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Electric interactions: A study of cellulose

Stenqvist, Björn

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LUND UNIVERSITY

PO Box 117
221 00 Lund
+46 46-222 00 00

Electric interactions

A study of cellulose

Björn Stenqvist



LUND
UNIVERSITY

Doctoral Thesis

The thesis will be publicly defended on Tuesday 31st of May 2016, 10.30
in lecture hall B, Center for Chemistry and Chemical Engineering, Lund

Faculty opponent

Professor Jiří Kolafa, University of Chemistry and Technology, Prague,
Czech Republic

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Doctoral Thesis

Division of Theoretical Chemistry
Department of Chemistry
Faculty of Science
Lund University

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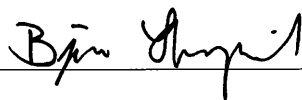
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List of Papers

This thesis is based on the following papers, which will be referred to in the text by their Roman numerals. The papers are appended at the end of the thesis.

I Faunus - a flexible framework for Monte Carlo simulation

Björn Stenqvist, Axel Thuresson, Anıl Kurut, Robert Vácha, Mikael Lund

Molecular Simulation, **39**, 1233-1239 (2013)

II Cellulose-Water Interactions: Effect of electronic polarizability

Björn Stenqvist, Erik Wernersson, Mikael Lund

Nordic Pulp & Paper Research Journal, **30**, 26–31 (2015)

III The mechanism of cellulose solubilization by urea studied by molecular simulation

Erik Wernersson, Björn Stenqvist, Mikael Lund

Cellulose, **22**, 991–1001 (2015)

IV Direct summation of dipole-dipole interactions using the Wolf formalism

Björn Stenqvist, Martin Trulsson, Alexei I. Abrikosov, Mikael Lund

J. Chem. Phys., **143**, 014109 (2015)

V General moment cancellation: Long-ranged electrostatic interaction summation using a pair-potential

Björn Stenqvist, Mikael Lund

submitted (2016)

VI Evidence for dissociation of cellulose hydroxyl groups in alkali

Erik Wernersson, Björn Stenqvist, Yuan Fang, Åsa Östlund, István Furó, Mikael Lund, Björn Lindman, Diana Bernin

Manuscript

List of Contributions

- I I was responsible for everything concerning anisotropic particles, and wrote parts of the paper.
- II I was responsible for the article as a whole, performed the quantum mechanical calculations, wrote the simulation software, produced most of the presented data, and wrote major parts of the paper.
- III I performed the quantum mechanical calculations, and wrote the corresponding part of the paper.
- IV I was responsible for the article as a whole, developed the majority of the theory, wrote parts of the simulation software, produced the majority of the presented data, and wrote major parts of the paper.
- V I was responsible for the article as a whole, developed the theory, wrote the simulation software, produced the presented data, and wrote major parts of the paper.
- VI I performed the quantum mechanical calculations, wrote the corresponding part of the paper, and performed some of the analysis.

Preface

The following work is a scientific anthology with the aim to describe a journey starting almost five years ago. It initializes in framing the context by introducing various subjects, all essential to properly understand the subsequent articles.

The path I have ventured to arrive at this moment, has taken me to places I had never been and introduced me to people I had never met. On the journey I have been guided and counselled chiefly by my supervisor Mikael Lund. I will now tell you a story about the time he obtained results from an anonymous form, that the people of his group filled out regarding his leadership skills. He almost blushed and evadingly said we were too kind, but we were not! I am very glad and feel privileged to be a Ph.D. student of yours. I wish you the very best, though I know you do not need it, and hope that even though our paths will now diverge, that at some point they will cross again!

This thesis is not the sum of my efforts alone but rather the result from collaborations with others. Without the authors of the included articles, this work would literary not have been possibly. Therefore, I deeply thank you for generated interest, heated discussions, and contributions resulting to this. During the development of the articles, a thought of mine has taken shape, stipulating no interaction too small to be essential. Sadly, it is not possible to include gratitude to every one in this short passage. Therefore I write this general *and* specific salutation to YOU.

There are many who know that without you this thesis faced certain defeat. The articles won't give you any honors, the thesis won't mention you, but I will not forget!

Björn

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Populärvetenskaplig sammanfattning

Detta arbete har haft som målsättning att fördjupa vår kunskap om cellulosa och hur denna polymer reagerar i olika miljöer. Cellulosa är det vanligaste organiska materialet på jorden vilket gör att det är relativt lätt-tillgängligt, billigt, och miljövänligt. Genom att öka vår förståelse av de egenskaper som cellulosa besitter kan det bli möjligt att utveckla nya användningsområden, men också kvalitativt förbättra nuvarande applikationer, där cellulosa används.

För detta ändamål har vi använt atomistiska modeller och teori om elektromagnetiska krafter. Det har då blivit möjligt att simulera och beräkna egenskaper på olika system, i detta fall; cellulosa, vatten, och möjligtvis någon ytterligare partikel. Metoderna som använts är helt generella vilket gör att det i princip är möjligt att använda samma tillvägagångssätt på vilket molekylärt system som helst.

Att arbeta på en atomär nivå innebär dock att det är möjligt att se på partiklar på olika sätt, antingen som vanliga makroskopiska objekt beskrivna av klassisk mekanik, eller att de beskrivs av sannolikheterfunktioner som följer kvantmekaniska regler. Båda dessa perspektiv har för- och nackdelar varvid vi har använt dem till olika saker. Genom att karakterisera atomer enligt kvantmekanik och propagera dem genom klassiska ekvationer har det varit möjligt att någorlunda legera det bästa från två världar i en procedur.

Genom att använda de föregående nämnda metoderna går det att utforska många aspekter av cellulosa. Detta arbete har emellertid fokuserat på (o)lösligheten av detsamma och mekanismerna bakom detta fenomen.

Chapter 1

Introduction

The purpose of this work is to model and gain insights regarding the cellulose molecule. Cellulose is a major constituent of plants and thus the most common organic material on the planet. Since cellulose is very common, it is of course significant to properly understanding how it interacts. Doing so might enable us to use cellulose for purposes currently unavailable, but perhaps more important, it may allow us to increase the quality of the products at use today. For us to successfully complete this mission it is essential to have access and proper knowledge of suitable techniques and tools. For these reasons our tale begins very long ago in a place far away, it starts with an element so small and tiny that it could not be divided, or so they thought...

We speak of course of the atom, the existence of which has been anticipated in Greece and India since at least 5-4th century BC. Nevertheless, the first reported evidence^{1,2} of this theorised entity came in the early twentieth century. Since then more refined models have been presented by including electrons, protons and neutrons.^{3,4,5} These particle models enhance the possibilities of extracting accurate information without any other specific prior data about the system at hand. However, even though our knowledge of the geometry and consistence of a system has increased, we still need to know how the elements interact with one another. Currently there are four known forces; electromagnetic, gravitational, weak nuclear, and strong nuclear. At the atomistic scale the three latter ones are most often negligible, which is also the case throughout this work. Based on electronic forces alone we will attempt to describe evolutions of atomistic systems. The relatively weak magnetic force will not be discarded altogether but merely included in analysis of static systems.

Calculations at this level of theory, when including more than a few

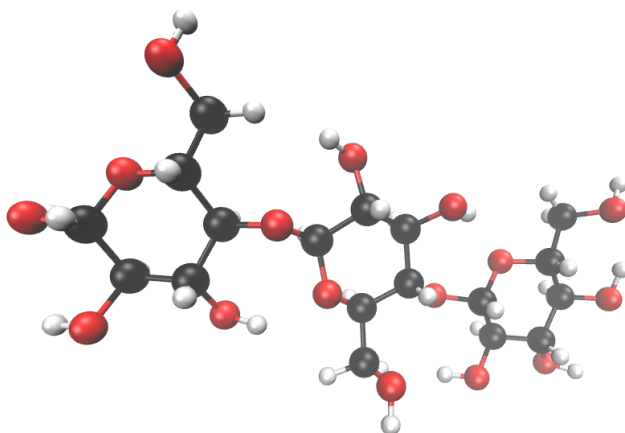


Figure 1.1: A cellulose molecule with three rings (cellotriase (C₆H₁₀O₅)₃). The spheres symbolise atoms where; black is carbon (C), red is oxygen (O) and white is hydrogen (H).

particles, are generally incomprehensible for any human being. Alas, computers have to be used to execute the calculations and simulations needed to resolve such issues. Computer operations are based in a finite numerical framework where most often exact analytical results are impossible to get. Consequently, methods dealing with computational problems and the interpretation of the output data by suitable analysis methods will also be addressed.

To sum up, by using an atomistic approach we set out to model cellulose molecules, see Fig. 1.1, in order to gain further understanding. Our understanding of reality is based on models, therefore, it is important for these models to be as accurate yet as simple as possible. Accurate such that agreement is reasonable with the modelled entity and simple enough such that we can properly understand them. There are characteristics of cellulose well described by more simple so-called coarse-grained models.⁶ However, for detailed molecular analysis, of for example binding sites, an atomistic description is surely needed. By mainly using theory of electrostatic interactions this work tackles the issue of the (in)solubility of cellulose molecules, an area subjected to current research.^{7,8}

Chapter 2

Electric interactions

When determining the propagation of a system on an atomistic scale it is necessary to include contributions due to electric interactions to retrieve accurate results. To properly do so we need a theoretical frame to work within. Thus, we start this chapter by stating a general theorem saying; if all sources and circulation densities (i.e. curl) in a vector field (i.e. a space) are known then that vector field is uniquely determined.⁹ Moreover, the base of electric theory is the empirically established Eq. 2.1, called Coulomb's law.

$$\mathbf{F}(\mathbf{r}) = -\frac{qq^*}{4\pi\epsilon_0} \nabla \left(\frac{1}{r} \right) \quad (2.1)$$

Here \mathbf{F} is the force vector between two by r distanced particles with point charges q and q^* , and ϵ_0 the vacuum permittivity. From here on we will use SI units if not stated otherwise. Also, bold notation is used for tensors and normal fonts for their norms. By using Coulomb's law it is possible to show that the curl in any electrostatic field vanishes. A curl-free field is also known as a conservative field, meaning that any lines connecting the same initial and final coordinates will yield indistinguishable line integrals. A physical way to interpret this, is that the work necessary to move a particle from one place to another is independent of the specific path it takes. Since the curl vanishes it is the potential $\Phi(\mathbf{r})$ which solely and uniquely describes the vector field at a position \mathbf{r} . By knowing the charge-density $\rho(\mathbf{r})$, the potential can be retrieved through Eq. 2.2 which is called Poisson's equation.

$$\nabla^T \nabla \Phi(\mathbf{r}) = -\frac{\rho(\mathbf{r})}{\epsilon_0} \quad (2.2)$$

Though we know a solution to exist, the solution is most often unfathomable even in many simple systems. Therefore, we need approxima-

tions and simplifications of the problem to arrive at a comprehensible result. So we start off by considering a single point charge q . For the set-up presented in Fig. 2.1 the potential is expressed as Eq. 2.3.

$$\Phi(\mathbf{r}'' - \mathbf{r}') = \frac{1}{4\pi\epsilon_0} \frac{q}{|\mathbf{r}'' - \mathbf{r}'|} = \frac{1}{4\pi\epsilon_0} \frac{q}{r_{>}} \sum_{n=0}^{\infty} \left(\frac{r_{<}}{r_{>}} \right)^n P_n(\cos(\theta)) \quad (2.3)$$

Here $r_{>}$ is the greater of the \mathbf{r}' and \mathbf{r}'' lengths, converse for $r_{<}$, θ is the angle between the two vectors, and P_n are Legendre polynomials. The potential is now described in two parts; (i) a radial part and (ii) an angular part. By decomposing a whole system into single particle sub-systems, as described above, solutions can (often) be retrieved easier since they now share a common origin and the solution is parted in different spatial groups. Moreover, if we know the surroundings of this sample not to be vacuum but rather a dielectric medium with permittivity ϵ_r , then the charge will induce a reaction potential described by Eq. 2.4 where R is the radius of the spherical cavity centred in the origin. We now have a description of not only the potential from a single charge in vacuum but also from a single charge in a macroscopic environment.

$$\Phi_{\text{RP}}(\mathbf{r}'' - \mathbf{r}') = \frac{(1 - \epsilon_r) q}{4\pi\epsilon_0 R} \sum_{n=0}^{\infty} \frac{n+1}{n + \epsilon_r(n+1)} \left(\frac{r_{>} r_{<}}{R^2} \right)^n P_n(\cos(\theta)) \quad (2.4)$$

Now we have a potential that shows great promise for both conceptual understanding and precise determination of electrostatic systems. Before moving on to describe energies we for future use introduce the field which is a (fairly) macroscopic entity connected to both the Coulomb force and the potential as depicted in Eq. 2.5.

$$\mathbf{E}(\mathbf{r}) = \lim_{q \rightarrow 0} \left(\frac{\mathbf{F}(\mathbf{r})}{q} \right) = -\nabla\Phi(\mathbf{r}) \quad (2.5)$$

2.1 Energy

Energy is, as the potential, a tangible entity we all have some relation to. On the atomistic scale one often divides the total energy into distinguishable parts coupled with some specific effect or mechanism. To do this we first need a mathematical construction linking to the previously mentioned Coulomb's law. For our purposes the definition of energy is

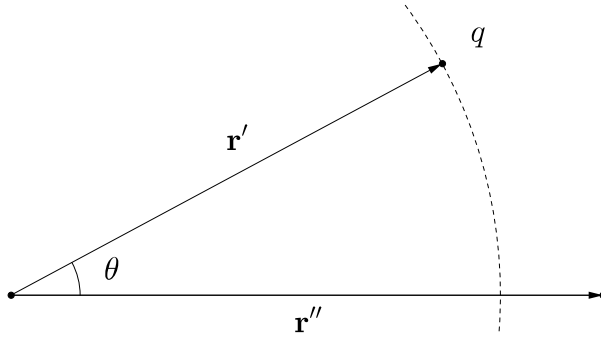


Figure 2.1: The charge q is disposed r' from the origin giving the potential in Eq. 2.3 at the position r'' .

that which is needed to get from one point to another given a force driving the course of action. This definition together with Coulomb's law gives the particle interaction energy difference u as Eq. 2.6 where infinite separation is the reference state.

$$u(r) = \frac{qq^*}{4\pi\epsilon_0 r} \quad (2.6)$$

So far we have mainly used the notion of discrete charges. In a real system however the charge distribution is not discrete but rather continuous. Instead of a sum of discrete particle interactions one thus gets an integral expression of the continuous charge distributions. This expression can be divided into different parts. The origin of all these parts comes from Eq. 2.6 but they give rise to different nanoscopic phenomena. Usually the different system energies E_X , where X is the corresponding phenomenon, are linked as in Eq. 2.7.

$$E_{\text{Total}} = E_{\text{Electrostatic}} + E_{\text{Induction}} + E_{\text{Dispersion}} + E_{\text{Repulsion}} \quad (2.7)$$

The electrostatic part is, as it sounds, a contribution based on the *static* electric structure of the system. Externally *inducing* a transformation of the static electric structure gives rise to the induction energy term. Even though no external perturbation is at hand, the motion of the charges themselves induces local variations which rapidly *disperse*. It is from these local variations the attractive dispersion energy term emerges. Finally, The Pauli principle¹⁰ states that no more than one fermion (e.g., an electron, proton, or neutron) can occupy a given quantum state. Thus if two such particles spatially converge they will increasingly *repel* each other, giving the repulsion energy term.

2.2 Two-body interactions

Before we go into detail about these specific phenomena, we need to bring up one of the most common approximations used in atomistic system descriptions, which is that the total atomic interaction is the sum of all pair (two-body) interactions. That is, the interaction between two particles is treated as if they were independent from any other particle. Though not true, the approximation yields adequate accuracy for many a problem. Since the total energy (or force or field) now consists of a sum of every pair interaction, the total calculation can be parted into smaller independent calculations which can later be assembled to a final result. This division can greatly decrease the time needed to evaluate the total interaction if parallelization is possible. Not only that but (perhaps) primarily, the interaction formulas are generally more simple than for example triple (three-body) interactions.^{11,12}

2.3 Electrostatics

The interaction between atoms is a result from integrated interactions of their intrinsic electric structures. Most often these structures are too complex to represent in their entirety, whereby approximations are needed. A common approach is to characterize electrostatics of an atom by a single-valued entity, the charge. This entity is the 0:th order electrostatic moment of the atom or the *monopole*. Being a single value the effect from a monopole is isotropic, i.e., independent of direction and thus the one ($3^0 = 1$) degree of freedom (df) is the distance from it. The first correction to the monopole contribution is the anisotropic, i.e., dependent of direction 1:st order moment or *dipole*. The dipole moment has three (3^1) components, one for every spatial degree of freedom. It can be represented by two oppositely charged poles, thus di-pole. Further corrections come from quadrupoles (3^2 df), octupoles (3^3 df), hexadecapole (3^4 df) etc. These corrections go by their common name *multipoles*.

A mathematical way of obtaining multipole moments is to treat the charge distributions as a perturbation with respect to its center. This is a valid approach only if the location for observing the structure is sufficiently far away. Eq. 2.8 describes the potential at a distant point \mathbf{r} from N discrete charges positioned close to the origin, at δ_n respectively. For simplicity we have omitted the factor of $1/(4\pi\epsilon_0)$ in Eq. 2.8. The total charge q , dipole moment μ and quadrupole moment Q are defined in

Eq. 2.9, and in Eq. 2.10 the interaction tensor is introduced.

$$\Phi(\mathbf{r}) = \sum_{n=1}^N \frac{q_n}{|\mathbf{r} - \delta_n|} = q\mathbf{T}_0(\mathbf{r}) - \boldsymbol{\mu}\mathbf{T}_1(\mathbf{r}) + \frac{1}{2}\mathbf{Q}\mathbf{T}_2(\mathbf{r}) - \dots \quad (2.8)$$

$$q \equiv \sum_{n=1}^N q_n, \quad \boldsymbol{\mu} \equiv \sum_{n=1}^N q_n \delta_n, \quad \mathbf{Q} \equiv \sum_{n=1}^N q_n \delta_n \delta_n^T. \quad (2.9)$$

$$\mathbf{T}_n(\mathbf{r}) = \nabla^n \left(\frac{1}{|\mathbf{r}|} \right), \quad \mathbf{T}_n(\mathbf{r}) \in \mathbb{R}^{3^n}. \quad (2.10)$$

By multiplying any given charge with the potential $\Phi(\mathbf{r})$, the interaction energy with the described electric structure is obtained. Furthermore, by using more and more terms from Eq. 2.8 our calculated interaction energy more closely matches the true interaction energy. Lastly we acknowledge that Eq. 2.8 essentially is a multi-charge tensor-formed representation of the single-charged Eq. 2.3 using $|\mathbf{r}''| \gg |\mathbf{r}'|$.

2.4 Induction

Pair-potentials are, as depicted, often an apt and simple way to describe the interactions in a system. Even so, there may be essential many-body effects giving qualitatively differing results to those illustrated by simple pair interactions. A way of introducing such many-body effects is to include polarizable particles. Thus the particles may induce multipole moments on one another. The induced moments are determined by the polarizability tensor $\boldsymbol{\alpha}$ of the particles and its experienced external field \mathbf{E} . In theory it is possible to induce any electric multipole moment, though this work has included solely the induced dipole-moment $\boldsymbol{\mu}_{\text{Ind}}$ according to Eq. 2.11.

$$\boldsymbol{\mu}_{\text{Ind}} = \boldsymbol{\alpha}\mathbf{E} \quad (2.11)$$

2.5 Dispersion / Repulsion

A simple and common expression approximating both dispersion and repulsion is the Lennard-Jones ((m,n)LJ) pair-potential¹³ given in Eq. 2.12.

$$u(r) = \frac{\tau_n}{r^n} - \frac{\tau_m}{r^m} \quad (2.12)$$

Both τ_n and τ_m are positive parameters based on the types of the interacting particles. Hence the first term corresponds to the repulsion and the

second to the dispersion energy. The dispersion energy is a quantum-mechanical phenomenon and the derivation of the dispersion term is based on quantum mechanics too. It has been shown¹⁴ that the leading contribution to dispersion energy is proportional to r^{-6} whereby m is typically chosen to be six. Even though the repulsion term is also a quantum-mechanical phenomenon, there is no theoretical equivalence for its energy. For this reason it is subjected to empirical or conceptional models. Due to computational advantages it is common¹⁵ to chose $n = 2 \cdot m = 12$ which accounts for the infinite repulsion at infinitesimal distances. Another model is the exponential $P(r)e^{-r/\varrho}$ potential, where $P(r)$ is a polynomial and ϱ a parameter. Such potentials have been proposed based on (empiricism and) theory of overlapping electron shells.¹⁶ The potential fails to mimic infinite repulsion at infinitesimal distances although it coincides with experimental results at somewhat larger distances. We have regarded qualitative repulsion at close distances more important than accurate long-range repulsion and thus the (6,12)LJ-potential has been used throughout this work.

Finally, it is possible to include the, attractive, averaged electrostatic contribution throughout configuration space in τ_6 by incorporating the Boltzmann weighted dipole-dipole and ion-quadrupole interactions as written in Eq. 2.13.[†] The domains of validity for these contributions are shown in Eq. 2.14.[‡] Here we have introduced the indexes A and B for particle types, k_B as the Boltzmann constant, T as the absolute temperature, and finally λ as the eigenvalues of the quadrupole-moment tensor.

$$\tau_6^{\mu\mu} = \frac{\mu_A^2 \mu_B^2}{3(4\pi\epsilon_0\epsilon_r)^2 k_B T}, \quad \tau_6^{qQ} = q^2 \frac{3\text{Tr}(\mathbf{Q}\mathbf{Q}^T) + \text{Tr}(\mathbf{Q})^2 - 6\text{Tr}(\text{adj}(\mathbf{Q}))}{10(4\pi\epsilon_0\epsilon_r)^2 k_B T} \quad (2.13)$$

$$r \gg \sqrt[3]{\frac{\mu_A \mu_B}{4\pi\epsilon_0\epsilon_r k_B T}}, \quad r \gg \sqrt[3]{\frac{|q|}{4\pi\epsilon_0\epsilon_r k_B T} \max_i (|\lambda_i - \text{Tr}(\mathbf{Q})|)} \quad (2.14)$$

[†]The averaged ion-quadrupole interaction is obtained by the same method as for the standard averaged dipole-dipole interactions.

[‡]The interval of validity for the averaged ion-quadrupole interactions is obtained by acknowledging the maximum value of $\mathbf{r}^T \mathbf{Q} \mathbf{r}$ to be retrieved when $\mathbf{r}/|\mathbf{r}|$ is the eigenvector to \mathbf{Q} corresponding to its largest eigenvalue.

Chapter 3

Quantum Mechanics

So far we have used what is called *classical* mechanics to describe particles, however, a more accurate description comes from *quantum* mechanics (QM). Since QM is the most accurate of the two then, theoretically, we should always use it. Even so, for macroscopic object descriptions the discrepancies between the two are negligible. For small objects such as sub-atomic particles, a classical description is not even valid whereby we are left with QM alone. It seems QM is the ideal choice for any given system, but there is a practical hindrance in that quantum calculations are much more demanding than classical ones. Usually about a couple of hundred atoms is the limit where after the computational cost becomes insurmountable. In this work the model systems are in the atomic domain, thus making them eligible for both approaches. The choice therefore stands between quantum accuracy and classical rate. We will see later on that it is possible to combine the best qualities of both approaches in order to get quantum-mechanical features in classically propagated systems.

3.1 Basics

The base of QM is Eq. 3.1, also known as the time-dependent Schrödinger equation.¹⁷ Here \hat{H} is the Hamiltonian operator, Ψ is the spatial state wave function, t the time, and \hbar the reduced Planck constant.

$$\hat{H}\Psi = i\hbar \frac{\partial}{\partial t} \Psi \quad (3.1)$$

In this work only stationary states are of interest, whereby we only use the simplified time-independent Schrödinger equation as in Eq. 3.2.

$$\hat{H}\Psi = E\Psi \quad (3.2)$$

In QM it is not the position and momentum of the particles *per se* which describes the state of the system but rather their wave function Ψ . \hat{H} describes the interactions in the system which acting on Ψ gives its energy E . Thus there are two interlinked aspects to consider, the Hamiltonian and the wave-function. Most often the Hamiltonian is built up by summing the kinetics of, and electric interactions between, the particles in the system in addition to external contributions. The usual approach concerning the wave function is to split it into two independent nuclei- and electron-functions. This is called the Born-Oppenheimer approximation¹⁸ and is based on the assumption that electrons re-arrange instantly with a nuclear translation. Moreover, the electron wave function has to obey the Pauli principle. By using a Slater-determinant of orbital functions this antisymmetric property is fulfilled. Lastly, the variational principle claims that no trial wave function has a lower eigenvalue than the true one. Thus by minimizing the energy, a fair approximation of the wave function is often retrieved.

Now we will introduce some numerical methods whereby QM problems may be solved. These methods are sufficiently sound for our needs, however, for greater accuracy (and thus complexity and time needed), methods such as configuration interaction¹⁹ (CI), coupled cluster²⁰ (CC), and complete active space self consistent field²¹ (CASSCF) are available.

3.2 Hartree-Fock

The base of many (if not most) numerical approaches in QM is the Hartree-Fock method^{22,23} (HF). The main idea behind the method is to initiate the system with an approximate wave-function where after the energy is minimized in a self-consistent manner, thus the method is sometimes also referred to as the self-consistent field method (SCF). It uses the mean field of the surrounding electrons as an approximation by which there will be a loss of electron correlation (i.e. dispersion energy) but also a reduction of complexity of the problem at hand.

Møller-Plesset perturbation theory

Losing the electron correlation is sometimes a viable option although for many problems it is essential to include. The Møller-Plesset perturbation theory²⁴ (MPPT) captures some of the correlation lost in HF. When using perturbation theory one needs an approximation of the true solution from which the correlation correction is considered to be a perturbation from

the same. Consequently the approximate solution used in MPPT is the HF result. The theory is valid for any higher order perturbations, however, analytical expressions give the first order correction nil. A generic feature of even-number order perturbations is the inherent lowering of energy which is not guaranteed with odd number order perturbations such as three. Thus, the only reliable orders to incorporate would be two, four, six, etc. The exponential computational cost with number of particles which further increases with order of perturbation, together with the disused void first order correction thus gives the most usual order of perturbation as two (MP2).

3.3 Density Functional Theory

A fairly simple and computationally fast method for QM-calculations is Density Functional Theory²⁵(DFT). Rather than dealing with the state wave function of the system, as in HF, it uses the electron density $\rho(\mathbf{r})$. It has been shown that there does exist a functional (i.e. a function of a function) $F(\rho(\mathbf{r}))$ which yields the ground-state energy and that the properties of the ground-state can be uniquely retrieved using the electron density. Even so, the method somewhat lacks electron correlation and in its original form it is insufficient to describe excited states. These deficiencies have however been resolved to some extent.^{26,27}

3.4 Basis Sets

In large-scale computer calculations it is usual to not use analytical expressions but rather linear algebra to solve equations. Therefore the state wave function needs to be described in terms of standard shapes. A basis set is a toolbox of standard orbital functions which combined should be able to approximate any function, for example the wave function. For a diverse infinite basis set this is obviously true, however, a computer is limited to only a finite number of orbitals from which only an approximate description may be obtained. Though we can increase the number of standard orbital functions the computational cost of using a basis set is exponential to its size. Accordingly, we aim to use small sets in our calculations in order to gain efficiency.

3.5 Nuclear Magnetic Resonance

Nuclear magnetic resonance (NMR) is a spectroscopy technique used to study molecular structures immersed in a strong magnetic field \mathbf{B} by means of radio-frequency electro-magnetic radiation. Many elemental particles have magnetic spins, and consequently, atoms (and isotopes) may also have this intrinsic property. In a magnetic field, the spin removes the degeneration of the nucleus energy-levels, seen in Eq. 3.3, and the spins will align accordingly.

$$E_i = -\frac{m_i \gamma h}{2\pi} B \quad (3.3)$$

Here the energy E_i relates to the i -component of the magnetic moment m_i , the gyromagnetic ratio γ , and the Plank constant h . Usually a strong field is used to increase the difference between discretization levels. NMR techniques relies on measurements of transitions between such non-degenerate energy-levels. Eq. 3.4 gives the energy difference between two discrete levels as a function of the frequency ν of an emitted photon. Thus, given a specific frequency, it is possible to calculate the localized magnetic field at a nucleus, and implicitly the electron distribution around the same.

$$\Delta E = h\nu \quad (3.4)$$

By further use such frequencies it is possible to define the chemical shift δ between a sample and a reference as in Eq. 3.5.

$$\delta = \frac{\nu_{\text{sample}} - \nu_{\text{reference}}}{\nu_{\text{reference}}} \quad (3.5)$$

The main difficulty of the computational approach is to get gauge-independent vector potentials. Specifically it is the basis set which needs to be treated in order no nullify unwanted effects introduced by the external magnetic field. The gauge-invariant atomic orbital (GIAO) method²⁸ proposes a solution to this problem where the basis set is field-dependent. This correction removes most of the undesired effects in the resulting chemical shielding tensor σ_{ij} , see Eq. 3.6 where j index spatial component. This tensor is directly proportional to the chemical shift δ .

$$\sigma_{ij} = \left. \frac{\partial^2 E}{\partial m_i \partial B_j} \right|_{\mathbf{B}=0} \quad (3.6)$$

Chapter 4

Statistical mechanics

As it sounds statistical mechanics is a *statistical* approach to a given problem. Through studies of microscopical states, their probabilities to be occupied, and mechanics governing their behaviour, the physical properties of macroscopic observables can be predicted. Yet we start by using only probabilities and see that statistical inference alone will eventually give results interpretable as statistical mechanical results.

Let us assume that there is a state i occupied with the probability ρ_i . We denote the measure of uncertainty of such a system state as $H(\rho_1, \dots, \rho_\nu)$ where ν is the total number of states. This uncertainty H we assume; (i) to be continuous in each ρ_i , (ii) monotonically increasing with an increase of equal probable states, (iii) to be the product of the uncertainties of the (possible) subsystems. It has been shown²⁹ that the only function to obey these criteria is the one in Eq. 4.1 where K is a positive constant amounting to a unit of measure.

$$H(\rho_1, \dots, \rho_\nu) = -K \sum_i \rho_i \log(\rho_i) \quad (4.1)$$

If we know a system to be in a specific state, say $\rho_k = 1$, then we have $H = 0$ and thus no uncertainty. For any other distribution of probabilities $H > 0$ and we have some uncertainty. This relation between the uncertainty H and the probabilities ρ_i has an analogy in statistical mechanics³⁰ where the entity H is denoted S and called entropy, and K is the Boltzmann constant. However, for us to obtain the same result using statistical mechanics we need to adopt a rule or *postulate* which we take for granted as fact (though we do not know if so). This postulate is called the *ergodic hypothesis*. It says that the result from sampling the ensemble of states in phase space equates the samples from an eternally physically propagated system in the same space.³¹ That is, we have a one-to-one or *bijective* cor-

respondence between a system propagated in time and an equal system propagated in space.

4.1 Thermodynamics

So far we have not used but rather described the foundation of statistical mechanics. Now we will apply it to real systems, starting in a system with constant number of particles (N), volume (V), and energy (E). The set of systems with these specific entities kept constant is called the *microcanonical ensemble*. The number of occupational possibilities in these systems is called the microcanonical *partition function* and is denoted $\Omega_{N,V,E}$. We now state a second postulate which is called *equal a priori probability*. It says that an isolated system in equilibrium has an equal probability of being in any state. Hence we have $\rho_1 = \dots = \rho_v = 1/v$ which incorporated into the statistical mechanical version of Eq. 4.1 collapses to Eq. 4.2.

$$S = k_B \log(\Omega_{N,V,E}) \quad (4.2)$$

A measure of the entropy, or uncertainty, of a system under these conditions is now apparent. By this quantity we can further define the chemical potential (μ), pressure (P), and absolute temperature as is defined in Eq. 4.3 respectively where the subscripts implies constant quantities during the differentiation.

$$-\frac{\mu}{T} = \left. \frac{\partial S}{\partial N} \right|_{V,E}, \quad \frac{P}{T} = \left. \frac{\partial S}{\partial V} \right|_{N,E}, \quad \frac{1}{T} = \left. \frac{\partial S}{\partial E} \right|_{N,V} \quad (4.3)$$

Now we see that S is not merely an abstract measure of uncertainty but also intrinsically coupled to every-day concepts. A fundamental property of the total entropy in the microcanonical ensemble is that it never decreases. Therefore if the entropy rises during a process then that process is *irreversible*. In other words if we lose information (i.e. increase the uncertainty) then we can not re gain it.

The concepts brought forward so far are conceptually accurate, however, for convenience other ensembles are more common to use. Such an example is the *canonical* ensemble. Eq. 4.4 presents its partition function in which number of particles, volume, and temperature are kept constant.

$$Q_{N,V,T} = \sum_E e^{-E/k_B T} \quad (4.4)$$

$$A = -k_B T \log(Q_{N,V,T}) = E - TS \quad (4.5)$$

For such an ensemble it is not the entropy that will inherently increase but instead the quantity known as Helmholtz free energy, see Eq. 4.5, will strive towards the minimum. Likewise we can further define the *isobaric-isothermal* partition function in Eq. 4.6 where now not the volume but the pressure is constant. This time it is neither the entropy nor Helmholtz free energy that assumes an extreme value but rather Gibbs free energy, as shown in Eq. 4.7, is minimized.

$$\Delta_{N,P,T} = \sum_E e^{-E/k_B T} \sum_V e^{-PV/k_B T} \quad (4.6)$$

$$G = -k_B T \log(\Delta_{N,P,T}) = E - TS + PV \quad (4.7)$$

There are more ensembles, although in this work we have only made explicit use of the latter two. With the use of the partition functions we can define average values of different quantities. The average value of an arbitrary quantity X can be expressed as in Eq. 4.8. The probabilities are presented in Eq. 4.9 and the summation goes over every microstate, energy, or energy *and* volume with their corresponding X -state using the microcanonical, canonical, and isobaric-isothermal ensemble respectively.

$$\langle X \rangle = \sum X \rho \quad (4.8)$$

$$\rho = \frac{1}{\Omega_{N,V,E}}, \quad \rho_i = \frac{e^{-E_i/k_B T}}{Q_{N,V,T}}, \quad \rho_{ij} = \frac{e^{-E_i/k_B T} e^{-PV_j/k_B T}}{\Delta_{N,P,T}} \quad (4.9)$$

Lastly we introduce the *grand canonical*(GC) ensemble with its partition function as Eq. 4.10. This ensemble constraints the chemical potential, volume, and temperature to be constants. In the next section we will (for this work at least) implicitly need the concept of the GC ensemble. The grand potential, Eq. 4.11, is the entity which should be minimal for the GC ensemble in thermal equilibrium.

$$\Xi_{\mu,V,T} = \sum_E e^{-E/k_B T} \sum_N e^{N\mu/k_B T} \quad (4.10)$$

$$\Lambda = -k_B T \log(\Xi_{\mu,V,T}) = E - TS - \mu N \quad (4.11)$$

Kirkwood-Buff theory

The procedure of assessing binding affinities is one of great difficulty but similarly great importance. With the use of Kirkwood-Buff theory³² it is however possible to get such, thermodynamically well-defined, results

quantified. The theory focuses on the ability to link microscopic descriptions to macroscopic states, based on the GC ensemble. Here it connects chemical potential (and osmotic pressure) derivatives to the fluctuations in average number density, see Eq. 4.12, which are in turn connected to the normalization conditions for the radial distribution functions in the GC ensemble. In this equation ρ symbolises particle densities, δ the Kronecker delta, X an arbitrary particle type, and G_{AB} is described in Eq. 4.13, also called the Kirkwood-Buff integrals (KBI), by the radial distribution function $g_{AB}(\mathbf{r})$.

$$\frac{k_B T}{V} \left. \frac{\partial N_A}{\partial \mu_B} \right|_{\mu_X \neq \mu_B, N, T} = \frac{\langle N_A N_B \rangle - \langle N_A \rangle \langle N_B \rangle}{V} = \rho_A \rho_B G_{AB} + \rho_A \delta_{AB} \quad (4.12)$$

$$G_{AB} = \int (g_{AB}(\mathbf{r}) - 1) d\mathbf{r} \quad (4.13)$$

KBI for different particle distribution functions can be combined giving the preferential binding parameter Γ in Eq. 4.14 where C index particle type. This is a measure of the *difference* in preferential binding of the particles and in this work a vital article. The KBI can further be used to derive expressions for partial molar volumes, compressibility, and activity derivatives.

$$\Gamma_{BC} = \rho_C (G_{BC} - G_{BA}) = \left. \frac{\partial \left(\frac{N_C}{N_A} \right)}{\partial \left(\frac{N_B}{N_A} \right)} \right|_{T, \mu_A, \mu_C} \quad (4.14)$$

We have seen that particle fluctuations are important in KB theory and thus the GC ensemble is expediate to use. In many considerations this is however a cumbersome ensemble to use. Therefore it is common to use an other type of ensemble and regard a sub-system of the same as GC.³³ Since the studied 'grand canonical' system has a specific size it means the total system needs to be a fair amount larger to accurately mimic a true GC system. This together with a necessity for precise radial distribution functions results in large systems simulated for a long time when evaluating the theory.

Lastly, we want to mention inverse Kirkwood-Buff theory which has somewhat completed the concept by being capable of predicting microscopic behaviour based on macroscopic data.³⁴

Chapter 5

Simulations

Throughout this work computer simulations have been used. The word simulation originates from the Latin *simulatus* meaning ‘to make like’. This is exactly what simulations aim to do, to mimic or imitate something. In principle this could be done to any system, although we are trying to mimic the behaviour of atoms. This can be done by setting up a space comprised of atoms and stating rules for their interactions. After this set-up we can observe how the system evolves. Obviously it is important for the system to be properly conformed, and for correct interactions to be used, if accurate information is to be gained. There are two main schemes with regard to the propagation of an atomistic system; Molecular Dynamics (MD) and Monte Carlo (MC).

5.1 Schemes

The MD approach is based on calculating *forces* between atoms. These (usually Newtonian) forces will move the atoms some distance during a predetermined time step. By performing this procedure over and over, the system will behave fairly similar to a real system, that is given correctly adjusted settings such as the size of the time step. When running MD simulations the calculated forces need to be treated such that they are in balance with the surroundings of the simulation space, if any. It is thus not unusual for a thermostat³⁵ and/or barostat³⁶ to be needed in order to meet these criteria. Molecular Dynamics has many advantages, one of which is that we may observe how the system evolves over time, however, there are also pitfalls such as getting stuck in a local energy-minima.

In MC simulations the system is propagated through random displacements. If we explore every possible configuration using this ap-

proach, the MC and MD results are assumed to converge. This is what we earlier called the ergodic hypothesis. Unfortunately the computation time it would take to explore a large enough region of the configuration space, giving interpretable results, would be impractically long. Nevertheless, we are not interested in all information about the system but rather about some specific entities. Thus if we chose configurations of large importance to those entities more often than others we may speed up the calculations. In our cases we are interested in Boltzmann-weighted averages which are ratios rather than absolute values, see Eq. 4.8-4.9. In these cases a representative region of states is given if the probability of accepting a configuration change is chosen according to Eq. 5.1.^{37,38}

$$P = \min \left(e^{-\Delta E/k_B T}, 1 \right) \quad (5.1)$$

Here ΔE is the difference in configurational energy brought about from a displacement. A drawback with MC is that time-dependent entities are quantitatively impossible to sample. On the other hand, using properly chosen displacements the risk of getting caught in energy minima is small.

5.2 Electric summation methods

When simulating a system it is only possible to give it a finite size. Even (currently) large particle systems ($N \sim 10^6$) are too small to neglect long-ranged electric effects. Thus it is imperative to accurately account for the excluded contributions from (the implicit) outside of the simulation-space. To do this, we first need a description of the properties of the outside space itself. The most common plan of attack is to use periodic boundary conditions (PBC). That is a centred box as the simulation space, which is replicated in every direction filling infinite space. This approach has the mathematical advantage of periodicity but drawbacks with artificial long-ranged order. Another approach is to model the surrounding as a continuum, where matter as a whole is uniformly described, but here artefacts may enter at the interface between the two realms. Yet another approach is to put the three-dimensional simulation space as the edge of a four-dimensional hypersphere, thus there are no boundaries at all. Even so, the hypersphere approach is valid only for sufficiently large spheres where curvature artefacts are small. It seems none of the models are perfect, all the same, at the moment this is what we have to work with, which is why we now concentrate on techniques to aggregate the electric

contributions using such environments. Though many more exist^{39,40,41} we present only three approaches; the standard Ewald summation, the reaction field method, and Wolf summation. Each one has pros, cons, similarities, and differences to one another and as such the final choice about formalism and boundary condition is often based on the specific structure of the system at hand.

Ewald summation

The Ewald method^{42,43} uses PBC and separates the conditionally convergent system energy into absolute convergent short- and long-ranged interaction energies via a splitting function. The long-range interactions are Fourier-transformed and evaluated in reciprocal space while the short-ranged ones are summed in real space. For practical reasons there is need of a cut-off in both spaces, i.e., the most long-ranged contributions in real space are neglected and conversely in reciprocal space. Even with these cut-off's a drawback with the Ewald summation is the computational time it demands, growing quadratically with the number of particles in the system. This exponential cost has however been somewhat reduced as of late.⁴⁴ Historically the Ewald summation was introduced as a way of obtaining crystal energies where it obviously benefits from the intrinsic periodicity of the formalism.

Reaction field method

The reaction field method models infinite space as a continuum with some relative permittivity wherein the system particles are enclosed in a cavity.^{45,46,47} The particles in the cavity act upon this dielectric entity and polarize the same. The induced field of the polarized continuum in return acts on the particles, hence a *reaction field*. It is thus vital for the continuum relative permittivity, also known as the dielectric constant, to be accurately parametrized such that the correct field is induced. This task is not trivial since the generic features of the same is nebulous on small scales. Therefore, the evaluation of the dielectric constant has been subjugated to a lot of research.^{48,49,50} The continuum model often gives a fair representation of macroscopic liquids and hence it is within this regime the formalism is usually preferred. Since only particles within the cavity have to be dealt with explicitly, the computational time needed is roughly proportional to the number of particles in the system.

Wolf formalism

The Wolf method is based on charge neutralization. It has been noticed⁵¹ that for a given cut-off the resulting potential energy error is proportional to the aggregated charge within that sub-system. Therefore, if the sum is zero, the error is approximately zero. By pairing every particle with an oppositely polarized image particle, neutrality is thus always assured. The Wolf formalism locates these image particles at the cut-off sphere. It is however often necessary to introduce a damping-factor in the formalism, introducing a not yet fully explored damping-parameter space, the analogy of which is thoroughly researched for Ewald sums.^{52,53} Like the Ewald method, Wolf summation was introduced to retrieve crystal energies and like the reaction field method its complexity is of order $\mathcal{O}(N)$.

Discussion

As we have seen there are different approaches to find a solution to the problem of summation of long-ranged electrostatic interactions. This section is included as a general discussion about such interactions and implications of the methods used to account for their long-ranged contributions. We start by discussing the standard PBC approach.

Methods using the PBC replication usually try to explicitly include all interaction in infinite space, for example Ewald sums and the Fast Multipole Method⁵⁴ (FMM). Therefore these methods are in some sense 'brute-force' methods with no long-range *correction* but rather they try to avoid the need for correction altogether. If all such interactions are accounted for, the methods themselves are of course perfectly accurate and invalid results can only be attributed to the choice of boundary conditions. However, in both methods there is a need for one or more cut-off's. This limits Ewald sums to cases where small distant errors (real space cut-off effect) and small proximal errors (reciprocal space cut-off effect) can be neglected without further implications. In a similar way FMM suffers from long-ranged errors but also from errors at every length scale due to the impossibility of including infinite multipole moments interactions in the summations, a criterion which should be met for the formalism to be exact. It is of course not strange that it is impossible to reach the aim of including infinitely many interactions using finite computer resources. Even so, the Ewald method and FMM have proven to yield proper results in many regards and most often it is not the methods themselves but indeed the choice of boundary condition that is to blame for invalid

results.⁵⁵

The solution to Poisson's equation for a particular geometry is⁵⁶ Eq. 2.4 in addition to Eq. 2.3. This approach is the reaction field method which in practice truncates the infinite sum of Eq. 2.4. Thus the reaction field does indeed give an *exact* solution in the limit of infinite contributions and an accurate dielectric constant. It is not possible to include infinitely many higher order terms, however, by sequentially include more and more terms, we may reveal an important feature of the system: how long-ranged the interactions really are, and maybe which angular moments to be important. Therefore, even though the evaluation of the external dielectric constant may be problematic, the method have valuable properties.

The Wolf summation method has been described as an ensured charge neutralization of every spherical region surrounding a particle. The physical interpretation of this is straightforward, however, the mechanism behind the neutralization has not yet been contemplated as far as we know. The method seems to be restricted to fairly conductive systems with relatively isotropic particle distributions. If we have a particle at some position r from the origin embedded in a cavity of a conductive sphere with radius R , an equal mathematical description would be to simply have the particle and an image particle at position R^2/r oppositely polarized and charge-scaled with a factor of R/r . This image charge will induce a charge on the surface of the cavity equal in size but oppositely polarized to the original particle. Thus, the charge-neutralization condition in the Wolf method might only be a consequence of conductive boundary conditions. This obviously limits the method for its general applicability. Even so, it has been noted that to ensure fast converging results, for a crystal, the method needs a damping function, typically the complementary error-function. We now look back to Eq. 2.4 which can be further expanded by using Eq. 5.2. The lower order terms of these sums are generally of larger importance than higher-order ones whereby two main approaches will be used; (') use only the $n = 0$ term but all k -terms, and (") use only the $k = 0$ term but all n -terms. The resulting reduced charges, positioned at R^2/r , can be seen in Eq. 5.3.

$$\frac{n+1}{n+\varepsilon_r(n+1)} = \frac{1}{\varepsilon_r+1} \sum_{k=0}^{\infty} \frac{1}{(\varepsilon_r+1)^k (n+1)^k} \quad (5.2)$$

$$q' = - \left(1 - \frac{1}{\varepsilon_r}\right) \frac{R}{r} q, \quad q'' = - \left(\frac{\varepsilon_r-1}{\varepsilon_r+1}\right) \frac{R}{r} q \quad (5.3)$$

In the limit $\epsilon_r \rightarrow \infty$ both approaches are indeed equal to the original Wolf method. For other values of ϵ_r there is an effective damping, not of the direct contribution but of the image charge. Such an approach has been successfully tested for a Wolf-like potential used on a diversity of systems including water.⁵⁷ Nevertheless, it included only seemingly arbitrary chosen damping parameters with no direct physical connection. Here, instead of using an arbitrary damping parameter we suggest a direct physical connection to the properties of the immediate environment. Since no true system is a perfect conductor the original Wolf method will present inherently erroneous result. Even so, if we have an arbitrary large dielectric constant the approximation of the second approach is basically void, resulting in a exact result. Hence, by using an infinite dielectric constant, the correction from higher order ϵ_r -terms but also from higher order n -terms terms fails to signify. If lower dielectric constants are used then the Wolf method seems to suffer significantly from lost contributions in both categories. However, to evaluate which to be of more importance requires further studies. Using this narrative we see the original Wolf method not to be an independent method based on neutralization, but rather as a version of the reaction field method using conducting boundary condition.

Chapter 6

Cellulose

Cellulose was isolated over a century ago and at that time named from the french 'consisting of cells'.⁵⁸ It originates from plants and thus is a renewable material, accessible throughout the globe (notably in the form of wood pulp), and is fairly economical. One of the first approaches to utilize wood for pulp production on an industrial scale was the soda process in the middle of the nineteenth century. Not long thereafter the Kraft process added sodium sulphide to the aqueous sodium hydroxide in the soda process, which made the process more effective in separating cellulose fibres from the lignin. Today one focus lie in the further dissolution of cellulose crystals inherent to the wood pulp. The systematic name of the cellulose polymer is (1→4)- β -D-Glucan. Here the numbers indicate linked carbon atoms between the anhydroglucose units (see Fig. 6.1), β the link type and D the monomer form. Even though almost two centuries have passed and the subject has been extensively investigated, there is no consensus regarding important aspects of cellulose structures. Even so, by starting from the beginning we will see that some progress has indeed been made.

6.1 Structures

Starting at a large scale and going smaller, general trends in cellulose structures can be observed. Small string-like cords accumulate in semi-crystalline forms where outlying chains are incorporated or intertwined with other similar block structures,⁵⁹ thus the result is a two-phase system consisting of both crystalline and non-crystalline matter. The aim of this work has not been to study these relatively large-scale structures, but rather concentrate on small polymer units. It is of such chains the

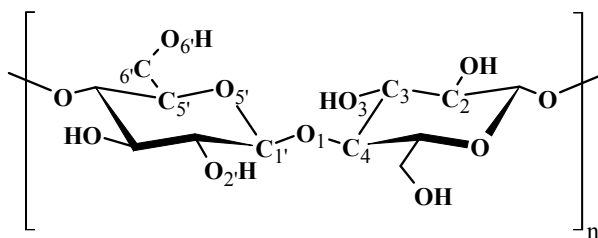


Figure 6.1: The structure of cellulose where n is the number of repeated dimer units. The left atoms are indexed with a prime to separate them from the otherwise identical right unit atoms.

crystalline sheets which we now address are composed of.

The first distinction between nanoscopic cellulose crystals was the one between cellulose I and II. While cellulose I is found in the native cellulose extracted from pulp, cellulose II is retrieved from the latter by mercerization or regeneration. Mercerization is intracrystalline swelling of cellulose in aqueous alkali followed by washing while regeneration is dissolution of cellulose which then recrystallises. Both processes yield cellulose II complexes though structural discrepancies have been noted.⁶⁰ It was further shown that part of the disputes about cellulose native structure stemmed from the presence of not one but two further different cellulose complexes, the α and β allomorphs.^{61,62} Furthermore, by treating cellulose with ammonia it is possible to retrieve types III₁ and IV₁ from cellulose I and types III₁₁ and IV₁₁ from cellulose II.^{63,64} In this work we have primarily focused on cellulose I and II whereby we leave the structures of cellulose III and IV for the interested reader to review. Thus we now investigate cellulose I _{α} , cellulose I _{β} , and cellulose II.

Before we go into detail about cellulose we backtrack to Fig. 1.1 where we observe the hydroxymethyl-groups to have different orientations with respect to the pyranose oxygen (O5') and the adjacent pyranose carbon (C5'). It is common to define the dihedral angles $\omega = \text{O5-C5-C6-O6}$ and C4-C5-C6-O6 which give rise to three main configurations; trans-gauche (tg), gauche-gauche (gg) and gauche-trans (gt). Moreover, the angles $\Phi = \text{O5'-C1'-O1-C4}$ and $\Psi = \text{C1'-O1-C4-C5}$ report on the linkage torsion between the monomers and are thus also of importance. We will later see that different dihedral angles give rise to vastly different structures and behaviour in cellulose samples.

The two cellulose I polymorphisms stem from both primitive organisms such as algae for I _{α} and higher lifeforms such as plants for I _{β} .⁶² It is however possible to convert the meta-stable cellulose I _{α} to the stable I _{β}

complex.^{65,66} A common feature of the two is a parallel chain arrangement⁶⁷ and tg-conformations of the hydroxymethyl-groups.^{68,69} For such crystals, the specific hydrogen-bonding pattern^{68,69} gives cellulose I α a triclinic unit cell with one chain while cellulose I β has a monoclinic unit cell with two chains.^{67,70,69} The main difference between cellulose I and II is the bonding network, both intra- and inter-chain and intra- and inter-sheet. Another aspect is the hydroxymethyl-groups which are gt in cellulose II in contrast to the tg conformation of cellulose I. The alignment of the polymer chains, parallel in cellulose I and anti-parallel^{71,60} in cellulose II, is an important aspect contributing to the bonding pattern. Lastly, the process of converting cellulose I to cellulose II is an irreversible procedure and the former is, thus, a meta-stable form.

6.2 Dissolution

It has been known since the middle of the nineteenth century⁷² that tetraamminediaquacopper dihydroxide, or Schweizer's reagent, is a working solvent for cellulose. Not long after, in 1892, the viscose process⁷³ was invented. It stipulates a pretreatment of the sample in sodium hydroxide after which carbon disulphide is added, resulting in the forming of sodium cellulose xanthate. This intermediate product is dissolved in more sodium hydroxide which finally yield dissolved cellulose chains. These processes do all have some disadvantages, either they are environmentally unsound, ineffective, or yield inadequate fibre strengths. For those reasons we want to find other processes and solvents which fit all of the criteria and in order to do so we need to understand the dissolution mechanism(s).

There are different approaches to cellulose dissolution. Two main groups of approaches with regard to the end result are; derivatizing and non-derivatizing solvents. That is, the resulting cellulose structure is either perturbed in some manner or it is not. A second division may be a separation in aqueous and non-aqueous solvents. In the following paragraphs some approaches within the non-derivatizing groups will be addressed starting with aqueous solvents. Derivatizing solvents have not been studied explicitly during this project whereby the interested reader is referred elsewhere.⁷⁴ Table. 6.1 includes examples of the, to be, mentioned molecules which can be used to dissolve cellulose.

The cuprammonium process is an approach where cupraammonium hydroxide (Cuam) dissolves cellulose. A proposed possible explanation

Non-derivatizing aqueous	
[Cu(NH ₃) ₄](OH) ₂	Cuam
NaOH	Sodium hydroxide
CO(NH ₂) ₂	Urea
Non-derivatizing non-aqueous	
[C ₅ H ₁₁ NO ₂] ₂ H ₂ O	NMNO
(CH ₃) ₂ SO	DMSO
[(C ₄ H ₉) ₄ N] ⁺	TBA
[C ₆ H ₁₁ ClN ₂] ⁺	C2mim

Table 6.1: The table shows different solvents or molecules used to dissolve cellulose. The left column shows the chemical formula while the right gives the name or abbreviation.

for this feature is the weakening of the intra-molecular hydrogen bonds.⁷⁵ Further conjecture about cellulose-cuam interaction suggests deprotonation of the former which is double-bonded to C2 and C3 of the latter.⁷⁶ Other examples of aqueous co-solvents are NaOH⁷⁷ (and LiOH⁷⁸). It is believed that the alkali atom complexes with water and that this structure causes cellulose to eventual break the inter-chain hydrogen-bonds. However, in this work we consider the dissolution to be due to deprotonation of cellulose hydroxyl groups by the alkali, see Paper VI. On a side note, suggestions have been made where the decreasing alkali ion size increases cellulose solubility, starting with potassium samples which did not dissolve at all.⁷⁹ Onwards, the sodium-water complexes have been shown to vary in structure with concentration and temperature.⁸⁰ It seems that cellulose dissolution using NaOH is restricted to such structures produced at low temperatures. Even so, sodium hydroxide is often used as a pre-treatment in which it induces swelling of the cellulose sheets. This swelling does often increase the likelihood/efficiency of dissolution using other co-solvents. For example, by adding ZnO or urea to a NaOH-cellulose solution the dissolution process was shown to improved in efficiency.⁸¹ The influence of zinc-oxide further showed that oxidized cellulose greatly improves solubility either with or without NaOH inclusion. These results hints to charging of the cellulose molecule being essential for its dissolution, a conjecture implicitly suggested by the previously mentioned formation of cellulose-cuam complexes. Even so, the solutions with zinc-oxide eventually gelled.

The *N,N*-dimethylacetamide/LiCl combination is a candidate in the non-derivatizing non-aqueous solvents category giving dissolution with low or no degradation. Unfortunately, however, there seems to be no ex-

planation for the mechanism taking place.⁸² Moving on to single component solvents the *N*-methylmorpholine-*N*-oxide (NMNO) complex have shown promise. It is a hygroscopic molecule and it has been shown that NMNO-monohydrate dissolves cellulose at around 100°C while the corresponding disesquihydrate structure at any temperature does not.⁸³ The dissolution mechanism has been conjectured to be the integrated result from the ability of NMNO to tripple-hydrogen-bond with the hydroxyl-groups of C2, C3, and C6 on the cellulose polymer.⁸⁴ Because of the satisfactory features of the NMNO-process yielding fibres and industrial popularity the resulting product has been given a name, Lyocell. Dimethyl sulfoxide (DMSO) is another solvent which together with many co-solvents, one of which is tetrabutylammonium fluoride (TBAF), forms binary solutions capable of dissolving cellulose. One advantage is the solubility of cellulose of relatively high degree of polymerization (i.e. chain length) without the use of pretreatments at room-temperature.⁸⁵ It has also been reported that no dissolution occurs when changing the halide of the complex to chloride or bromide, however, replacement with the acetate ion gives successful results. The TBA⁺-F⁻ salt is chemically similar to an ionic liquid (IL) but is not itself liquid in pure form. It has been shown that many ILs are favourable for cellulose dissolution. For example, both 1-butyl-3-methylimidazolium with a spectrum of anions⁸⁶ and 1-ethyl-3-methylimidazolium (C2mim) using either acetate or chloride⁸⁷ have been shown cellulose to dissolve. For the C2mim-acetate IL, MD-simulations suggest the dissolution mechanism to be due to anion-binding to cellulose hydroxyls, which is strong relative to that of water hydrogen bonding, and that the cation binds through hydrophobic interactions.⁸⁸

In this last paragraph we engage the suggestions that cellulose is an amphiphilic molecule,^{89,90} i.e., it has both hydrophobic and hydrophilic parts. It is the equatorial orientation of the hydroxyl groups which gives cellulose a distinct ability to form hydrogen-bonds while the face of the pyranose ring has a hydrophobic trait. This amphiphilic property has been acknowledged to prohibit cellulose dissolution.⁹¹ Therefore, it may be possible for amphiphilic solutions and solvents to reduce the hydrophobic interactions in water solutions and thus increase cellulose solubility, a feature we have already seen ILs able to reproduce in the non-aqueous solutions group of solvents. One agent capable of mitigating such hydrophobic interactions in water-solutions is urea.⁹² It has been shown that urea together with alkali dissolves cellulose, but in that study dissolution was attributed to hydrogen bonding⁷⁹ which has further been con-

firmed from MD-simulations.⁹³ Even so, it has also been shown through MD-simulations⁹⁴ that urea does indeed mitigate the hydrophobic effect without disturbing the capability of the anhydroglucose hydroxyls to form hydrogen-bonds.

6.3 NMR on cellotriose

In Paper VI we have shown deprotonation of cellobiose to be important in alkali solutions, and in this section we will further explore the narrative of (de)protonation effects. The following presents results from DFT calculations of a β -cellotriose chain immersed, using the polarizable continuum model,^{95,96} in implicit water. The geometries were optimized using the B97-2 functional⁹⁷ and 6-311++g(d,p) basis set.^{98,99} However, for the NMR chemical shift calculations, the pcSseg-2 basis set¹⁰⁰ was used together with the gauge-independent atomic orbitals method.²⁸ The studied property was how (de)protonation affects a neutral polymer. The original structure was an optimized β -cellotriose which was (de)protonated and re-optimized for the different incidents accordingly. Initial studies showed a general trend for the energies according to $gt < gg < tg$ whereby the minimum energy configuration of tripple-gt was used as the base molecule for the coming calculations. The aim was to gain insight into cellooligomer features. Hence, to avoid effects induced by the ends of the chain, the NMR analysis was carried out on the middle monomer alone. In Table. 6.2 the results can be seen where the energies were calculated according to Eq. 6.1.



Here $X = \{1, 3\}$ indicate the state of the (de)protonated cellulose, an approach which obviously is rough using a polarizable continuum model.

In the unperturbed structure, a hydrogen-bond is present between O6 at the central monomer and O3 at the reducing end. This is unchanged by (de)protonation of O3 and also for deprotonation of O2. When protonating O2 however, a new hydrogen-bond forms between the O3 hydrogen and the non-reducing end the central O6 one. For either (de)protonation of O6 the effect is a broken hydrogen bond and thus there are none left.

Energetically, the calculations seem to favour both protonation and deprotonation with respect to a neutral cellotriose chain. The approximation of the surrounding as a polarized continuum can not, generally, reproduce effects emerging from hydrogen-bonds. This feature may be

	ΔE	C1	C2	C3	C4	C5	C6
O2-H ⁺	-9.6	8.0	7.2	5.2	1.5	0.5	0.6
O3-H ⁺	-3.8	2.0	7.2	9.5	11.0	0.3	1.1
O6-H ⁺	-0.7	-1.3	0.5	0.6	-0.3	11.8	10.9
O2+H ⁺	-2.6	-6.3	15.3	-3.4	3.4	-0.2	-0.7
O3+H ⁺	-13.5	-0.8	-3.9	7.9	1.9	-2.9	-0.2
O6+H ⁺	-10.8	-1.6	-0.3	-0.3	-1.2	-5.1	11.1

Table 6.2: C¹³ chemical shifts differences in ppm in response to deprotonation or protonation of hydroxyl oxygens in the six far right columns. The energies are in kcal/mol and taken from the geometry optimization calculations.

critical, nevertheless, it is an approximation which is not unlikely to affect the different configurations in a similar way. A uniting characteristic for the different configurations is the number of hydrogen bonding sites accessible on the respective (perturbed) hydroxyl group. The deprotonated polymer may hydrogen-bond twice through the remaining oxygen, the uncharged chain through one oxygen and one hydrogen, and the protonated through both hydrogen atoms. These interactions are obviously different but nevertheless they are all hydrogen-bonds.

In Table. 6.2 we can see a generally higher chemical shift at the carbon atoms due to deprotonation. The exception is deprotonation of O6 which gives lower shifts at C1 and C4, whose common feature is their linkage to an adjacent anhydroglucose unit. Moreover, deprotonation of O2 and O3 seems to induce larger effects in their closest link-atom than they do the non-link atoms. By observing the protonation effects a general lowering of the chemical shift is seen. This time, however, there are several exceptions; C2 and C4 for protonation of O2, C3 and C4 for protonation of O3, and C6 for protonation of O6. We further observe that the C4 atom behaves qualitatively the same regardless of deprotonation or protonation at any given location. This hint that the C4 atom occupies an extreme state in the neutral chain, a state which immediately changes when modifying the polymer charge.

For a truly infinite polymer, the angles between the monomers would supposedly be the same. For our reference trimer, however, there are discrepancies, primarily in the Ψ -angle (126.8 versus 104.9 degrees). This initial state might explain the fairly different changes for the angles. Even so, we see generally larger twists represented by the Ψ -angle than for Φ , suggests that the electronic structure around C4 is preferentially changed to that of C1. This, again, exposes C4 as a central atom to study for proper

	$\Delta\Phi_N$	$\Delta\Phi_R$	$\Delta\Psi_N$	$\Delta\Psi_R$	$\Delta\omega$
O2-H ⁺	0.4	1.1	-2.1	-5.2	-1.6
O3-H ⁺	3.9	-1.5	-7.7	-2.3	-1.9
O6-H ⁺	-1.1	-1.9	1.9	-21.6	12.5
O2+H ⁺	-6.6	-3.0	29.6	0.4	1.9
O3+H ⁺	0.5	1.5	48.2	4.0	1.6
O6+H ⁺	2.0	-1.0	-0.5	31.7	2.2

Table 6.3: Changes in angles in degrees from that of the unperturbed polymer. N symbolises the angle between the middle and non-reducing end while R represents the middle to reducing end angles.

understanding of the cellulose molecule. The remarks from the current section is in line with the results of Paper VI where deprotonation of cellobiose seems favorable.

Chapter 7

Conclusions

In this project the common thread has been electric interactions. The *modus operandi* has been computer simulations of systems at an atomic level of theory. In order to gain insights of the cellulose molecule, such systems have been allowed to evolve and were sampled by different computer simulations techniques. The particles used have been parametrized through quantum mechanical approaches after which the systems have been propagated using classical mechanical interactions. Statistical mechanics has generated criteria for proper sampling of phase space if needed, and thermodynamics have been used as the analysis tool from which interpretable data could be extracted.

Secondly, static cellulose systems have been analysed using computational NMR. In Sec. 6.3 the thesis presents hints of favorable interactions between the polymer and its water-like environment by ionizing the same. Furthermore, the C4 atom was revealed as key for properly understanding both twisting and electric rearrangements of the chain.

Thirdly, summation methods for long-ranged electrostatic interactions have been developed for both isotropic and anisotropic potentials. A discussion about electrostatic summation methods in Sec. 6.2 suggests a direct physical connection between the damping parameter in the Wolf method and the permittivity of the surrounding medium.

Lastly, at the next page we present a compilation of the results from the different papers.

- I Anisotropic functionality was implemented in our in-house Monte Carlo simulation package. That code (with further updates) was then the backbone used throughout the main project.
- II The study concluded electric polarizability to indeed play a significant role at interfacial waters and hydroxyl groups in cellulose-water systems. Also, an indication of proper long-range electrostatic summation was noticed for an expanded Wolf formalism.
- III We found urea to mitigate the hydrophobic effect at the faces of an infinitely replicated cellulose-chain immersed in water. This binding did not interfere with the solvating shells around the equatorial hydroxyl groups, and the process was exothermic.
- IV Conceptual realizations of the expanded formalism included a (semi-)definite density interval of validity and the existence of a so-called saturated cut-off in addition to the parametrization of the method.
- V It was shown that multipole cancellation in itself is only a valid approach for summation of long-ranged isotropic interactions whereas summations of anisotropic particle interactions require further theory.
- VI A general tendency towards deprotonation of the hydroxyl groups in cellobiose by comparing computational and experimental NMR data was noticed. Deprotonation of the C1 hydroxyl group of the reducing end seemed the most favourable which, possibly, is followed by a second deprotonation at the non-reducing end.

Chapter 8

Outlook

Electric interactions have been under investigation for centuries and will of course be subject of a lot of interest in the future. At the moment the multiple approaches for isotropic summation methods do not by any means capture the full picture one by one, but should rather be amalgamated into a sole concept, which should be possible since they all describe the same thing. Therefore, a comprehensive yet conceptual review of the pair potentials based on summation of long-ranged electrostatics might be worthwhile to pursue. Furthermore, the direction of future electrostatic developments might advance by focusing more on anisotropic interactions. Not only may anisotropic interactions be of larger importance than is generally recognised, but also since their inherent nature can give conceptual insights that can not be gained by investigating isotropic interactions.

When it comes to cellulose, quantum mechanics seems essential in understanding and discovering dissolution mechanisms. However, this in conjunction with entropic contributions will allow a further exploration of phase space. Thus a fruitful approach might be DFT-MD calculations in which thermal aspects may be considered. As with the electrostatic interactions mentioned above, a proper review of cellulose solvents and co-solvents may both illuminate older but still up-to-date knowledge and save time in not exploring the same mistakes (or successes) again. Moreover, since this work has shown charging effects of cellulose molecules to play a not insignificant role, newcomers (or other) to the cellulose field are encouraged to scan the heap of older literature regarding this subject.

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