Investigation into the impact of solid surfaces in aqueous systems

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To my wife and family.
My pillars of support.
Scientific environment

The research in this PhD thesis have been performed at the University of Bergen, Institute of Physics and Technology in the group for thermodynamic modeling. My main supervisors have been Professor Bjørn Kvamme and Professor Tatiana Kuznetsova have been my co-supervisor.

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The rest, those I forgot or neglected to mention; your name should probably be right about here. In the list of all those names, all those friends, colleagues, acquaintances and family members, the ones that have supported me, helped me and distracted me when necessary ...

Thank you all!
Abstract

Global warming is upon us. The scientific community is searching for methods of slowing down, preventing and reversing its effects. Carbon dioxide have been at the center of attention the last few decades, being the main contributor to man-made global warming. Carbon capture and sequestration is one of the potential tools in this undertaking of mitigation. By capturing carbon dioxide and transporting it to injection sites for subsurface storage the amount released can be reduced.

This thesis approaches several of the topics involved in transport and sequestration of carbon dioxide. Carbon dioxide transport to injection site will likely be by pipelines. In arctic regions the potential for ice-like structures known as clathrates, or hydrates, to form due to the high pressure and low temperature conditions is significant. Reducing the risks of hydrate formation calls for knowledge of the decisive factors. Thus, this work participates in the development of more robust strategies for hydrate prediction and consequently prevention.

In pipelines, oxidized carbon steel surfaces are readily available. These have proven to be excellent adsorption sites for water in the gas stream. Carbon dioxide is an hydrate former, capable of stabilizing hydrate cavities of water molecules as a guest molecule. Here the chemical potential of water, carbon dioxide and hydrogen sulfide is examined under realistic pipeline conditions. These results are used to predict if, in which phase, and from which phases, hydrate will form. It was found that water will adsorb onto the hematite (rust) surface. The water layers closest to the hematite have too low chemical potential for hydrates to form. However, as the distance to the hematite increases, water regains more and more of its bulk properties, where hydrates are possible. Adsorbed impurities like hydrogen sulfide is shown to assist carbon dioxide in forming stable hydrates. We draw the conclusion that relying solely on dew-point calculations may underestimate the risk of hydrate formation.

Reducing the risk of hydrate formation can also be done by gas dehydration. As the hydrate cavities consists of hydrogen bonded water molecules, reducing available water will serve as a method of hydrate prevention. Linde Type A zeolites is often used in processing industry for gas dehydration. However, detailed information on kinetics such as rate of loading, diffusion and poisoning can still be improved. This work investigates the interfacial termination of Linde Type A zeolites. Furthermore, the effects of partial atomic charges in the interface region on diffusion, flux and water orientation and structuring are determined.

It was found that while the termination mattered, the charge distribution dominated and significantly affected the kinetics in the interface region. Likewise, improper balancing of partial atomic charges led to disturbances in the inter-cavity motion of water molecules. Depending on the distribution of charges in the interface the rate of loading were reduced by as much as half.
List of publications

Papers


International presentations


Contents

Scientific environment iii
Acknowledgements v
Abstract vii
List of publications ix
Abbreviations xv
Chemicals xvii
Symbols xix

1 Introduction 1
  1.1 Objectives and outline of thesis ........................... 2

2 Background 5
  2.1 Global warming ............................................. 5
    2.1.1 Summary of key observations .......................... 5
    2.1.2 Greenhouse gases ...................................... 6
  2.2 Carbon capture and sequestration ............................ 7
  2.3 Pipeline transport challenges ................................ 10
  2.4 Gas dehydration ............................................. 12

3 Theory of molecular simulation 15
  3.1 Molecular dynamics .......................................... 15
    3.1.1 Statistical mechanics ................................... 15
    3.1.2 Governing equations ..................................... 17
    3.1.3 Integration of motion .................................... 18
    3.1.4 Periodic boundary conditions ............................ 19
    3.1.5 Electrostatic interactions in periodic systems ........... 20
    3.1.6 Temperature control ..................................... 23
    3.1.7 Free energy calculations ................................ 24
  3.2 Force fields .................................................. 25
    3.2.1 Bonded interactions ..................................... 25
    3.2.2 Non-bonded interactions ................................ 27
## Contents

4 Simulation constituents and details  
4.1 Gas, liquid and solid constituents ........................................... 31  
4.1.1 Gas and liquid constituents .............................................. 32  
4.1.2 Solid constituents ....................................................... 36  
4.2 Simulation analyzes .......................................................... 42  
4.2.1 Self-diffusion ................................................................. 42  
4.2.2 Electrostatic potential energy maps ...................................... 43  

5 Introduction to the papers ....................................................... 45  

6 Conclusions ............................................................................. 49  

7 Suggestions to future work ...................................................... 51  

8 Scientific results ...................................................................... 57  

9 Appendix A ............................................................................. 133
List of Figures

3.1 Periodic Boundary Conditions ........................................... 20
3.2 Bond ball-and-spring model with harmonic and Morse potential .... 26
3.3 Illustration of ball-and-spring model for angles ...................... 27
3.4 Illustration of dihedral angles .......................................... 27
3.5 Comparison of Buckingham and Lennard-Jones 12-6 potentials .... 29
4.1 Illustration of the carbon dioxide (CO$_2$) molecule .................. 32
4.2 Illustration of the hydrogen sulfide (H$_2$S) molecule ............... 34
4.3 Illustration of the water (H$_2$O) molecule ............................ 35
4.4 Illustration of calcite unit cell ........................................ 38
4.5 Illustration of the LTA windows ........................................ 39
4.6 Illustration of LTA zeolite framework .................................. 40
**Abbreviations**

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>AR4</td>
<td>fourth assessment report</td>
</tr>
<tr>
<td>AR5</td>
<td>fifth assessment report</td>
</tr>
<tr>
<td>CCS</td>
<td>carbon capture and sequestration</td>
</tr>
<tr>
<td>CPU</td>
<td>central processing unit</td>
</tr>
<tr>
<td>EOR</td>
<td>enhanced oil recovery</td>
</tr>
<tr>
<td>fSPC</td>
<td>flexible simple point charge</td>
</tr>
<tr>
<td>GHG</td>
<td>greenhouse gas</td>
</tr>
<tr>
<td>GMST</td>
<td>global mean surface temperature</td>
</tr>
<tr>
<td>GPGPU</td>
<td>general purpose graphical processing unit</td>
</tr>
<tr>
<td>HSE</td>
<td>health, safety and the environment</td>
</tr>
<tr>
<td>IPCC</td>
<td>Intergovernmental Panel on Climate Change</td>
</tr>
<tr>
<td>LTA</td>
<td>Linde type A</td>
</tr>
<tr>
<td>LTA-3A</td>
<td>Linde type A zeolites with potassium counter-ions</td>
</tr>
<tr>
<td>LTA-4A</td>
<td>Linde type A zeolites with sodium counter-ions</td>
</tr>
<tr>
<td>MD</td>
<td>molecular dynamics</td>
</tr>
<tr>
<td>MOF</td>
<td>metal organic framework</td>
</tr>
<tr>
<td>MSD</td>
<td>mean squared displacement</td>
</tr>
<tr>
<td>PBC</td>
<td>periodic boundary conditions</td>
</tr>
<tr>
<td>ppb</td>
<td>parts per billion</td>
</tr>
<tr>
<td>ppmV</td>
<td>parts per million by volume</td>
</tr>
<tr>
<td>RF</td>
<td>radiative forcing</td>
</tr>
<tr>
<td>SPC</td>
<td>simple point charge</td>
</tr>
<tr>
<td>SPC/E</td>
<td>extended simple point charge</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>--------------------------------</td>
</tr>
<tr>
<td>syngas</td>
<td>synthesis gas</td>
</tr>
<tr>
<td>Tcl</td>
<td>tool command language</td>
</tr>
<tr>
<td>vdW</td>
<td>van der Waals</td>
</tr>
<tr>
<td>VMD</td>
<td>Visual Molecular Dynamics</td>
</tr>
<tr>
<td>WMGHG</td>
<td>well-mixed greenhouse gas</td>
</tr>
</tbody>
</table>
Chemicals

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca$^{2+}$</td>
<td>calcium ion</td>
</tr>
<tr>
<td>CaCO$_3$</td>
<td>calcite</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>methane</td>
</tr>
<tr>
<td>$\left[M_{12}^{n+/n}\right][Al_{12}Si_{12}O_{48}]_8$</td>
<td>LTA (generic formula)</td>
</tr>
<tr>
<td>CO</td>
<td>carbon monoxide</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>carbon dioxide</td>
</tr>
<tr>
<td>CO$_3^{2-}$</td>
<td>carbonate ion</td>
</tr>
<tr>
<td>Fe$^{2+}$</td>
<td>ferrous ion</td>
</tr>
<tr>
<td>FeCO$_3$</td>
<td>siderite</td>
</tr>
<tr>
<td>H$_2$</td>
<td>hydrogen gas</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>water</td>
</tr>
<tr>
<td>H$_2$S</td>
<td>hydrogen sulfide</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>hematite</td>
</tr>
<tr>
<td>MgCO$_3$</td>
<td>magnesite</td>
</tr>
<tr>
<td>N$_2$O</td>
<td>nitrous oxide</td>
</tr>
<tr>
<td>TEG</td>
<td>tri-ethylene glycol</td>
</tr>
</tbody>
</table>
Symbols

\[ \alpha \] Morse potential well width
\[ \beta \] Ewald coefficient
\[ \delta_{ij} \] scaling factor for interaction between \( i \) and \( j \)
\[ \varepsilon \] Lennard-Jones well depth or strength of interaction
\[ \varepsilon_{ij} \] \( \varepsilon \) for interaction between atoms \( i \) and \( j \)
\[ \varepsilon_r \] relative permittivity
\[ \phi \] dihedral angle
\[ \sigma \] Lennard-Jones parameter
\[ \sigma_{ij} \] \( \sigma \) for interaction between atoms \( i \) and \( j \)
\[ \theta \] angle between bonded atoms A–B–C
\[ \theta_{eq} \] equilibrium angle between bonded atoms A–B–C
\[ \zeta \] Nosé-Hoover thermodynamic friction coefficient
\[ \langle A \rangle \] ensemble average of property A

\( A \) Buckingham potential exponential pre-factor (repulsive)
\( \mathcal{A} \) System in state \( \mathcal{A} \)
\( A(t) \) value of property A as function of time, \( t \)
\( \langle A(t) \rangle \) time-average of property \( A(t) \)

\( B \) Buckingham potential parameter (in exponential function)
\( \mathcal{B} \) System in state \( \mathcal{B} \)

\( C \) Buckingham potential parameter (attractive)

\( D_e \) Morse potential well depth

\( E \) energy

\( \mathbf{F} \) force

\( i \) particle iterator

\( j \) particle iterator
Symbols

$k_b$ force constant for a bond
$k_f$ force constant for an angle

$N$ number of particles

$p$ pressure
$p$ momentum
$p_s$ time-scale conjugated momentum

$Q$ Nosé-Hoover thermostat parameter
$q$ position
$q_c$ partial atomic charge of particle
$Q_i$ partial atomic charge of particle $i$
$Q_j$ partial atomic charge of particle $j$

$r$ bond or separation length
$R\bar{3}c$ a trigonal crystallographic space group
$r_{eq}$ equilibrium bond length
$r$ vector between two particles

$s$ time-scale variable

$T$ temperature
$t$ time

$U$ potential energy
$U_{angle}$ potential energy from angle bending
$U_{bond}$ potential energy from bond stretching
$U_{dihedral}$ potential energy from twisting a dihedral angle
$U_{el}$ potential energy from electrostatic interactions
$U_{vdW}$ potential energy from van der Waals interactions

$V$ volume
$V_1 \ldots V_3$ dihedral force constants

$X$ number of independent degrees of freedom in $q$ and $p$
Chapter 1: Introduction

CO$_2$ have been at the center of attention the last few decades, being the main contributor to man-made global warming. In 1997 the Kyoto Protocol [1] was adopted. In the Kyoto Protocol the parties agreed to reduce the carbon dioxide equivalent emissions by at least 5% from the 1990-level, in the period 2008-2012.

To reduce the carbon dioxide emissions renewable energy sources must be utilized while weakening fossil fuel dependence. Reduction of CO$_2$ emissions by post-combustion capture is also viable. Large stationary carbon dioxide sources, like coal power plants, are good candidates for carbon capture and sequestration (CCS). By scrubbing the flue-gas for carbon dioxide, the CO$_2$ can be captured and stored in geological formations. While technology for capturing carbon dioxide (i.e. natural gas treatment with amines) was first disclosed in 1959 by Bertheir [2], subsurface storage is in need of some attention from the research community.

When injecting carbon dioxide in geological formations, proper sealing of the reservoir is key. The site has to be thoroughly examined to identify faults in the cap-rock, designating regions that potentially should be avoided. To further add to a complex picture, carbon dioxide can dissolve into water and lower the pH. For subterranean sequestration of CO$_2$ where depleted hydrocarbon reservoirs are among the more obvious choices, the mineral composition of the reservoir rock is important. One of the more abundant minerals in earth crust, calcite (CaCO$_3$), can be dissolved by aqueous carbon dioxide. This give rise to the possibility of fractures being widened, permeabilities that may change due to dissolution or precipitation, or eventually leakage.

For off-shore subsurface storage carbon dioxide has to be transported to the injection site. While pipelines likely is the best option for such transport, it is not without problematic issues. Pipeline transport of CO$_2$ may be complicated by the presence of trace amounts of water. If the pipeline happens to be located on the sea-floor, or in arctic areas, the low temperatures combined with the high pressures inside may cause clathrates to form. Formation of hydrates (clathrates) can lead to blocking of the pipeline, with the consequences that may have.

Gas hydrate consists of water forming the cavities and guest molecules filling the cavities and stabilizing the hydrates. Without water, guest molecules or correct pressure and temperature conditions, hydrates cannot form. There exists several strategies for preventing hydrate formation. One could be to operate with pressure and temperature conditions that will not allow for hydrates to form. Another would be to inject chemicals, like methanol or ethylene glycol, diethylene glycol or triethylene glycol. These prevent hydrate formation by favorable hydrogen bonding to water, lowering the chemical potential of the aqueous phase. However, just like hydrate inhibitors may prevent hydrate formation, surfaces and interfaces may contribute to promote hydrate formation.
In daily life interfaces play a crucial role in an abundance of processes, from biological to chemical and further to physical processes. Interfaces, like cell-membranes, are vital for life as we know it. Interfaces are also present in industrial systems. For instance in oil-water gravitational separators, distillation columns, packed column absorption systems and even in pipelines. In short, all systems containing more than one phase has to have at least one interface.

While a pipeline wall macroscopically might seem like a uniform surface, microscopically it is quite complex. The surface might have been exposed to water, or humidity, and as a consequence rusted. Or, it might have been coated with an surface active agent. Between the rusty spots, or surface, there might be small gaps or wide bands of unoxidized iron. On a molecular scale, all these surfaces have different properties, resulting in disparate interactions between the surface and neighboring molecules. For instance, the rusty surface will be highly hydrophilic, while the surfactant coated surface can be hydrophobic. The differences in interactions between water and seemingly similar surfaces is controlled at the atomistic/molecular, or even quantum, level. Understanding hydrate formation, and proper prevention, requires knowledge of how surfaces affect hydrate constituents, stability and structure.

As water has to be present for hydrates to form, simply drying the gas and removing water from the fluid is a viable option. Gas drying can be achieved in different manners. One of the methods involves using zeolites to adsorb the water. The benefit of this method is that it can be tuned to selectively adsorb water, while ignoring for instance carbon dioxide.

A zeolite often used for drying of natural gas is the Linde type A (LTA) zeolite. LTA zeolites is a cubic structure with cavities inside. By ion-exchange different counter-ions can be introduced into the zeolite, effectively blocking part of the entrances. Consequently, the zeolite works as a molecular sieve, only allowing molecules with physical dimensions below certain sizes access to the interior. For instance, Linde type A zeolites with sodium counter-ions (LTA-4A) will allow both water and methane access, where Linde type A zeolites with potassium counter-ions (LTA-3A) will only allow water of the two.

While LTA zeolites have received considerable attention the last decade or so, questions still remains when it comes to its kinetic properties. In particular there has been a lack of attention on how the interface is terminated, the effect of the termination, and how the interface facilitates or prevent poisoning of the zeolite.

1.1 Objectives and outline of thesis

The focus of this thesis is within the realm of CCS to examine the potential for hydrate formation when CO₂ is subjected to pipeline transport, subterranean injection and storage. Furthermore, to investigate LTA zeolites, to eventually optimize the loading and reduce potential poisoning of the zeolites.

From the main objective the following sub-objectives have been derived:

- Determine the structure and chemical potential of water on calcite surface
- Determine the structure and chemical potential of water on hematite
1.1 Objectives and outline of thesis

- Evaluate the potential for hydrate formation on said surfaces
- Investigate the impact of LTA zeolite termination on water interaction and adsorption

With this in mind the following systems are studied in this thesis:

I Calcite with water and carbon dioxide
II Hematite with water and carbon dioxide
III Hematite with water and hydrogen sulfide
IV Linde Type A zeolites with water (both potassium and sodium counter-ions)

The rather wide scope of the main objective does imply that this is part of a larger work. Thus, the focus in this thesis is mainly on the zeolite and effect of termination and charges in those systems. However, the first papers were on systems with calcite and hematite where I contributed by writing analysis routines, extending software and implementing free energy calculation methods, and running simulations with subsequent post-processing. It ends with the two papers on LTA zeolites, where the focus is on the water-zeolite interactions, the electrostatic interactions and the effect of termination and charge distributions in the interface.

The whole thesis could easily have been dedicated to just one of the sub-goals. Nevertheless, it has to fit into a larger scope.
Chapter 2: Background

2.1 Global warming

According to overwhelming international consensus, and backed up by the massive reports from the Intergovernmental Panel on Climate Change (IPCC), climate change is happening right now, and the humankind is to blame. IPCC’s fifth assessment report (AR5) states that it is certain that the global mean surface temperature (GMST) has increased during the last 100–150 years [3]. Stocker et al. [3] further states that each of the last three decades have successively been warmer at the earth’s surface than the last.

The report uses a set of specific terms to indicate the likelihood of the assessments given in Table 2.1. For instance, in AR5 one can read that:

It is also virtually certain that maximum and minimum temperatures over land have increased on a global scale since 1950.

From Table 2.1 it is clear that this means that the probability of this statement being true is evaluated to being in the range of 99–100%. While the quote from IPCC’s AR5 is a nice demonstration of their usage of the terms to ensure consistency when treating uncertainties, it is also a quote worth to consider. Clearly, the international community of scientists agree that global warming is real, and that it constitutes a real problem.

2.1.1 Summary of key observations

As technology has been developed sensors have been put into the field, allowing for precise measurements to be made. Thus, at least since the 1970s there exists good quality datasets available to the climate researchers.

Table 2.1: Description of terms used to quantify likelihood in the technical summary of IPCC’s fifth assessment report [3]. The terms are typeset in italics.

<table>
<thead>
<tr>
<th>Term</th>
<th>Likelihood of outcome [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Virtually certain</td>
<td>99–100</td>
</tr>
<tr>
<td>Very likely</td>
<td>90–100</td>
</tr>
<tr>
<td>Likely</td>
<td>66–100</td>
</tr>
<tr>
<td>About as likely as not</td>
<td>33–66</td>
</tr>
<tr>
<td>Unlikely</td>
<td>0–33</td>
</tr>
<tr>
<td>Very unlikely</td>
<td>0–10</td>
</tr>
<tr>
<td>Exceptionally unlikely</td>
<td>0–1</td>
</tr>
</tbody>
</table>
Summing up the key observations during these decades shows that in the northern hemisphere we have very likely had the warmest 30-year period from 1983–2012 of the last eight centuries. Furthermore, it was likely the warmest period the last fourteen centuries [3]. Globally, it is virtually certain that the troposphere has warmed during the last 50–60 years, and that the stratosphere has cooled. The change in temperature is not only confined to the atmosphere. Stocker et al. [3] asserts that it is virtually certain that the upper part of the ocean, down to 700 m, have warmed in the period 1971–2010. In the longer perspective, they believe it likely warmed from 1870–1971.

In the Arctic, Stocker et al. [3] affirms with very high confidence that the extent of the sea ice has decreased in the period 1971–2012, and that the rate of change very likely was between 450 000–510 000 km\(^2\). To put this in perspective, the area of Norway is 385 171 km\(^2\), including Svalbard and Jan Mayen [4]. I.e. each decade the extent of Arctic sea ice is reduced with an area corresponding to at least 1.15 times the area of the kingdom of Norway.

One of the more troubling conclusions from the Technical Summary found in AR5 is that the Earth has been in radiative imbalance since at least about 1970 [3]. They declare it virtually certain that the Earth has gained substantial energy by radiation from the Sun entering the Earth’s atmosphere, without a similar amount exiting.

One of the consequences of global warming is the potential for rising sea levels as the Antarctic and Greenland glaciers melts. AR5 asserts with very high confidence that glaciers all over the world are diminishing. For the last two decades the Antarctic ice sheet has been losing ice, and there is a high confidence that acceleration of outlet glaciers is to blame. To make matters worse, the current climate and glaciers are not in equilibrium, ensuring further future melting. The report states that even if the current temperature increase were to subside, the glaciers will continue to ebb.

This is in spite of trends towards, and observations of larger floods due to, heavier precipitation.

2.1.2 Greenhouse gases

Greenhouse gases (GHGs) like carbon dioxide, methane (CH\(_4\)), H\(_2\)O, nitrous oxide (N\(_2\)O) and halocarbons are gases that adsorb (and can emit) infrared radiation, and thus trap heat in the atmosphere by adsorbing and reemitting the radiation [3].

While both carbon dioxide and water (along with methane and nitrous oxide) are natural occurring, where water is the most abundant, carbon dioxide is the one receiving the attention. When burning fossil fuels, the hydrocarbon chains breaks down into CO\(_2\) and H\(_2\)O (along with heat). Fossil fuels can be considered as chemical stable CO\(_2\) containers; when it is extracted and consumed CO\(_2\) is released into the atmosphere. By releasing the CO\(_2\), the atmospheric concentration of CO\(_2\) is increased, and the greenhouse effect increases as a consequence. The increased net radiative flux, or radiative forcing (RF) as it is known as [3], of all well-mixed greenhouse gas (WMGHG) was in 2011 estimated to be \((2.83 \pm 0.29)\) W\(\text{m}^{-2}\), for CO\(_2\) by itself the number is \((1.82 \pm 0.19)\) W\(\text{m}^{-2}\) from the industrial era. Carbon dioxide on its own makes up for more than half of the RF. This makes CO\(_2\) an important focus for reducing emissions in the effort to halt the global warming.

Again turning to Stocker et al. [3], the concentration of GHGs measured in 2011 exceed recorded concentrations from the past 800 000 years (stemming from polar ice
core samples). It is estimated that the CO$_2$ emissions from fossil fuel use and cement production between 1750 and 2011 was $(375 \pm 30) \times 10^{15}$ g of carbon, where $1 \times 10^{15}$ g of carbon is corresponds to $3.6675 \times 10^{15}$ g of CO$_2$. If the emissions from land use is included the number rises to $555 \times 10^{15}$ g carbon released, where $(240 \pm 10) \times 10^{15}$ g carbon accumulated in the atmosphere. The remainder re-adsorbed into the oceans or used by plants in photosynthesis and trapped, etc.

As the atmospheric concentration of CO$_2$ increases, the concentration in the oceans are bound to rise too. Stocker et al. [3] states that it is very likely that the total oceanic content of carbon increased from 1994 to 2010. As briefly mentioned in the introduction, the dissolution of CO$_2$ in water leads to a lowering of the pH. AR5 (and references therein) determines that the pH of the oceanic surface water has decreased by 0.1 since the beginning of the industrial era. Since pH is a logarithmic scale, the rather small decrease of 0.1 actually corresponds to a 26% increase in H$^+$ concentration.

Methane is another greenhouse gas that has had increasing atmospheric concentrations during the industrial era. The concentration has increased from the 1750s where it was $722 \pm 25$ to $1803 \pm 4$ parts per billion (ppb) in 2011. Stocker et al. [3] asserts with very high confidence that the increase is caused by human activities. Methane atmospheric concentrations has had a period of little to no increase, but recently the concentrations has started to increase again. Consequently the RF increased by 2% from fourth assessment report (AR4) to fifth assessment report, very likely making the RF from CH$_4$ larger than that of the halocarbons as a class in total.

2.2 Carbon capture and sequestration

As given above in subsection 2.1.2, CO$_2$ is the cause of more than 50% of the radiative forcing. At the same time, the majority of CO$_2$ is released from use of fossil fuels. Since some of the worst polluters are coal power plants, which are large single source polluters, capturing and sequestrating the CO$_2$ currently released from these is a viable option.

Carbon capture

By capturing the GHGs, and CO$_2$ in particular, the rate of global warming can be slowed down. Capturing CO$_2$ can be done via different methods, and is usually categorized into three different branches of technology [5].

**Post-combustion**  CO$_2$ capture from flue gas after combustion. Can be done through amine-extraction processes.

**Pre-combustion**  Capture of carbon prior to combustion, usually through production of hydrogen gas (H$_2$) as an energy-carrier.

**Oxy-combustion**  Generation of high CO$_2$ concentration flue gas through combustion in an oxygen-rich atmosphere mixed with recycled flue gas.

The most common method, the post-combustion capture where the carbon dioxide is separated from from the flue gas, has the advantage that it can be retrofitted to existing coal power plants. However, there are several disadvantages such as low concentration
of CO₂ in the flue gas (harder to separate out), and low pressure flue gas, which mandates the compression of CO₂ for pipeline transport and/or subsurface injection [5]. While CO₂ reaction with amines have been the traditional method of extraction, and is still being researched and improved on, there are several other emerging methods such as carbonate-based systems, aqueous ammonia, separation by membranes, capture by sorbents, adsorption in metal organic frameworks (MOFs), CO₂ reactions with enzymes and the use of ionic liquids [5]. While the future for post-combustion carbon capture may be promising, the disadvantages mentioned above are general and apply to all these systems.

Removal of the carbon prior to combustion is known as *pre-combustion* capture. The process works by gasification of the fuel under high temperature and pressure with the addition of oxygen. The result is synthesis gas (syngas), in essence consisting of carbon monoxide (CO) and H₂. By adding steam to the syngas in a shift converter the CO reacts with the H₂O-gas and turns into CO₂ and H₂. Prior to combustion of the hydrogen gas the carbon dioxide has to be separated out. Given the difference in physical size and chemical properties, membrane separation of H₂ and CO₂ is, if not exactly an easy process, at least manageable. The advantage of pre-combustion methods is that the exhaust from the subsequent combustion of the H₂ is pure H₂O. Furthermore, the syngas-process is a high-pressure process, meaning that the need for increasing the CO₂ pressure prior to pipeline transport/injection is reduced. The higher concentrations of CO₂, compared to post-combustion concentrations, also makes for easier separation. The disadvantage is cost of the system and the inability of retrofitting, which limits its use to new plants [5].

The third option, *oxy-combustion*, relies on burning the fuel in a very oxygen-rich atmosphere (above 95 %) mixed with recycled flue gas [5]. In this process the CO₂ concentration in flue gas is increased significantly, by the continuous recycling, to the point where it consist almost exclusively of CO₂ and H₂O, with traces contaminants. The advantages are the high concentration of CO₂ in the flue gas and that this technology can be retrofitted, much like the post-combustion technologies. However, there are several challenges with this technology. First, a high demand of oxygen for injection into the combustion process makes a on-site cryogenic oxygen-plant a prerequisite, for which the cost of operation may be formidable. Similarly to that of the post-combustion methods, the pressure of captured carbon dioxide is low which calls for compressors for obtaining the necessary pressure for transport or injection.

**Sequestration**

Carbon sequestration can be sorted into two main groups, biotic and abiotic sequestration. For the purposes of this text the focus will be exclusively on the managed abiotic carbon sequestration. Lal [6] lists four main methods of abiotic managed sequestration:

- Mineralization
- Oceanic injection
- Chemical scrubbing
- Geological sequestration
Chemical scrubbing can be the same process as the post-combustion amine extraction discussed above in subsubsection 2.2. However, in the carbon capture process, the amines (or carbon scrubbers in general) are usually regenerated, where the CO\textsubscript{2} is released from the absorbent. By choosing not to regenerate the absorbent the captured CO\textsubscript{2} remains absorbed, and as such it could conceivably be considered a sequestration method. Nonetheless, chemical scrubbing is usually only viewed as a part of the capture process due to the cost of absorbents, and will not be further discussed here.

Mineralization is an interesting process and one that inherently may be considered a part of many geological sequestration projects through for instance generation of calcite. Carbon sequestration by means of mineralization is the process of binding CO\textsubscript{2} to other elements such as calcium or magnesium, thus forming minerals, in this case calcite (CaCO\textsubscript{3}) and magnesite (MgCO\textsubscript{3}). Both of these are examples of mineral carbonation. Carbon dioxide mineralization is not limited to only these two processes, and several other reactions can occur. These are examples of natural processes, that takes place by themselves. The challenge lies in industrialization of the processes, by speeding up the slow rates of reaction [6]. Accelerating the rate of reactions can be done by increasing temperature and pressure, but that has its own cost in form of energy input.

It is well-known that oceans cover 71% of the earth’s surface. The large bodies of water makes oceanic injection of CO\textsubscript{2} a tempting prospect. According to Lal [6], the initial proposals were made in the late 1970s. It is prudent to note that the AR5 asserts that the oceanic pH has decreased since the start of the industrial era, and that dissolution of carbon dioxide is the likely cause of this decrease. With that in mind, oceanic injection of CO\textsubscript{2} may not be all that clever [6], and could have some detrimental consequences for the ecosystem.

The most promising technique for carbon sequestration is that of geological injection. Geological injection of CO\textsubscript{2} has been commercially utilized since 1996 in Statoil’s Sleipner Vest CO\textsubscript{2} disposal project [7]. In this project CO\textsubscript{2} had to be removed from the natural gas produced from the wells to meet the customer product specifications. Releasing the carbon dioxide into the atmosphere would have incurred significant expenses due to the CO\textsubscript{2}-quota system. Thus, from a business point of view, it made economical sense to inject the captured CO\textsubscript{2} into the Utsira formation.

Carbon dioxide has further uses within the oil and gas sector. Injection of CO\textsubscript{2} in oil reservoirs is an effective method of enhanced oil recovery (EOR). The injected CO\textsubscript{2} can work as an highly effective solvent for small hydrocarbons and aromatics [8], and lower the viscosity of the solution. With lower viscosity, the hydrocarbons can achieve higher flow-rates which in turn can result in increased production. Similarly, injection of CO\textsubscript{2} into deep subsurface coal seams with concurrent natural gas production can displace CH\textsubscript{4} and increase production while the CO\textsubscript{2} remains trapped. The benefit of this method is to offset the cost of carbon sequestration by the energy gained from the CH\textsubscript{4}. Several field tests were successfully carried out using variations of this technique in the mid 1990s in the San Juan Basin (non-exhaustive list) [8].

A third candidate for geological sequestration is injection in deep saline aquifers of which are widespread and thus lessens the distance of transportation. In the deep saline aquifers CO\textsubscript{2} can be trapped in different manners. Under the right conditions CO\textsubscript{2} can form its own gas phase from the brine, and when prevented from rising higher in the formation due to cap-rock (or a low permeability layer), the CO\textsubscript{2} is constrained.
to the natural hydrodynamic gradient [8]. This is known as hydrodynamic trapping. Carbon dioxide can also dissolve into the brine and become solubility trapped. Dissolving CO$_2$ into brine results in lowering of the pH. Calcite, for instance, dissolves in acidic solutions. The potential for dissolution of the mineral matrix, poses some potential problems. The worst case scenario is weakening of the cap-rock, or increase in the permeability in low permeability zones, allowing for migration of CO$_2$ to the surface. Dissolution with subsequent precipitation or carbonization of minerals may change the permeability in near-injection well areas. If the permeability is reduced, higher injection-pressure might be necessary to inject at the same rate, with the potential for inducing fractures in the mineral matrix. Finally, injected carbon dioxide may be subjected to mineral trapping. Dissolved CO$_2$ can undergo an chemical reaction with cations and form mineral particles that precipitate from the solution. While the side-consequences as described above may be undesirable, mineral trapping is the most stable underground trapping.

To conclude, there are many methods of carbon sequestration. Subsurface sequestration seems not only to be the most promising, but is also a proven method.

### 2.3 Pipeline transport challenges

For any carbon sequestration to take place, pipeline transport of some kind is almost a given necessity. Assuming subsurface injection, be it in a deep coal seam, saline aquifer, depleted hydrocarbon reservoir or even as part of an EOR project, the CO$_2$ has to be transported to the injection site.

Pipeline transport is by no means a new technology. Hydrocarbons as gas, liquid and multiphase fluids, have been successfully transported through pipelines over long distances for quite a substantial time. Prior to hydrocarbon transport, water and sewer-systems were (and still are) highly dependent on effective pipeline distribution systems. Despite pipeline transport being a proven and well-known technology, both old and new challenges arises and must be handled when dealing with CCS. Several challenges have to be considered, evaluated and solved prior to effective pipeline transport of carbon dioxide from capture-site to injection-site. In no particular order, some of the challenges are:

- Erosion
- Corrosion
- Hydrate formation

**Erosion**

In Norway, carbon sequestration will very likely be carried out by injection into depleted hydrocarbon reservoirs, saline aquifers or as part of enhanced oil recovery. Thus, the pipelines will have to be put on the seafloor for efficient transport to take place. This further complicates some of the problems. Erosion, where solid particle within the fluid phase transported in the pipeline works as an abrasive, can over time weaken pipeline wall to the point of failure. Such a failure would incur considerable cost of repair, not
to mention the downtime where CO$_2$ would likely have to be released to the atmosphere rather than injected due to no viable alternative transportation. Fortunately, in most capture-scenarios there are few sources for particulates to enter the fluid stream and as such, while the consequences may be severe, the likelihood of this failure-mode occurring is not very high.

**Corrosion**

More problematic is the issue of corrosion. Flue gases inherently contain H$_2$O which in contact with iron pipeline walls readily cause corrosion. The fact that CO$_2$ is present as well does nothing to improve on the situation, as CO$_2$ can result in very high corrosion rates when dissolved in water [9]. Corrosion of the pipeline walls can lead to severe weakening to the point where the structure no longer can withstand the high internal pressure. CO$_2$ corrosion is dependent on a multitude of parameters. Among these are T, p, pH and water wetting [9]. In a pipeline the temperature is usually beyond the operator’s control and is given by the ambient temperature of the surroundings. With pressure there can be some leeway, but it has to be sufficiently high for injection to occur, while being low enough to avoid unintentional fracturing of the rock matrix. In the field this means that both T and p are more or less fixed due to the environment and are not parameters that can be tuned to reduce the impact of corrosion. The pH has a dual effect on corrosion. It affects the electrochemical reactions and can accelerate or decelerate the rate of corrosion. At higher pH, the solubility of ferrous ion (Fe$^{2+}$) is reduced. The reduction of Fe$^{2+}$–solubility can accelerate the precipitation of siderite (FeCO$_3$) that can form a protective film on the surface, decelerating further corrosion. Again it is prudent to mention that CO$_2$ dissolved in water lead to a lower pH and as such may prevent the precipitation of FeCO$_3$. Uncoated carbon steel or mild iron surfaces are water wetting surfaces. The presence of both a water film and CO$_2$ is necessary for CO$_2$–corrosion, but can also result in a transparent corrosion surface film which is protective against corrosion. Despite the protection, corrosion failures, predominantly due to CO$_2$–corrosion, account for $\sim$25% of all safety incidents in the oil and gas industry [9].

**Hydrate formation**

Pipeline surfaces, whether corroded or not, are water wetting surfaces. This makes the surfaces susceptible to adsorption of a thin water film, if water is present in the fluid stream. Clathrates, or gas hydrates, has long been a challenge for the oil and gas industry. Gas hydrates exists in several forms, but are essentially networks of hydrogen-bonded water molecules that form cavities which are stabilized by guest molecules. CO$_2$ is one of the guest molecules capable of stabilizing the cavities and thus contribute to hydrate formation. In fact, CO$_2$ has proven to be a more aggressive hydrate former than, for instance, CH$_4$. The presence of H$_2$O and CO$_2$ makes hydrate formation plausible if the thermodynamic conditions are such that hydrates will be stable. The low ambient temperature on the seafloor are within the hydrate stability zone for CO$_2$–hydrates. As are the high pressures usually associated with pipeline transport [10]. With both temperature and pressure within the hydrate stability zone, hydrate formation can present a serious problem for future CO$_2$–pipelines. It is well-known within
the oil and gas industry that plugging of pipelines due to hydrate formation presents challenges both in the form of accidents (health, safety and the environment (HSE)—risk) and the staggering costs associated with shutting down the pipeline and rectifying the issue. Thus, the potential for hydrate formation under such conditions surely need more research to ensure prior knowledge of proper operating conditions and hydrate formation risks.

2.4 Gas dehydration

Water has to be present for hydrates to form. Its presence is also a major contributor to corrosion. Without water there is no molecules to form the hydrogen bonded network of cavities which trap the guest molecules in hydrates. Since carbon dioxide is a guest molecule and surely present in a CO₂—pipeline, water removal from the gas stream is the only viable option for hydrate prevention through removal of hydrate constituents. Water removal can also be important in preventing corrosion.

Removing water from a gas can be carried out by different means such as absorption, adsorption, condensation or selectively permeable membranes. The oil and gas industry has extensive knowledge of absorption of water from gas streams using glycols (for instance tri-ethylene glycol (TEG)). Here the gas stream is fed through an absorber where the water in the gas comes into contact with the glycols and is absorbed into the liquid glycol phase, which is circulated through a stripping process where the absorbed water is boiled out of the TEG. The regenerated TEG is then pumped back to the absorber. Generally, absorption by glycols are used for bulk removal of water down to approximately 60 parts per million by volume (ppmV) [11], but it is possible to lower the water content to as little as a few ppmV [12]. As a side note there are some cases where glycols are injected into critical parts of gas processing plants without a separate dehydration unit or in critical parts prior to dehydration units. That is, however, considered a method of reducing hydrate formation risk, and not as a dehydration method.

Condensation by cooling the gas is another option. By, for instance, utilizing the Joule-Thompson effect, water can condensate out from the gas when the pressure is lowered. The liquid water is then removed from the gas stream. The disadvantage is that the dehydrated gas stream will have to undergo re-compression before pipeline transport. In a CCS scenario, the flue gas is likely already as atmospheric pressure, thus requiring the flue gas to be compressed twice.

The third option is dehydration by adsorption. Here silica gels and molecular sieves are often used. Molecular sieves, such as LTA zeolites, can selectively allow water to enter into the cavities and adsorb there, while blocking access to other molecules. While molecular sieves can achieve a dry gas with very low water content, a low as 0.03 ppmV [12], they are more expensive to install, require batch operation, the adsorbent must be replaced from time to time, and the regeneration process requires more energy in form of added heat than a glycol absorber/stripper-plant. The required energy depends of course on the adsorption characteristics of the zeolite in question and the required degree of regeneration.

However, even though molecular sieves are susceptible to attack by acids, they perform better with sour gas than glycols. The main reason being that for instance LTA-4A
can adsorb both CO$_2$ and H$_2$S, thus removing the sour gas components from the gas stream. This is an advantage when considering the damage that can be incurred by corrosion. When dealing with a CO$_2$-pipeline LTA-4A is likely not a good choice for a molecular sieve for dehydration due to CO$_2$ being capable of entering the cavities. In that case LTA-3A may be a better choice, as CO$_2$ has a harder time entering the cavities due to the larger counter-ions blocking the entrances. More on this in subsubsection 4.1.2, Simulation constituents and details, which deals specifically with zeolites.
Background
Chapter 3: Theory of molecular simulation

3.1 Molecular dynamics

Alder and Wainwright [13] stated in the abstract of their paper that "A method is outlined by which it is possible to calculate exactly the behavior of several hundred interacting classical particles." This is in essence molecular dynamics (MD) described in a sentence. The limits on how exactly the behavior can be calculated depends in a large degree on the choice of force fields and computational methods. As with most other model-based methods in physics, as well as pretty much every other branch of science, it has its shortcomings. MD is, nonetheless, a very powerful tool for generating molecular trajectories, statistical information and mapping out portions of phase space.

3.1.1 Statistical mechanics

Statistical mechanics is a branch of physics that connects the interactions and momenta of particles to thermodynamic observables, or variables. It has been widely successful in explaining physical observable phenomenons from the atomistic origin. Statistical mechanics is also the theoretical basis for molecular dynamics, in the way statistical mechanics couples the microscopic fluctuations, configurations and motions to macroscopic observable properties.

In thermodynamics we observe the macroscopic system and the corresponding macroscopic properties. For a macroscopic system in a given macrostate, there is an exceedingly large number of corresponding microstates. The microstates are defined by, and constrained to, the macroscopic variables. An isolated system has a fixed number of particles ($N$), a fixed volume ($V$), and a certain amount of energy ($E$). The variables $N$, $V$ and $E$ define the constraints on the system, and the corresponding microstates. Every microstate belonging to the macrostate thus have to have the same number of particles, total energy and volume.

Ensembles in statistical mechanics

In statistical mechanics there are several ensembles. The microcanonical, canonical and grand canonical ensembles are the most known. For each of these ensembles there is a set of fixed variables, the macroscopic thermodynamic observables that define the constraints on the system (see Table 3.1).

For each of the ensembles a partition function can be derived. The partition functions are crucial in statistical mechanics as they hold a wealth of information about the system. They are also the path to the thermodynamic quantities.
Table 3.1: Ensembles and partition functions in statistical mechanics [14, pp. 78, 138, 268]. $\mathcal{H}$ is the Hamiltonian, $M_N$ the microcanonical normalization factor and $C_N$ the canonical normalization factor.

<table>
<thead>
<tr>
<th>Ensemble</th>
<th>Variables</th>
<th>Partition function</th>
</tr>
</thead>
<tbody>
<tr>
<td>Microcanonical</td>
<td>$N, V, E$</td>
<td>$\Omega(N, V, E) = M_N \int dx \delta(\mathcal{H}(x) - E)$</td>
</tr>
<tr>
<td>Canonical</td>
<td>$N, V, T$</td>
<td>$Q(N, V, T) = C_N \int dx e^{-\beta \mathcal{H}(x)}$</td>
</tr>
<tr>
<td>Grand canonical</td>
<td>$\mu, V, T$</td>
<td>$Z(\mu, V, T) = \sum_{N=0}^{\infty} e^{\beta \mu N} Q(N, V, T)$</td>
</tr>
</tbody>
</table>

For instance, in the simple case of the microcanonical ensemble it is possible to define $\Omega(N, V, E)$ as the number of microstates belonging to the macrostate such that:

$$\Omega(N, V, E) = \text{number of microstates with } N, V \text{ and } E \text{ in } [E, E - \delta E].$$  (3.1)

If we assume that all microstates are equally probable at thermodynamic equilibrium, then

$$P_v = \frac{1}{\Omega(N, V, E)}$$  (3.2)

is the probability, $P_v$, of being in microstate $v$. The entropy is then defined as

$$S = k_B \ln \Omega(N, V, E),$$  (3.3)

where, $S$ is the entropy and $k_B$ is Boltzmann’s constant.

Returning to Table 3.1, each ensemble has a set of fixed variables. For the microcanonical ensemble the system, with fixed number of particles, volume and energy, is completely isolated. There is no change in volume, no particles may enter or leave the system nor may energy. The canonical ensemble on the other hand has fixed temperature instead of energy. This difference allow for energy to be exchanged with the surroundings, keeping the temperature constant. It is usual to visualize this as if the system was connected to, or lowered into, a heat bath with infinite potential. With the grand canonical ensemble the concept is somewhat more complex. With the chemical potential, volume and temperature is fixed, the system can exchange matter with its surroundings. Thus, mass, energy and pressure of the system may fluctuate as matter enters or leaves the system, as long as the chemical potential, volume and temperature remain fixed. It is in connection with a reservoir containing an infinite large number of particles.

**Phase space**

The classical Hamiltonian is given as the sum of potential and kinetic energy in the system,

$$\mathcal{H}(\mathbf{q}, \mathbf{p}) = U(\mathbf{q}_1, \ldots, \mathbf{q}_N) + \sum_{i=1}^{N} \frac{p_i^2}{2m_i},$$  (3.4)

where for particle $i$ $\mathbf{q}_i$ is the position, $\mathbf{p}_i$ is the momentum and $m_i$ is the mass. Note that the potential energy is a function of the positions only, while the kinetic energy is
a function of the momenta. It is usual to talk about them belonging to \textit{configurational space} and \textit{momentum space} which are the vector spaces spanned by the positions and momenta, respectively. For a system of N particles, phase space – the space spanned by both positions and momenta – the points in phase space are then defined by:

\[
(q^N, p^N) := (q_1, q_2, \ldots, q_N; p_1, p_2, \ldots, p_N)
\] (3.5)

Phase space is thus a $6N$ dimensional space, encompassing all possible positions and momenta. In the microcanonical ensemble the constraints (N,V,E) limit the possible points for the given system in phase space to a complex surface. If we were to follow the time-evolution of such a system, the trajectory would trace a path on that surface.

**Ergodicity**

A concept in statistical mechanics is that of \textit{ergodicity}. The general idea is that if we follow the time-evolution (or the trajectory) for a sufficiently long enough time, we will eventually pass through all points on the phase-space surface (constrained by the ensemble variables), or at least close to. Mathematically we have that the ensemble average, $\langle A \rangle$, is equal to the time-average, $\bar{A}(t)$, when the time goes towards infinity (see Eq. (3.6)).

\[
\lim_{t \to \infty} \bar{A}(t) = \langle A \rangle
\] (3.6)

This hypothesis is what we are exploiting in MD. Based on the hypothesis one makes the assumption that the systems partition function is sampled proportional to the ensemble’s partition function, and the systems observables are approximating the ensemble observables. Key for this to be valid are that a proper force field is used and that the observation period is sufficiently long. In the context of molecular dynamics simulations this is somewhat more complicated as the user, and indeed the implementation itself, may disrupt the system or sampling.

**3.1.2 Governing equations**

The design of MD is to model the interactions of particles, such as atoms or molecules, using Newton’s laws. By assigning potentials to atoms, the potential energy $U(r)$ between two atoms separated by a distance $|r|$ can be calculated. The force acting on the atoms can then be found using Eq. (3.7)

\[
F(r) = -\nabla U(r),
\] (3.7)

where $F$ is the resulting force vector, $U$ is the potential energy and $r$ is the vector from atom $i$ to atom $j$. By summing up all contributions for each particle the acceleration for each and every particle is then calculated from Newton’s second law.

To obtain the potential energy, the force field (see section 3.2) comes into play. Force fields contain the means, in form of functional forms and parameters, to calculate the potential energy of the particles. While the algorithms of and in MD are important, the choice of a force field may be crucial to succeed.
3.1.3 Integration of motion

From application of the force fields one get the potential energy. By Equation 3.7 and Newton’s second law one obtain the acceleration. But to advance the system in time an integration algorithm for the particles is needed. Luckily, of these there are many. There is the Verlét algorithm, velocity Verlét, leapfrog and all the Runge-Kutta methods. Some are more stable than others, some are computationally less costly than others and some are more convenient than others. In the end, they are supposed to solve the same task, advance the system in time.

Verlét algorithm

One of the simplest algorithms, and perhaps best known, is the Verlét algorithm. The derivation of this algorithm is fairly easy. Write down the Taylor expansions of the position of particle $i$, $q_i$, for time $(t \pm \Delta t)$

$$q_i(t + \Delta t) = q_i(t) + \left( \frac{d\mathbf{q}_i}{dt} \right)_t \Delta t + \frac{1}{2} \left( \frac{d^2\mathbf{q}_i}{dt^2} \right)_t (\Delta t)^2 + \ldots$$

(3.8)

$$q_i(t - \Delta t) = q_i(t) - \left( \frac{d\mathbf{q}_i}{dt} \right)_t \Delta t + \frac{1}{2} \left( \frac{d^2\mathbf{q}_i}{dt^2} \right)_t (\Delta t)^2 + \ldots$$

(3.9)

Add Equation 3.8 and Equation 3.9, and with some rearranging one get

$$q_i(t + \Delta t) = 2q_i(t) - q_i(t - \Delta t) + \left( \frac{d^2\mathbf{q}_i}{dt^2} \right)_t (\Delta t)^2,$$

(3.10)

which is the Verlét algorithm. One of its interesting features, which is somewhat hard to see here since this derivation stopped the Taylor expansion after the second order, is that the third order expansions cancels, just like the first order (the velocity) did. Thus the truncation error of this algorithm is to the fourth order. The disadvantage is that the velocity disappeared. The latter can easily be rectified by

$$v_i(t) = \frac{q_i(t + \Delta t) - q_i(t - \Delta t)}{2\Delta t},$$

(3.11)

or by using the slightly different velocity Verlét algorithm.

Leapfrog algorithm

The leapfrog algorithm is another method. This method does return both the position and velocity. However, at each point in time one only has the position or the velocity. This may again easily be corrected along the lines of Equation 3.11. In the leapfrog algorithm one start with the Taylor expansions over the velocities at time $(t \pm \frac{\Delta t}{2})$,

$$v_i \left( t + \frac{\Delta t}{2} \right) = v_i(t) + \left( \frac{d\mathbf{v}_i}{dt} \right)_t \frac{\Delta t}{2} + \frac{1}{2} \left( \frac{d^2\mathbf{v}_i}{dt^2} \right)_t \left( \frac{\Delta t}{2} \right)^2 + \ldots$$

(3.12)

$$v_i \left( t - \frac{\Delta t}{2} \right) = v_i(t) - \left( \frac{d\mathbf{v}_i}{dt} \right)_t \frac{\Delta t}{2} + \frac{1}{2} \left( \frac{d^2\mathbf{v}_i}{dt^2} \right)_t \left( \frac{\Delta t}{2} \right)^2 + \ldots$$

(3.13)
These equations are then subtracted from each other and rearranged to yield

\[ v_i \left( t + \frac{\Delta t}{2} \right) = v_i \left( t - \frac{\Delta t}{2} \right) + \left( \frac{dv_i}{dt} \right) \Delta t + \ldots, \]  

(3.14)

which is the velocity part of the leapfrog algorithm. Repeating the procedure for the positions, but now for time \( (t + \frac{\Delta t}{2}) \pm \frac{\Delta t}{2} \) and one get

\[ q_i \left( t + \frac{\Delta t}{2} + \frac{\Delta t}{2} \right) = q_i \left( t + \frac{\Delta t}{2} \right) + \left( \frac{dq_i}{dt} \right) _{t + \frac{\Delta t}{2}} + \frac{1}{2} \left( \frac{d^2 q_i}{dt^2} \right) _{t + \frac{\Delta t}{2}} \left( \frac{\Delta t}{2} \right)^2 + \ldots \]  

(3.15)

and

\[ q_i \left( t + \frac{\Delta t}{2} - \frac{\Delta t}{2} \right) = q_i \left( t + \frac{\Delta t}{2} \right) - \left( \frac{dq_i}{dt} \right) _{t + \frac{\Delta t}{2}} + \frac{1}{2} \left( \frac{d^2 q_i}{dt^2} \right) _{t + \frac{\Delta t}{2}} \left( \frac{\Delta t}{2} \right)^2 + \ldots \]  

(3.16)

subtracting Equation 3.16 from Equation 3.15 and the position part of the leapfrog algorithm come out as

\[ q_i \left( t + \frac{\Delta t}{2} + \frac{\Delta t}{2} \right) - q_i \left( t + \frac{\Delta t}{2} - \frac{\Delta t}{2} \right) = \Delta t \left( \frac{dq_i}{dt} \right) _{t + \frac{\Delta t}{2}} + \ldots, \]  

(3.17)

which by some rearranging and substitution becomes the usual equation for the positions in the leapfrog algorithm:

\[ q_i (t + \Delta t) = q_i (t) + v_i \left( t + \frac{\Delta t}{2} \right) \Delta t + \ldots \]  

(3.18)

As one now easily can see, the velocities are calculated at times \( t + \frac{\Delta t}{2} \), with positions calculated at times \( t + \Delta t \). This is the gist of the name "leapfrog", where the velocities leaps over the positions and vice versa.

### 3.1.4 Periodic boundary conditions

In molecular dynamics and scientific computation in general, a significant amount of effort goes into making the code, computation or application as efficient as possible. periodic boundary conditions (PBC) is one of the methods that can be utilized to simulate a system of infinite size while keeping a low number of actual particles. It is also a method that prevents the system from being dominated by the influence of particles.
constantly colliding with walls of the simulation box. This allows for simulation of bulk properties, even in a smaller system with limited number of particles.

The general concept is quite simple and is illustrated in two dimensions in Figure 3.1. When a particle, visualized as circles in Figure 3.1, moves outside the simulation box it reenters from the opposite side. This can be considered as if the particle moves into another box, and that a new particle enters the simulation box from a third box. In effect, one obtains a seemingly infinite simulation system, free from wall effects, with constant number density, capable of reproducing bulk properties.

### 3.1.5 Electrostatic interactions in periodic systems

As mentioned in subsubsection 3.2.2, Ewald summation methods are often used to calculate the long-range electrostatic interactions in periodic systems. These methods are employed as conventional methods, i.e.: using Coulomb’s law, has a poor computational performance. If one wants to increase the performance, the introduction of a cut-off distance is required, with the then added inaccuracy.

In Ewald summation methods, here in the flavor of the smooth particle mesh of Essmann et al. [15], the contributions to the electrostatic potential energy is divided into three terms. These are the direct contribution Equation 3.19, which is calculated in normal space, the reciprocal contribution Equation 3.20, calculated in reciprocal space and the correction term Equation 3.21 which corrects for both intra-molecular interactions and self-interactions.

$$U_{dir} = \frac{1}{2} \sum_n^+ q_i q_j \text{erfc} \left( \beta \frac{|r_i - r_j + n|}{|r_i - r_j - n|} \right)$$ (3.19)
\[ U_{\text{rec}} = \frac{1}{2\pi V} \sum_{m \neq 0} \frac{\exp(-\pi^2 m^2/\beta^2)}{m^2} S(m)S(-m) \] (3.20)

\[ U_{\text{corr}} = -\frac{1}{2} \sum_{(i,j) \in M} q_i q_j \text{erf}(\beta |\mathbf{r}_i - \mathbf{r}_j|) - \frac{\beta}{\sqrt{\pi}} \sum_{i=1}^{N} q_i^2 \] (3.21)

In Equation (3.19)–(3.21) \text{erf}(\cdot) and \text{erfc}(\cdot) is the error function and the complementary error function, respectively, \( \beta \) is the Ewald coefficient and \( \mathbf{n} \) is the periodic image vector. The Equation 3.21 is easy to calculate, given that one has the list of "masked pairs", \( M \). As the interesting parts are in the reciprocal contributions (Equation 3.20) the section below, subsubsection 3.1.5, is devoted to solving that equation.

To sum it up, the total electrostatic potential energy is then given as:

\[ U = U_{\text{dir}} + U_{\text{rec}} + U_{\text{corr}}. \] (3.22)

**Smooth particle mesh Ewald summation**

The equations and formalism below is based on the work of Essmann et al. [15]. It is included here as it was necessary to develop a utility to build a map of the electrostatic potential energies. The utility used the smooth particle mesh Ewald summation method.

Let: \( \mathbf{a}_\alpha \), where \( \alpha = 1, 2, 3 \), form the edges of a unit cell. \( \mathbf{a}_\alpha^* \) is the conjugate reciprocal vectors defined by \( \mathbf{a}_\alpha^* \cdot \mathbf{a}_\beta = \delta_{\alpha\beta} \) for \( \alpha, \beta = 1, 2, 3 \), where \( \delta_{\alpha\beta} \) is the Kronecker delta. The unit cell is filled with \( N \) point charges \( q_1, q_2, \ldots, q_N \), with positions \( \mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N \). Corresponding fractional coordinates \( s_{\alpha i} \), for point charge \( i \) is given by \( s_{\alpha i} = \mathbf{a}_\alpha^* \cdot \mathbf{r}_i \). Since the point charges interact not only with the neighboring charges, but also with all their periodic images as well (but not itself or its image), a vector \( \mathbf{n} = n_1 \alpha_1 + n_2 \alpha_2 + n_3 \alpha_3 \), where the integers \( n_1, n_2, n_3 \) cannot be all 0 at the same time, give the position of the periodic images. Finally we need to define the reciprocal lattice vectors \( \mathbf{m} = m_1 \alpha_1^* + m_2 \alpha_2^* + m_3 \alpha_3^* \), where \( m_1, m_2, m_3 \) are integers that cannot all be 0 at the same time.

With the definitions above now in place, the structure factor \( S(\mathbf{m}) \) in eq. (3.20) is defined as

\[ S(\mathbf{m}) = \sum_{j=1}^{N} q_j \exp(2\pi i \mathbf{m} \cdot \mathbf{r}_j) \]

\[ = \sum_{j=1}^{N} q_j \exp(2\pi i [m_1 s_{1j} + m_2 s_{2j} + m_3 s_{3j}]). \] (3.23)

We define the three positive integers, \( K_1, K_2, K_3 \). Then for any point charge, a scaled fractional coordinate is defined by \( u_\alpha = K_\alpha \mathbf{a}_\alpha^* \cdot \mathbf{r} \). Since periodic boundary conditions are used, one can assume that \( 0 \leq u_\alpha < K_\alpha \). Then the exponentials from (3.23) can be expressed as:

\[ \exp(2\pi i \mathbf{m} \cdot \mathbf{r}) = \exp(2\pi i \frac{m_1 u_1}{K_1}) \cdot \exp(2\pi i \frac{m_2 u_2}{K_2}) \cdot \exp(2\pi i \frac{m_3 u_3}{K_3}). \] (3.24)
Using Cardinal B-splines, the exponentials on the right hand side of equation (3.24) can be approximated as
\[
\exp(2\pi i \frac{m_i u_i}{K_i}) \approx b_i(m_i) \sum_{k=-\infty}^{\infty} M_n(u_i - k) \cdot \exp(2\pi i \frac{m_i k}{K_i}),
\]
where \(M_n\) is the Cardinal B-spline defined by
\[
M_2(u) = \begin{cases} 
0 & \text{for } u < 0 \text{ or } u > 2 \\
1 - |u - 1| & \text{for } 0 \leq u \leq 2 
\end{cases},
\]
and
\[
M_n(u) = \frac{u}{n-1} M_{n-1}(u) + \frac{n-u}{n-1} M_{n-1}(u-1),
\]
for any spline order \(n > 2\). The function \(b_i(m_i)\) in equation (3.25) is now given by
\[
b_i(m_i) = \exp(2\pi i (n-1)m_i/K_i) \times \left[ \sum_{k=0}^{n-2} M_n(k+1) \exp(2\pi i m_i k/K_i) \right].
\]
We define two new arrays:
\[
B(m_1,m_2,m_3) = |b_1(m_1)|^2 \cdot |b_2(m_2)|^2 \cdot |b_3(m_3)|^2,
\]
where \(b_i(m_i)\) is given by equation (3.28), and
\[
C(m_1,m_2,m_3) = \frac{1}{\pi V} \exp(-\frac{\pi^2 m^2}{\beta^2})
\]
for \(\mathbf{m} \neq 0\), with \(C(0,0,0) = 0\). Note that \(\mathbf{m}\) is redefined in the definition of \(C(m_1,m_2,m_3)\) as \(\mathbf{m} = m'_1 a'_1 + m'_2 a'_2 + m'_3 a'_3\), where \(m'_i = m_i\) for \(0 \leq m_i \leq K/2\) and \(m'_i = m_i - K_i\) elsewhere. With all this in place, the pair potential \(\theta_{rec}\) is given by the forward Fourier transform of \(B \cdot C\), i.e. \(\theta_{rec} = \mathcal{F}(B \cdot C)\). At this point the only part missing is the "charge grid array"
\[
Q(k_1,k_2,k_3) = \sum_{i=1}^{N} \sum_{n_1,n_2,n_3} q_i M_n(u_{i1} - k_1 - n_1 K_1) \\
\quad \quad \times M_n(u_{i2} - k_2 - n_2 K_2) \\
\quad \quad \times M_n(u_{i3} - k_3 - n_3 K_3).
\]
Finally the approximate reciprocal energy is calculated as
\[
\tilde{U}_{rec} = \frac{1}{2\pi V} \sum_{\mathbf{m} \neq 0} \exp(-\frac{\pi^2 m^2}{\beta^2}) B(m_1,m_2,m_3) \\
\quad \cdot F(Q)(m_1,m_2,m_3) F(Q)(-m_1,-m_2,-m_3) \\
= \frac{1}{2} \sum_{m_1=0}^{K_1-1} \sum_{m_2=0}^{K_2-1} \sum_{m_3=0}^{K_3-1} Q(m_1,m_2,m_3) \\
\quad \cdot (\theta_{rec} \ast Q)(m_1,m_2,m_3),
\]
(3.32)
where $\theta_{rec} \ast Q$ denotes the convolution of $\theta_{rec}$ and $Q$.

### 3.1.6 Temperature control

Molecular dynamics natural ensemble is the micro-canonical ensemble, i.e. constant $N$, $V$ and $E$. For comparison with experimental data this is inconvenient as most experiments are performed in the canonical ensemble with constant $N$, $V$ and $T$. Thus it is desirable to run simulations with a constant $T$.

Thermostatting in MD simulations can be achieved through different methods, from the simple velocity scaling to the more complex methods such as Andersen thermostatting [16] or the Nosé-Hoover thermostat [17, 18]. Temperature is a measure of the velocity of particles through the well known relation

$$\frac{1}{2}mv^2 = \frac{3}{2}k_B T,$$

where $m$ is the mass, $v$ is the velocity and $k_B$ is Boltzmann’s constant. It’s through this mechanism that the thermostats work. For the simple case of velocity scaling the velocity would be scaled up or down to a match a set system temperature. To avoid excessive system disturbance the velocities are usually only scaled when the measured temperature deviates by a set limit from the temperature of interest. While velocity scaling is an easy approach to simulations with constant temperature it is not a good approach. The method fails to generate the canonical partition function and the action of scaling the velocity makes phase space trajectories discontinuous.

A better method is to use the Andersen or Nosé-Hoover thermostats. Andersen’s method relies on stochastic collisions imparting momenta to the particles, one particle at the time. Still, this has the disadvantage of making the phase space trajectories discontinuous whenever a particle experience such an event. The Nosé-Hoover thermostat does not make the trajectories discontinuous. It works by expanding the systems Hamiltonian by adding an additional degree of freedom;

$$\hat{H}_{\text{Nosé}} = \phi(q) + \sum \frac{p^2}{2ms^2} + (X + 1)k_B T \ln s + \frac{p_s^2}{2Q},$$

where $q$ is the position and $p$ the momenta. The variable $s$ is a time-scale variable, originally used by Nosé [17] to scale time, and $p_s$ its coupled momentum [18]. $Q$ behaves as a virtual mass for the variable $s$, and has dimensions energy $\cdot$ time$^2$ [17].

Now, the Nosé thermostat as it was proposed had a disadvantage. It relied on scaling time. For MD simulations, where average quantities and properties, and more importantly time-average quantities and properties may be of interest, variable time is an inconvenience. Thus, Hoover [18] improved somewhat on Nosé’s formulation and simplified the resulting equations of motion such that

$$\dot{q} = \frac{p}{m}, \quad \dot{p} = F(q) - \zeta p$$

$$\dot{\zeta} = \frac{\left[ \sum \frac{p^2}{m} - X k_B T \right]}{Q},$$

(3.35)
where $\zeta$ is the thermodynamic friction coefficient [18]. The parameter $X$ should be equal to the number of independent degrees of freedom in $q$ and $p$. Note that Equation 3.35 does no longer rely on time-scaling and are easier implemented in MD software.

### 3.1.7 Free energy calculations

The work in this thesis entailed calculating chemical potential of different species. As the chemical potential is not a natural variable/quantity in MD simulations this required some additional effort.

There are, as usual in the world of MD, multiple methods of estimating chemical potential. Of the more known methods are thermodynamic integration methods, both temperature and polynomial path thermodynamic integration[19] and Widom particle insertion [20]. In this work the focus have mainly been on the thermodynamic integration methods, with particular focus on the polynomial path thermodynamic integration. This due to the relatively ease one could implement this method into the MD simulation software of Lyubartsev and Laaksonen [21].

Tuckerman [14, pp. 315] states that for a system in state $\mathcal{A}$ transforming into state $\mathcal{B}$ with potential energy functions $U_A(r_1,\ldots,r_N)$ and $U_B(r_1,\ldots,r_N)$, respectively, we can define

$$U(\lambda,r_1,\ldots,r_N) = f_1(\lambda)U_A(r_1,\ldots,r_N) + f_0(\lambda)U_B(r_1,\ldots,r_N),$$

where $f_1(\lambda)$ and $f_0(\lambda)$ are switching functions defined such that

$$f_1(0) = f_0(1) = 0$$
$$f_1(1) = f_0(0) = 1.$$ (3.37)

The easiest case where this holds true is for $f_0(\lambda) = 1 - \lambda$ and $f_1(\lambda) = \lambda$, where $\lambda \in [0,1]$. In effect this will switch the state from $\mathcal{A}$ to $\mathcal{B}$. In the polynomial path thermodynamic integration formalism from Mezei [19] the choice of $\lambda$ is somewhat different as seen in Equation 3.38.

$$f_1(\lambda) = \lambda^k$$ and $f_0(\lambda) = (1 - \lambda)^k$ (3.38)

The free energy difference can be found by integrating over $\lambda$

$$\Delta A = A_1 - A_0 = \int_0^1 \left\langle \frac{\partial U(\lambda,r_1,\ldots,r_N)}{\partial \lambda} \right\rangle d\lambda.$$ (3.39)

Inserting Equation 3.38 into Equation 3.39 and calculating the partial derivative results in

$$\Delta A = \int_0^1 k[(1 - \lambda)^{k-1}\langle U_A\rangle_\lambda + \lambda^{k-1}\langle U_B\rangle_\lambda] d\lambda.$$ (3.40)

In Mezei [19]’s work the idea is to integrate over a polynomial path evaluated using Gaussian quadratures.
3.2 Force fields

The governing equations of MD are Newton’s laws and known to be conservative, thus particles will continue along the direction of their velocity vector unless they interact with other particles or fields. The interaction parameters for particles are given by force fields, describing the interactions in form of equations and force constants, the latter which determines the strength of the interaction. The force fields are a requirement in MD. Thus a major part of running molecular dynamics simulations is to obtain, by finding or creating, a suitable force field for the application in hand.

The task of doing so may seem trivial at first, but is one of utmost importance and harder than it might look. More time is spent on choosing the correct force field, and to verify that the force field is suitable, than for instance the construction of the simulation systems. Water, which only contains three atoms, is a small molecule. In spite of its size, it is surprisingly difficult to simulate. There exists a multitude of different models, yet none of them are capable to correctly display all the properties of water. Some models are good at replicating the diffusional properties in liquid state, others are tailored to obtain the correct crystal structure as ice. However, no model – at this time – is capable of replicating the true behavior of water. With this in mind is should be clear that choosing force fields is crucial for quality simulations and and important aspect of molecular simulations.

Rather than forces, the force field give the means to calculate the potential energy ($U$), when the positions of all the particles in the system is known. The forces are then obtained by taking the negative gradient of the potential energy (see subsection 3.1.2). A general expression for the potential energy is

$$ U = U_{el} + U_{vdW} + U_{bond} + U_{angle} + U_{dihedral}, \quad (3.41) $$

where the contributions are from electrostatic interactions ($U_{el}$), and van der Waals interactions ($U_{vdW}$), bond stretching ($U_{bond}$), angle bending ($U_{angle}$) and twisting of dihedral angles ($U_{dihedral}$), respectively. Further terms could also be included, such as cross-interactions when both stretching a bond and bending an angle.

3.2.1 Bonded interactions

The different contributions in Eq. (3.41) are often split into two groups. Non-bonded and bonded interactions, where $U_{bond}$, $U_{angle}$ and $U_{dihedral}$ are bonded interactions. Bonded interactions are usually\(^1\) intra-molecular interactions, while non-bonded interactions can be both intra- and inter-molecular interactions.

Bonds

Chemical bonds between atoms are often modeled as harmonic bonds, where the two bonded atoms are connected by a virtual spring. This is the well-known ball-and-spring model, and it uses Hooke’s law to describe the potential energy;

---

\(^1\)There are special circumstances, or cases, where one could use for instance an harmonic pseudo-bond to ensure that a molecule stays within a certain distance from a surface, molecule, et cetera; making the interaction inter-molecular.
where $k_b$ is the bond force constant, $r$ is the length of the bond and $r_{eq}$ is the equilibrium bond length. Another common potential for bonds is the well known Morse potential:

$$U_{bond}(r) = D_e(1 - \exp(\alpha[r_{eq} - r]))^2,$$  \hspace{1cm} (3.43)

where $D_e$ is the well depth and $\alpha$ is the width of the well. Unlike the harmonic potential, Morse potential can model bond dissociation, as the potential energy approaches the dissociation energy\(^2\) when the bond stretches far enough. This is in contrast to the harmonic potential which, by nature, has no upper limit, see Figure 3.2.

Figure 3.2: Left: Ball and spring model for bond between atom A and B. The equilibrium bond length, $r_{eq}$, is measured from center to center, $k_b$ is the force constant for the spring (see Eq. (3.42)).

Right: Comparison of a harmonic potential for bond stretching (solid) and a Morse potential (dashed). The units are arbitrary, but both have the minimum at 2.5 on the horizontal axis. Note how the potential energy from the Morse potential approaches a limit as the bond is being stretched.

### Angles

Angles are usually modeled using a harmonic style potential, analog to the bonds, but the dependent variable, $\theta$, is now the angle between atoms A–B–C,

$$U_{angle}(\theta) = \frac{1}{2} k_f(\theta_{eq} - \theta)^2,$$  \hspace{1cm} (3.44)

where $\theta_{eq}$ is the equilibrium angle and $k_f$ is the angle force constant.

### Dihedral angles

Dihedral angles are usually modeled in a slightly more complex manner, utilizing Fourier series:

\(^2\)This is somewhat simplified in the text. The dissociation energy obtained from the Morse potential is in fact slightly larger than the true value, due to the zero-point-energy stemming from the bond vibrations (see [22, p. 515]).
3.2 Force fields

A dihedral angle is the angle between two planes. The dihedral angle, $\phi$, is the angle between the two planes stretched by ABC and BCD, respectively. For a molecule to have a dihedral angle, a minimum of four atoms has to be attached in sequence.

$$U_{dihedral}(\phi) = \frac{V_1}{2} \left[ 1 + \cos(\phi) \right] + \frac{V_2}{2} \left[ 1 - \cos(2\phi) \right] + \frac{V_3}{2} \left[ 1 + \cos(3\phi) \right],$$

(3.45)

where $\phi$ is the dihedral angle between atoms A, B, C and D. $V_1 \ldots V_3$ are the force constants used to describe these somewhat more complex potentials.

3.2.2 Non-bonded interactions

In addition to the bonded interactions there is also non-bonded interactions. These are interactions that can be both intra- and inter-molecular. The non-bonded interactions can be classified in different manners. We can talk about short-range and long-range interactions or van der Waals (vdW) interactions and electrostatic interactions.
van der Waals interactions

The van der Waals interactions, or the short-range interactions, consists of three parts: the Keesom interaction, the Debye interaction and London dispersal forces. Each of these corresponds to a different electrostatic interaction:

**Keesom** Permanent dipole – permanent dipole interaction.

**Debye** Permanent dipole – induced dipole interaction.

**London** Induced dipole – induced dipole interaction.

In sum, we know from statistical mechanics that these interactions, which are all attractive potentials, falls off as a function of $1/r^6$, thus classifying them as short-ranged.

Along with the vdW interactions, a fourth term is merged into the short-range potentials in molecular simulations. This fourth term is repulsive in nature and stems from both Paulie’s exclusion principle — that no two electrons may occupy the same spin-orbital — and electrostatic repulsion. Note that the potential for Paulie’s exclusion principle is exponential in form.

To model the short-range interactions the Lennard-Jones 12-6 potential is by far the most used and popular potential (see Eq. (3.46)). The Lennard-Jones potential consist of an attractive part, falling off as $1/r^6$, stemming from the vdW interactions, and a repulsive part, falling off as $1/r^{12}$ describing the repulsive part of the potential:

$$U_{ij}(r) = 4\varepsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{|r_{ij}|} \right)^{12} - \left( \frac{\sigma_{ij}}{|r_{ij}|} \right)^6 \right] \delta_{ij},$$

where indices $i$ and $j$ enumerates two different atoms, $\varepsilon_{ij}$ is the well-depth of the potential, $\sigma_{ij}$ is the van der Waals radius and $\delta_{ij}$ is a scaling factor. The scaling factor is used in some force field to soften intra-molecular interactions between atoms separated by three bonds (1–4 interactions) and in some cases 1–5 interactions and beyond. $\delta_{ij} \in [0, 1]$, as an example the Optimized Potentials for Liquid Simulations (OPLS) by Jorgensen et al. [23] uses a factor of 0.5 for 1–4 interactions and 1.0 for 1–5 interactions and beyond. For atoms separated by less than three bonds the scaling factor is 0.0, or one simply neglects to calculate the interaction, as they are embedded in the bond and angle contributions. It is also prudent to point out that the 12-exponent in the Lennard-Jones potential does not have a true physical meaning. Rather, it was chosen for computational efficiency as it is easy to square the 6-exponent contribution. As mentioned above, the repulsive contribution is exponential in form.

While the Lennard-Jones 12-6 potential is the most popular, the Buckingham potential is also widely used. Similarly to the Lennard-Jones potential, the attractive part falls off as $1/r^6$. The advantage of the Buckingham potential is that the repulsive part is represented by a exponential form. While it is an advantage when thinking of replicating the physical form of the interaction, it is computationally far more expensive.

---

3 Some people, like Atkins and Paula [22, see p. 696], include the repulsion as a fourth term in the van der Waals forces. Yet others reserve the van der Waals forces for attractive interactions only.
\[ U(r) = A \times \exp(-B|\mathbf{r}|) - \frac{C}{r^6}, \] (3.47)

where \( A, B \) and \( C \) are constants that determine the strength and shape of the interaction. In some formulations of the Buckingham potential the constant \( B \) is given as \( B = 1/\rho \) and has units Å. These constants are dependent on which two atoms, or atom types, that interact. See Figure 3.5 for a comparison of the Buckingham potential and the Lennard-Jones 12-6 potential. Another potential draw-back with the Buckingham potential is the infinite attractive well when two atoms are closer than a critical distance (see Figure 3.5). While normally not an issue it can be a cause for some difficulties when initializing a system, or when using some potentials which have a very limited repulsion.

Fig. 3.5: Lennard-Jones 12-6 potential (black) and Buckingham potential (dashed gray) in arbitrary units. In this case the Buckingham potential was fitted to reproduce the Lennard-Jones potential. Thus the potentials more or less agree, but the repulsive part differs, with the Buckingham potential being less steep. Also note how the Buckingham potential has a maximum at \( r \approx 0.75 \). If two particles get closer than this they fall into an infinite attractive potential well.

**Electrostatic interactions**

Atoms, unless they are ionized, have zero net charge; the same is valid for molecules. However, in a molecule such as water we still observe a dipole moment. To replicate the observed dipole moment in water partial atomic charges are introduced on each atom. That is, permanent point charges are assigned to each atom within a molecule, such that observed dipole – or higher multipole – moments can be reproduced under the constraint that the sum of partial charges within the molecule is zero. The implication of this is that electrostatic interactions are reduced to simple point charge – point charge interactions which easily can be calculated using Coulomb’s law (Eq. (3.48)):
The disadvantage with the use of fixed partial atomic charges is that it leaves the model molecule unable to be polarized, by for instance an external electric field, or nearby molecules, atoms or charged surfaces. Some models allow for polarization of the individual atoms. This may increase the qualitative predictions of the simulations but comes at a significant computational cost.

While it is possible to calculate an approximate potential energy arising from electrostatics utilizing Coulomb’s law, for large and periodic systems this is computationally very expensive. As electrostatic interactions are long-ranged, they are slow to fall off and is one of the more expensive calculations. Thus, Coulomb’s law is often used for the electrostatic interaction within a short range, with a given cut-off radius. Ewald summation methods, or similar methods, which have some addition benefits, are often utilized beyond the cut-off radius (see subsection 3.1.5). This allows for faster electrostatic calculations without introducing artificial artifacts from cutting the tail of the long-ranged interaction.
Chapter 4: Simulation constituents and details

Molecular dynamics is nothing new. One of the first, if not the first paper detailing molecular dynamics simulations is from 1959 by Alder and Wainwright [13]. Alder and Wainwright also wrote a letter to the editor in The Journal of Chemical Physics in 1957 where they described how they had used a computer to exactly solve the classical equations of motion for a system consisting of several hundred particles [24]. In the early days they relied on hard sphere, and square well potentials. With time, and computational advances, the potentials have become more complex as well. The advent of more not only more complex, but also a wider selection of, force fields has made the task of selecting the appropriate one for the system in hand a much harder one than in the early days of molecular simulations.

Beyond the rather trivial part of actually running the simulations there are the more non-trivial actions, such as setting up the simulation systems and creating and running post-processing analyzes. This chapter is intended to shed some light on the models used (see section 4.1) and a short physical description of what is being modeled. In the analyzes section (see section 4.2) some analyses will be given in detail along with the concept and idea behind it. I’ve opted to do this to illustrate the amount of work hidden in figuring out how to best analyze a system, and creating the analyzes.

4.1 Gas, liquid and solid constituents

The majority of my work consists of simulations of complex systems in the way that they include both fluids and solid surfaces. All constituents in any system has to be described by a model, i.e. have some force field parameters assigned. As a side note; a particle without any force field parameters is a particle without any interaction. Such particles are known as ghost particles. While such a particle may seem superfluous there exists a use for them (for instance in particle insertion methods for estimating chemical potentials).

Just as the physical counter-parts to the models have physical properties that differs between them, particularly if they exists in other states, so do the models have different properties in terms of functional form and parameters. Gas and liquids usually have functional forms that are more alike and are often utilizing Lennard-Jones interactions and mixing-rules to estimate cross-interactions. Solids, minerals in particular, seems to be described more in terms of pair-potentials, where parameters are given for each particular interaction (often derived from ab initio calculations), rather than relying on the use of mixing rules. This use of pair-potentials make force fields for solids more cumbersome to use, in terms of choosing the correct set of parameters, the system setup and in terms of determining cross-interactions. Thus I’ve elected to separate the
constituents into two subsections, one for gas and liquid constituents and one for solid constituents.

4.1.1 Gas and liquid constituents

For the most part the fluids have been restricted to water with dissolved carbon dioxide or hydrogen sulfide. Depending on the system pressure and temperature the constituents have been in gas or liquid state. In some cases, the temperature and/or pressure conditions have been such that one or more of the constituents have been super-critical. In such cases one may have to pay particular attention to the selection of an appropriate force field.

Carbon dioxide

Carbon dioxide is readily available in nature and the main contributor to man-made global warming. To mitigate the impact of global warming the scientific community is focused on reducing the amount released into the atmosphere. This work deals with the subject through molecular modeling. With molecular simulations there may be several different models for even simple molecules. Due to the limitations of classical models the parameters are fitted to replicate the environment of interest. Simulations of CO\(_2\) as a gas may utilize one model with one set of parameters while simulation where CO\(_2\) exists as a super-critical fluid requires a different set of parameters.

The lack of a uniform, fit-all scenarios model can be troublesome. A models that gives excellent performance in a bulk water system may simply be unable to replicate the behavior when it approaches the surface. Such complexities must always be at the attention of the scientist.

Figure 4.1: Illustration of the carbon dioxide molecule.

While the subject of models may have some complexities as mentioned above, the CO\(_2\) molecule is a rather small molecule consisting of three atoms. Consequently, the models does not contain dihedral angles. As can be seen in Figure 4.1, carbon dioxide is a linear molecule, making the angle approximately 180 degrees. Beyond that, there is a short-range interaction site on each atom, as well as a partial atomic charge. All this, with the bond length and force constants make up the different CO\(_2\)-models employed.

In our work we employed different models for CO\(_2\). The EPM2-model from Harris and Yung [25], which is using the Lennard-Jones potential (see Table 4.1 for values), and the Buckingham potential-based model of Tsuzuki et al. [26]. The Buckingham model was primarily used for interactions towards hematite (Fe\(_2\)O\(_3\)) as quite a few of
Table 4.1: Selected model parameters for CO₂. Bond and angle parameters are specified in the references. (a) Lennard-Jones parameters for the CO₂ EPM2 model by Harris and Yung [25] and Buckingham parameters from the work of Tsuzuki et al. [26]. (b) Lennard-Jones parameters and partial atomic charges from Panhuis et al. [27].

<table>
<thead>
<tr>
<th>Atom</th>
<th>$q_c$ [e]</th>
<th>$\varepsilon$ [kJ mol$^{-1}$]</th>
<th>$\sigma$ [Å]</th>
<th>$A$ [kJ mol$^{-1}$]</th>
<th>$B$ [Å]</th>
<th>$C$ [kJ Å$^6$ mol$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$^a$</td>
<td>0.6512</td>
<td>0.2339</td>
<td>2.757</td>
<td>909.23</td>
<td>0.3704</td>
<td>1491.6</td>
</tr>
<tr>
<td>O$^a$</td>
<td>−0.3256</td>
<td>0.6694</td>
<td>3.033</td>
<td>1483 3000.00</td>
<td>0.2273</td>
<td>1629.9</td>
</tr>
<tr>
<td>C$^b$</td>
<td>0.6172</td>
<td>0.51369</td>
<td>3.2618</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O$^b$</td>
<td>−0.3086</td>
<td>0.81057</td>
<td>3.0145</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 4.2: A summary of some important physical properties of carbon dioxide. Values at 298.15 K and 101.325 kPa (when relevant) Values from "CRC Handbook of chemical properties" [28] if not otherwise specified.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Critical pressure</td>
<td>7.375</td>
<td>MPa</td>
</tr>
<tr>
<td>Critical temperature</td>
<td>304.13</td>
<td>K</td>
</tr>
<tr>
<td>Density</td>
<td>$1.799 \times 10^{-3}$</td>
<td>g cm$^{-3}$</td>
</tr>
<tr>
<td>Molecular weight</td>
<td>44.010</td>
<td>g mol$^{-1}$</td>
</tr>
<tr>
<td>Solubility in H₂O</td>
<td>1.5</td>
<td>mol%</td>
</tr>
<tr>
<td>Sublimation point</td>
<td>194.686</td>
<td>K</td>
</tr>
<tr>
<td>Triple point</td>
<td>216.592</td>
<td>K</td>
</tr>
</tbody>
</table>

the mineral models rely on Buckingham potentials. The model by Tsuzuki et al. [26] is optimized for a supercritical fluid, a vital point worth noticing. Fitting a Lennard-Jones potential to a Buckingham potential can be done, and was one of the solutions chosen in Paper I, but the agreement will never be perfect due to the differences in the repulsive part. It may, however, be acceptable within the potential well, see Figure 3.5. After some experimenting, the switch to a Buckingham potential for CO₂ versus CaCO₃ was made. In the later work where we estimated free energies of CO₂ in water we utilized the model of Panhuis et al. [27], which was optimized for water-carbon dioxide systems.

### Hydrogen sulfide

Hydrogen sulfide has been a problem for the oil and gas industry for a number of years. It is toxic, there are strict limits to how much is allowed in fuel, it is also a very aggressive hydrate former as well as being corrosive. In sum, H₂S is a contaminant and something we would rather not see in process equipment or a pipeline. Nonetheless, H₂S is present in many natural gases, making it unavoidable. If it is present it has to be taken into account when considering flow assurance.

Clathrates are known to be capable of blocking pipelines, creating hazardous situations and process downtime. Hydrogen sulfide, as mentioned above, is a well known
Table 4.3: A summary of some important physical properties of hydrogen sulfide. Values at 298.15 K and 101.325 kPa (when relevant). Values from "CRC Handbook of chemical properties" [28] if not otherwise specified.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boiling point</td>
<td>213.60</td>
<td>K</td>
</tr>
<tr>
<td>Critical pressure</td>
<td>9.00</td>
<td>MPa</td>
</tr>
<tr>
<td>Critical temperature</td>
<td>373.1</td>
<td>K</td>
</tr>
<tr>
<td>Density</td>
<td>$1.393 \times 10^{-3}$</td>
<td>g cm$^{-3}$</td>
</tr>
<tr>
<td>Melting point</td>
<td>187.65</td>
<td>K</td>
</tr>
<tr>
<td>Molecular weight</td>
<td>34.081</td>
<td>g mol$^{-1}$</td>
</tr>
<tr>
<td>Solubility in H$_2$O[29]</td>
<td>$1.848 \times 10^{-3}$</td>
<td>mol %</td>
</tr>
</tbody>
</table>

and very aggressive hydrate former. Any pipeline streams within the hydrate stability zone containing H$_2$S has significant chance of experiencing hydrate-related problems.

Figure 4.2: Illustration of the hydrogen sulfide molecule.

Hydrogen sulfide as a molecule looks structurally similar to water. It consists of three atoms, two of which is hydrogen atoms bonded to the central sulfur atom (see Figure 4.2). Sulfur, being the next element below oxygen in the periodic table has twice the atomic weight. This give H$_2$S a molecular weight nearly twice that of water (see Table 4.3). Nonetheless, H$_2$S is a gas at standard temperature and pressure conditions, where water predominantly exists as a liquid.

In this work H$_2$S has been modeled using the model from Kristóf and Liszi [30] (see Table 4.4). It is a four-site model, meaning that it contains an additional particle. In this case that particle is a point-charge that lies in the H-S-H plane. The point-charge does not have any short-range interactions. Furthermore, the model only has one short-range interaction site, namely the sulfur atom. Just like the point-charge, the hydrogen atoms are only graced with partial atomic charges without any short-range interactions. The model description contains bond lengths and angles, but in this work the H$_2$S has exclusively been modeled as a rigid molecule. Thus H$_2$S has only had rotational and translational degrees of freedom. This does leave somethings to be desired, as the effect of bond-vibrations and bending of angles will not be included in the simulations. Yet it is always a matter of consciously deciding what is strictly necessary for achieving the goal. In the simulations where I used H$_2$S the conclusion was that for the properties of interest the necessity of a flexible model was not present. A rigid model would yield a computational advantage when considering speed. The latter ended up trumping any
4.1 Gas, liquid and solid constituents

Table 4.4: Model parameters for hydrogen sulfide by Kristóf and Liszi [30]. The Lennard-Jones interactions are centered on the sulfur atom, with the hydrogens having only Coulomb interactions. This model also includes a fourth point-charge (PC) in the H-S-H plane.

<table>
<thead>
<tr>
<th>Charges</th>
<th>Lennard-Jones</th>
<th>Bond and angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>$q_S$</td>
<td>$q_H$</td>
<td>$q_{PC}$</td>
</tr>
<tr>
<td>[e]</td>
<td>[e]</td>
<td>[e]</td>
</tr>
<tr>
<td>0.40</td>
<td>0.25</td>
<td>-0.90</td>
</tr>
</tbody>
</table>

Table 4.5: A summary of some important physical properties of water. Values at 298.15 K and 101.325 kPa (when relevant). Values from "CRC Handbook of chemical properties" [28] if not otherwise specified.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boiling point</td>
<td>373.124</td>
<td>K</td>
</tr>
<tr>
<td>Critical pressure</td>
<td>22.06</td>
<td>MPa</td>
</tr>
<tr>
<td>Critical temperature</td>
<td>647.10</td>
<td>K</td>
</tr>
<tr>
<td>Density</td>
<td>997.0 $\times 10^{-3}$</td>
<td>g cm$^{-3}$</td>
</tr>
<tr>
<td>Molecular weight</td>
<td>18.015</td>
<td>g mol$^{-1}$</td>
</tr>
<tr>
<td>Triple point</td>
<td>273.16</td>
<td>K</td>
</tr>
</tbody>
</table>

Potential advantage of a flexible model. It is also prudent to mention that keeping point-charges fixed in plane has previously turned out to be quite troublesome in flexible models.

Water

Water, and modeling water, is an area of great interest by itself. So great that there are books devoted to the subject alone [31]. The deceptively small and simple molecule has a number of different features that has turned out to be of great importance. For instance, water has its greatest density at around 4 °C. Not to mention that ice has a lower density than liquid water. These two properties alone ensures that fresh water lakes and ponds may avoid freezing solid, thus enabling fish to thrive beneath a cover of ice. It is also these complex properties of water that make modeling water troublesome.

Figure 4.3: Illustration of the water molecule.
Simulation constituents and details

Table 4.6: Model parameters for water. Note that the Lennard-Jones, bond and angle parameters are identical for the two first models. The fSPC model is more advanced than the SPC model in terms of allowing flexible bonds and angle, but utilizes the same charges.

<table>
<thead>
<tr>
<th>Model</th>
<th>Charges</th>
<th>Lennard-Jones</th>
<th>Bond and angle</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$q_o$</td>
<td>$q_H$</td>
<td>$\varepsilon$</td>
</tr>
<tr>
<td>SPC</td>
<td>$-0.82$</td>
<td>$0.41$</td>
<td>$0.6507$</td>
</tr>
<tr>
<td>SPC/E</td>
<td>$-0.8476$</td>
<td>$0.4238$</td>
<td>$0.6507$</td>
</tr>
<tr>
<td>fSPC</td>
<td>$-0.82$</td>
<td>$0.41$</td>
<td>$0.6507$</td>
</tr>
</tbody>
</table>

In the majority of my work I’ve relied on three water models, namely the simple point charge (SPC) model, extended simple point charge (SPC/E) model and flexible simple point charge (fSPC) model. These are all well-known and renown models. The SPC model is a simple rigid water model. It consists of three point charges with a single short-range interaction site centered on the oxygen atom (see Table 4.6). The O–H bonds are fixed along with the angle, allowing only for translational and rotational degrees of freedom. Later on Berendsen et al. [33] improved on his model and published the extended simple point charge (SPC/E) model. The newer model had some minor changes to the partial atomic charges, but remained otherwise identical to the SPC model. Toukan and Rahman [34] made a flexible model in 1985, where they improved on the SPC model by allowing bonds and angles to be flexible. The fSPC model also contains cross-terms as well as using Morse potential for the bond stretching. In sum, it is considerably more complex than the SPC-model and their paper make for a interesting read.

Many other different water models can be found in the literature, like the TIP4P and TIP5P models. These are four- and five-site models, respectively. The extra sites are additional point charges similarly to the H$_2$S-model. The TIP5P model was only released as recently as in year 2000 [35]. The authors state that the TIP5P model is capable of reproducing the trend of waters maximum density at 4 °C, which is an improvement over the TIP3P and TIP4P models. More complex models with four and five sites increases the computational demands, which is partly why their development have been held back. Recent advances in computational power makes the computational cost of these models more acceptable. However, the fact that point charges have zero mass makes for some computational difficulties in some code implementations. This did to some extent prevent the use of the TIP4P and TIP5P models in this work.

4.1.2 Solid constituents

The solid constituents in this work has been calcite (CaCO$_3$), hematite (Fe$_2$O$_3$) and Linde type A (LTA) zeolite ($\begin{array}{|c|c|c|}
| M^{12+}_n & 12 & 12 \\
| Al_{12}Si_{12}O_{48} & 8 & 8 \\
| \end{array}$). Calcite and hematite is readily available in nature. CaCO$_3$, for instance, is one of the more abundant minerals. On the other hand, LTA zeolites are synthesized through a rather simple process. Fortunately, when modeling these compounds the origin is not a factor of importance.
Calcite

CaCO\textsubscript{3} is a well-known mineral. It can have a wide variety of crystal shapes and colors. One of the more common forms is as limestone formed from marine sediments. Due to the porosity of limestone it may accommodate gas, liquids or even gas hydrates within the rock matrix. If the pores are interconnected and the permeability is sufficiently high, it may even allow for fluids to flow.

In this work the choice to focus on calcite as the reservoir rock came from it being widespread in known oil and gas reservoirs and aquifers. As such it is a likely target for sub-surface carbon sequestration. It is also interesting as it is known to dissolve in low pH environments. Carbon dioxide can react with water and calcite to dissolve the calcite (CO\textsubscript{2} + CaCO\textsubscript{3} + H\textsubscript{2}O ⇌ Ca\textsuperscript{2+} + 2 HCO\textsubscript{3}−) [36]. This reaction could potentially over time dissolve CaCO\textsubscript{3} to an extent where the risk of leakage through a fault line is increased.

Conversely, dissolved CaCO\textsubscript{3} may precipitate again further from the injection well resulting in reduced porosity and permeability. In theory, a severe reduction in permeability may demand an increased injection pressure, to the point where the increased pressure may fracture the rock matrix. Fracking, or hydraulic fracturing as it is also known, is a technique to modify (increase) the permeability of a reservoir rock through the creation of fractures in the matrix. The technique, when used correctly, can have a significant impact on reservoir flow. However, it is difficult to predict to which extent the rock matrix will fracture, and in which directions the newly formed fractures will go. An unintended fracturing may cause undesirable leakage. It should be noted that this is probably the worst case scenario, and hopefully one that the (injection site) operator would be aware of.

Beside the dissolution and/or precipitation of CaCO\textsubscript{3} there is the potential for clathrates to form within the pores of the reservoir or aquifer rock. For hydrate formation to occur the temperature and pressure conditions must be within the hydrate stability zone. Carbon dioxide hydrates are more stable than for instance a methane (CH\textsubscript{4}) saturated hydrate. As such, it can form hydrate a conditions where natural gas hydrates would not be formed. A benefit of the increased CO\textsubscript{2} hydrate stability is the potential for exchanging CH\textsubscript{4} guest molecules with CO\textsubscript{2}. Injecting CO\textsubscript{2} into a reservoir containing CH\textsubscript{4} hydrate can be used as a method of producing CH\textsubscript{4} through hydrate reformation [37, 38, 39]. CO\textsubscript{2} has a lower chemical potential as a guest molecule than what CH\textsubscript{4} has. The difference in chemical potential give rise to the increased CO\textsubscript{2} hydrate stability and is a driving force for guest–guest exchange.

The calcite mineral has a crystallographic structure belonging to the trigonal crystal system and the R\textsuperscript{3}c space group. Its unit cell has sides with lengths a = b = (4.988 ± 0.001) Å and c = (17.061 ± 0.001) Å [40]. The angles are α = β = 90° and γ = 120° (see Figure 4.4). Stoichiometrically it consists of a calcium ion (Ca\textsuperscript{2+}) and carbonate ion (CO\textsubscript{3}−). By correctly replicating the unit cell one can construct a large block of calcite. For use in the simulations this is exactly what has been done. A crystallographic information file (.cif) with calcite parameters were downloaded from the "American Mineralogist Crystal Struture Database" [41]. This contained the information needed to construct a large crystal which was subsequently cleaved to expose the 10\textsuperscript{1}4 crystallographic plane of interest.

When setting up such a system the total system size in terms of physical size and
number of atoms must be kept in mind. Too small and the system may experience unintended self-interactions (through proxy atoms). Too large and the computational demands will make the simulations unfeasible due to time constraints. After the construction of a calcite crystal, force field parameters must be assigned to the atoms (see Table 4.7).

During the simulations carried out within this work, the calcite model was kept fixed. This means that the calcium and carbonate ions did not have any translational or rotational degrees of freedom. It also means that the surface dynamics will be somewhat affected by this as well as the surface structuring of adsorbed molecules. However, the work of Heberling et al. [42] shows that the surface relaxation and restructuring of calcite is relatively small. Thus, the choice of a rigid, fixed, CaCO$_3$ is not unwarranted.

**Hematite**

Hematite is one of the most thermodynamic stable and abundant iron oxides [45, 46]. It can be found in nature, in the earth’s crust and in the industries. When iron surfaces oxidizes they are inevitably covered by a layer of iron oxides, or rust. The pipelines traditionally used in the oil and gas industry are made of carbon steel. Due to outside storage and exposure to the elements prior to being installed they may come preequipped with a surface layer of iron oxides.

The crystallographic structure of hematite is a hexagonal unit cell belonging to the trigonal crystal system, with the $R\bar{3}c$ space group [47]. This is the same one as
Table 4.8: Hematite-water parameters from Leeuw and Cooper [48] with charges from ab initio calculations Kvamme et al. [49]. The pure Lennard-Jones parameters stems from CLAYFF [50]. Subscript "w" indicates oxygen in water, oxygen in Fe₂O₃ is without subscript.

<table>
<thead>
<tr>
<th>Interaction</th>
<th>(q_i) ([\epsilon])</th>
<th>(\varepsilon_{ij}) ([\text{kJ mol}^{-1}])</th>
<th>(\sigma_{ij}) ([\text{Å}])</th>
<th>(A) ([\text{kJ mol}^{-1}])</th>
<th>(B) ([\text{Å}])</th>
<th>(C) ([\text{kJ Å}^6 \text{mol}^{-1}])</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe–Fe</td>
<td>1.31</td>
<td>(3.7781 \times 10^{-5})</td>
<td>2.355</td>
<td>103.47</td>
<td>42549.82</td>
<td>0.3299</td>
</tr>
<tr>
<td>O–O</td>
<td>-0.87333</td>
<td>0.6502</td>
<td>3.1655</td>
<td>2196380.31</td>
<td>0.1490</td>
<td>2790.34</td>
</tr>
<tr>
<td>Fe–O(_w)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O–O(_w)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 4.5: Illustration of the 8R (left), 6R (middle) and 4R (right) windows. The numbers 8, 6 and 4 refers to the number of oxygen atoms (red spheres) in the window. The silver and yellow spheres are aluminum and silicon atoms respectively.

for calcite, but for Fe₂O₃ the sides have lengths: \(a = b = (5.038 \pm 0.002) \text{ Å}\) and \(c = (13.772 \pm 0.012) \text{ Å}\) (see Figure 4.4). The angles remain the same as for calcite. Unlike calcite which was cleaved to expose the 10\(\overline{1}4\) surface, the 0001 surface of hematite was studied here, based on the arguments presented in Leeuw and Cooper [48] and the abundance of experimental data available for that surface.

The force field employed is given in Table 4.8, and similarly to the CaCO₃ systems the Fe₂O₃ atoms where kept fixed during simulation runs.

Linde Type A zeolites

Linde Type A zeolites consists of a framework built by interconnected aluminum, oxygen and silicon atoms. In these structures aluminum and silicon atoms are bonded to four oxygen atoms, making a tetrahedra. Aluminum and silicon are thus known as T-atoms in the realm of zeolites. LTA zeolites belong to the cubic crystal system and have sides \(a = b = c = (24.555 \pm 0.002) \text{ Å}\) with angles \(\alpha = \beta = \gamma = 90^\circ\) [51].

The aluminum, oxygen and silicon atoms can form different ring structures, denoted 4R, 6R and 8R windows, depending on the number of oxygen atoms in the ring (see Figure 4.5). Combining the rings in the correct structure and you get the LTA framework illustrated in Figure 4.6. Here you see how the 8R-windows allows access into
the alpha-cavities. The central beta-cavities (aka sodalite cavities) can only be accessed through 4R- or 6R-windows. The 4R-windows are too small to allow water molecules to pass. For a framework neutralized by counter-ions, the center of the 6R-windows is one of the favorable counter-ion sites, effectively blocking off the window. In a neutral unit cell there are one counter-ion in each 8R-window and another one in each 6R-window. Additionally, there is a counter-ion inside each alpha-cavity that positions itself floating slightly above a 4R-window, this is not a fixed position. This last counter-ion can move around inside the cavities.

![Figure 4.6: Illustration of LTA zeolite framework.](image)

LTA zeolites are synthesized in a relatively easy process. The product from the process is Linde type A zeolites with sodium counter-ions. To obtain LTA-3A zeolite one has to perform an additional process known as ion exchange, where the sodium ions are exchanged with potassium ions. The larger potassium ion reduces the effective opening into the 8R-windows. LTA zeolites are used in a wide range of applications. They are used in laundry detergents, water purifications, water softening, dehydration processes (both industrially and in home appliances), separation, as membranes and as catalysts. The numerous applications has ensured that scientists have devoted lots of interest in the subject, both experimentally and theoretically.

The force field employed on the zeolite simulations stems from the work of Faux et al. [52]. It utilizes a mixture of Buckingham potential and Lennard-Jones potential
4.1 Gas, liquid and solid constituents

Table 4.9: Short-range potentials for framework atoms from [52], potassium parameters from [53]. Water-zeolite potential from [54], and are indicated by subscript "w" on water atoms. Water-water interactions modeled using the flexible single point charge model (SPC) [34]. Non-listed interactions are set to 0.

<table>
<thead>
<tr>
<th>Interaction</th>
<th>Buckingham</th>
<th>Lennard-Jones</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al–O</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al–O$_w$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al–H$_w$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O–K</td>
<td>96514.28</td>
<td>0.3620</td>
</tr>
<tr>
<td>O–Na</td>
<td>563159.47</td>
<td>0.2387</td>
</tr>
<tr>
<td>O–O</td>
<td>2196392.25</td>
<td>0.1490</td>
</tr>
<tr>
<td>O–Si</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O–O$_w$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O$_w$–K</td>
<td>96514.28</td>
<td>0.3620</td>
</tr>
<tr>
<td>O$_w$–Na</td>
<td>563159.47</td>
<td>0.2387</td>
</tr>
<tr>
<td>O$_w$–O$_w$</td>
<td>2633780.0</td>
<td></td>
</tr>
</tbody>
</table>

for the short-range interactions. The Lennard-Jones interactions are given as

$$u(r) = \frac{A_{LJ}}{r^{12}} - \frac{B_{LJ}}{r^6},$$

where $A_{LJ}$ and $B_{LJ}$ are the repulsive and attractive terms given in Table 4.9, respectively. Generally one can transform the parameters from the form given here to the more commonly known $\sigma$ and $\varepsilon$ form of the Lennard-Jones potential (see Equation 3.46). To transform back and fourth Equation 4.2 and Equation 4.3 can be used. The calculation of $\sigma$ and $\varepsilon$ is complicated in the case of aluminum-oxygen due to the interaction not having any attractive part ($B_{LJ}$). This changes the functional form making the two formulations inequivalent, yet in some cases an approximation can be made by curve fitting. Thus approximate values for $\varepsilon$ and $\sigma$ can be obtained if desirable.

$$A_{LJ} = 4\varepsilon \sigma^{12}, \quad B_{LJ} = 4\varepsilon \sigma^6$$

$$\varepsilon = \frac{B_{LJ}^2}{4A_{LJ}}, \quad \sigma = \left(\frac{A}{B}\right)^{1/6}$$

The force field by Faux et al. [52] should in theory be capable of replicating a flexible framework. However, in my work the software limited my options to the point where this was unfeasible without significant modifications to the source code. As such, the framework was kept fixed during simulations, only allowing for the counterions and water molecules to move.
4.2 Simulation analyzes

Molecular simulation is data generation and gathering. The goal of the simulation is to generate data that hopefully replicates what can be observed in the physical world. On our case that means that we sample the positions, velocities, energies and other properties for atoms, molecules and the system as a whole. These data, generated by the simulation, is the foundation that we through different methods try to analyze and extract information from. It can be as simple as counting or as complex as mapping and evaluating the average potential energy of the system. All to gain a better understanding of the systems and the physics involved. During my research I have had to write several algorithms for analyzing data. Amongst these are algorithms for unfolding the trajectories, calculating mean squared displacements (MSDs), calculating order parameter of water, measuring flux, measuring retention times and for mapping out the potential energy surface with and without short-range interactions. Since this have very much been a part of my day to day work I have opted to write a small text on two of these.

4.2.1 Self-diffusion

There are several methods of estimating self diffusion of molecules in a fluid. Measuring the MSD and using Einstein’s relation is one. Using the velocity autocorrelation and integrating the area beneath the curve is another. In my work I used the first method.

To calculate the MSD in a large system is fairly easy. Simply put, to calculate the MSD you take the difference between the position, \( r(t) \), at time \( t \) and the position, \( r_0 \), at an initial point in time, \( t_0 \), and square this difference. If you have more than one particle, which is the case of molecular simulations you average over the number of particles, i.e.:

\[
\text{MSD}(t) = \left\langle (r(t) - r_0)^2 \right\rangle
\] (4.4)

However, in most of my systems the molecules would pass through one or more periodic boundaries. This complicates the calculations since the particles suddenly jump from one end of the box to another. If the particles passes through the boundary in the x-direction the x-coordinate will change from for instance 9.99 to -9.99 in a single time step. Given that the particle continues to travel unabatedly in the same direction the uncorrected MSD will diminish as the particles closes up on its original position.

Due to the complication described above it is necessary to either track the particles as they cross the PBC, or unfold the trajectory prior to running the MSD calculations. Since most simulations consists of a large number of particles, and an even larger number of snapshots in time which the calculations are based on, both of these solutions are quite time consuming. Initially I wrote a tool command language (Tcl) script for the Visual Molecular Dynamics (VMD) application [55] that unfolded the trajectories. However, this was only capable of unfolding the trajectories as long as the particles did not pass through several periodic boundaries. Not only that, due to it being a scripting language, and being run inside VMD, it turned out to be very slow.

In the end I had to write a tool to read the trajectory data, keep track of all the particles, and how many boundaries each had passes in all dimensions to be able to
calculate the MSDs in this work. In the LTA-systems this was further complicated by
the need to exclude the non-mobile water molecules within the $\beta$-cavities. This was
necessary for having comparable results to that of Faux [56].

4.2.2 Electrostatic potential energy maps

In the zeolite systems I ran into an issue which I assumed was due to electrostatic
potential energy gradients within the simulation system. This was something that had
to be confirmed, both to bring the issue to the attention of other researchers wishing to
go down a similar path, and to figure out a solution to the problem.

While the hypothesis was clear there were no good tools for visualizing the elec-
trostatic potential energy surface. In theory it is quite simple, move a test particle with
a known charge on a grid and record the calculated energy at each point. However,
once again the PBC complicates the situation. Using Coulomb’s law to calculate ev-
ery interaction for all the grid points would have been very slow. Furthermore, that
approach would require some sort of cut-off. A too short cut-off distance and the re-
sults would be very poor, too long cut-off distance and the computation would become
exceedingly slow. A better approach would be to implement a form of Ewald summa-
tion methods. Ewald summation is capable to calculate the electrostatic interaction to
an arbitrary precision in periodic systems. It is widely used in molecular dynamics.
However, Ewald summation is not particularly fast. It is significantly faster (and more
precise) than using Coulomb’s law, but there are faster options. The smooth particle
mesh Ewald summation method Essmann et al. [15] is one of these methods and the
one that was implemented. The gist of this implementation is given in Appendix A (9)
and all the relevant equations can be found in subsection 3.1.5.

Initially the program was written to run on the central processing unit (CPU) rather
than the general purpose graphical processing unit (GPGPU). However, once the utility
was completed it turned out to be much too slow. Due to the massive amounts of calcu-
lations involved in creating maps with the desired resolution it would have taken way
too long. Rewriting the important parts of the algorithm to run on the GPGPU turn out
to be fairly easy and a tremendous time saver.
Chapter 5: Introduction to the papers

As mentioned in section 1.1 the focus has been on examining the potential for hydrate formation during transportation and subsurface storage, with emphasis on using zeolites for gas dehydration as hydrate prevention.

Thus, the papers can be divided into three groups. Paper I deals with water and carbon dioxide interactions with calcite and hydrate surface. Paper II and Paper III covers hydrate formation in and during pipeline transport. These two papers were part of a larger project and as such a group effort. They are based on the rather large written report submitted at the end of the project. The third group consists of Paper IV and Paper V which are focused on zeolites.

**Paper I: Molecular dynamics study of calcite, hydrate and the temperature effect on CO2 transport and adsorption stability in geological formations**

Subsurface storage of CO$_2$ can be of the utmost importance to reduce the rate of global warming and man-made climate change. But is the effects of injecting CO$_2$ into the formations understood all that well?

In this paper we study the interactions, adsorption and structuring of H$_2$O and CO$_2$ on the *in situ* dominant calcite surface. The system is set up with two solid phases, a CaCO$_3$ and a CO$_2$ hydrate, to glean important information regarding the potential competition for CO$_2$. The hydrate surfaces were initially coated by a thin water layer separating it from the carbon dioxide phase. Calcite was coated by a much thicker water layer.

During the simulations two different force field approaches were studied. We started with a hybrid Lennard-Jones/Buckingham force field, and later switched to a purely Buckingham based force field. The differences introduced by the two difference force field approaches were analyzed and compared.
**Paper II: Consequences of CO$_2$ solubility for hydrate formation from carbon dioxide containing water and other impurities**

Transporting CO$_2$ to injection sites can be accomplished in different manners, depending on injection site. On-shore injection sites can rely on trucks, trains or pipelines, while off-shore sites may utilize large tankers or pipelines. For large volumes over a long period of time pipelines are the superior option, despite the greater initial cost.

Traditionally the industry have used water dew-point calculation for hydrate risk evaluation. In a pipeline transporting CO$_2$ and impurities to the injection site – in low temperature and high pressure conditions – the risk of hydrate formation may be given by other factors than the dew-point of water. Here we investigate and formulate a strategy for hydrate risk evaluation in these conditions.

The paper deals with the formalities of absolute thermodynamics, estimation of chemical potentials as a basis for evaluating if hydrate formation will occur or not. We have also included H$_2$S, an aggressive hydrate former, as an impurity in the gas stream. For each of the paths to hydrate formation given in the paper, the thermodynamic equations necessary are given.

The implications of hydrophilic surfaces, such as oxidized pipeline walls, are investigated in terms of the potential for water adsorbing onto the surface earlier than dictated by dew-point calculation estimates.

**Paper III: Water-wetting surfaces as hydrate promoters during transport of carbon dioxide with impurities**

In the same settings as for Paper II the effect of water-wetting surfaces, more specifically hematite (Fe$_2$O$_3$), on hydrate formation is examined. Where Paper II concentrated more on the concept and formalism we extend this here and take a closer look at the adsorption of CO$_2$ and H$_2$S onto Fe$_2$O$_3$.

The focus is on the total chemical potential for adsorbed carbon dioxide and hydrogen sulfide estimated from molecular dynamics simulations. These are compared towards the total chemical potential for adsorbed water and water participating in hydrate cavities. Finally, the preferential orientation of H$_2$S adsorbed on hematite is studied.
**Paper IV: The impact of electrostatics in bulk Linde type A zeolites**

The focus now shifts towards LTA zeolites and their properties depending on the choice of counter-ions. A flexible water model was introduced in the zeolite and comparisons were made towards previous work by other groups. The paper reports results from calculations of self-diffusivities and water distributions for the flexible water model in both LTA-3A and LTA-4A.

Initial attempts to move towards more realistic interfacial systems are also made. The efforts reveal that interfacial termination and electrostatics are vital for correct modeling.

We then visualize the electrostatic potentials present in the interfacial system and examines the possibility, and effect, of reducing the partial atomic charges.

**Paper V: The effect of interfacial charge distributions and terminations in LTA zeolites**

Progressing from Paper IV the study of LTA zeolites are moved to more complex interfacial systems. Larger interfacial systems consisting of two unit cells in the longitudinal direction, not including the interfacial termination, are set up. The systems get two different terminations, noted as S4R and D4R terminations. Additionally the D4R systems are ran with six different charge distributions in the interface.

Initially the systems are only partially hydrated, containing only 224 water molecules in total, corresponding to half of the experimentally determined usual loading. On the outside of the zeolite there is a large water phase, capable of supplying the zeolite with more than enough water to become fully hydrated.

The effects of termination and interfacial charge distributions on water structuring, densities and rates of loading are examined. Extending on the previous work, the consequences of improperly handling of partial atomic charges are visualized and identified.
Introduction to the papers
Chapter 6: Conclusions

Our study of the calcite surface adsorption and structuring of carbon dioxide and water showed that temperature were of importance, in terms of both interface and adsorption stability. The study also highlights the importance of proper potentials and the need for better experimental data for comparison and fitting purposes.

When considering pipeline transport of carbon dioxide proper hydrate risk evaluation is critical for proactive hydrate prevention. Thus, more complex models than simple dew-point calculations should be considered. The strategy illustrated may be one such viable method. The work in Paper II and Paper III show that water adsorbing onto solid surfaces may be the deciding factor. While it is shown that the chemical potential of the innermost layers, those directly adsorbed to the surface, prevents hydrate formation those layers rapidly approach what is free water. Thus, hydrate has a real possibility of forming on the outskirts of the adsorbed water layers. There the guest molecules will be readily available too, simplifying mass transport, while the adsorbed water and solid surface can allow for effective heat dissipation.

While hydrogen sulfide is an aggressive hydrate former on its own, it is in low concentrations not capable of forming stable hydrate on its own, but rather assists in stabilizing carbon dioxide-hydrate. hydrogen sulfide was found to adsorb strongly onto the hematite surface, but this may still fail to prevent it from forming a mixed hydrate with carbon dioxide.

Since water has shown such a strong affinity for hematite, adsorbing prior to reaching the dew-point drop out concentrations, dehydration of the gas stream may be necessary to prevent hydrate formation. Linde Type A zeolites have been widely used for dehydration purposes. As carbon dioxide is capable of entering the zeolite when using sodium as counter-ions to balance the structure, it was desirable to extent the studies to potassium counter-ions. We show that the larger counter-ions drastically affects the water diffusion. Furthermore, the accessible volume for water is significantly reduced. When modeling interfacial systems proper surface-termination and corresponding charge distribution is key.

We conclusively visualize and demonstrate how interface termination, and perhaps even more importantly charge distribution affect water structuring, rates of loading as well as interfacial and bulk dynamics. Poor choices, such as changing bulk charges to compensate for interfacial imbalance, skews the dynamics of the system.
Chapter 7: Suggestions to future work

The Achilles’ heel of molecular simulations are the force fields. Without proper force fields the results may be biased one way or the other. This make the need for often lacking representative experimental data grave. While fitting potential parameter to experimental results may be very fruitful, employing other means such as Car-Parrinello [57] molecular dynamics or Born-Oppenheimer molecular dynamics may be another approach. While these methods are more demanding with regards to computational complexities, they can form a basis for fitting potentials or reference state in lack of experimental information.

Investigation and calculation of chemical potential is tricky at best. For instance, In the polynomial path thermodynamic integration approach the interactions are scaled, in essence, from their real potential to 0. This, when in presence of a surface and competing species will eventually lead to the molecules being desorbed from the surface. Thus, the contributions sampled after desorption is very likely from a different state or phase. Exploring different methods may be necessary to get better estimates for chemical potential. Perhaps particularly so for hydrogen sulfide, which displayed this exact behavior. More advanced methods could perhaps more precisely predict the adsorbed water layer thickness necessary for hydrate formation to become favorable. Such information can further improve our abilities to predict, and prevent, hydrate formation.

The calcite systems, while the work has been advanced later on by others in the group, could benefit from an increase in complexity. While the effect of a flexible crystal, or flexible surface layers may not be of critical importance for simple systems, the inclusion of ionic species (Ca$^{2+}$, HCO$_3^-$, H$_3$O$^+$, OH$^-$) can potentially skew the CO$_3^{2-}$ orientation to a greater extent than water. These are ionic species that inevitably will be present in a system with water and dissolved carbon dioxide. It is prudent to recall the effect of strong electrostatic gradients in the interface regions of these systems, or in the case of defects in the crystal structure.

Linde Type A zeolites, while their structure is very well known and understood still presents a significant amount of questions. Not the least when considering the surface. Experimental results, scanning electron microscopy imaging, indicates that the D4R surface termination is the correct termination. However, it does not tell if the aluminum and silicon atoms on the termination are hydroxylated (a not unreasonable assumption). Again I propose that we return to \textit{ab initio} methods for clarification. And while it is being done getting estimates for the partial atomic charges in the interface, although not an exact science, might be a good idea.

Another potentially fruitful approach is to set up systems in which the zeolite is a membrane separating water in a high-pressure reservoir from a low-pressure region. This would allow for measuring the flux of water molecules through the LTA zeolite. Such experimental results are readily available. Thus, they can possibly give indica-
tions on which terminations and charge distributions are yielding results closest to the experimental data, and thus give confirmation by proxy.

As the concentration of water in the gas/liquid outside the zeolite is reduced, the chemical potential decreases. Grand canonical molecular dynamics can be an approach to investigate the kinetics of such a system for different levels of chemical potential for water. The concept of having a particle source in the outer fluid phase is intriguing.


[48] N. H. de Leeuw and T. G. Cooper. “Surface simulation studies of the hydration of white rust Fe(OH)2, goethite α-FeO(OH) and hematite α-Fe2O3”. In: *Geochimica et Cosmochimica Acta* 71.7 (2007), pp. 1655 –1673. DOI: http://dx.doi.org/10.1016/j.gca.2007.01.002.


Chapter 8: Scientific results
Appendix A

Smooth particle mesh algorithm

The main part of the utility (Algorithm 1) loads the coordinates of all atoms into a vector of objects of type Atoms. The atom class is a simple class, holding the name of the atom, its index, total number of atoms, x, y and z coordinates and the partial atomic charges.

Algorithm 1: Main function calls in utility

The algorithm takes as input the desired resolution of K-space along with the periodic boundary conditions (dimensions in x, y and z), and the grid resolution for the test particle. Furthermore, the user specifies the spline order and the $\beta$-parameter.

Once the necessary input is provided, the utility continues to calculate the values for $B, C$ and $Q$ arrays, according to equations 3.29, 3.30, 3.31, respectively via algorithm 2. After this point it proceeds to calculate the reciprocal contribution to the systems energy, $\tilde{E}_{\text{rec}}$. 
Algorithm: FillArrays  
**Data:** Vector of Atoms, Spline-object, Arrays  
**Result:** Populated B, C and Q-Arrays  

for $k_1 = 0 \rightarrow K_1$ do  
  for $k_2 = 0 \rightarrow K_2$ do  
    for $k_3 = 0 \rightarrow K_3$ do  
      $B(k_1,k_2,k_3) = BC\text{alculate}();$  
      $C(k_1,k_2,k_3) = CC\text{alculate}();$  
      $Q(k_1,k_2,k_3) = QC\text{alculate}();$  
    end  
  end  
end

Algorithm 2: Function FillArrays(), populates the arrays used in calculation of the electrostatic energies.

Algorithm: CalculateEReciprocal  
**Data:** B, C, Q, K_1, K_2, K_3  
**Result:** $\tilde{E}_{rec}$, $(B \ast C) \cdot Q$-array  

$F^{-1}(Q) = \text{FFT3D}(Q);$  
for $k_1 = 0 \rightarrow K_1$ do  
  for $k_2 = 0 \rightarrow K_2$ do  
    for $k_3 = 0 \rightarrow K_3$ do  
      $BCQ^{-1}(k_1,k_2,k_3) = B(k_1,k_2,k_3) \cdot C(k_1,k_2,k_3) \cdot F^{-1}(Q)(k_1,k_2,k_3);$  
    end  
  end  
end

$BCQ = \text{FFT3D}(BCQ^{-1});$  
for $k_1 = 0 \rightarrow K_1$ do  
  for $k_2 = 0 \rightarrow K_2$ do  
    for $k_3 = 0 \rightarrow K_3$ do  
      $\tilde{E}_{rec} += K_1 \cdot K_2 \cdot K_3 \cdot BCQ(k_1,k_2,k_3) \cdot Q(k_1,k_2,k_3);$  
    end  
  end  
end

return $0.5 \cdot \tilde{E}_{rec};$

Algorithm 3: Function CalculateEReciprocal() - Does the inverse Fourier transform of Q-array, multiplies B and C arrays with $Q^{-1}$-array, and then does a forward Fourier transform of the product. The resulting array is stored for further use.
The reciprocal contribution to the systems energy is calculated by the function CalculateEReciprocal, shown in Algorithm 3. This function performs an inverse Fourier transform of the "grid charge array", $Q$, and returns $F^{-1}(Q)$. In the CUDA accelerated implementation for generating the electrostatic map, the convolution of $B$ and $C$-arrays, multiplied with the $F^{-1}(Q)$-array is needed. This is calculated here and stored for later use. Thus the function loops over $K_1$, $K_2$ and $K_3$, and performs the element-wise multiplication of $B$, $C$ and $F^{-1}(Q)$-arrays. A forward Fourier transform is then carried out on the resulting array, returning a new array denoted as BCQ, see algorithm 3.

Now $\tilde{E}_{rec}$ can be calculated by once again looping over $K_1$, $K_2$ and $K_3$, and summing up the product of the $BCQ$-array with the $Q$-array and $K_1$, $K_2$, $K_3$. Finally, $\tilde{E}_{rec}$ is multiplied by the prefactor of 0.5 from Eq (3.32) and the reciprocal contribution is returned.

To generate the electrostatic map, a test particle has to be placed at the desired grid points. The resolution for the number of grid points for the test particle, is provided as input by the user. Then the utility generates $xSteps \cdot ySteps \cdot zSteps$ points in space, and subsequently the same number of $Q_{test}$-arrays (see algorithm 4). For each new grid point, a new set of scaled fractional coordinates were calculated for the test particle. These were then transferred to the GPU memory and a $Q_{test}$-array was computed based on equation (3.31), containing only the contributions from the test particle. Then, for each $Q_{test}$-array, i.e. each grid point, $\tilde{E}_{rec}$ is computed on the GPU using equation (3.32).

Algorithm 4: Function ComputeOnCUDA() - Generates the electrostatic maps. Implemented on a nVIDIA GPU in the CUDA language.
In the end, one has \( x_{\text{steps}} \cdot y_{\text{steps}} \cdot z_{\text{steps}} \) points with calculated energies, depending on the position of the test particle. The CUDA implementation allows for the multiplication of the arrays, as well as the generation of the \( Q_{\text{test}} \)-arrays to be computed within an acceptable time frame.

Now that the reciprocal contribution to the electrostatic energies are calculated, a similar scheme for the direct contributions is needed. This is calculated according to eq. (3.19), and is straightforward to implement. Again, this was done using CUDA to ensure rapid calculations. The energies for each grid point was stored for later output and processing.

The array containing the energies, both the direct and reciprocal contributions, is eventually stored in a DX formatted file, allowing for visualization in VMD. A utility was written for extracting layers from the .DX-file and plotting of maps by interfacing into gnuplot.