function (OPDF) at 343 molecules for different pressures: For 205 MPa (blue squares) the minimum in the center of the OPDF is too high, hence we know this pressure is below $P_c$. For 210 MPa (green circles) the minimum of the OPDF is too low what suggests that this pressure is above $P_c$. Our estimation of $P_c = 206 \pm 3$ MPa originates from the red triangles which fit best the three dimensional Ising OPDF (shown in black), coming from Ref. [53]. As the red triangles are obtained by histogram reweighting for temperature and pressure, also the pressure has an error bar.
4.4. Localization of the Critical Point

Fig. 4.18: Order parameter distribution function (OPDF) for $N = 343$, $N = 512$ and $N = 729$ molecules. The critical pressure and temperature for which the order parameter distribution function fits best with the one of the Ising model is presented in Table 4.4. As field mixing parameter $s = -27.6 \frac{g}{cm^3}$ has been the best choice for all sizes.
4.5 Finite Size Analysis

Here we will study how different variables depend on system size. First we will check whether the observations about first order phase transition and Widom lines made in section 4.7 will also be valid in the thermodynamic limit. We will do this by a finite size scaling of the Challa-Landau-Binder parameter. This will then prove that a first order phase transition ends and that therefore a critical point does exist. Furthermore we will scale the amplitudes of the order parameter distribution function, to verify the hypothesis that the critical point falls into the three dimensional Ising universality class. Finally we will show that the LDL phase is a liquid and the critical point is therefore a liquid-liquid critical point.

The investigated Challa-Landau-Binder parameter is defined as

$$\Pi = 1 - \frac{\langle X^4 \rangle}{3\langle X^2 \rangle^2},$$

where $X$ can either be the energy $u$ or the density $\rho$, here it is shown for the density, but the same calculations have also been done using the energy. A system near to the Widom line shows a monomodal distribution of $X$ and $\Pi$ is then equal to $2/3$. At the first order phase transition however the histogram of $X$ is bimodal and $\Pi$ therefore below $2/3$. The Challa-Landau-Binder parameter is therefore a good parameter to distinguish between a line of first order phase transitions and its Widom line. In finite systems however, a bimodal distribution can also occur on the Widom line. Therefore finite size scaling is performed to see how the Challa-Landau-Binder parameter would behave in the thermodynamic limit.

For every pressure and system size the Challa-Landau-Binder parameter has been taken at its minimum, since this is at the temperature where the phase transition respectively its Widom line is expected (see Fig. 4.19).

These minima are presented in Fig. 4.20 for different pressures and system sizes. We see that for the pressure of 190MPa the minimum of the Challa-Landau-Binder parameter increases with system size reaching $2/3$. For the pressure of 210MPa the minimum of the Challa-Landau-Binder parameter is still increasing but does not reach $2/3$ anymore. It therefore can be concluded that the line of first order phase transitions ends between these two pressures and hence also the critical pressure is
Fig. 4.19: Challa-Landau-Binder parameter at 200MPa (subcritical pressure) for three different sizes, as function of temperature. The Challa-Landau-Binder parameter drops as the temperature comes close to the Widom temperature $T_W$. The temperature for which the Challa-Landau-Binder parameter is lowest is expected to be where the Widom line crosses this pressure.

located inside this interval. This is consistent with the location of the critical point using the order parameter distribution function in section 4.4.

The amplitude of the order parameter distribution function scales like $L^{\beta/\nu}$, see Ref. [104]. For the three dimensional Ising model it is known that $\beta/\nu \approx 0.518$ [71]. The amplitudes obtained in section 4.4 are plotted in Fig. 4.21 and compared to a fitted function with an exponent of $\beta/\nu$. Showing that an exponent of 0.518 is consistent with our data.

It now can be safely assumed that the a critical point falls into the three dimensional Ising universality class and that the liquid-liquid critical point exists in ST2 water
4. Investigation of Supercooled ST2 Water

Fig. 4.20: The value of the Challa-Landau-Binder parameter $\Pi$ at the Widom temperature, respectively the temperature of the phase transition is shown for different system sizes and pressures. For 190MPa the Challa-Landau-Binder parameter in the thermodynamic limit tends to $2/3$ i.e. the value for a monomodal distribution and therefore a state on the Widom line. For 210MPa however the extrapolation of $B_4$ to the thermodynamic limit is below $2/3$ what indicates a bimodal distribution and hence a first order phase transition. See Fig. 4.19 for how the value of the Challa-Landau-Binder parameter is chosen. The lines are guides to the eyes.

at $P_c \approx 206$MPa.

It remains to show that the two phases are really liquid. This has not been disputed for the high density phase, but has been questioned for the low density phase in Ref. [51]. Here it will be shown that LDL is really a liquid phase by showing that the order parameter $Q_6$ as defined in section 2.3.2.1, goes to zero as $N^{-1/2}$
4.6 LDL a Liquid that Can Be Equilibrated

I study the LDL phase at the supercritical pressure of 210MPa and a temperature of 243K. The systems are thermalized for 100ns. In figure 4.15 I showed that the

with increasing system size unlike a crystal where a finite value is expected in the thermodynamic limit. Simulations of 1000ns will be studied in the LDL phase for different system sizes and it will be shown that they equilibrate. Stability against crystallization in the thermodynamic limit is of course not possible for a super-cooled fluid as the very definition of a super-cooled liquid is to be meta-stable against crystallization.

Fig. 4.21: Scaling of the amplitude of the order parameter distribution function. The amplitudes are shown in red triangles, the theoretical scaling \( L^{\beta/\nu} \) \([104]\), \( \beta/\nu \approx 0.518 \) for the three dimensional Ising universality class) is shown as a black line. The result is consistent with this scaling law specially if one considers that the system sizes are small and therefore higher order corrections are probably relevant.

4.6 LDL a Liquid that Can Be Equilibrated

I study the LDL phase at the supercritical pressure of 210MPa and a temperature of 243K. The systems are thermalized for 100ns. In figure 4.15 I showed that the
4. Investigation of Supercooled ST2 Water

Fig. 4.22: Dependence of the density and the size of the largest crystal on time for the simulations used in Fig. 4.23 to show the scaling of \( Q_6 \) for LDL. This plot shows that: at this state point the phase is really in LDL. Correlation times are smaller than these 100 ns and the phases can therefore be equilibrated. To show that the system is really in the LDL phase the time behavior of the different simulations is exhibited for the four system sizes in Fig. 4.22, and shows that for all four system sizes the density lies below 0.95 g/cm\(^3\) up to some spikes for the smallest system size. In the same figure the size of the largest cluster is shown for the four system sizes. It shows that no big crystal is forming. To demonstrate that LDL is really a liquid I did a finite size scaling of the \( Q_6 \) order parameter. \( Q_6 \) is constant for different system sizes for crystals, but decreases with the square root of the number of particles for liquids. In Fig. 4.23 the histograms of \( Q_6 \sqrt{N} \) are shown for the four system sizes. The collapse indicates the scaling with \( 1/\sqrt{N} \) and therefore confirms the liquid phase of our LDL simulations.

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Fig. 4.23: Histogram of the scaled structural order parameter $Q_6 N^{1/2}$. The collapse of the histograms shows that $Q_6$ is scaling like $N^{-1/2}$, as it is expected for a liquid, and does not have a finite value in the thermodynamic limit as would be expected for a crystal. The scaling is presented for four system sizes at a pressure of 200MPa and $T = 244K$. 

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4.6. LDL a Liquid that Can Be Equilibrated
4.7 Phase Transition Introduces Changes in the Structure

In this section it is shown how different structure measurements change by changing the phase from LDL the HDL at both: the first order phase transition (higher pressure than \( P_c \), supercritical fluid) and at the Widom line (lower pressure than \( P_c \), subcritical fluid). This will be done for the radial pair correlation function \( g_{OO}(r) \) of the oxygen atoms, and for the intermediate scattering function of the oxygen atoms \( S_{OO}(q) \).

Let us start with the radial pair correlation function: For that we check the change of \( g(r) \) with increasing temperature at the subcritical pressure of \( 200\text{MPa} < P_c \). As we can see in Fig. 4.24 the structure changes smoothly with increasing temperature from the LDL to the HDL structure. This again is consistent with the location of the critical point in 4.4 and the idea of crossing the Widom line. From this Fig. 4.24 it is clear that the LDL structure (for example the red curve for 244K) is more pronounced than the HDL structure (for example black curve for 250K). This is specially true for the long ranges where HDL does not show any structure but LDL does. It helps to understand why some people misunderstand this LDL phase as a crystalline phase.

For a system at the supercritical pressure of \( 210\text{MPa} > P_c \) the LDL and HDL look similar as at 190MPa but the change is not smooth anymore, but quite sharp, see Fig. 4.25.

The same comparison is done for the intermediate scattering function \( S_{OO}(q) \) and a sub- and supercritical pressure. Its change with temperature for the subcritical pressure of \( 190\text{MPa} < P_c \) is shown in Fig. 4.26 and for the supercritical pressure of \( 210\text{MPa} > P_c \) is shown in Fig. 4.27. As for \( g(r) \) also the intermediate scattering function changes smoothly between LDL and HDL in the subcritical region but immediately in the supercritical region. Main differences between the structures can be observed in the first and the second peak: Going from LDL to HDL by increasing the temperature the first peak shrinks and comes closer to the second
4.7. Phase Transition Introduces Changes in the Structure

Fig. 4.24: Radial pair correlation function between the oxygen atoms \( g_{OO}(r) \) at the subcritical pressure of \( 200 \text{MPa} < P_c \) for a system using \( N = 729 \) molecules. The structure changes smoothly with increasing temperature from the LDL to the HDL structure.

peak until it is hardly a peak anymore, but more a dominant shoulder of the now first peak. The second peak in LDL is also shrinking as the liquid is going towards HDL. Together with the peaks also the minima between the peaks are becoming less pronounced near to HDL. Also a shoulder on the third peak in LDL is vanishing. It is vanishing much before the first peak finished to lower (the shoulder has definitely vanished for \( T = 250\text{K} \), when the first peak is still separated from the second peak by a pronounced minimum). The simulations at the supercritical pressure (Fig. 91...
4. Investigation of Supercooled ST2 Water

Fig. 4.25: Radial distribution function between the oxygen atoms $g_{OO}(r)$ at the supercritical pressure of 210MPa $> P_c$ for a system using $N = 729$ molecules. The structure quite sharply changes with increasing temperature from the LDL to the HDL structure. The structures of LDL and HDL are similar to the structures found for lower pressure in Fig. 4.24.

4.27) can be used to estimate the temperature of the phase transition: The first five temperatures show a pronounced first peak, they definitely are in the LDL phase. The sixth temperature (245K) shows a less pronounced first peak, but more significantly has lost the shoulder in the third peak, it is therefore between LDL and HDL. the last four figures show a very weak first peak, a low second peak and no shoulder in the third peak, so they are definitely in the HDL phase.
4.7. Phase Transition Introduces Changes in the Structure

Fig. 4.26: Intermediate scattering function for systems at $P = 190\text{MPa} < P_c$ and a system size of $N = 729$ molecules. As in Fig. 4.24 the structure is changing smoothly between LDL and HDL. Three characteristics differ between LDL and HDL: 1) LDL has a higher first peak which is lowering and shifting towards the second peak in the HDL phase. 2) the second peak is higher in the LDL phase than in HDL and 3) the third peak has a tiny shoulder in the LDL phase. With the lower maximum in the HDL phase the minima are becoming less deep. All in all LDL is more structured than HDL.

We have seen that in simulations close to the Widom line the system is switching back and forth between the two states, as for example in the not crystallized systems in Fig. 4.12. Can we follow the structural change in such simulations? An analysis for a simulation at $200\text{MPa}$ and $T = 248\text{K}$ with $N = 343$ molecules is performed,
4. Investigation of Supercooled ST2 Water

Fig. 4.27: Intermediate scattering function for systems at $P = 210\text{MPa} > P_c$ and a system size of $N = 729$ molecules. Unlike in Fig. 4.24 the structure not changing smoothly between LDL and HDL, but quite abruptly. The first five temperatures are definitely in the LDL phase. For 245K the structure is much closer to the LDL phase according to the first two peaks, but already lost its shoulder in the third peak, it is therefore the temperature of the phase transition. This fits with the observation in Fig. 4.17 of estimating the phase transition temperature of 210MPa using the order parameter distribution function. The last four temperatures show HDL structure also according to the first two peaks.

where the system is changing phase twice between 30ns and 60ns, see Fig. 4.28. Fig. 4.29 shows the intermediate scattering function for six different intervals during these 30ns. In the first interval 30ns – 35ns the system is in the LDL phase as
Fig. 4.28 shows. For the same interval we can see the LDL behavior also in the intermediate scattering factor with two high first peaks and a tiny shoulder in the third peak. In the second interval the density shows peaking into HDL and going back to the LDL phase. The structure (red curve for the second interval) shows now a much lower first peak, but also the height of the second peak is lower and the shoulder in the third peak vanished. However the first peak is still higher than in the pure HDL phase, what makes sense since the system is not purely HDL between 35ns – 40ns. The time dependence of the density shows a LDL phase for the whole third interval, what can again be observed in the structure (green curve). The structure is even more pronounced than in the first interval. As the density is increasing in the fourth interval, the structure shows again HDL properties where again the first peak is slightly too high. The first peak is then moving towards the HDL shape during the fifth interval (cyan curve) as the density is continuously in the HDL phase. During the sixth interval the density is decreasing again and the structure still showing HDL properties, only the first peak becomes more LDL like. In conclusion we see: the structure is indeed changing with the transition from HDL to LDL including fluctuations between HDL and LDL during a single simulation. We also see that the first peak does not lose his whole height of LDL unless it is pure HDL, however it looses the LDL’s third peaks shoulder and a good portion of the heights of the first two peaks quite fast.

4.8 Structural Order Parameters

In order to find the structural order parameter, which distinguishes best between HDL, LDL and crystal, I tested several order parameters as $q_3$, $\psi_3$, $Q_3$, $Q_6$ and $q_6$, as defined in section 2.3.2. Let us call $q_6$ and $Q_6$ the order parameter on the first coordination shell, defined using the first four nearest neighbors and $q_6'$ and $Q_6'$ the order parameters on the second coordination shell defined using the first 16 neighbors, excluding the first coordination shell. In Fig. 4.30 we present the change of these order parameters with time for the same simulation as used for figures 4.28
4. Investigation of Supercooled ST2 Water

Fig. 4.28: Time dependence of the density fluctuations in a simulation near the Widom line (200MPa < P_c, T = 248K) with a system size of N = 343 molecules. In the interval 30ns – 60ns the system is switching twice between LDL and HDL. The change in the intermediate scattering function for this run can be followed in Fig. 4.29.

and 4.29, namely 343 molecules at 200MPa and T = 248K. The global parameters as Q_3, Q_6 and Q'_6 are quite noisy, the local structural order parameters: q_3, ψ_3, and q_6 however give a clear picture of which phase is sampled. Also for the local order parameters using the second coordination shell q'_6 gives the clearest results. It should be mentioned that unlike the other parameters, Q_3 and φ_3 are large for the HDL phase and small for the LDL phase.

The histogram of different structural order parameters for the HDL, LDL and two
crystalline structures will be analyzed. All four system have 343 molecules. One of the crystalline structures has a density below 0.90g/cm³ lets call it low density crystal (LD crystal). The other crystal has a density higher than 0.90g/cm³ hence it will be called medium density crystal. The LDL phase comes from a state point at 200MPa and 243K. The HDL phase comes from a state point at 200MPa and 252K. For both liquids the first 100ns have been removed as thermalization time. The LD crystal is the crystal shown in Fig. 4.13 with an initial density of 0.90g/cm³, for which the time interval from 400ns to 1000ns has been used. The MD crystal has also been observed in Fig. 4.13 for an initial density of 0.93g/cm³. For this crystal the time interval was 900 − 1000ns (after the second crystallization event, which is visible in Fig. 4.13). The density evolutions for these two crystals are shown in Fig. 4.12.

The different structural order parameters are defined in section 2.3.2. In Fig. 4.31 it is shown how the parameter $q_3$ is changing for the four structures calculated on the first coordination shell. For the HDL phase the histogram is monotonously growing from 0 at 0.2 to about 5 at around 0.68 and then falling down again to 0. The LDL phase follows the same scheme, growing to a higher value ($\approx 12$) at a later time ($\approx 0.7$). Growing to an even higher value at an even later time is the histogram for the crystals. The LDL phase seems therefore to be just an intermediate scattering between HDL and the crystals. Note that the two different crystalline structures differ by the fact that the medium density crystal has a small peak at $\approx 0.42$. The order parameter $q_3$ can also be calculated for the second coordination shell as done in Fig. 4.32. This has several effects on $q_3$: the values are lower and the order of which structures has the lowest value is reversed. But most importantly the difference in the histogram for the different structures is more pronounced especially the averages of the histograms are different too, what is important when analyzing $q_3(t)$.

Next the structural order parameter $d_3$ is used to analyze our four different structures. The result is shown in Fig. 4.33. The HDL structure has a very broad histogram. The histogram of LDL is less broad and has a small minimum in the
center. For the LD crystal this becomes more pronounced. It has one peak close to $-1$ and one close to $-0.1$. The difference between the two structures is however quite large as the y axis is logarithmic and hence the first peak close to $-1$ for the LD crystal is dominating its whole histogram. The change to lower values as the structure changes from LDL to HDL can be explained by the fact that small clusters with the structure of a crystal appear in the LDL phase. They are not growing further and melting again as could be seen in figures 4.13, 4.14 and in 4.22 for exactly this LDL simulation. The $d_{3}$ parameter is used to calculate the size of the largest cluster using a cutoff of $-0.87$. The histograms for the $\phi_{3}$ order parameter are shown in Fig. 4.34. The HDL and LDL phases have Gaussian shaped histograms, nicely separated. The histograms of the crystalline structure have a strong peak at low values close to $-1$. So $\phi_{3}$ is a very useful order parameter to distinguish between LDL and crystals. To investigate the hexagonal structure the order parameter $q_{6}$ is investigated in Fig. 4.35. Similar as for the parameter $q_{3}$, the histograms of the four different structures do not differ much, but calculating in the second coordination shell helps to distinguish LDL from HDL and from the crystals, as Fig. 4.36 shows.

It has turned out that the best parameter to distinguish LDL from the two tested crystals is the $d_{3}$ parameter, as its histogram shows a peak below $-0.87$ nearly an order of magnitude higher, than for LDL or HDL.
Fig. 4.29: Intermediate scattering function for the same system as Fig. 4.28 (200MPa < P_c, T = 248K with a system size of N = 343 molecules). The structure is shown for different time intervals of size 5ns. Comparing with Figs. 4.28 and 4.26 or 4.27 shows how clearly the structure is changing as the system switches between HDL and LDL.
4. Investigation of Supercooled ST2 Water

Fig. 4.30: Different structural order parameters and the volume (from top to bottom) 1) volume, 2) $q_3$, 3) $Q_3$, 4) $\psi_3$, 5) $q_6$, 6) $Q_6$, 7) $q'_6$, 8) $Q'_6$, where ' means calculated on the second coordination shell as defined in the text. The parameters are shown for a run using 343 molecules at 200MPa and $T = 248\, K$, the same as in figures 4.28 and 4.29. Averaged quantities as $Q_3$, $Q_6$ and $Q'_6$ exhibit much more noise and are therefore not ideal to distinguish between LDL and HDL. Among these, $Q'_6$ gives the clearest results. For the local order parameters using the second coordination shell gives the clearest results ($q'_6$). It should be mentioned that unlike the other parameters $Q_3$ and $\phi_3$ are large in the HDL phase and small in the LDL phase (as the density).
Fig. 4.31: Histogram of the structural order parameter $q_3$ for HDL, LDL a crystal with low density (below 0.90g/cm$^3$ called LD Crystal) and a crystal with intermediate density (above 0.90g/cm$^3$ called MD Crystal). The LDL phase comes from a state point at 200MPa and 243K. The HDL phase comes from a state point at 200MPa and 252K. For both liquids 100ns have been skipped as thermalization time. The LD crystal is the crystal observed in Fig. 4.13 with an initial density of 0.90g/cm$^3$, for the evaluation the time interval from 400ns to 1000ns has been used, this is after the crystallization event. The MD crystal has also been observed in Fig. 4.13 but for the run with initial density of 0.93g/cm$^3$. For this crystal the time interval used for evaluation was 900 – 1000ns (after the second crystallization event). The time behavior of the density for these two crystals can be found in Fig. 4.12. For this structural order parameter the shape of the two crystals is very similar, but also the shape of HDL and LDL are not much different. The LDL phase looks like an intermediate phase between HDL and the crystals.
Fig. 4.32: Histogram of the structural order parameter $q_3$ in the second coordination shell, for HDL, LDL, a crystal with low density (below 0.90g/cm$^3$ called LD crystal) and a crystal with intermediate density (above 0.90g/cm$^3$ called MD crystal). These are the same structures as used in Fig. 4.31 and discussed in its caption. Using the second coordination shell the $q_3$ values shift to lower values. The HDL, LDL and the crystals can now be differentiated also by the mean value of $q_3$. 

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Fig. 4.33: Histogram of the structural order parameter $d_3$ defined between bonds of molecules, for HDL, LDL, a crystal with low density (below 0.90g/cm$^3$ called LD crystal) and a crystal with intermediate density (above 0.90g/cm$^3$ called MD crystal). These are the same structures as used in Fig. 4.31 and discussed in its caption. The difference between the histogram is larger than in Fig. 4.31. Especially the peak of the two crystals (note the logarithmic scale for the y axis) helps to distinguish between crystals and LDL respectively HDL. The parameter $d_3$ is the one used in this work to define the biggest crystal in run.
4. Investigation of Supercooled ST2 Water

Fig. 4.34: Histogram of the structural order parameter $\phi_3$, for HDL, LDL, a crystal with low density (below 0.90g/cm$^3$ called LD crystal) and a crystal with intermediate density (above 0.90g/cm$^3$ called MD crystal). These are the same structures as used in Fig. 4.31 and discussed in its caption. Also this structural order parameter distinguishes clearly between HDL, LDL and the crystals. HDL and LDL are bell-shaped curves but have a different mean value what is convenient to distinguish HDL and LDL by the mean value of $\phi_3$. Crystals show a clear peak close to $-1$, what makes them easy to detect especially since both: HDL, nor LDL have a very low percentage at these values.
Fig. 4.35: Structural order parameter \( q_6 \) in the first coordination shell for LDL, HDL, a crystal with low density (below 0.90g/cm\(^3\) called LD crystal) and a crystal with intermediate density (above 0.90g/cm\(^3\) called MD crystal). These are the same structures as used in Fig. 4.31 and discussed in its caption. As for \( q_3 \) (see Fig. 4.31), also for \( q_6 \) the LDL phase looks like an intermediate situation between HDL and a crystal.
Fig. 4.36: Structural order parameter $q_6$ defined on the second coordination shell for LDL, HDL, a crystal with low density (below 0.90g/cm$^3$ called LD crystal) and a crystal with intermediate density (above 0.90g/cm$^3$ called MD crystal). These are the same structures as used in Fig. 4.31 and discussed in its caption. As it was true for the $q_3$ parameter, it is also true for the $q_6$ parameter that the histogram of the order parameter calculated on the second coordination shell can better distinguish between the different structures. Especially also the mean values differ more significantly, what is important if the time behavior of $q_6(t)$ is investigated as in Fig. 4.30.
Discussion and Outlook

Water as liquid exhibits more than 62 different anomalies including the fact that the response functions as the specific heat, the compressibility and the thermal expansion coefficient are strongly increasing when lowering the temperature. In 1992 the existence of a critical point in deeply supercooled water separating so-called low density liquid (LDL) and high density liquid water (HDL) has been proposed to explain the strong increase of the response functions. This hypothesis has been proven to be extremely hard to investigate using experiments, as the suggested critical point lies deeply in the “no mans land”, a region above the glass crystallization temperature and below the homogeneous crystallization line, where liquid water can not be accessed in experiments. Using molecular dynamics simulations however the system is pure and small enough to investigate this region and has been studied heavily. Although a huge amount of research has been done, the existence of this liquid-liquid critical point in water is still disputed. Claims that the LDL phase is not a liquid but a crystal or at least that LDL is unstable against crystallization arose.

In this thesis this liquid-liquid critical point in water has been investigated by performing molecular dynamics simulations in both the NVT and the NPT ensemble using the ST2 water model. As the correlation times are huge, simulation times up to $1\mu$s are needed what corresponds to $10^9$ time steps. In both ensembles the
phase transition between the HDL and LDL has been confirmed, for the NVT ensemble by coexistence, in the NPT ensemble by flipping between the states. These flipping states have been observed the first time and are a strong evidence for the existence of the liquid-liquid critical point for ST2. In the constant volume simulations the critical point has been located using the crossing of the isochors. In the NPT ensemble several methods have been applied giving consistent results: Using finite size scaling it has been shown that the universality class is consistent with the universality class of the three dimensional Ising model. Using orientational order parameters the structures of the LDL and the HDL phase have carefully been analyzed to check for crystallization. Small crystallites growing up to 10% of the system size, which melt again completely have been found. Three out of a hundred simulations did fully crystallize forming a mixed crystal between cubic and hexagonal symmetry. The structures of LDL and HDL phases have been analyzed using the intermediate scattering structure function and the radial correlation function.

In conclusion the liquid-liquid critical point has been found in the NVT as well as the NPT ensemble confirming previous work [53, 77]. Using finite size scaling it has been shown that the existence of a critical point is not due to a finite size effect and confirms the universality class of its critical point. For the first time phase flipping in the supercritical region has been observed. Simulation times of $1\mu$s made it possible to equilibrate the LDL phase for which it is shown that it is different from solid phases and stable against crystallization as small crystallites growing up to 10% of the system size melt again completely. This proved that the LDL phase is really a liquid, unlike proposed by others. Of course both LDL and HDL are not stable phases, as they are super-cooled liquids and therefore unstable against crystallization. However during the time scale of our simulations of 1000ns HDL and LDL are stable against crystallization and as the liquids are thermalized within the simulated time, there is a time scale for which the two metastable phases, HDL and LDL, are equilibrated stable phases against crystallization.

The simulations could be extended in different manners: Bigger system sizes, probably coupled with more advanced techniques as umbrella sampling, can give more
accurate results. For a proposed liquid-liquid phase transition in carbon it turned out that only ab-initio calculations could show that for carbon this hypothesis is wrong [103]. It would therefore be important to also have some ab-initio simulation for super-cooled water. This however would need a huge improvement in ab-initio techniques in both speed and accuracy for water. Analysis of the hydrogen network of HDL, LDL and specially the time dependent network of the transition could give additional insights about the mechanisms triggering the liquid-liquid critical point (LLCP) on top of insights gained by studying other models as the Jagla potential. The same is true for the study of how changes in the water potential change the LLCP. The final proof for the existence of the LLCP in water will be an experimental confirmation.
5. Discussion and Outlook
References


Curriculum Vitae

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List of Publications:
Investigation of the liquid-liquid critical point in st2 water using finite size scaling.
accepted by Scientific Reports

Nanoscale dynamics of water near its liquid-liquid critical point.
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