Computational Studies of Cellulose-based Materials

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Description of the cover: frontside is a representative snapshot of TEMPO CNCs in aqueous solution, and backside is a snapshot from the cellulose regeneration process.

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Abstract

Cellulose is a remarkable organic biopolymer and sustainable raw material existing in nature. Over the past several decades, the study of cellulose materials has attracted significant attention in chemistry, physics, biomedicine, and engineering fields. The unique properties of cellulose such as high tensile strength, biocompatibility, and renewability, enabled its applications in numerous industries, including textiles, construction, biomedicine, pulp production, energy, and even electronics. However, in-depth research on the performance of cellulose-based materials and devices is still in high demand due to the complexity of cellulose and its derivatives.

This thesis uses a theoretical modelling method to explore the cellulose-based materials structure, morphology and properties, and predict cellulose-based devices performance. The method is efficacious in understanding natural phenomena and solving practical problems through mathematical modelling, computer engineering, and data analysis.

This thesis focuses on three computational studies: (I) cellulose nanomaterials, (II) cellulose composites, and (III) cellulose-based ion exchange membranes in aqueous organic redox flow batteries (AORFBs). The first part presents theoretical insights into cellulose nanocrystal (CNC), surface modifications, and regenerated cellulose. The second part includes numerical models of light propagation in cellulose composites such as transparent wood, and the third part involves modelling and simulation of AORFBs.

In part (I), we constructed Martini 3 coarse-grained (CG) molecular dynamics (MD) models describing different crystalline structure of CNCs (including Iβ/II/III). Subsequently, we investigated the dispersion and aggregation properties of COO\(^{-}\) modified CNC Iβ in NaCl aqueous solutions and found that the results are consistent with experimental observations. Also, based on topologies developed for cellulose Iβ/II, we studied the regeneration process of cellulose crystallites. The X-ray diffraction (XRD) was used to monitor structural changes and microcrystal formation during regeneration. The XRD results indicate that the regenerated cellulose crystallites are cellulose II, which are in line with the experimental measurements. In part (II), we explored light propagation in transparent wood (TW), i.e., cellulose/PMMA composite materials, using TW models developed by us. The models were built by identifying cellulose fiber structures in SEM images. We employed ray tracing, a
relatively simple but proven accurate and efficient technique, and rigorous electromagnetic methods to analyze the light propagation in TW and extract the refractive index of the TW. In part (III), we constructed a model of an AORFB based on the Tertiary-Current-Distribution/Nernst-Planck equations implemented in COMSOL. Then we simulated the charge-discharge and capacity loss curves of the AORFBs. The simulation results are consistent with the experimental measurements.

We believe that the results reported in the thesis provide better understanding of cellulose-based materials and devices, advance the computational methods for modelling and simulations of cellulose, and promote the sustainable development of technology and industry.
Populärvetenskaplig sammanfattning

Cellulosa är ett av de mest förekommande materialen på jorden och finns främst i trä, halm, bomull, lin med mera. Cellulosaprodukter som textilier och papper har använts i tusentals år. På senare år, med framstegen inom materialvetenskap och teknik, kan hållbara cellulosamaterial, inklusive naturlig cellulosa och regenererad cellulosa, användas inom förnybar energi, miljöskydd, biomedicin och många andra områden. Fortsatt fördjupad förståelse och forskning om cellulosa och dess kompositmaterial är dock fortfarande nödvändig.


Avhandlingen består av tre delar: (I) cellulosa-nanomaterial, (II) cellulosa-kompositmaterial och (III) cellulosa-jonbytesmembran i vattenhaltiga organiska redox flödesbatterier (AORFB). Den första delen behandlar teoretiska insikter i cellulosa-nanokristaller (CNC), ytmodifieringar och regenererad cellulosa. Den andra delen inkluderar numeriska modeller för ljusutbredning i cellulosa-kompositer, och den tredje delen presenterar modellering och simulerings av AORFB.

I den första delen konstruerade vi modeller av CNC för att analysera deras struktur, morfologi och egenskaper. Vi undersökte dispersionen och aggregeringen av COO$^-$ modifierade CNC i vattenlösningar av NaCl och fann att resultaten överensstämmer med experimentella observationer. Därefter undersökte vi cellulosa-regenerering och använt röntgendiffraktion (XRD) för att övervaka mikrostrukturaella förändringar under denna process. XRD-resultaten visar att de regenererade cellulosasakristalliterna har cellulosa II-struktur, vilket överensstämmer med experimentella mätningar. I den andra delen studerade vi ljusutbredning i genomsnittligt trä (TW). TW framställdes genom att ersätta lignin i trä med ett kemiskt material vars brytningsindex är nära cellulosans. Vi undersökte förhållandet mellan ljusspridning i TW och brytningsindexet för kemiska material med hjälp av spårning av ljusstrålar och rigorösa elektromagnetiska metoder. I den tredje delen konstruerade vi en modell för AORFB baserat på elektrochemiska ekvationer. Vi studerade laddnings- och
urladdningskurvor samt kapacitetsförlusten för AORFB. Simuleringsresultaten överensstämmer med experimentella mätningar.

Denna avhandling främjar förståelsen för cellulosa-baserade material och komponenter och främjar hållbar utveckling av teknik och industri.
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Norrköping, 2023

Jiu Pang
List of Included Publications

**Paper I:** Martini 3 model of surface modified cellulose nanocrystals: investigation of aqueous colloidal stability  
Jiu Pang, Aleksandar Y. Mehandzhiyski, Igor Zozoulenko  
Cellulose, 2022, 29, 9493.  
Contribution: Carrying out coarse-grained simulations, analyzing simulation results, creating visualizations, and writing the manuscript draft.

**Paper II:** A computational study of cellulose regeneration: Coarse-grained molecular dynamics simulations  
Jiu Pang, Aleksandar Y. Mehandzhiyski, Igor Zozoulenko  
Carbohydrate Polymers, 2023, 313, 120853  
Contribution: Carrying out coarse-grained simulations, analyzing simulation results, creating visualizations, and writing the manuscript draft.

**Paper III:** Light Propagation in Transparent Wood: Efficient Ray Tracing Simulation and Retrieving an Effective Refractive Index of Wood Scaffold  
Jiu Pang, Adil Baitenov, Céline Montanari, Archana Samanta, Lars Berglund, Sergei Popov, and Igor Zozoulenko  
Advanced Photonics Research, 2021, 2, 2100135.  
Contribution: Carrying out optics simulations, analyzing simulation results, creating visualizations, and writing computational part of the manuscript draft.

**Paper IV:** Controlling the rate of posolyte degradation in all-quinone aqueous organic redox flow batteries by sulfonated nanocellulose based membranes: the role of crossover and Michael addition  
Sanna Lander*, Jiu Pang*, Johan Erlandsson*, Leena Korhonen, Mikhail Vagin, Tobias Abrahamsson, Penghui Ding, Viktor Gueskine, Aleksandar Mehandzhiyski, Igor Zozoulenko1, Lars Wågberg, Xavier Crispin, Magnus Berggren (*Authors contributed equally)  
In manuscript.  
Contribution: Carrying out redox flow battery simulations, analyzing simulation results, creating visualizations, and writing computational part of the manuscript draft.
List of Abbreviations

CNC  Cellulose Nanocrystal
RFB  Redox flow battery
AORFB  Aqueous organic redox flow battery
CG  Coarse-grained
AA  All-atom
MD  Molecular dynamics
XRD  X-ray diffraction
TW  Transparent wood
FEM  Finite element method
AI  Artificial intelligence
COO−  Carboxylate group
TEMPO  2,2,6,6-tetramethylpiperidinyloxy
vdW  van der Waals
PBC  Periodic boundary condition
LJ  Lennard-Jones
PDEs  Partial differential equations
1d  One-dimension
2d  Two-dimension
3d  Three-dimension
SDGs  Sustainable Development Goals
SO3−  Sulfonate group
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Part II Scholarly Articles
Part I Background
1. Introduction

This thesis aims to develop theoretical models of cellulose-based materials based on advancing computational methods and to apply the models to analyze specific questions. The significance of this research lies in its potential to advance the understanding of cellulose-based materials and their potential applications, which can promote the development of various sustainable and efficient cellulose-based products. This chapter provides a background on the cellulose-based materials, computational methods, and the motivations behind the thesis.

1.1 Motivation and research background

The topic of sustainable development has been discussed for decades. Based on the requirements for materials research outlined in the 2030 Agenda for Sustainable Development, the development of sustainable and eco-friendly materials, efficient use of resources, low-carbon materials, and increased focus on recycling and circularity are an important way forward in academia and industry. One typical kind of sustainable and eco-friendly material is the cellulose-based material. Cellulose is a naturally-occurring, abundant, renewable, and biodegradable organic biopolymer which has gained significant attention in recent years due to its unique properties and potential applications in a wide range of fields, including energy storage, biomedical engineering, environmental remediation, etc\(^1\)–\(^4\).

In recent years, computational studies have become an important component of experimental and theoretical works in different fields, providing a powerful tool for examining and predicting the behavior of material and device systems\(^5\)–\(^6\). It enables the exploration of materials’ properties and phenomena at various scales, from the atomistic to the macro scales. The critical advantage of computational studies is that it offers insights that may be impossible or challenging to observe in experiments. As a result, scientists can have a deeper understanding of the target systems. This can be helpful for the developments of advanced materials and devices in experiments by dissecting and comprehending the systems and optimizing the variables and parameters.

Depending on the system scales, various computational methods can be applied to study the materials’ properties and device’s performances, such as molecular dynamics (MD), finite element method (FEM), density functional theory (DFT), etc\(^7\)–\(^9\). Computational studies have become an integral part of scientific research
and are likely to play an increasingly important role. With the advancement of algorithms, artificial intelligence (AI), and computational power, we can expect to see many exciting discoveries and applications of computational studies in the coming years.

1.2 Aim and structure of the thesis

This thesis aims to develop computational models of cellulose-based materials and devices by MD and FEM, predicting the corresponding materials’ properties and device’s performance.

The research focuses on two main aspects of cellulose-based materials: The fundamental material properties and the application performances. A basic knowledge of the involved cellulose-based materials and devices are presented in Chapter 2.

The main goal of this thesis was to develop novel computational models for cellulose-based materials and devices that keep pace with the advancing computational methods and techniques. The modelling steps and computational methods used and developed in this thesis are presented in detail to ensure the reproducibility, transparency, and comprehensibility. Chapter 3 presents the algorithms and computational details of MD and force fields, as well as the essential analysis tools. Chapter 4 presents the details of FEM modelling and computational process, along with the governing equations and boundary conditions involved. Subsequently, the summary of the papers is described in Chapter 5. Finally, the potential applications and future prospects of the computational models and studies are presented in Chapter 6.

Then, in Part II, the scholarly articles presenting the results of our projects are listed. In Paper I, we constructed the cellulose nanocrystal (CNC) \( \text{I}_\beta \) and COO\(^-\) (TEMPO) surface modified CNC \( \text{I}_\beta \) models and studied the dispersion properties of TEMPO CNCs in NaCl aqueous solutions. As a follow-up study, in Paper II, the cellulose morphologies (CNC \( \text{I}_\beta, \text{II}, \text{and III} \)) were studied, and the cellulose regeneration process were observed from dissolved cellulose chains in aqueous solutions. Paper III presented the computational study of light propagation in transparent wood (TW). The refractive index of TW was fitted by comparing the normalized light intensity in simulations and experimental measurements. Finally, Paper IV presented the modelling of aqueous organic redox flow batteries (AORFBs). The capacity curves of AORFBs were simulated and compared with experimental results to explore the kinetics of the Michael addition reaction (MAR) in all-quinone AORFBs.
2. Cellulose materials and applications

This chapter provides an overview of the fundamental concepts of cellulose-based materials and devices. The materials discussed in this thesis include pristine cellulose, chemically modified cellulose, regenerated cellulose, and cellulose composite materials. The applications of cellulose materials in this thesis include transparent wood (TW) and an ion-exchange membrane of aqueous organic redox flow batteries (AORFBs).

2.1 Natural cellulose

Cellulose, a complex carbohydrate, or polysaccharide, composed of D-glucose units linked by β-(1,4) glycoside bonds \((\text{C}_6\text{H}_{10}\text{O}_5)_n\), as shown in Figure 2.1a\(^1\). Cellulose chains have a flat and linear conformation. Cellulose fibrils, which can reach lengths of several micrometers and have diameters of several to tens of nanometers, are comprised by crystalline domains (where cellulose chains are arranged in a highly ordered manner) and amorphous (disordered manner) domains\(^1\), as shown in Figure 2.1b. Cellulose nanocrystals (CNCs) (also known as nanowhiskers, nanorods, or rod-like cellulose crystals), are extracted from these crystalline domains, and represent a novel class of high aspect ratio renewable nanomaterials (diameter is 3~5 nm and length is 50~500 nm)\(^1,3\). The CNC has many advantages, such as high production rate, high strength and stiffness, and biodegradability, etc\(^1\). These properties enable CNC to be applied in fields of renewable energy, environmental protection, biomedicine, just to mention a few\(^10\).
Naturally available cellulose, i.e., cellulose I, primarily originates from plants like trees, cotton, flax, and algae\textsuperscript{11}. Cellulose I has two polymorphs: the triclinic crystal structure (I\textsubscript{α}) and the monoclinic crystal structure (I\textsubscript{β}). Cellulose I\textsubscript{α} is mainly found in algae and bacteria, and cellulose I\textsubscript{β} primarily exists in plant cell wall and tunicates\textsuperscript{12}. Previous studies have demonstrated that cellulose I\textsubscript{α} is metastable and can be converted into cellulose I\textsubscript{β} through various chemical treatments\textsuperscript{12}. Though the number of cellulose chains in the CNC is still in debate\textsuperscript{13}, the model of CNC with 36 chains (square) is widely accepted for higher plants\textsuperscript{14–16}, see Figure 2.2. In CNC I, the packaging pattern of cellulose chains are parallel (1-4 link glycoside bonds points to same direction), as illustrated in the Figure 2.1a. By specific chemical treatments, cellulose I can be irreversibly transformed into cellulose II and III\textsubscript{I/II} \textsuperscript{1,14,17–19}. In the process of dissolving and regenerating cellulose I to cellulose II, the cellulose chains intermingle and rearrange to form an antiparallel chain stacking pattern (see Figure 2.2b). Cellulose II is considered the most stable among all other cellulose crystal structures thus far\textsuperscript{20}.

Figure 2.1  a) The schematics of repeated units in cellulose chain, the 1-4 link glycoside bond is shown by arrow; b) the crystalline and disordered regions in a cellulose microfibril; c) the diagram of CNCs extracted from the cellulose microfibril. The figures are reproduced from Reference\textsuperscript{1} with permission from The Royal Society of Chemistry.
2.2 Surface modified CNCs

The unique structures of CNCs make it hard to blend them with a majority of nonpolar and hydrophobic polymer matrices\textsuperscript{21}. In order to address this issue, researchers have investigated a range of techniques to modify the surface structures of CNC, aiming to alter/control its surface properties. These chemical modifications extend the CNC applications to areas such as advanced engineering and biomedicine\textsuperscript{22,23}.

The key reaction sites for modifying the CNC are the surface hydroxyl (−OH) groups. The primary objectives of surface modification of CNC include: (1) introducing hydrophobic or hydrophilic groups on the surface to improve its compatibility; (2) incorporating negative or positive functional groups on the surface to enhance its dispersion properties in aqueous solutions\textsuperscript{25}. The TEMPO-oxidized CNCs, which converts the surface primary −OH groups of CNCs into carboxyl (−COO\textsuperscript{−}) groups, see Figure 2.3, was first reported by Araki et al\textsuperscript{26}. The
negative charges of $-\text{COO}^-$ groups oppose attraction between CNCs caused by van der Waals forces, preventing the aggregation of CNCs and allowing them to disperse evenly in water. Hayaka et al. observed that the TEMPO-oxidized cellulose nanofibrils dispersion maintained its dispersed state up to 50 mM NaCl and formed aggregated gel particles at 100 mM NaCl aqueous solutions\textsuperscript{27}. Subsequently, Antti et al. investigated the behavior of two TEMPO-oxidized CNCs in NaCl aqueous solutions by all-atom (AA) MD simulations\textsuperscript{22}. However, the effects of salt concentrations in their MD models were not studied and the morphology of aggregated CNCs can not be simulated due to the size limitations of AA MD models.

2.3 Regenerated cellulose

Cellulose is an essential raw material resource for future industrial production, which can contribute to the circular economy and sustainable development of society. In recent years, regenerated cellulose materials have been extensively used in the key commercial sectors, such as polymers, membranes, textiles, and coatings industries\textsuperscript{23,25,28}. The research on cellulose dissolution and regeneration strategies has been conducted through experimental methods and molecular simulations\textsuperscript{29}. Various regenerated cellulose materials retain excellent biodegradability and mechanical properties\textsuperscript{30}. On a molecular level, the strength and stability of cellulose structures are primarily explained by the hydrogen bonding between cellulose chains\textsuperscript{31}. It is worth noting that the stacking interactions, including van der Waals (vdW) interactions and hydrophobic forces\textsuperscript{32,33}, make a comparable contribution to the cellulose stability\textsuperscript{34}.

**Figure 2.4** a) Hydrophilic areas between the equatorial direction of the glucopyranose ring; b) hydrophobic areas of the axial direction of the glucopyranose ring.
The cellulose chains possess hydrophilic and hydrophobic characteristics in the equatorial and axial directions respectively\textsuperscript{35}, see Figure 2.4. This amphiphilic characteristic of cellulose chains affects the regeneration pattern of cellulose in aqueous solutions\textsuperscript{35-37}. Isobe et al.\textsuperscript{38} monitored the regeneration process of cellulose by synchrotron-radiation X-ray in experiments. They found that the cellulose sheets were first formed due to the hydrophobic interactions, and then the sheets line up to form cellulose crystallites by hydrogen bonding. Heasman et al. has proved these hypotheses of cellulose regeneration process by AA MD simulations\textsuperscript{39}. However, the number of cellulose chains in AA models is severely limited by the computational resources. To accurately describe the structures and morphologies of regenerated cellulose crystallites, larger MD models for cellulose regeneration are still needed.

2.4 Transparent wood

Transparent wood (TW), a unique cellulose composite material, preserves its mechanical properties while introduces a new feature—high optical transparency. Functionalized TW can be used in smart buildings, decoration, design, and photovoltaics. TW is produced in two main steps. First, lignin is removed from the wood materials; second, a polymer material (such as PMMA, thiolene, or similar materials) that has a refractive index closes to the one of cellulose is infiltrated into the delignified wood substrates, see Figure 2.5.

![Figure 2.5](image)

*Figure 2.5* a) Schematic of the fiber structures of wood. The TW was prepared by removing lignin and filling specific polymer materials. b) a common wood sample transforms to a highly transparency TW sample. The figures are reproduced from Reference\textsuperscript{40} with permission from John Wiley and Sons.
The match of refractive index between the polymer filler and the cellulose scaffold is a key point that guarantees the transparency of TW, because the mismatch of the refractive index will lead to non-negligible light scattering in TW\textsuperscript{41,42}. Thus, to produce TW products with high transparency, it is crucial to correctly estimate the refractive index of the cellulose substrate and choose a suitable polymer filler. Though there are various methods to measure the refractive index of cellulose substrates in experiments, the refractive index depends on the specific type of raw wood and the measured refractive index may not align with actual TW material\textsuperscript{43–46}. Therefore, it is crucial to develop optical models for TW samples to predict the refractive index of cellulose scaffolds to facilitating the development of TW products.

2.5 Redox flow battery application

Redox Flow battery (RFB) is one of the most promising large-scale energy storage technology available today, particularly in the context of integrating renewable energy sources into the power grid\textsuperscript{47,48}. The renewable energy such as solar and wind powers has intermittency, which leads to fluctuations in power supply. Thus, the energy storage devices such as rechargeable batteries or supercapacitors are needed to store the excess energy during peak production times and compensate in periods that natural power generation is insufficient.

A typical RFB consists of several cells connected in series or parallel. Usually, each cell includes an anode, a cathode, and an ion exchange membrane separator, as shown in Figure 2.6. The ion exchange membrane prevents the cross-mixing of positive and negative electrolytes while allowing the transport of proton ions. An ideal ion exchange membrane usually needs high selectivity, excellent proton conductivity, and high chemical stability, especially in strong acidic environments\textsuperscript{49}. Among the numerous RFB systems, the Vanadium Redox Flow Battery (VRFB) is one of the most successful RFB technologies along with many commercial achievements\textsuperscript{50–52}. However, the low solubility of vanadium ions, which results in the low energy density of VRFBs, and the high cost of vanadium restrict its application in many fields, such as electric vehicles and portable electronics.
Organic materials, due to the diverse molecular structures, high tunability, and low material cost, stand out and are considered as one of the novel electrolytes and membranes in RFBs. Sanna et al. found that the sulfonated nanocellulose membranes possesses low porosity and excellent ionic transport properties, and the aqueous organic redox flow batteries (AORFBs) with sulfonated cellulose membrane show superior battery performance. The AORFBs still have significant capacity losses, and the research of AORFBs with cellulose-based membranes are under developments in recent years.

Figure 2.6 The schematics of a redox flow battery (RFB).
3. Molecular dynamics

Molecular dynamics (MD) is a useful computational method for studying the molecular/materials properties. It can provide valuable insights into the structures and properties of materials and monitor molecular interactions at the atomistic level. This chapter briefly overviews the fundamental principles and critical techniques used in MD simulations. The modelling, computation, and results analysis for cellulose-based materials are presented.

3.1 A brief summary of MD

Molecular Dynamics (MD) is a pivotal computational methodology enabling simulations of molecules and material behavior at nanoscale under various conditions, such as in solutions, at interfaces, or at specific temperatures and pressures. This method has many practical applications in various fields, including physical chemistry, material science, molecular biology, etc.

Importantly, MD simulations can track the spatial dynamics of atoms to record the precise trajectories of molecules. This enables researchers to gain valuable insights into the structures and properties of the materials and therefore makes it possible to predict molecular behaviors that are difficult to observe in experiments.

The basic principle of building an MD model is using particles to construct molecular structures. The atoms were represented by these particles and linked via chemical bonds. The interactions between the particles are described by potential energy functions, also known as force fields, which quantify the energy associated with the arrangement and interactions of the particles.

By using classical mechanics, particularly Newton’s equations of motion, the acceleration of each particle can be calculated based on the forces acting on them:

$$ F_i = m_i a_i = m_i \frac{dv_i}{dt} = m_i \frac{d^2r_i(t)}{dt^2} \quad (3.1) $$

Here, $i$ is the index number of the particles in the MD model, and $m$ is particles’ mass. The $a$, $v$, and $r$ represent the acceleration, velocity, and position of the particle, respectively. The force acting on each particle at a given time ($t$) depends on the particle’s relative position among other particles (disregarding external...
forces). The forces determine the acceleration and velocity of particles and then in the next time step the changes of the particles’ positions leading to the changes of forces. Thus, the forces, accelerations, and velocities need to be recalculated at every instant. The changes of the acceleration and velocity of particles over time steps are computed using numerical integration methods.

Leap-Frog integration is a typical numerical integration method because it is fast, accurate, and stable. For a known state, the positions are updated every $\Delta t$ step:

$$r(t + \Delta t) = r(t) + v\left(t + \frac{\Delta t}{2}\right)\Delta t$$  \hspace{1cm} (3.2)

where $r(t)$ represents the position vector of a particle at time $t$; $\Delta t$ is the timestep; The velocity is updated every $\Delta t/2$ and “leapfrog” ahead the positions:

$$v\left(t + \frac{\Delta t}{2}\right)\Delta t = v\left(t - \frac{\Delta t}{2}\right)\Delta t + a(t)\Delta t$$  \hspace{1cm} (3.3)

The current velocities are computed by averaging the velocities before and after the current time, which is given by:

$$v(t) = \frac{v\left(t + \frac{\Delta t}{2}\right) + v\left(t - \frac{\Delta t}{2}\right)}{2}$$  \hspace{1cm} (3.4)

Then, the $F$ and $a$ of each particle can be recalculated step by step at its updated position. By repeating this process, the coordinates of particles are generated as a function of time, allowing to trace particles’ trajectories. The MD simulations end when the predetermined time is reached, and then the resulting output files can be employed to analyze various aspects of the material, including its structural characteristics, dynamic properties, intermolecular interactions, etc.

### 3.2 Ensembles

A simulation box is needed to place the molecular and solvent particles in MD models. The most common type of simulation box is a cuboid that uses periodic boundary conditions (PBC). In PBC, the box is considered a unit cell in an 12
infinitely repeating grid - imagine the box replicated endlessly in all directions, as shown in Figure 3.1. When a molecule leaves the box through one side, an identical molecule enters from the opposite side. This mimics an infinitely large system, making the simulation more realistic and reducing edge effects.

Figure 3.1 The schematic diagram of the periodic boundary conditions of two-dimensional simulation box. The green box represents the pristine unit cell.

Thermodynamics ensembles represent the possible states of a system under certain thermodynamic constraints\textsuperscript{62,63}. As shown in Figure 3.2, there are three typical physical ensembles used in MD simulations and each maintains different constant conditions. The NVT ensemble has fixed number of particles (N), volume (V), and temperature (T). The T is stabilized by periodically adjusting the velocities of the particles. The NPT ensemble has fixed N, pressure (P) and T. The P is controlled by adjusting the dimensions (length, width, and height) of the simulation box. The NVE ensemble is used for simulating isolated systems under fixed constant energy (E), N, and V.
Figure 3.2 Visual representation of the typical physical ensembles for MD simulations: NVE, NVT, and NPT. NVE stands for Number-Volume-Energy, NVT for Number-Volume-Temperature, and NPT for Number-Pressure-Temperature. Each ensemble shows the constant conditions: N, number of particles; V, volume; E, energy; T, temperature; P, pressure.

3.3 Force fields

3.3.1 Potentials

For the force fields (potential energy functions) of MD simulations, the forces \( F \) acting on atoms/particles can be computed from:

\[
F = -\nabla V_{total} \tag{3.5}
\]

where \( V_{total} \) represents the total potential energy of the interactions. The \( V_{total} \) contains potential energy of non-bonded and bonded interactions:

\[
V_{total} = V_{non-bonded} + V_{bonded} \tag{3.6}
\]

The non-bonded interactions are described by the Lennard-Jones (LJ) and Coulombic equations:

\[
V_{non-bonded} = V_{LJ}(r_1 \cdots r_n) + V_{Coul}(r_1 \cdots r_n) \tag{3.7}
\]
The LJ potential $V_{LJ}(r_1 \cdots r_n)$ mainly describes the van der Waals forces (attraction) and Pauli exclusion forces (repulsion) between electrically neutral atoms and is given by:

$$V_{LJ}(r_1 \cdots r_n) = \frac{1}{2} \sum_i \sum_{j \neq i} 4\varepsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right]$$ (3.8)

The $\sum_i \sum_{j \neq i}$ represents the summation over all unique pairs of atoms $i$ and $j$ in the system. The $r_{ij}$ represents the distance between particles $i$ and $j$. The $\sigma_{ij}$ donates the distance between atoms $i$ and $j$ at which the interatomic potential energy is zero. The term $\left( \sigma_{ij}/r_{ij} \right)^{12}$ describes the repulsive forces due to Pauli exclusion, while the $\left( \sigma_{ij}/r_{ij} \right)^{6}$ describes the attractive van der Waals forces.

The diagram for the LJ potential curve is plotted in Figure 3.3. The LJ potential curve shows how the potential energy changes as the distance between the beads varies from infinity to the point of minimum distance. When $r_{ij}$ is larger than $\sigma$, the potential energy is negative, corresponding to attractive forces between the two particles. When $r_{ij}$ is smaller than $\sigma$, the potential energy is positive, corresponding to repulsive forces between the two particles.

![Lennard-Jones Potential](image)

**Figure 3.3** LJ potential curve illustrates the variation of potential energy between two particles as a function of the inter-particle distance.

For atoms that are not electrically neutral, the Coulomb potential $V_{Coul}(r_1 \cdots r_n)$, is used to account for their electrostatic interactions and is given by:
where \( q_i \) and \( q_j \) represent the electric charges of atoms \( i \) and \( j \) in the MD models, and \( \epsilon_0 \) represents the permittivity of free space.

The bonded interactions include the bond stretching (2-body), bond angle (3-body), and dihedral angle (4-body) interactions. A special type of dihedral angle to maintain the planar of the structures or to prevent the configuration transitions is called improper dihedral angles. The bonded interactions are computed by:

\[
V_{bonded} = V_{bonds} + V_{angles} + V_{improper} + V_{dihedral} \tag{3.10}
\]

where \( V_{bonds} \), \( V_{angles} \), \( V_{improper} \), and \( V_{dihedral} \) represents the bond, angle, improper dihedral angle, and dihedral angle contributions to the bonded interactions. The harmonic potential of the bond stretching interaction between covalently bonded atoms is calculated by:

\[
V_{bonds} = \sum_{bonds} \frac{1}{2} K_b (r_{ij} - r_0)^2 \tag{3.11}
\]

where the \( \sum_{bonds} \) represents the summation over all bonds in the system; \( i \) and \( j \) represents the number of atoms in the bonds, respectively; \( K_b \) donates the force constants of the bonds; \( r_0 \) represents the equilibrium value of the bonds. The harmonic potential of angle between atoms \( i \), \( j \) and \( k \) can be computed by:

\[
V_{angles} = \sum_{angles} \frac{1}{2} K_\theta (\theta_{i,j,k} - \theta_0)^2 \tag{3.12}
\]

where the \( \sum_{angles} \) represents the summation over all angles in the system; \( \theta_{i,j,k} \) and \( \theta_0 \) are the actual and equilibrium angles of atoms \( i \), \( j \) and \( k \); \( K_\theta \) represents the force constants of the angles. The harmonic potential of the improper dihedral angles can be calculated by:

\[
V_{improper} = \sum_{improper} \frac{1}{2} K_{\theta_{ij}} (\theta_{ij} - \theta_{0ij})^2 \tag{3.13}
\]
\[ V_{\text{impropers}} = \sum_{\text{impropers}} \frac{1}{2} K_d (d_{i,j,k,l} - d_0)^2 \]  

where the \( \sum_{\text{impropers}} \) represents the summation over all improper dihedral angles in the system; \( d_{i,j,k,l} \) and \( d_0 \) represent the actual and equilibrium improper dihedral angles of atoms \( i, j, k \) and \( l \); \( K_d \) is the force constant of the improper dihedral angles; The potential of dihedral angles can be calculated by:

\[ V_{\text{dihedrals}} = \sum_{\text{dihedrals}} K_d (1 + \cos(n d_{i,j,k,l} - d_0)) \]  

### 3.3.2 Atomistic force fields

Force fields are essentially sets of equations and parameters that are taken from experiments in physics and chemistry or from calculations in quantum mechanics, which are used to calculate the potential energy of a system. The choice of force field plays a pivotal role in MD simulations since different force fields usually have specific applicability and mismatched force field may lead to discrepant simulation results, influencing the accuracy and reliability of MD simulations. The commonly used force fields in MD simulations include AMBER, OPLS, CHARMM, GROMOS, etc.\(^6\)\(^7\)\(^6\)\(^7\)\(^0\). The AMBER force field is designed explicitly for simulating carbohydrates and glycoproteins and offers an improved description of conformational changes of sugar rings, which is widely used for the simulations of biomolecules and possess superior precision and computational efficiency\(^6\)\(^9\). In Paper II, the GLYCAM06 force field\(^7\)\(^1\), a branch of the AMBER, was chosen to optimize the atomistic structures of regenerated cellulose crystallites. The GLYCAM06 force field is designed explicitly for simulating carbohydrates and glycoproteins and offers an improved description of conformational changes of sugar rings. Besides, the OPLS force field aims at optimizing parameters for liquid systems, which is broadly utilized in simulating solvated biomolecules and small organic molecules\(^7\)\(^0\). In Paper I, the OPLS force field was used for calculating the potential of the mean force (PMF) between two TEMPO CNCs in aqueous solutions. One must recognize that MD simulations may not always perfectly align with experimental outcomes. For instance, a study
by James et al. observed a difference in the results of simulations of cellulose I\textbeta microfibrils with different force fields\textsuperscript{72}. The results from CHARMM and GLYCAM06 were closer to experimental observations than from GROMOS at high temperatures. This underscores the importance of selecting a suitable force field based on the system and the objectives of the study.

3.3.3 Coarse-grained method

Despite the implementation of advanced parallel algorithms and the use of faster supercomputers, the simulation of real-world physical processes remains a substantial challenge. This is because solving Newton's equations of motion for real physical systems requires massive calculations. Though classical atomistic MD simulations can provide good insights into the complex interactions at the atomic level, for larger systems (like colloidal solutions of CNCs), all-atom (AA) MD can only handle limited system sizes. For instance, a CNC of 50 nanometers in length that is composed of 36 cellulose chains roughly contains 3600 glucose molecules (C\textsubscript{6}H\textsubscript{10}O\textsubscript{5}), amounting to approximately 75600 atoms. When surrounded by solvent molecules, a cubic water box of 50 nanometers would contain about four million water (H\textsubscript{2}O) molecules. Simulations at this scale would consume significant computational resources, including processors, memory, and storage, posing an enormous challenge even for large-scale clusters with multiple nodes.

Researchers have developed coarse-grained (CG) methods which can simulate larger MD systems compared to AA MD simulations. CG MD methods are computational techniques that are extensively applied to study biomolecular systems. They simplify the complexity of large biomolecules by mapping atoms or groups to larger particles (also called beads), that is, combining several to dozens of atoms into a single bead or particle. An ideal CG model aims at not only better understanding the interest properties of the system, but also eliminating non-essential details to enhance computational efficiency. By ignoring what is deemed as "unnecessary" atomic details, CG models enable the investigations of the dynamical and structural characteristics of target system on larger scales than AA models.

Another important consideration in speeding up MD simulations is the choice of integration time steps (\Delta t). Both in AA and CG MD simulations, employing larger integration \Delta t for sampling the simulation trajectory can accelerate simulation speed. However, it should be noted that too large \Delta t could destabilize the system. Generally, \Delta t should be about 5~10 times smaller than the fastest
oscillation in the system. For example, in AA simulations of biomolecular materials, O-H bonds typically have the fastest oscillations, with a period of approximately 10 femtoseconds (fs)\textsuperscript{73,74}. Therefore, to ensure the stability of the integration of the motion equations in AA biomolecular simulations, $\Delta t$ is generally set between 1 fs to 2 fs. In CG simulations, because the ‘beads’ represent groups of atoms and have a larger mass, the vibrations are slower. This inherently leads to a reduction in the frequency of the fastest oscillations in CG models, allowing for the use of larger $\Delta t$. In CG simulations, $\Delta t$ can be increased to 10 fs, 20 fs, or even larger. It is worth noting that when designing CG models and preparing force field files, one should ensure the stability of molecular structures, which is the basis for stably running MD simulations at large $\Delta t$.

3.3.4 Martini 3 CG force field

The Martini force field is a popular CG force field initially designed to simulate lipids and other biomolecular systems\textsuperscript{75}. With the continuous development of the Martini force field, its application has been extended to many fields, such as biology, physics, biomedicine, nanotechnology, and material design\textsuperscript{76–79}. The CG models developed based on Martini force field can reproduce the structural and thermodynamic characteristics of the AA model. It balances accuracy and computational efficiency, making it an attractive choice for long-time simulations of large-scale systems.

Martini 3 is the newest version of the Martini force field that has been recently released\textsuperscript{80}. The updated force field can predict molecular aggregations and general interactions with better accuracy than that of Martini 2. Martini 3 reparametrizes the CG beads, enriches the types of CG beads, and improves and optimizes all non-bonded interaction terms.

Martini 3 contains seven bead types: apolar (C), intermediate/non-polar (N), polar (P), monovalent ions (Q), divalent ions (D), water (W), and halo-compounds (X). Each bead can be assigned to regular (R), small (S), or tiny (T) sizes. The C, N, P, Q, and X beads have subtypes which are numbered by the relative degree of polarity from 1 (lower polarity) to a maximum of 6 (higher polarity), see Figure 3.4. It should be noted that Martini 3 has defined several labels for the beads under various situations, including hydrogen bonding, electron polarizability, positive/negative, cross-interactions, self-interaction, and partial charge. Martini 3 force field provides rich interaction levels for these bead types to have a more accurate representation of the atomistic structures and
molecular interactions. In Martini 3 simulations by GROMACS software, the non-bonded and bonded interactions are discussed in Chapter 3.3.1.

In the modelling of molecules, the initial bead types can be determined by the default bead assignments for molecules/fragments in Martin 3. Then, the bead types can be refined based on the comparison of the solute-solvent interactions, solvation free energies, and oil/water transfer free energies, to AA simulation results or experimental results. Besides, the molecular structures in the model can be mended by the properties of the models, such as lattice parameters, mechanical properties, etc.

![Image of bead types](image)

**Figure 3.4** Summary of the different bead types in Martini 3 force field: a) organic beads (except the X-beads); b) X-beads designed for halo-compounds; c) ion beads; The figures are reproduced from Reference 80 with permission from Springer Nature.

### 3.4 Preparing Martini 3 CG CNC models
#### 3.4.1 Pristine CNC

The process of constructing a CG cellulose model is shown in **Figure 3.5**. The **Step 1** is to determine and understand the atomic structure of cellulose. AA models of cellulose molecules have been widely studied in previous works 81–83. Customized cellulose nanocrystal (CNC) models can be constructed and downloaded from the Cellulose Builder tool 83. The .gro file of AA CNC model 20
contains essential information such as atom names, coordinates, and charge magnitudes.

The CG models are generally constructed by mapping from AA models. In **Step 2**, following the general procedure of Martini CG modelling, we constructed small molecules (cellobiose) and reproduced thermodynamic parameters (octanol/water partition coefficients) to help in determining and fine-tuning the bead types. Cellobiose is formed by combining two glucose units to a molecule, as shown in Figure 3.6a, and cellulose chains is formed by combining hundreds or thousands of cellobiose units to a longer molecule/chain.

Then, in **Step 3**, the CG model of cellulose chain is constructed. The bead types of CG cellulose chain are inherited from CG cellobiose molecule. **Figure 3.6c** presents a short cellulose chain that contains 6 cellobiose units (disregarding the ends). The SN3a beads (orange beads) are used to represent the chain backbone of cellulose chain and the TP1 beads (grey beads) are used to represent the hydroxyl groups.

Subsequently, in **Step 4**, we need to design the bonded (bond, angle, and dihedral angles) parameters of the Martini 3 CG cellulose chain and optimize these parameters by comparing them with the bonded parameters obtained from the AA simulations of CNC. When constructing Martini CG cellulose model, it is necessary to carefully determine which molecular bonds in the atomic structure need to be retained and which can be omitted.
Finally, in **Step 5**, we fit the structure and properties (e.g., lattice parameters, Young’s modulus, etc) of CG CNC with AA/experimental results to do further optimizations.

![Diagram of celllobiose molecule and mapping relations](image)

**Figure 3.6** a) Illustration showing the mapping relations between atomistic representations and CG beads in a celllobiose molecule; b) the representations of atoms and Martini 3 CG beads; c) mapping relations between atomistic representations and CG beads in a short cellulose chain that contains 6 celllobiose units.

Overall, optimizing the parameters of the Martini 3 CG model is a critical step for developing accurate and reliable CG cellulose models. This involves two key aspects: optimizing the parameters related to covalent bonds (bond, angle, and dihedral angle parameters), namely bonded parameters, and those parameters related to interactions between particles that are not covalently bonded, namely non-bonded parameters. The non-bonded parameters describe the non-bonded interactions, such as van der Waals forces, Pauli exclusion forces, electrostatic forces, etc., as discussed in detail in **Chapter 3.3.1**.

### 3.4.2 TEMPO CNC

The TEMPO (2,2,6,6-tetramethylpiperidinyloxy) CNC material\(^{22,27}\), obtained by modifying the surface of CNC with carboxyl groups (COO\(^{-}\)), represents one of the typical functional cellulose-based materials. The modelling of TEMPO CNC has two steps. First, we focused on the pristine cellulose in NaCl aqueous solution fitting the interaction between Na\(^{+}\) beads and neutral beads (pristine cellulose and water beads) to reproduce the AA results. As all beads in pristine CNC model were electrically neutral (uncharged), the non-bonded interactions among the CNC and salt beads were only calculated via the Lennard-Jones (LJ) potential.
Second, we focused on the TEMPO CNCs fitting the interaction between Na\(^+\) beads and charge group beads (COO\(^-\) surface groups). When charged beads (COO\(^-\)) were included in the system, the computation of non-bonded interactions among TEMPO CNC and Na\(^+\) beads involved both the LJ and Coulomb potential\(^{80}\). The fitting, validating, and optimizing processes of CNC models with COO\(^-\) groups and Na\(^+\) beads were presented in detail in Paper 1. It should be noted that the Na\(^+\) ions are in dynamical association/dissociation equilibrium on the surface of TEMPO CNCs in the aqueous, and they can be exchanged between the TEMPO CNCs and water. This is an important characteristic because the freely moving Na\(^+\) ions in solution results in the double layer repulsive force between charged colloidal particles (CNCs with COO\(^-\) groups). To correctly describe this phenomenon, we reproduced this association/dissociation equilibrium by fitting Martini 3 parameters to reproduce the atomistic density profiles. However, only modifying the LJ parameters proved to be insufficient to reproduce the atomistic results. Note that various attempts were done to reproduce the interactions between Na\(^+\) and TEMPO CNCs to fit with AA results, including changing types of charged beads, sigma and epsilon parameters in Martin 3, simulation settings, etc. We found that only by increasing the screening constant \(\epsilon_r\) to 50, which is usually set as 15 or 20 in the Martini models for lipid systems, the density curves of Na\(^+\) reproduces the AA results well and can achieve the association/dissociation equilibrium of Na\(^+\) ions. Moreover, the potential of mean forces (PMF) between two CNCs can be described correctly using the larger \(\epsilon_r\). Thus, \(\epsilon_r = 50\) was used for the CG simulations in this thesis when charged beads (COO\(^-\)) presented in the system.

### 3.5 MD computation process

The main steps to run an MD simulation are illustrated in Figure 3.7. The process of running a MD simulation starts with Step 1: Prepare the model, which contains the coordinates of the particles. In this thesis, the GROMACS package is used for MD simulations\(^{84,85}\), and the input model file is in the .gro format. The particles coordinate file can be either downloaded from databases or constructed using molecular modelling tools/scripts (details on model construction are provided in Chapter 3.4).
The main steps in running an MD simulation.

In **Step 2**, one needs to choose an appropriate force field that matches the MD model and generates corresponding topology (.itp) files.

In **Step 3**, one needs to prepare the MD parameter (.mdp) files, a critical input file that includes all parameters and settings, such as time steps, ensembles, cutoff values, etc. The configuration of specific parameters and settings is based on study purpose, and the simulations’ unique requirements and characteristics.

In **Step 4**, after the above essential input files are prepared, the MD simulation is ready to run. It should be noted that certain internal stresses or geometrical inconsistencies in the model, referred to as strains, could result in MD system instabilities. Thus, the initial model must undergo energy minimization to reduce the system strains entirely before performing actual simulations. After the actual MD simulations are done, the data obtained can be used to analyse the structures and properties of the simulated materials.

### 3.6 X-ray diffraction method

X-ray diffraction analysis (XRD) is a powerful technique to investigate the crystallographic structure of materials. It is based on the interaction between X-rays and materials to measure the diffraction angles and intensities of X-rays within the materials. The information about the atomic arrangement within the material, in particular the lattice types, lattice constants, interplanar spacing, etc., can be obtained. These parameters are crucial to understand the structures and properties of materials.

XRD is the main method for identifying cellulose crystal structures and phases. The cellulose nanocrystal (CNC) has several morphologies, as shown in **Figure 3.8**, commonly referred to as cellulose I, II, and III. These morphologies have distinct crystal structures and arrangements of cellulose chains. XRD can
identify these different forms based on the diffraction patterns that they produce when X-rays are incident on the cellulose sample. The positions and intensities of the diffraction peaks are analyzed to obtain information of the crystal structures and phases present in the sample.

Figure 3.8 XRD curves of experimental and Martini 3 CNC I, II, III crystals. The crystal structures (g, h, and i) are reproduced from Figure 2.2.

The Debyer, a XRD software package based on Debye scattering equation is usually used for analysing the results of MD simulations (https://github.com/wojdyr/debyer). The Debye scattering equation describes the total contribution to the scattering from all scattering centres. The equation was proposed by physicist Peter Debye in 1915\(^87\) and is mainly used to analyse the structures of amorphous or semi-crystalline materials. \(I(Q)\) represents the scattering intensity:

\[
I(Q) = \sum_i \sum_j f_i f_j \frac{\sin(Qr_{ij})}{Qr_{ij}} \tag{3.15}
\]

The double summation symbols \(\Sigma_i\) and \(\Sigma_j\) represent summing over all pairs of scattering centers. \(f_i\) and \(f_j\) are scattering factors of scattering centers, depending on the electron cloud distribution and wavelength of the center. \(Q\) is the scattering vector, proportional to the difference between the incident wave vector and the scattered wave vector. \(r_i\) and \(r_j\) are the positions of scattering centres.
3.7 Backmapping method

After the CG simulation is done, backmapping the CG results to all-atom (AA) results facilitates obtaining insight on an atomistic scale\textsuperscript{88,89}. The primary advantage of CG simulations lies in their efficiency, as they can handle system sizes and time scales far beyond those of AA simulations. However, this also brings some challenges. A significant challenge is that an important information at the atomic level is lost, which inevitably reduces the accuracy of the simulation results under certain situations. The backmapping of CG results is intended to overcome this problem.

The fundamental idea of backmapping is to convert CG particles to original atomic ones through certain algorithms and constraints. Backward, a flexible backmapping approach, is usually used for converting the Martini 3 CG models to AA models\textsuperscript{90}. The steps of backmapping from a Martini CG cellulose chain to AA cellulose chains include:

**Step 1**: Prepare an appropriate conversion template that contains the correspondence between Martini 3 beads and atoms. Prepare the appropriate force field file for the output AA model files.

**Step 2**: Each CG bead in the MD cellulose model will be replaced by several atoms. These atoms will be sequentially placed with controlled relative positions by the backward tool. The placement algorithm is flexible, meaning that it allows for various configurations, such as trans, cis, chiral, etc., to define the relative positions of the atoms. It is important to note that the relative positions of these atoms must be accurately determined to ensure the correct structures of sugar rings in the AA cellulose model.

**Step 3**: Energy minimization and short MD simulations are carried to optimize the positions of atoms and stabilize the MD system.

Due to the high level of simplification of the Martini model, backmapping may not be able to fully restore the original AA model. Thus, the atom model obtained from backmapping is typically an approximate model rather than an exact atomic model. Despite this problem, the backmapping from CG to AA is considered as a very useful tool, as it allows us to utilize the computational efficiency of CG simulations to investigate/explore the chemical process, and gain insights of the simulation results at the atomistic scale.
4. Finite Element Modeling and Simulation Using COMSOL Multiphysics

Finite Element Method (FEM) is a numerical technique for solving partial differential equations extensively utilized in academic research, engineering design, and scientific analysis. The chapter provides a concise overview of the fundamental principles and methods of finite element modelling and simulation using COMSOL Multiphysics for modelling of optical properties of transparent wood and cellulose based electrochemical devices.

4.1 A brief summary of FEM

Partial differential equations (PDEs) are often used to describe physical phenomena that are dependent on space and time, such as mass transfer, heat transfer, fluid flow, and electromagnetic fields. However, it is challenging to find an analytical solution for PDEs in most cases. In recent decades, a numerical technique, Finite Element Method (FEM), has been developed to deal with PDEs through a series of mathematical tools and processing techniques. FEM plays a pivotal role in understanding, predicting, and optimizing engineering designs and processes in science and industry.

First, FEM converts the PDEs from their “strong form” into an integral form, referred to as the “weak form”, and integrates over the entire modeling domain. Subsequently, the model needs to be discretized through a process known as mesh generation, where the computational domain is divided into numerous small fragments of simple shapes called “elements,” and the physical quantities will be calculated at the vertices of these elements.

The next step is to introduce trial functions (generally simple polynomials) to integral equations to approximate the unknown physical properties, such as displacements, temperatures, pressures, etc. Finally, assembling the equations over all elements, a set of algebraic equations can be obtained. By such process, FEM transforms the continuous physical problem into a discrete mathematical problem, which can be easily solved using numerical methods on a computer.

4.2 COMSOL Multiphysics

COMSOL Multiphysics is a finite element simulation software designed for coupling multiple physical fields, and it is adept at solving complex problems...
across various domains, such as electromagnetics, fluid dynamics, chemical engineering, and structural mechanics. It has had widespread applications in academic research, engineering design, and scientific analysis in recent years.

4.3 Geometry construction

Creating an effective geometric model is vital for the successful simulation of physical problems using COMSOL Multiphysics. COMSOL supports one-dimensional (1d), two-dimensional (2d), and three-dimensional (3d) models, yet with gradually increased demand of computational resources. When determining the dimensionality of the geometric model (1d, 2d, 3d) in COMSOL, it is necessary to consider the geometric shape, the physical questions, computational resources, accuracy requirements, etc. For models with relatively simple structures, geometry can be directly created, modified, and combined using the built-in geometry construction tools in COMSOL.

COMSOL allows for importing complex external models from software such as CAD or MATLAB. In Paper 3, we established a complex 2D wood model that is consistent with the experiment, based on SEM images of transparent wood samples (Figure 4.1a). In previous studies, due to the complexity of the wood structure, the propagation of light rays in transparent wood was typically computed using simplified structures, as shown in Figure 4.1b. In our work, we used the ImageJ tool to extract the fiber structures of the wood (Figure 4.1c), and then utilized MATLAB to identify the black (fiber structure) and white regions, and employed the LiveLink™ for MATLAB® interface in COMSOL to create a finite element model, see Figure 4.1d. This “realistic” modeling of experimental samples can yield more accurate simulation results. It is noteworthy that during the creation of the geometric model, modifications such as eliminating sharp angles may be required.
4.4 Mesh generation

The fundamental principle of mesh generation involves subdividing a complex geometric model into numerous simpler shapes, such as triangles and quadrilaterals in 2d and tetrahedrons or hexahedrons in 3d. These simple shapes are referred to as elements. Mesh generation is essential in FEM as it influences the accuracy and efficiency of the simulations. A finer mesh can deliver more accurate results although at the expense of computational time and resources, whereas a coarser mesh may yield results more swiftly but with less compromised accuracy.

The reliability of the generated mesh depends on several factors, such as the chosen of mesh type, element size and distribution, and solver settings, etc. Conducting sensitivity analysis and mesh convergence studies are standard practices for evaluating the reliability of simulation results. A common practice in FEM is to increase the density of the mesh (i.e., finer mesh) incrementally and
then compare the simulation outcomes. If the results change significantly with a finer mesh, it implies that the simulation is highly sensitive to mesh size. In this case, a further finer mesh is needed to guarantee the accuracy of the simulation results. Conversely, if the results are stable within a specific range of mesh sizes, it can be concluded that a mesh convergence has been achieved. By refining the mesh progressively and monitoring the variations in results, one can assess the impact of mesh size on outcomes and identify a balance point where an acceptable accuracy and computational efficiency can be achieved.

4.5 Solvers

Solvers are central components of FEM and are responsible for solving complex engineering and scientific problems. COMSOL Multiphysics offers several solvers for tackling partial differential equations. When employing solvers in COMSOL, it is crucial to choose the appropriate solver and settings based on the specific problems and applications. COMSOL solvers can be categorized into direct and iterative solvers. The direct solvers, including NUMPS, PARDISO, and SPOOLES, are based on LU decomposition. Among these direct solvers, PARDISO is recognized for its swiftness, while SPOOLES is the slowest but uses the least amount of memory. COMSOL offers various iterative solvers, which fundamentally resemble the conjugate gradient method. Direct solvers work by running a large and complex computation, while iterative solvers work step-by-step. For a given model, iterative solvers have significantly lower memory requirements than direct solvers.

COMSOL will present a suitable solver according to the model's physical field and the problem's complexity. Generally, direct solvers, such as Gaussian elimination, are suitable for small to medium-sized problems, while iterative methods are more commonly utilized for large-scale problems. It should be noted that the types of solvers and their parameter configurations may require adjustments to enhance simulation efficiency, particularly in cases of convergence issues or memory limitations.

4.6 Optics Physical equations and Boundaries

4.6.1 Ray Optics equations

The Geometrical/Ray Optics module in COMSOL is used for analysing optical systems, primarily based on the approximation methods of geometrical optics. Geometrical optics deals with light propagation issues by neglecting wave effects
and considering light as rays propagating in straight lines. In Ray Optics module, the rays are computed using Hamilton's equations\textsuperscript{99}. When rays propagate through an interface between two materials, as shown in Figure 4.2, the angle of incidence $\theta_1$ is computed by:

$$\theta_1 = \cos \left( \frac{d_1 \cdot d_s}{|d_1||d_s|} \right)$$  \hspace{1cm} (4.1)$$

where $d_1$ is the unit vector of direction of the incident light and $d_s$ is a unit vector normal to the material interface.

**Figure 4.2** Diagram of incident, transmitted, and reflected light in a material interface. The material interface and normal are labelled.

Then, the direction of the transmitted ray ($d_2$) and the angle of the transmitted ray ($\theta_2$) can be calculated by:

$$d_2 = \eta d_1 + \gamma d_s$$  \hspace{1cm} (4.2a)$$

$$\gamma = -\eta \cos \theta_1 + \cos \theta_2$$  \hspace{1cm} (4.2b)$$

$$\eta = \frac{n_1}{n_2}$$  \hspace{1cm} (4.2c)$$

$$\theta_2 = \arcsin(\eta \sin \theta_1)$$  \hspace{1cm} (4.2d)$$

where $\eta$ equals to the ratio of the refractive indices of the first medium $n_1$ and the second medium $n_2$; $\theta_1$ is the angle of incident light; $\theta_2$ is the angle of transmitted light; The $\gamma$ is calculated from the incident and transmitted angles. The direction of the reflected ray was calculated by:
\[ d_r = d_1 - 2d_s \cos \theta_1 \quad (4.3) \]

When the intensity/power of the secondary rays (i.e., reflected rays) is lower than the user-defined Threshold, the secondary rays will not be released. The reflection coefficients for the rays can be computed by Fresnel equations:

\[
R_p = \frac{n_2 \cos \theta_1 - n_1 \cos \theta_2}{n_2 \cos \theta_1 + n_1 \cos \theta_2} \quad (4.4a) \\
R_s = \frac{n_1 \cos \theta_1 - n_2 \cos \theta_2}{n_1 \cos \theta_1 + n_2 \cos \theta_2} \quad (4.4b)
\]

where \( R_p \) and \( R_s \) are the reflection coefficients for the parallel (p) and perpendicular (s) polarizations of light, respectively. The transmission coefficients for the rays can be computed by Fresnel equations:

\[
T_p = \frac{2n_1 \cos \theta_1}{n_2 \cos \theta_1 + n_1 \cos \theta_2} \quad (4.5a) \\
T_s = \frac{2n_1 \cos \theta_1}{n_1 \cos \theta_1 + n_2 \cos \theta_2} \quad (4.5b)
\]

where \( T_p \) and \( T_s \) are the transmission coefficients for the parallel (p) and perpendicular (s) polarizations of light, respectively.

### 4.6.2 Accumulator equation

When the rays reach a boundary within the TW model, the total power of the rays can be determined using the accumulator, as given by:

\[ rpb_{new} = rpb + R \quad (4.6) \]

where \( R \) is the power of the individual ray; and the \( rpb \) represents the total accumulated power. The \( rpb \) increases each time a new ray enters the wall.

### 4.6.3 Wave Optics equations
In the studies of transparent wood (TW) models, the simulation focuses on the TW’s refractive index and light propagation. The effects of the relative permeability ($\mu_r$) and conductivity ($\sigma$) are ignored in the TW models ($\mu_r = 1$ and $\sigma = 0$). Consequently, the simulations of electromagnetic waves in the Wave Optics module by COMSOL is based on a form of Maxwell's equation:

$$\nabla \times (\nabla \times \mathbf{E}) - k_0^2 \varepsilon_r \mathbf{E} = 0$$  \hspace{1cm} (4.7)

where the vector differential operator $\nabla$ represents the variation in space; $\mathbf{E}$ is the electric field intensity; relative permittivity ($\varepsilon_r$) represents the response of a medium to an electric field; $k_0$ is the wavenumber in free space. In 2d optics models, the electric field can be described by:

$$\mathbf{E}(x, y, z) = \mathbf{\tilde{E}}(x, y)e^{-ik_z z}$$  \hspace{1cm} (4.8)

where $\mathbf{E}(x, y, z)$ represents the electric field at the spatial position $(x, y, z)$; The $\mathbf{\tilde{E}}(x, y)$ describes the spatial distributions of the electric field’s amplitude and phase in the $(x, y)$ plane; $-ik_z z$ is the exponent that describes the variation of the electric field along the $z$ direction; $i$ denotes the imaginary unit; $k_z$ is the wavenumber along $z$ direction; and $z$ represents the $z$-coordinate of the position. In essence, Eq 4.8 shows how $\mathbf{E}$ at a spatial position $(x, y, z)$ is composed of a spatially varying complex amplitude $\mathbf{\tilde{E}}(x, y)$ and an oscillatory phase change along the $z$ direction.

### 4.7 Electrochemistry Physical equations and Boundary conditions

The Tertiary Current Distributions, Nernst-Plank interface in COMSOL is used for calculating the transport of species and chemical reactions in AORFBs. The concentration of species flowing into and out of the cells were determined by Global Ordinary Differential Equations (ODEs) and Differential Algebraic Equations (DAEs) Interface. The Events Interface was used to switch the charge-discharge states. The chemical species and geometry model of AORFB are described in Chapter 5.4. The governing equations and boundary conditions of the AORFB model are labelled in Figure 4.3.
Figure 4.3 Governing equations and boundaries for the AORFB model.
4.7.1 Nernst-Planck equations

The Nernst-Planck equation, also known as the mass conservation equation, is a time-dependent continuity equation for the concentration of species:

$$\frac{\partial c_i}{\partial t} + \nabla \cdot J_i + u \cdot \nabla c_i = R_{i,tot} \quad (4.9)$$

where $R_{i,tot}$ is the total reaction rate of the species $i$; $u$ denotes the flow rate. Ion transport is typically governed by three primary processes: diffusion, migration, and convection. The $J_i$ represents the flux density of species $i$ due to diffusion and migration:

$$J_i = -D_i \nabla c_i - z_i \mu_{m,i} F c_i \nabla \Phi_l \quad (4.10)$$

where $D_i$ represents the diffusion coefficient of the species $i$; $z_i$ is its valence; $u_{m,i}$ denotes its mobility; $F$ is the Faraday constant; and $\Phi_l$ signifies the electrolyte potential. The mobility $\mu_{m,i}$ of species $i$ can be calculated by diffusion coefficient ($D_i$):

$$\mu_{m,i} = \frac{D_i}{RT} \quad (4.11)$$

4.7.2 Electrode and electrolyte current equations

In porous carbon electrodes, the current includes the electrolyte current due to the movement of charges in the liquid electrolytes and electrode current comes from the solid carbon materials. The electrolyte current ($i_l$) is calculated by:

$$i_l = F \sum_{i=1}^{n} z_i j_i \quad (4.12)$$

where $j_i$ represents the flux density of species $i$ due to diffusion and migration. The electrode current ($i_s$) is computed by:
where $\sigma_s$ is the conductivity of the porous electrode; $\phi_s$ represents the potential in the solid carbon materials.

4.7.3 Electrochemical reactions

For porous electrodes, the electrochemical reaction rates of different species can be computed based on Faraday's laws of electrolysis as follow:

$$ R_i = -a_v \frac{v_i i_{loc}}{nF} $$  \hspace{1cm} (4.14)

where, $a_v$ is the specific surface area of the porous electrode; $v_i$ denotes the stoichiometric coefficient; $i_{loc}$ represents the local current density; $n$ is the number of participating electrons.

For a specific reaction, the local current density ($i_{loc}$) can be computed using the activation overpotential. The activation overpotential, denoted as $\eta$, is given by the expression:

$$ \eta = \phi_s - \phi_l - E_{eq} $$  \hspace{1cm} (4.15)

Here, $E_{eq}$ represents the equilibrium potential; $\phi_s$ and $\phi_l$ represent the potential in the electrode and electrolyte, respectively. Then, the Butler-Volmer equation is used to compute the $i_{loc}$:

$$ i_{loc} = i_0 \left( \exp \left( \frac{a_a F \eta}{RT} \right) - \exp \left( -\frac{a_c F \eta}{RT} \right) \right) $$  \hspace{1cm} (4.16a)

$$ i_0 = i_{0,ref} \sum_{i:v_i>0} \left( \frac{c_i}{c_{i,ref}} \right)^{\frac{a_v v_i}{n}} \sum_{i:v_i<0} \left( \frac{c_i}{c_{i,ref}} \right)^{\frac{-a_v v_i}{n}} $$  \hspace{1cm} (4.16b)
where, \( i_0 \) represents the exchange current density; \( \alpha_a \) is the anodic charge transfer coefficient; \( \alpha_c \) is the cathodic charge transfer coefficient; \( i_{0,\text{ref}} \) is the reference exchange current density. The equilibrium potential \( (E_{eq}) \) is calculated according to:

\[
E_{eq} = E_{eq,\text{ref}} - \frac{RT}{nF} \ln \prod_i \left( \frac{c_i}{c_{i,\text{ref}}} \right)^{\nu_i}
\]  

(4.17)

where, \( E_{eq,\text{ref}} \) represents the reference equilibrium potential.

4.7.4 Non-electrochemical reactions

The AORFB device in Paper IV operates in an acidic environment. The model needs to consider the chemical equilibrium of the dissociation of \( \text{H}_2\text{SO}_4 \) species. The initial dissociation reaction (i.e., \( \text{H}_2\text{SO}_4 \rightarrow \text{H}^+ + \text{HSO}_4^- \)) is assumed to be fully completed in its entirety. The second step of the dissociation process (i.e., \( \text{HSO}_4^- \leftrightarrow \text{SO}_4^{2-} + \text{H}^+ \)) is computed via the dissociation source term \( (R_d) \), described by equation\(^\text{52}\):

\[
R_d = k_d \times \left( \frac{c_{\text{H}^+} - c_{\text{HSO}_4^-}}{c_{\text{H}^+} + c_{\text{HSO}_4^-}} - \beta \right)
\]  

(4.18)

where \( k_d \) is the coefficient of dissociation reaction; \( c_{\text{H}^+} \) and \( c_{\text{HSO}_4^-} \) represents the concentration of \( \text{H}^+ \) and \( \text{HSO}_4^- \) species; \( \beta \) signifies the degree of dissociation.

In addition, the Michael addition reaction (MAR) rate for quinone I reactants in the positive electrolyte is given by equation:

\[
R_{\text{MAR}} = k_{\text{MAR}} \times c_{\text{quinone},I}
\]  

(4.19)

Here, \( k_{\text{MAR}} \) is rate constant of MAR, and \( c_{\text{quinone},I} \) is the concentration of quinone I species in the model.

4.7.5 Electrolyte tank equation
The global equations under the Global ODE and DAE Interface can be defined to represent the tanks of the AORFB. The concentrations of species in tanks are determined by calculating the difference between the species flowing out and in of the AORFB cells:

$$\frac{V}{L} \frac{d}{dt} (c_i^{\text{in}}) = \int_{\text{outflow}} (J_i \cdot n) dS - \int_{\text{inflow}} (J_i \cdot n) dS$$

(4.20)

where $c_i^{\text{in}}$ represents the concentration of species $i$ in the electrolyte tank (the species in the tank are assumed to be good mixed); $L$ and $V$ are the height of electrode and total volume of the electrolyte. The $J_i \cdot n$ represents the molar fluxes of the species $i$ through the outflow and inflow boundaries. The integrals ($\int dS$) are calculated on the outflow and inflow boundaries.

### 4.7.6 Donnan boundary

The Donnan boundary describes the physicochemical phenomena occurring at the interface of an ion exchange membrane in AORFB models\textsuperscript{100}. The distribution of mobile ions is affected by the fixed charged groups within the ion exchange membrane. In the AORFB model, the Donnan boundary describes the relation between electrolyte potentials and concentrations of species:

$$\Phi_{i,m} - \Phi_{i,e} = -\frac{RT}{z_i F} \ln \left( \frac{c_{i,m}}{c_{i,e}} \right)$$

(4.21)

where $m$ and $e$ represent the ion exchange membrane and electrode regions, respectively.

### 4.7.7 Flow boundary

Flow boundaries define how species interact with and transfer across the boundaries in the AORFB model. Depending on different scenarios, various boundary conditions can be chosen to determine the transport of species:

$$n \cdot (J_i + uc_i) = n \cdot (uc_{0,i})$$

(4.22)
Where $c_{0,i}$ is the given upstream concentration of species $i$. The total flux is calculated by the Danckwerts condition. This boundary condition is typically used when the inflow concentration and flow velocity are known.

$$n \cdot D_i \nabla c_i = 0$$  \hspace{1cm} (4.23)

This equation represents that at the outflow boundary, the boundary does not affect transport; it only allows material to leave with the flow.

$$-n \cdot J_i = 0$$  \hspace{1cm} (4.24)

This equation represents a no flux boundary, i.e., species $i$ will not be transported across the boundary.

### 4.7.8 Insulation boundary

The insulation boundary is used to represent the electrical insulation interface:

$$-n \cdot i_S = 0$$  \hspace{1cm} (4.25)

$$-n \cdot i_l = 0$$  \hspace{1cm} (4.25)

The $i_S$ and $i_l$ represent the current densities of the electrode and electrolyte, respectively.
5. Summary of the Papers

Our research focuses on predicting and analyzing the properties and performance of cellulose-based materials and devices. We constructed the cellulose MD models and applied them to study dispersion properties of TEMPO CNCs and regeneration of cellulose materials. Besides, we constructed the FEM TW models to study light propagation and aqueous organic redox flow battery (AORFB) models to predict capacity performance. In this chapter, the results of Paper I–IV are summarized.

Paper I

**Martini 3 model of surface modified cellulose nanocrystals: investigation of aqueous colloidal stability**

Jiu Pang, Aleksandar Y. Mehandzhiyski, Igor Zozoulenko
Cellulose, 2022, 29, 9493.

Cellulose nanocrystals (CNCs), known for their biocompatibility and recyclability, are effectively utilized across various fields, such as biomedical engineering, wastewater treatment, and energy & electronics, etc. However, the dispersion of pristine CNCs in most non-polar and hydrophobic polymer matrices is not uniform. To mitigate this, the CNCs' surface primary hydroxyl groups are typically converted into functional groups, e.g., COO\(^{-}\), to enhance compatibility and dispersion properties.

Many coarse-grained (CG) molecular dynamics (MD) models for CNCs have been developed to study the structures and properties of cellulose-based materials. However, these models primarily focus on pristine CNC but miss the surface modifications that are typically presented in most experimental works. This omission significantly restricts the models' applications.

In Paper I, we developed new CNC and TEMPO CNC models using the Martini 3 force field. We calculated the lattice parameters and mechanical properties of the pristine CNCs and compared these results with experimental results. Our findings show a notable improvement over previous CG CNC models and approximate to the experimental measurements. Subsequently, we designed and investigated surface-modified CNC models with COO\(^{-}\) groups, which is called TEMPO CNCs, to study the aggregation and dispersion properties in aqueous
solutions with varied NaCl concentrations. We found that the Na$^+$ ions are in dynamical association/dissociation equilibrium on the surface of TEMPO CNCs in the aqueous, and this equilibrium leads to a double-layer repulsive force between charged colloidal particles. By altering non-bonded and bonded parameters, we reproduced this dynamic equilibrium in the CG model.

Then, we analyzed the dispersibility of TEMPO CNCs in an aqueous solution (weight ratio is 7%) with different NaCl concentrations. We assumed that the TEMPO CNCs are aggregated if the distance is smaller than 0.35 nm and quantified the systems’ state by counting the number of contacts among TEMPO CNCs within the time frame of $0 < t < 1000$ ns, as shown in Figure 5.1. The top and surface contacts between the CNCs are counted separately, given the absence of COO$^-$ charge groups on the end surfaces of CNC. Pristine CNCs exhibit a rapid onset of aggregation (within 50ns) in pure water, and the number of contacts remains stable after 500 ns. The CNCs show an arrested state; that is, several CNCs are aggregated and locked together and unable to move freely in aqueous solution (see Figure 5.1a). This is consistent with previous experimental observations. In contrast, TEMPO CNCs in low NaCl concentration aqueous solutions disperse and do not aggregate even within 1000 ns simulations, see Figure 5.1c and d. However, when the NaCl concentrations increase, equal to or over 100 mM, the number of contacts between TEMPO CNCs increases obviously (see Figure 5.1f). Similar aggregation trends were seen in previous experiments with sulfated CNCs in NaCl aqueous solutions.

In conclusion, our study represents a substantial advancement in CNC modeling, offering an accurate description of TEMPO CNCs in colloidal solutions. The work provides a flexible modelling method of CNCs with different surface functional group modifications and degrees of substitution. Our model serves as a promising tool for future explorations.
Figure 5.1 a) Representative snapshots and b) number of contacts over simulation time of pristine CNCs in aqueous solution; c) representative snapshots and d) number of contacts over simulation time of TEMPO CNCs in aqueous solution; e) representative snapshots and f) number of contacts over simulation time of TEMPO CNCs in a NaCl (100 mM) aqueous solution. The top contacts and lateral face contacts (excluding contacts between the end surfaces) between CNCs were plotted, respectively. The contact is determined by minimum distances (<0.35 nm) between CNCs.
Cellulose is a substantial raw material in industrial productions and contributes to the future circular economy and sustainable development. In recent years, the principles and strategies of cellulose dissolution/regeneration are explored via experiments and simulations. Although there are corresponding hypotheses and atomistic molecular dynamics (MD) models of regenerated cellulose, previous atomistic MD studies either contain too few cellulose chains or have too high weight ratio of cellulose chains, which can hardly study the morphologies of regenerated cellulose materials. Thus, a coarse-grained (CG) MD model of regenerated cellulose that can reach the system sizes and time intervals far exceeding those of atomistic MD simulations needs to be developed.

In **Paper II**, two cellulose self-assembly systems were designed to study the regeneration process. In the first system, cellulose chains were inserted into the computational box one by one. The snapshots of cellulose sheets consisting of 2, 4, 6, and 9 chains are shown in **Figures 5.2a**. With the number of chains increases, the cellulose sheets grow longer, resembling a fibril-like bundle structure.

In the second system, we simulated the cellulose regeneration process starting with totally dissolved 200 cellulose chains in aqueous solution (weight ratio is 1.4 wt%). **Figure 5.2b** shows snapshots (2 ns, 30 ns, and 400 ns) of the regenerated cellulose II. The cellulose chains are first attached to the closest chains to form cellulose sheets by stacking the glucopyranose ring plane due to the hydrophobic interactions. Then, the cellulose bundles, resembling fiber-like structures, form at around 30 ns and gradually grow longer. Similar behaviour is observed in the first system when inserting chains one-by-one. For the XRD curves of regenerated cellulose II, as shown in **Figure 5.2c**, the peak at 21 degrees in the XRD curves, which correspond to the 110/200 surfaces of cellulose II structure, gradually increases and becomes sharper over simulation time. The cross-sectional snapshots of the regenerated cellulose model, as well as simplified schematical structures based on the snapshots, are presented in **Figure 5.2d**. The images clearly show the characteristic structures of cellulose II with the respective interplane distances.
Finally, the regenerated CG cellulose models were transformed to AA cellulose models using backmapping method. The XRD curves of CG models, backmapped AA model, and experimental samples match closely, with all curves showing the same main peak at approximately 20–21 degrees, which correspond to the 110/200 planes of cellulose II crystallites. Our results demonstrate that CG MD simulations prove to be a powerful tool to provide a microscopic insight into the process of cellulose regeneration, which is not available with traditional experimental observations.

**Figure 5.2** a) A series of snapshots of the cellulose sheet regenerated by inserting chains one-by-one; b) a series of snapshots and c) XRD curves of the regenerated cellulose II crystallities that contains 200 chains; d) sectional view of the regenerated cellulose crystallities and its simplified stacking patterns.
Transparent wood (TW) is a novel material that is based on natural wood, keeping its mechanical properties, and bringing high optical transparency. The fabrication of TW starts with the removal of lignin and follows with the injection of a polymer material (PMMA, thiol-ene, or the similar) that possesses a refractive index closely matching the cellulose scaffolds. However, the previous experimental data of refractive index of cellulose materials can be influenced by wood species and chemical treatments, therefore these values might differ from an actual refractive index of the TW scaffolds. The mismatch of refractive indices between filling polymers and wood scaffolds in TW materials would cause a light scattering, consequently, shows strong non-homogenous haze. Thus, a numerical model is highly demanded to explore the light propagation in TW samples and retrieve the value of an effective refractive index.

In Paper III, we developed simplified and realistic numerical TW models and studied the light propagation. First, we used a simplified geometry model of TW structure where the cellulose scaffolds were represented by ring areas, and the filling polymer occupies areas inside and outside the rings, as shown in Figure 5.3a. Figure 5.3b shows normalized intensity for wave and ray optics simulations of the simplified TW models. Not only the shapes of the normalized intensities for the wave and ray optics calculations are very similar, but also absolute values of the calculated transmittance are very close (90.9% and 89.0%, respectively). This good matching proves the validity of the ray optics approach, a considerably simplified but accurate and efficient solution.

Then, a realistic TW model was designed using SEM images obtained from the TW samples in experiments. The light propagation in the near zone (i.e., the TW model region) simulated by the ray tracing methods. The thickness of the TW models and samples were 1nm, 2nm, and 3nm, respectively. With the thickness of TW samples increases from 1 mm to 3 mm, the total transmittance of the TW material gradually decreases due to enhanced light scattering during light propagation through the material. The light propagation in 1nm TW model is shown in Figure 5.3c. Light progressively scatters and becomes wider while it...
propagates through the TW model. The angular distributions of normalized intensity were counted in ray optics simulations and measured in experiments. We tested a series of values of refractive index of cellulose scaffolds and compared with experimental data. The normalized intensity curves for all TW models exhibit the best agreement with the experiment results when the refractive index of cellulose scaffolds is set to 1.54.

The methodology developed in this study holds promise towards realistic and practical wood modelling, serving as a plausible tool for material design and applications. It can be used for interpretation of experimental scattering phenomena, materials design, and the modelling of other transparent cellulosic materials.

**Figure 5.3** a) Simplified TW model and its partial enlarged view. Red arrows indicate the direction of light. b) The averaged normalized intensity curves of wave- and ray-optics calculations. c) Light propagation in 1 mm thickness TW models. The power of the optical rays ranging from 0 to $5 \times 10^{-5} \, \text{W/m}$ are represented by black to red curves. d) The angular distributions of normalized intensity curves in experimental measurements and simulations for 1 mm TW samples/models. RI represents the refractive index of cellulose substrate used in the optics models.
Paper IV

Controlling the rate of posolyte degradation in all-quinone aqueous organic redox flow batteries by sulfonated nanocellulose based membranes: the role of crossover and Michael addition

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In Manuscript

Aqueous organic redox flow battery (AORFB) is a promising solution towards the large-scale sustainable energy storage. However, in most AORFB systems, the crossover or side reactions of the reactants can lead to the degradation of battery performance, making recovery and regeneration of electrolytes impossible. Thus, quantitative investigations towards AORFBs are needed to gain further insights into the mechanisms of a capacity loss.

In Paper IV, we developd the AORFB model using the cell configuration, porous electrodes, compositions of posolyte and negolyte that utilized in the experiment section in this work, as shown in Figure 5.4. The negolyte contains \( \text{H}^+, \text{HSO}_4^-, \text{SO}_4^{2-} \), and both reduced and oxidized forms of ARS\(^{2-}\) species. Meanwhile, the posolyte contains \( \text{H}^+, \text{HSO}_4^-, \text{SO}_4^{2-} \), and both reduced and oxidized forms of Tiron\(^{2-}\) species. The oxidized form of Tiron\(^{2-}\) is also known as quinone I.

![Figure 5.4](image.png)

Figure 5.4 provides a schematic representation of the 2d AORFB model (enclosed within the red dotted rectangle). The boundary conditions and governing equations of the AORFB model are detail described in Chapter 4.7.
A stationary study was carried out to initialize the spatial distributions of the potentials and concentrations. Then, the charge-discharging of the AORFB was computed in time-dependent simulations by switching inward current density on the current collector of positive electrode. As shown in Figure 5.5a, the inward current density is set to 4 mA/cm$^2$ in charging stage and −4 mA/cm$^2$ in discharge stage to represent the galvanostatic charge-discharge in experiments. The AORFB voltage is charged to a maximum of 1.0 V and discharged to 0.5 V, as shown in Figure 5.5b. The number of charge-discharge cycles was set to 100 for both simulations and experiments. We then computed the capacity curve of the AORFB by multiplying the current in the collector and the discharging time in each cycle.

In the AORFB model, the rate of Michael addition reaction (MAR) of quinone I was fitted by comparing the capacity curves of simulations to the experimental measurements, as shown in Figure 5.5c. It should be noted that the crossover of organic species, (ARS$^{2−}$ and Tiron$^{2−}$) through the membrane is set to zero, and this work focused on studying the MAR influences on capacity loss in the AORFB model. When the rate factor of the MAR is set at 0.00011, the computed decay of the discharge capacity of the AORFB model closely aligns with the experimental curves. To explore the effect of the membrane on MAR, the posolyte part of the cell with and without narrow MAR domain were considered. The absence or presence of narrow MAR domain implies that MAR is defined in the bulk of porous positive electrode or at the surface of the membrane (i.e., orange region in Figure 5.4), respectively. The quinone I concentrations at the outflow/inflow boundary of the porous positive electrode phase show the appearance of the visible difference between the profiles computed for inert and active membrane (represented as without and with short MAR domain, blue and black curves, respectively, Figure 5.5d and e)). When the MAR is active only at the membrane’s surface, the concentration of quinone I becomes slightly lower in the area close to the membrane, see Figure 5.5e, creating a concentration gradient in the porous electrode. We also compared the capacity curves and concentration profiles of H$^{+}$ ions for the two cases when MAR happens in the whole electrode or at the surface of the membrane. The concentrations of H$^+$ ions and capacity curves remain identical, irrespective of where the MAR occurs. Besides, in our simulations, changing the thickness of the membrane (from 45 µm to 125 µm) and the concentration of fixed $\text{SO}_3^{−}$ charges (from 200 to 2000 mol/m$^3$) does not significantly influence the charge-discharge and capacity curves of the AORFBs.
By enhancing our understanding of the chemical reactions, species concentrations, and material properties within an AORFB, our model provides critical insights that can aid in the further development of this technology.

Figure 5.5 a) Depicts the inward current density of AORFB during the 1st and 100th cycles. The current density is set to 4 mA/cm² during the charging stage and −4 mA/cm² during the discharging stage; b) shows the calculated cell voltage curves for the 1st and 100th cycles; c) illustrates the capacity curves of galvanostatic charge-discharge from the cellulose membrane AORFB model. The capacity curves are calculated with different factor of MAR rates to fit experimental measurements. d) and e) presents the concentrations of quinone I (when the AORFB is charged to 1.0 V) along the cross section at the inflow and outflow boundaries of the AORFB model, respectively. The blue and black curves correspond to the cases that MAR takes place in the whole positive electrode domain or at the surface of the membrane, respectively.
6. Outlook

In the context of the Sustainable Development Goals (SDGs) for 2030, cellulose material is becoming an increasingly integral to the circular economy due to its biodegradability, renewability, and biocompatibility. The use of computational studies in the design, production, utilization, and recycling stages of cellulose-based materials and devices can potentially promote the circular economy and sustainable development.

Due to cellulose's excellent properties, cellulose materials have wide potential in numerous fields, such as clean energy, environmental remediation, textiles, construction, biomedicine, pulp production, and even electronics. We are optimistic that the performance of cellulose-based materials will be further optimized and enhanced in the future. This, in turn, will facilitate their applications in more fields and industries. Computational studies can speed up the design and optimization processes of cellulose-based materials and devices.

The research work in this thesis focuses on the computational studies of cellulose-based materials by molecular dynamics (MD) and finite element method (FEM). We constructed several cellulose-related models and performed a series of simulations. These efforts aim to improve the understanding of materials made from cellulose, support new ideas, guide experiments design, and lead to potential economic and social benefits. In MD studies, we investigated surface-modified cellulose nanocrystal (CNC) models, focusing on modified CNCs with carboxyl groups (COO⁻). In future research, it would be interesting to explore the effects of other functional groups, such as sulfonate (SO₃⁻). Additionally, an exciting extension of our work would be to explore the dispersion properties of surface modified CNCs in different salt solutions. While our current study modelled CNCs with a length of 16 nm due to the computational resource constraints, more advanced computing resources and algorithms could be utilized in future research to model longer CNCs, providing even more realistic representations of CNC materials.

In our FEM studies, we developed a two-dimensional (2D) realistic model of transparent wood (TW). We believe that transitioning from a 2D model to a three-dimensional (3D) model would represent a substantial improvement, capturing the intricate geometries and light propagations within the TW more accurately. Moreover, incorporating more factors such as heat transfer and structural mechanics into the simulation could provide deeper insights into the real-world behavior of the TW under varying conditions.
Regarding our construction of a 2D FEM model of an Aqueous Organic Redox Flow Battery (AORFB), one interesting question that can be explored in the future is the role of the ion-exchange membrane in influencing device performance. There is limited understanding of this effect, and it warrants further investigation.

The significance of simulations in material and device fields should not be overstated. While they are helpful tools, it's very important to use them prudentially and be aware of their limitations and potential issues. Constructing reliable computational models and choosing appropriate simulation settings require highly specialized knowledge and skills. Additionally, simulation limitations, such as computational costs, time scales, and length scales, are usually present.

In recent years, the fast-growing development of artificial intelligence has shown possibility to combine machine learning and simulations. This combination is expected to promote the efficiency and accuracy of simulations, reduce study costs, assist in the selection of simulation parameters, enhance design and innovation, etc. Based on this, we believe that the computational studies of materials and devices will play a more and more important role and reach an unprecedented level.
References


Part II  Scholarly Articles
Papers

The papers associated with this thesis have been removed for copyright reasons. For more details about these see:

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Computational Studies of Cellulose-based Materials

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