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Modelagem e Caracterização de Sistemas Nanofluídicos Através de Simulações Moleculares em Multiescala

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Design and Characterization of Nanofluidic-Based Systems by Multiscale Molecular Simulations

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Abstract

The unusual physical properties exhibit by fluids within nanoscopic porous media play an important role in the plethora of chemical, geochemical and environmental processes. Currently, many aspects of the structure and dynamics of the spatially constrained fluids are still poorly understood. Additionally, the interfacial phenomena considerably influences the processes occurring in nanoporous media, which can have a major effect on nanofluidics devices. These multiphase systems and multiphysics phenomena occurs at solid/solution interfaces, with electronic and dynamic effects taking place across size and time scales. Currently, a single methodology is not capable to disentangle all the complexity find in such systems because it is restricted to a specific scale or computationally demand. In addition, the usual computational modeling methodologies applied to investigate bulk phases, they are, in general, not suitable to systematically access the surface effects occurring at solid/fluid interfaces. The challenges imposed by the nanofluidics-based systems within the molecular modeling framework require innovative initiatives (among the available methodologies) to correctly access the interface properties. In this thesis, we integrate and apply novel computational approaches to properly design and characterize nanofluidics-based systems at atomic level. In this context, we introduced an hierarchical top-down multilevel method by combining molecular dynamics simulations with first principles electronic transport calculations to address the multiscale phenomena problem. The potential of this implementation was demonstrated in a case study involving the water and ionic (Na, Li, and CL) flow through a (6,6) carbon nanotube. We showed that the ionic trace, observed on the electronic transmittance, it may handle an indirect measurement of the ionic current that is recorded as a sensing output. We implemented also a layered version of hydrogen bond network analysis based on graph theory. With this approach, we were able to properly explore interface effects arising on spatially confined fluids. By combining molecular dynamics simulations with the layered hydrogen bond network analysis, we evaluated the extension of surface effects on the fluids dynamics properties and the interaction details at calcite/brine interface. With the developed approach, we have been able to isolate the specific features of the aqueous solutions ions on the hydrogen bond network. We showed that the surface layer near the calcite/brine interface displays similar network topology as observed in pure water, since the electrostatic and physical barrier displayed by this layer inhibit the adsorption of ions on the calcite surface. Outside that region, these ions affect the hydrogen bond network. We observed a more extended geodesic paths with respect to that observed in pure water. Such hydrogen bond branches may connect low to high dynamics molecules across the pore and hence, it may explain the glue-like mechanical properties observed in confinement environment. Our main contributions in this work relies on describing the structure of solvent and electrolyte aqueous solution at calcite/fluid interface and their physical indications and potential significance on the crystal growth and dissolution processes. Our implementations provide interesting contributions to the current understanding of processes occurring in porous media. Specially, it may contribute on the rational design of novel nanofluidics devices.

Keywords: nanofluidics; molecular modeling; multilevel approach; hydrogen bond network analysis.

Resumo

As propriedades físicas incomuns exibidas por fluidos confinados em meios porosos desempenham um papel importante em diversos processos químicos, geoquímicos e ambientais. Atualmente, muitos aspectos da estrutura e dinâmica dos fluidos espacialmente confinados ainda são pouco compreendidos. Nesse contexto, fenômenos interfaciais influenciam consideravelmente os processos que ocorrem em meios nanoporosos, podendo resultar em efeitos relevantes para o desenvolvimento dos dispositivos nanofluidicos. Esses sistemas multifásicos e com fenômenos multifísicos podem apresentar propriedades eletrônicas e dinâmicas envolvendo diferentes escalas de tamanho e tempo na interface sólido/fluido. Atualmente, uma única metodologia não é capaz de resolver toda a complexidade encontrada em tais sistemas pelo fato de cada qual estar restrita a uma escala ou demanda computacional específica. Além disso, as metodologias habitualmente aplicadas para investigar as fases *bulk* através da modelagem computacional, em geral, não são adequadas para acessar sistematicamente os efeitos de superfície que ocorrem na interface sólido/fluido. Os desafios impostos à modelagem molecular pelos sistemas nanofluidicos requerem iniciativas inovadoras (dentre as metodologias disponíveis) para acessar as propriedades de interface. Nessa tese, integramos e aplicamos abordagens computacionais em nível atômico a fim de modelar e caracterizar sistemas nanofluidicos. Nesse contexto, nós introduzimos um método multinível hierárquico top-down, que combina simulações de dinâmica molecular com cálculos de primeiros princípios de transporte eletrônico, para abordar fenômenos de multiescala. O potencial dessa implementação foi demonstrado em um estudo de caso envolvendo o fluxo de água e o transporte de íons através de um nanotubo de carbono tipo (6,6). Mostramos que o traço iônico pode representar uma mudança na condutância elétrica do nanocanal, e levar a uma medida indireta da corrente iônica. Também implementamos uma versão modificada da análise de rede de ligações de hidrogênio baseada em teoria de grafos, a fim de fazer o estudo das propriedades estruturais e dinâmicas em diferentes regiões do poro. Com essa abordagem, nós fomos capazes de explorar sistematicamente os efeitos de interface em fluidos espacialmente confinados. Combinando-se simulações de dinâmica molecular com a análise da rede de ligações de hidrogênio em camadas, nós pudemos avaliar a extensão dos efeitos de superfície nas propriedades dinâmicas e os detalhes da interface calcita/salmoura. Com a abordagem desenvolvida, conseguimos isolar os efeitos específicos dos íons da solução eletrolítica aquosa na rede de ligações de hidrogênio. Mostramos que a camada superficial exibe uma topologia de rede semelhante àquela observada em água pura, uma vez que a barreira eletrostática e física exibida nessa região, inibe a adsorção de íons na superfície da calcita. Fora dessa faixa, os íons influenciam consideravelmente a rede de ligações de hidrogênio: observamos a formação caminhos geodésicos mais extensos em relação àqueles observados em água pura. Esses ramos, que são formados por ligações de hidrogênio contíguas, podem conectar moléculas de baixa e alta dinâmica. Tal estrutura, pode explicar as propriedades mecânicas adesivas observadas em fluidos altamente confinados. Nossas principais contribuições decorrem na descrição da estrutura do solvente, dos íons da solução aquosa na interface calcita/fluido; e suas indicações físicas, bem como seu potencial significado nos processos de crescimento e dissolução de cristais. Nossas implementações fornecem contribuições relevantes para a compreensão atual dos processos que ocorrem em meios porosos. Especialmente, podendo contribuir para um desenvolvimento racional de novos dispositivos nanofluidicos.

Palavras-Chave: nanofluidica; modelagem molecular; abordagem multinível; análise de rede das ligações de hidrogênio.

“In science, as in the playing card experiment, novelty emerges only with difficulty, manifested by resistance, against a background provided by expectation.”

Thomas S. Kuhn in *The Structure of Scientific Revolutions*

“I could either watch it happen, or be part of it”

Musk, Elon

Dedicated to my father Lirio Kirch

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CHAPTER 1

INTRODUCTION

1.1 Nanofluidics

Nanofluidics is an interdisciplinary scientific research field interface, often involving physics, chemistry, biology and engineering. It concerns the study of the properties, manipulation, and control of fluids constrained within nanometer-sized environments^{1,2}. The most interesting physics displayed by nanofluidics-based systems occurs at or near the channel surface. In that region, the solid and fluid properties may be mutually influenced. Within the nanoscopic environment, the electrical potential arising from the interface atoms may determine the physical and chemical properties of the interacting systems. A physical quantity characterizing the extension of the surface potential is the Debye length, ranging from 1 to 100 nm¹. As a consequence, the fluid properties within nanometer-sized environments are significantly different from the usual bulk ones³⁻⁵. This feature is currently explored to the development of the so-called nanofluidics devices.

Several nanofluidics devices were already proposed in a broad range of applications. The potential of nanochannels to separate the solute from solvent was explored in water treatment applications⁶. In addition, devices based on field effect were recently proposed to control and/or select the transport of biological and chemical species through microchannels⁷. This and other functionalities are necessary, for instance, in several applications for the so-called lab-on-a-chip technology aimed to scale single or multiple lab processes down to chip-format, such as, drug delivery and discovery, and rapid diagnosis⁸. In addition, the ability to active and precisely manipulate or detect single ions/molecules in solution may favor several processes as chemical synthesis and catalysis.

Recently, channels have been produced experimentally^{9,10} in a downsize scale, with tailored endings reaching 10 nm. Such nanochannels were predicted to improve the functionality of the related devices. Transport process occurring at this size scale are those ones with the greatest potential for applications and the most exciting from the scientific perspective due to the emergent phenomena, such phase transition anomalies¹¹ and formation of ice-like structures¹². The investigation of the fluid properties under nanoscopic environments and how they may influence the electronic/mass transport through the nanochannels is essential for the development of nanofluidics devices, since such study opens a potential to explore new functionalities. It is also desirable to understand the underlying molecular mechanisms in porous media displayed in geochemical, synthetic and biological crystal growth process¹³, for instance.

1.2 Hydrogen Bond Network Analysis

Typical investigations within the molecular modeling framework usually describe the properties of fluids in porous media through global physical quantities, such as the viscosity and the mean-square displacement. However, the fluid properties are, in general, determined by local intermolecular interactions, as the hydrogen bonds in water. The knowledge of the specific features of the water organization at solid interface through a hydrogen bond network analysis could improve the understanding of the fluid properties within confined interfaces. Specially, water is a common solvent in nanofluidics-based systems found in porous rocks and biological nanochannels. Although the individual H_2O molecule has a very simple geometric structure, water exhibits highly complex phenomena resulting from the hydrogen bond network^{14,15}. Significant changes in the local hydrogen bond structure are expected in the interface with a distinct phase or within spatially confined environments¹⁶. Such structure is also temperature sensitive, exhibiting a more extensive tetrahedral clustering with crystalline forms at low temperature¹⁷. Therefore, it is operative to determine the fluid dynamic properties under the hydrogen bond network viewpoint.

Figure 1.1: Schematic illustration of an hydrogen-bonded structure mapped into a graph object formed by multiple edges and nodes. From the graph network, the water structure can be characterized by the degree of connections, geometric patterns (*e.g.* cyclic pentamers, hexamer books) and the geodesic, for instance.

A computational methodology is highly desirable to access the specific features of the hydrogen bond network, specially to disentangle its topology details near or at interfaces under spatially confinement. The information about such a structure could elucidate the relationships between the local fluctuations and the water global properties¹⁷. A novel systematized way to explore the network features in hydrogen-bonded systems was developed recently based on the graph theory¹⁷. In this approach, an hydrogen bond is considered under a geometric criteria and it is converted into a graph object formed by

edges and nodes, as shown in **Figure 1.1**. From the graph construction, it is possible to access the network structuring details, such as the net spread through the fluid and the degree of connections displayed by each node. Typical analyzed quantities are the graph geodesic, degree distribution and network patterns, such as: tetramers, pentamers and hexamers. This methodology has been applied in the study of several hydrogen-bonded systems in its bulk phase. However, to properly investigate nanofluidics-based systems, a layered analysis approach is desirable to systematically access the effects of spatially confined interfaces on the hydrogen bond network. Currently, such implementation is missing.

1.3 Computational Simulations

The progress achieved in nanofluidics through theoretical and experimental fronts can be expanded or complemented by computational simulations studies within an atomistic perspective. Such approach may contribute to a predictive understanding of some important aspects occurring at nanoscopic environment. In the computer simulation framework, the computing power has increased exponentially over the time and it is now possible to simulate systems with millions of molecules and longer time¹⁸. Nowadays, such approach can provide important details about the underlying physical mechanisms observed through some experiments¹⁹. In this context, computer simulations have benefited the scientific research in several areas. For instance, experimental investigations in the oil industry may involve high pressure, temperature, and toxic or flammable materials. As advantage, the computer modeling framework may provide a controlled, cost-effective, and safe environment for the research. In addition, it can reveal new phenomena occurring far from the current resolution level of experimental techniques applied to the nanofluidics (typically below to 10 nm)²⁰.

In materials science, a set of models were successfully developed along the time to understand and explore the systems in a broad scale, such as: quantum mechanics, molecular dynamics, coarse-grained and finite elements²¹(see **Figure 1.2**). The phenomena observed in spatially confined interfaces may occur across several size and time scales, *e.g.* mass flow may influencing the electronic transport. This imposes several challenges from the computational perspective, where usually each method depicted in **Figure 1.2** deals only with a specific scale because the computational cost and also the lack of a suitable methodology. Although such limitation is not usually a problem to investigate a specific phenomena, the different scales are indeed connected, with finer often governing processes seen at coarser scales and vice-versa. From the best of our knowledge, there is no single methodology capable to capture all the complexity of such phenomenon. The best strategy could be to combine the existing methodologies within a multilevel scheme by linking the constitutive laws and physical properties through the distinct resolution levels.

Methodologies belonging to different scales can be chosen and combined in a high level of consistency to properly describe the target physical quantities within a multilevel approach. At nanoscale, it is important to consider methodologies that are able to capture the discrete nature of the fluids. Therefore, a multilevel molecular computational approach, ranging from molecular dynamics to quantum mechanics calculations, is desirable. Thus, we can take the advantage of classical molecular dynamics simulations (MD) to handle the characteristic time and size at nanoscale, and first principles calculations for electronic and transport properties. This approach may lead to the development of nanofluidics from the computer simulation perspective, since it allows to investigate systems and properties not achieved by the isolated methods.

Figure 1.2: Diagram representing the main available computational methods as a function of the covered time and size scales. The inset pictures exemplify a typical system/property covered by each methodology. From bottom to up: 1) The quantum mechanics access the electronic structure of the system. The charge density difference plot (blue isosurface) suggest the electronic level of this calculations by showing the charge rearrangements resulting from the interaction between the partially hydrated ion within a carbon nanotube. 2) Molecular dynamics simulations deals with the thermodynamic properties of interacting atoms or molecules. The inset picture shows a snapshot of a box under periodic boundary conditions representing bulk water. 3) Discrete space phases using a distribution function (of macroscopic physical variables) by the lattice Boltzmann method²². The inset picture shows a snapshot of a multicomponent system used to investigate the oil (black) extraction efficiency from micro porous (gray) by brine injection (cyan). 4) Finite discrete space applied to the numerical solution of the Navier-Stokes equation. The inset picture represents the space discretization of an oil plumbing at macro scale.

1.4 Goals and Organization

Nanofluidics-based systems display interface effects because the interaction of different phases, such as observed between electrolyte aqueous solutions and solid nanochannel surfaces. In addition, the phenomena arising in spatially confined interfaces may occurs across size and time scales. A single methodology is often not capable to disentangle all the complexity found in these systems. In this context, the nanofluidics requires innovative approaches, often involving combined methodologies, to proper access the systems properties. Therefore, a study focusing on the development and application of novel computational simulations approaches may be essential to design and characterize nanofluidics-based systems at molecular level. These studies can benefit the nanofluidics in several aspects, specially in the development of devices, by providing a detailed quantitative elucidation of the fluid and nanochannel properties exhibited at the spatially confined interfaces.

In this thesis, we aim to investigate the effect of spatially confined interfaces and ions on the structure and dynamics of electrolyte aqueous solution, since it is currently poorly understood. This study may advance also the current understanding of crystallization and

dissolution processes, specially these ones involved on the calcite-based systems. Calcite, an anhydrous calcium carbonate polymorph, is a major component of carbonate reservoir rocks. Its interaction with fluids is important in geological processes as biomineralization, CO₂ sequestration, and oil exploration and production. This thesis approaches the topic from a novel computational simulation perspective focusing on the hydrogen bond network analysis based on the graph theory. This approach will be adapted to the nanofluidics problems to systematically access the effects of confined interfaces through a layered analysis. The consequences of the water hydrogen bond topology on fluid dynamics will be further shown and discussed.

Within our study of confined interfaces, we are considering also the effect of fluids on the nanochannels properties. The complexity displayed by these systems may involves electronic and dynamics aspects occurring across size and time scales, as discussed in previous section. Within the computational simulation framework, an unified procedure is currently missing. In this context, the thesis aims to show that it is possible to model, characterize and predict such system properties from a computational simulation perspective, overcoming the scale limits through a multilevel approach. The potential of the introduced approach will be demonstrated in a case study involving the brine flow thorough a carbon nanotube.

In summary, this thesis address key features that permeates the porous media by exploring the physics of spatially confined interfaces through a original perspective within the molecular computer simulation framework. We aim to bring important results towards the understanding of the phenomena occurring in nanofluidics-based systems that are fundamental to propose control or manipulation mechanisms. Overall, the advances achieved in the thesis may provide useful information to the experimentalists seeking for the rational design of novel nanofluidics devices.

To better organize our ideas, the thesis is structured as follows:

- **Chapter 1-Introduction:** This chapter introduces the topic of the thesis, showing the motivation and goals to be achieved;
- **Chapter 2-Multilevel Molecular Simulations:** It summarizes the multilevel molecular simulations methods employed in this study. We emphasize the hydrogen bond network analysis that is extensively explored on this thesis;
- **Chapter 3-Multilevel Molecular Modeling Approach for Rational Design of Ionic Current Sensors for Nanofluidics:** In this chapter, we introduce a top-down multilevel approach, which combines molecular dynamics simulations with electronic and transport first principles calculations. The capability of this approach is demonstrated in a case study.
- **Chapter 4-Hydrogen Bond Network Under Confinement Environments: the Case of Calcite Slit Pores:** We investigated the structural properties of confined water within calcite slit pores ranging from 6 to 1 nm. This study was performed by combining molecular dynamics simulations with the layered analysis of the hydrogen bond network.
- **Chapter 5-Fresh Molecular Look at Calcite-Brine Nanoconfined Interfaces:** The previous study was extended to investigate the structure of solvent and ions at calcite-electrolyte aqueous solution. In this chapter, we provide new insights into the nanofluidics by relating the topology details of the hydrogen bond network with the dynamical properties exhibit in the spatially confined interface.
- **Chapter 6-Conclusions and Outlook:** The last chapter summarizes the conclusions and perspectives.

CHAPTER 2

MULTILEVEL MOLECULAR SIMULATIONS

This chapter describes the methodologies employed in our research. The first section introduces the reader to the concept of multilevel modeling, followed by a brief description of each single method. We emphasize the basis of the hydrogen bond network analysis at the end of this chapter, since it is a relatively novel methodology and it has been extensively employed through the studies that integrate the thesis.

2.1 Multilevel Modeling

Multiscale phenomena appear in several research areas. In meteorology, for instance, multilevel modeling is used to investigate global weather systems (fluids) displaying different spatial and temporal scales that produces local weather characteristics²³. The multilevel modeling is particularly important in materials science, since it allows the prediction of the systems properties based on knowledge of the relationships between the process and the structural features²¹.

The importance of multilevel models to investigate chemical systems was recognized with the Nobel Prize in the 2013. In that year, Karplus, Levitt and Warshel²⁴ were laureate due to the development of a multilevel model method using both classical and quantum mechanical theory. These methodologies were used to model large complex chemical systems and reactions. This method describes part of a large system using first principles, quantum chemical models for a central part of the system and how to link this part to a surrounding media, which is modeled using classical particles.

Several multilevel flavors were developed to investigate a broad range of systems and properties. Horstemeyer²⁵ presented a historical review of the different multilevel modeling approaches applied to various research areas^{26–29}. In addition, Steinhäuser²¹ provides an overview of some of the basics of the underlying physical theories, the mathematical concepts used for the computational multiscale modeling of fluids and solids through several length and associated time scales. Besides these known multilevel flavors, the field of multiscale problems is open for the development of novel approaches or applications. As common to all the approaches, the multilevel strategy requires a link element between the levels of resolution, cf. **Figure 2.1**, such as:

Figure 2.1: Schematic representation of a generic multilevel modeling approach applied to the water investigation.

- I) Potential energy surface (energy and forces);
- II) Structure (characteristic time and length scales);
- III) Environment (electrostatic, hydrodynamics, elastic, ...).

The exchange of information through the link element requires a high level of consistency between the individual models to reproduce the system properties as accurate as possible. New ways to combine these methodologies within the multilevel approach have been proposed to explore a broad range of properties. Considering previous published research experiences²¹, some strategies to link the levels of resolutions are:

- I) Sequential: the simulations models over different scales are considered separately by simply transfer information (linker) between distinct levels of resolution. The information exchange can be from top (coarse) to down (fine) and vice-versa³⁰;
- II) Hybrid: different levels of resolution are running simultaneously with a direct link between them^{24,31};
- III) Adaptive: switch between the resolution levels realized on the fly³².

In this thesis, we propose a new multilevel approach by combining classical molecular dynamics simulations with first principles electronic and transport calculations. It consists of an hierarchical top-down scheme applied to the nanofluidics problems. In such systems, it is mandatory to include explicitly the solvent, since the discrete nature of the fluids is essential to correctly describe the involved properties. Our multilevel approach treat different scales of the system separately, each one by the best corresponding methodology in a fully atomistic way. The different levels were combined in a sequential way, and linked through the representative atomic configurations, within the classical potential energy surface. The implementation details will be discussed in **Chapter 3**.

The theoretical background of each of methodologies belonging to our multilevel approach is already well established and a extensive review material can be found in the

literature^{33–35}. Thus, in the following sections, we will give a brief description of these methodologies within our multilevel approach.

2.2 Electronic Structure Level

2.2.1 Density Functional Theory

The quantum mechanics is the fundamental theory of nature at electronic scale. A typical quantum system is characterized by the wave function Φ . It is the solution of Schrodinger’s equation:

$$H\Phi = E\Phi, \quad (2.1)$$

where H is the Hamiltonian and E are the eigenvalues. The time independent Hamiltonian of interacting atoms is given by:

$$H = T_e + V_{e-e} + V_{e-n} + T_n + V_{n-n}, \quad (2.2)$$

where T_e is the electronic and T_n is the nuclei kinetic energy; V_{e-n} is the electron-nucleus; V_{e-e} is the electron-electron, and $\hat{V}_{n-n}$ is the nucleus-nucleus potential energy.

For a many body system represented by the Hamiltonian H (2.2), the equation (2.1) does not have an analytical solution. Nowadays, the density functional theory (DFT) is the most successful approach to investigate the properties of a given system at ground state. This methodology is supported by the Hohenberg and Kohn³⁶ theorems and the Kohn-Sham (KS) equations³⁷. The DFT describes the energetics of an interacting system via the electronic density instead the many-body wave function. For a given system with N electrons, it means that the basic variable — the density — depends only on the three spatial coordinates, rather than the $3N$ degrees of freedom of the wave function.

In practice, approximations are required to implement the theory, such as for the electronic exchange and correlation interactions E_{xc} . A typical approach is the local density approximation (LDA)³⁸. It considers the known exchange-correlation energy from the uniform homogeneous electron gas e_{xc}^{unif} at the same density $n[r]$ established inside each infinity volume element d^3r in the original system:

$$E_{xc}[n] = \int e_{xc}^{unif}(n[r])d^3r \quad (2.3)$$

The practical implementation of Kohn–Sham theory may display several flavors according to the choice of the basis set. Plane waves functions are a natural choice to describe delocalized electrons in solids with periodic boundary conditions. A rational choice of the basis set may decrease the computational cost. In the Siesta code^{39,40}, employed in our DFT calculations, the electronic states are represented in terms of a linear combination of localized atomic orbitals (LCAO)⁴¹. Whereas the plane waves approach uses a similar accuracy to describe the vacuum region as the region where the atoms are, the LCAO are centered in the atomic sites without need to extend the atomic orbitals in the vacuum region, which decreases the computational cost considerably.

The radial component of the atomic orbitals exhibits exponential decay away from the atomic nucleus in the form $e^{-\zeta r}$. The ζ controls the width of the orbital (large ζ gives a tight function, small ζ gives a diffuse function). A single- ζ basis set (SZ) has one single radial function per angular momentum channel. It offers quick calculations. However, the minimal basis set lack the flexibility to adjust to different molecular environments. In this context, the combination of multiple basis functions allows the electron density

Figure 2.2: Flow-chart depicting a generic DFT calculation in a self-consistent way.

to adjust its spatial extent to fit the particular molecular environment. A basis set in which there are multiple basis functions corresponding to each valence atomic orbital are called valence double, triple- ζ , and so on, basis sets. More sophisticated basis sets consider the polarization effects of atoms in the angular momentum. Polarized orbitals are constructed in Siesta code from perturbation theory. They are defined in such a way that there are not occupied orbitals with the same angular momentum l in the valence shell of the ground-state atomic configuration.

The computational cost related to solution of KS equations can be lowered by the pseudopotential technique⁴². Electrons in high energy levels (valence electrons) determine the chemical bonds and the electronic properties. Core electrons, near the nuclei, do not contribute directly to the electronic properties of the system. Thus, they are not considered explicitly within the DFT framework. Valence electrons interact with a lower potential (pseudopotential) due to the screening effect imposed by core electrons.

Within the DFT formalism, the integrals performed in real space are generally replaced by integrals over the (finite) first Brillouin zone in the reciprocal space. This is achieved by applying of Bloch⁴³'s theorem. Such integrals are performed by summing the function values of the integrand (for instance: the charge density) at a finite number of points in the Brillouin zone, called the k -point mesh. The k -mesh governs the fineness of the Brillouin zone sampling⁴⁰. In this context, some methods were developed to achieve an optimal grid sampling, such as the Monkhorst and Pack⁴⁴. In addition, a parameter regulating the basis set size is the mesh cut-off. Mesh cut-off is the highest energy of plane wave that can be represented with such grid. In a LCAO basis set, it is the equivalent the plane wave energy cut-off for the given k -mesh⁴⁰.

The Kohn-Sham equations are solved in a self-consistent way to reach the electronic configuration with the lowest energy at the ground state (seen **Figure 2.2**). An initial guess for the electronic density $n_0(r)$ is attributed to start the cycle, leading the calculation of the effective potential $v_{KS}(r)$, since $v_{KS}(r)$ is a functional of the electronic density $n(r)$. This potential plus the kinetic term constitute the Kohn-Sham Hamiltonian $\hat{H}_{KS}$. The electronic density is updated from the solution of KS equations. Output quantities such as energy, forces and charge can be extracted following the electronic density convergence³³.

Figure 2.3: (a) Schematic representation of a generic system setup for the electronic transport investigation as implemented in Transampa code. (b) Flow-chart depicting the self-consistently cycle of a typical electronic transport calculations with NEGF technique coupled to the DFT.

2.2.2 Non-Equilibrium Green's Functions

Electronic transport properties were investigated at electronic level through the Non-equilibrium Green's functions (NEGF) technique coupled to the DFT methodology. This approach was successfully implemented on the Transampa code^{45,46} by our research group. A schematic representation of a typical system for the ballistic electronic transport investigation is shown in **Figure 2.3(a)**. The system is constituted by semi-infinite periodic arrangement of cells — representing the metallic leads — with Hamiltonian H_{LL} and H_{RR} for the left and the right sides, respectively. Each cell is coupled with its two neighbors by the potential terms V_{LL} (V_{RR}) within the LCAO basis set. The central region H_{CC} — representing the scattering center — is coupled with left and right leads, where $(H_{LC(CR)})$ are the coupled terms.

In a typical transport system, the lack of a translational symmetry hinders the Bloch's⁴³ theorem application for the evaluation of the Kohn-Sham eigenstates in terms of the Bloch's wave functions. The NEGF⁴⁷ formalism is a successfully alternative for the DFT eigenvalue problem to evaluate the electronic density (see **Figure 2.3(b)**). In this context, the KS Hamiltonian is extracted from DFT calculation to build the Green's function. The electronic density updated $n(r)$ is achieved through the NEGF technique, following the self consistently cycle, as it is depicted in **Figure 2.3(b)**.

The transmittance is an essential output quantity extracted after the electronic density convergence in the NEGF framework for the open system⁴⁸. The transmittance function $T(E)$ at energy E is evaluated by means of the recursive Green's-function approach using a two-terminal device configuration with contacts represented by the semi-infinite and periodic ideal leads. It is given by:

$$T(E) = Tr \left[\Gamma_L G_S^\dagger \Gamma_R G_S \right], \text{ with } \Gamma_{L/R} = i \left(\Sigma_{L/R} - \Sigma_{L/R}^\dagger \right), \quad (2.4)$$

where G_S is the retarded Green's function for the scattering region⁴⁹, given by:

$$G_S[\epsilon^+ S_S - H_S - \Sigma_L - \Sigma_R]^{-1}. \quad (2.5)$$

In this expression, H_S is the Hamiltonian (and overlap matrix S_S) for the scattering region; $\Sigma_{L/R}$ stand for the self-energies coupling the scattering region to the left (L) and right (R) leads⁴⁹, while $\epsilon^+ = E + i\eta$, with $\eta \rightarrow 0$. The transmittance is interpreted as the probability that an electron with energy E has to ballistically cross the electronic transport system⁴⁸. In practice, the transmittance analysis may indicate changes in the system electronic structure when exposed to the a charge density perturbation. Such physical quantity can be related directly to the electronic current intensity. Within the Landauer-Büttiker formalism^{50,51}, the expression for the electric current intensity for the one-dimensional case⁵² is given by:

$$I = \frac{e^2}{h} \int_{-\infty}^{\infty} T(E) \left[f_{FD}(E - \mu_L) - f_{FD}(E - \mu_R) \right] dE, \quad (2.6)$$

where e is the elementary charge; h is the Planck's constant; $\mu_{L/R}$ are the leads chemical potentials; $f_{FD}(E)$ is the Fermi Dirac function.

2.3 Atomistic Level

2.3.1 Molecular Dynamics

Atomistic computer simulations within the classical molecular dynamics (MD) framework were performed in this thesis to investigate the structural and thermodynamic properties. MD simulations primarily consists of the numerical solution of the Newton's second law equation of motion for a N particles interacting system:

$$m_i \frac{d^2 \vec{r}_i}{dt^2} = - \sum_{j \neq i}^N \nabla_{\vec{r}_i} U(|\vec{r}_i - \vec{r}_j|), \quad i = 1, \dots, N, \quad (2.7)$$

where m_i is the particle mass, $\vec{r}_i$ is the position of each i particle and $U(|\vec{r}_i - \vec{r}_j|)$ is the potential energy for a given atomic configuration.

Forces are derived from the potential energy surface in the equation (2.7). The force field is the collection of consistently fitted parameters and functions describing the classical potential. Parameters adjusting such potential to a particular system are usually derived from first principles calculations or experimental data. Several works were addressed to determine the force field for a variety of systems aimed to reproduce its properties observed experimentally.

The class of potentials used in our research can be described by bonded and non-bonded terms. Bonded interactions are usually characterized by bond and/or angle dependent contributions⁵³. Such potential ensures the bond distance and/or angle equilibrium, where the potential energy is a minimum. In particular, the force fields that describe water molecules usually are bonded, and can either be rigid or flexible. The potential model employed for water molecules in in our research consists of a modified SPC model⁵⁴. It is described in detail in the **Appendix B.1** and **Appendix B.2**.

Additionally, non-bonded interactions between the chemical species are described in our study by pairwise interactions comprising of Coulomb and van der Waals terms⁵⁵. The last one displays long range dispersive and short range repulsive forces. The dispersive term is

Figure 2.4: a) Flow-chart depicting a generic MD simulation cycle. b) Simulation protocol employed in our studies.

due to the instantaneous dipoles, which arises during the fluctuations in the electron cloud. An instantaneous dipole in a molecule can induce charge rearrangements in neighboring atoms, giving rise to an attractive effect. At short internuclear distances, the potential energy increases due to the Pauli exclusion principle^{56,57}. A typical example of a van der Waals potential function is the Lennard-Jones potential⁵⁵, which is given by:

$$V(r_{ij}) = 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] \quad (2.8)$$

where $V(r_{ij})$ denotes the pairwise potential energy, as a function of the separation distance r_{ij} . In the Lennard-Jones potential, the attractive part varies as r_{ij}^{-6} and the repulsive part changes as r_{ij}^{-12} . The collision diameter σ_{ij} is the separation distance, where the V_{ij} energy is zero, whereas ϵ_{ij} is the well depth parameter. The resulting parameters for the interactions between different atom types are obtained from the mixture of the pure atoms values. In the Lorentz-Berthelot mixture rules⁵⁸, for instance, the collision diameter σ_{ij} for the $i - j$ interaction is equal to the arithmetic mean of the values for the two pure species. In addition, the well depth ϵ_{ij} is given by the geometric mean (see **Appendix B.1**).

Other typical contribution in the force field is the Coulomb potential used to describe the interaction between charged atoms. Due to the Coulomb potential, a particle interacts with all the other charged ones in the system. The calculation scales with N^2 , which quickly accumulates when N became large. To overcome this limitation, the potential displayed by remote particles is calculated in the reciprocal space through a Fourier transform in the particle-mesh methodology. The charge density resembles a Gaussian distribution, which can be solved through the Poisson equation (Ewald summation⁵⁹). In particular, the particle-particle-particle-mesh (PPPM)⁶⁰ is currently the most efficient methodology to calculate the Coulomb potential of N interacting particles, and it is also employed in our calculations. The PPPM approach divides the interacting particles in two sets. Then, it calculates the potential through a direct sum for particles that are closer. Then, it employs

the particle-mesh method for the other ones.

Time integration algorithms are required to solve the equation (2.7), *cf.* **Figure 2.4a**, to determine the atomic positions and velocities with respect to the time. Such algorithms are based on the finite difference methods, where time is discretized on a finite grid, with a infinitesimal time step, typically $\sim 10^{-15} s$. By iterating the procedure, the time evolution of the system can be followed for longer times. The Velocity Verlet⁶¹, used in our calculations, has the ability to accurately conserve the energy of the system. In addition, it is particularly advantageous for scaling calculations⁶², being it essential to simulate large systems across CPU (Central Processing Unit) and GPU (Graphics Processing Unit) computational resources.

Molecular dynamics simulations explore the time evolution properties of a system. Based on the ergodic hypothesis, the time averages are equivalent to ensemble averages. Then the time averages obtained in a MD simulation are equivalent to ensemble averages. It may be desirable to perform the simulations under some thermodynamic constraints, such as temperature and pressure. The two most common ensembles are the canonical (NVT) and isobaric-isothermal (NPT) ones. Typical molecular dynamics simulations under the NPT/NVT ensemble need a mechanism to control the temperature and pressure. The Nosé-Hoover method^{63,64} was extensively employed in our simulations. This method considers the heat bath (NPT or NVT) as an integral part of the system. Basically, this method adds to the energy function a fictitious degree of freedom s , which represents a heat bath. The thermal energy associated with s is $(3N + 1)k_B T \ln s$, where $3N + 1$ is the total number of degrees of freedom of the N particles, T is the temperature and k_B is the Boltzmann constant. The kinetic energy related to s is $Q(ds/dt)/2$, where Q plays the role of fictitious mass. With this approach, an extended system within the microcanonical ensemble includes the real system and a heat bath represented by s . As a consequence, the extended system produces a canonical ensemble in the real system because the energy exchange between the fictitious degree of freedom and the real system. The coupling between the two is controlled by Q . In this context, small Q leads to high frequency oscillations of energy coupled with s . In addition, in the limit of large Q , the microcanonical ensemble of the real system is retained.

To keep both the temperature and pressure constant during a MD simulation by mimicking a isothermal-isobaric ensemble, the volume of the simulation cell has to be controlled in addition to the temperature. Such response was produced in this thesis by the Nosé-Hoover barostat. In line with the integral thermostat one can introduce a new degree of freedom into the system, which controls volume fluctuations. It is achieved in the Nosé-Hoover approach by the introduction of a frictional coefficient, that evolves in time, to minimize the difference between the instantaneous pressure, and that one of an external reservoir. In analogy to basic thermostating, these fixes can also create a chain of thermostats coupled to the barostat variables. The barostat can be coupled to the overall box volume, or to individual dimensions. The equations of motion used are those of Shinoda et al.⁶⁵, which combine the hydrostatic equations Martyna et al.⁶⁶ with the strain energy proposed by Parrinello and Rahman⁶⁷.

Modeling of nanofluidics-based systems usually requires the evaluation of the properties averaged over a set of configurations of the solvent at thermodynamical equilibrium, for instance. It can be achieved following a simulation protocol for minimizing the molecular arrangement and equilibrate the system and subsequently production run, when the desired information is collected, *cf.* **Figure 2.4b**. The protocol details will be described in the next chapters. For each procedure stage, the resulting velocities, positions and the cell dimensions until the temperature (measured through the kinetic energy) and the pressure

are updated and taken as input to the Newtons' equation (2.7). The cycle shown in **Figure 2.4a** is repeated until a termination condition imposed by the chosen simulation time, usually within the nanoseconds scale.

Several structure and thermodynamic properties can be analyzed after or during the MD simulations (see **Figure 2.4a**). For instance, MD trajectories may provide useful guidelines for the derivation of dynamical properties, such as the NMR order parameters⁶⁸ and mean square displacement (MSD) described on **Appendix C**. Besides these features, the MD simulations are a powerful tool to evaluate structural properties, i.e. the radial pair distribution function (RPDF)⁶⁹, which describes how density varies as a function of distance from a reference particle. In this thesis, we focus on the hydrogen bond network analyzed over instantaneous geometric arrangements of water molecules extracted during the MD simulations.

2.3.2 Hydrogen Bond Network Analysis

An hydrogen bond (HB) is a directional intermolecular interaction operative in determining several fluid properties. It can be found in a vast number of chemical systems ranging from inorganic to biological⁷⁰. In spite of much work, many of the hydrogen-bonded system properties are still puzzling. In this short review, we highlight important aspects for the interpretation of our results taken from the the hydrogen bond network analysis based on the graph theory.

An hydrogen bond is understood as a type of interaction occurring when a hydrogen atom (H) — bonded to a strongly electronegative atom, such as O, F or N (X-H) — exists in the vicinity of another electronegative atom or molecule A (X-H $\cdots$ A). When an hydrogen atom of a molecule participates in the hydrogen bond, that molecule is called an hydrogen bond donor (D); conversely, the other molecule is known as an hydrogen bond acceptor (A) (see **Figure 2.5a**). In the perfect tetrahedral structuring, each water molecule can form two bonds as a donor and two as an acceptor (see **Figure 2.5b**). As highlighted by Urbic⁷¹, when two water molecules form an hydrogen bond, the charge redistribution occurs on both of them. In addition, the bond formation changes the feasibility of further hydrogen bonding in comparison to an individual water molecule⁷¹. According to these authors, the water molecule that donates the hydrogen atom in the hydrogen bond increases the electron density on oxygen. This leads to the hydrogen bond acceptance. In addition, the water molecule that accepts the hydrogen has reduced electron density on hydrogen atoms. It is beneficial for further donating of hydrogen atoms⁷². These electron density changes are the reason for the so-called cooperativity or anticooperativity in hydrogen bond formation in water hydrogen bond networks⁷³.

As a result, an hydrogen bond interaction may display potential energy values between ordinary dipole-dipole/dispersion forces (low) and true covalent or ionic bonds (high). Therefore, it can vary continually between 0.2 and 40 kcal/mol⁷⁴. In water, this quantity depends on several factors. It was shown that the strength of the hydrogen bond between two water molecules depends on the number of water molecules bonded to both water molecules and those on the second coordination shell⁷⁵. This occurs because hydrogen bonds do not normally occur as isolated entities, but form networks. Within these networks, hydrogen bond energies are not always additive⁷⁵. Other study showed that the introduction of ions to the local environment increases or decreases the HB strength depending on type of ion and to which water molecule the ion is bonded⁷¹. In addition, it has been shown through computer simulations that the HB strength in ice is greater than in liquid water^{76–78}, since the water molecules stay connected in optimal geometry, as shown in

Figure 2.5: a) Hydrogen bond geometric criteria, representing also the donor and acceptor molecules. b) Water ice Ih structure with tetrahedrally coordinated molecules in optimal geometry configuration, displaying two donor and two acceptor molecules. Figure adapted from <https://archive.cnx.org>.

Figure 2.5b.

As observed by Bondi⁷⁹, in the resulting $O - H \cdots O$ interaction, the intermolecular distance is shortened by around 1 Å compared to the sum of the van der Waals radii for the H and O atoms. This feature indicates there is a substantial overlap of electron orbitals. Furthermore, the authors argued that despite the charge transfer in the hydrogen bond¹, the interaction is dominantly electrostatic, which leads to a pronounced flexibility in the bond length and angle. Indeed, the total energy of an hydrogen bond (E_{tot}) may be split into electrostatics (E_{el}), polarization (E_{pol}), charge transfer (E_{ct}), dispersion (E_{disp}), and exchange repulsion (E_{er}) contributions. The distance and angular variation effects of these constituents are very different from each other. Specially, Bondi⁷⁹ identifies that the electrostatic term is directional and the long range largest term. The van der Waals force is also present, and in some specific interactions, the dispersion may contribute as much as the electrostatics term to the total bond energy. As argued by Coombes et al.⁸¹, purely electrostatic plus van der Waals models, as considered in our calculations, are indeed quite successful for describing hydrogen bonds occurring in water system, despite their simplicity.

In a set of hydrogen bonds between chemically identical groups, the shortest are not always the strongest. As observed by Huš and Urbic⁷⁵, the strongest hydrogen bonds are those ones closest to optimal geometry. Indeed, distances and angles may vary over a wide range even with a constant donor/acceptor combination⁷⁴. According to Steiner⁷⁴, the broad range can be a consequence of crystal-packing forces that affect each hydrogen bond in a different ways. The main structural features distinguishing the hydrogen bond from the purely van der Waals interaction is the preference for linearity in the interactions (160 to 180°)⁷⁴. These are the angles that occurs most frequently in ice crystals according to Steiner⁷⁴. The shortest distances occur at relatively linear angles, whereas longer bonds are observed with a larger angular range. In practice, a geometric criterion based on bond distance and orientation angle is considered to differentiate the bonded from the non-bonded interactions. Such definition was demonstrated to be equivalent to other

¹The amount of charge transferred is predicted to be about 0.5% of an electron in the dimmer, $\sim 1\%$ in clusters, and 2% in the crystal⁸⁰.

Figure 2.6: Potential energy surface resulting from the dimmer interaction. The Coulomb plus van der Waals potentials were considered in this calculations.

definitions based on energy¹⁷, for instance. Considering previous studies¹⁷, the more linear the hydrogen bond angle, the more defective the network is. However, according to Ozkanlar and Clark¹⁷, maximizing the number of waters participating in four hydrogen bonds by decreasing the angle between the molecules comes with the increase of those waters with five hydrogen bonds. To properly describe the water structure, it is necessary the equilibrium between the under and over coordination. Following Ozkanlar and Clark¹⁷'s studies, we considered an hydrogen bond whether two nearby water molecules satisfy two geometric criteria: 1) $r_{O...H}$ is less than 2.5 Å and simultaneously 2) the O-H...O angle is greater than $180^\circ > \theta > 150^\circ$ (see **Figure 2.5 a**). Such angular and bond distance yield an average total number of hydrogen bonds of 2.9, which is in excellent agreement with other results⁸². The **Figure 2.6** shows how the dimmer potential energy is related to the hydrogen bond angles and bond distances.

The hydrogen bond network evolves dynamically because of continuous dissociation and formation on time scales ranging from tens of femtoseconds to picoseconds. The thermal oscillations can influence the formation and break of hydrogen bonds¹⁷. The nearest neighbors with the reference water molecule have a residence time in the first solvation shell of a few picoseconds (1–7 ps)¹⁷. However, these nearest neighbor interactions generally exhibit an oscillatory behavior at short time scales, typically 10^{-15} s. According to Ozkanlar and Clark¹⁷, small angle perturbations to the orientation as a function of time indicate a predominance of librational motion that often temporarily breaks the hydrogen bond. The broken hydrogen bonds rapidly reforms often without exchange of hydrogen bonds partners. The average persistence of a single dimmer hydrogen bond in the network is predicted to be 120 fs⁸³.

There is a discussion in the literature about how water molecules are structured in liquid. Depending on which question to be asked, different models can emerge to explain the water properties⁸⁴. The conceptual views of water structure, drawn by experiments and computer simulations, have often been classified in mixture and continuum models^{76,85}. The mixture models conceive of liquid water as composed by two or more stable species

that differ in their hydrogen bonding configurations^{86–88}. Moreover, they predict the existence of intact and broken hydrogen bonds. In a two phase-mixture model, the d water is described considering water molecules being located in the caves of the ice lattice⁸⁵. In addition, the non-hydrogen-bonded species in these models are predicted to be much more mobile than the hydrogen bonded ones. In order to account for the fluidity of water, these models have to assume a considerable percentage of mobile non-hydrogen-bonded molecules⁸⁵. According to Krindel and Eliezer⁸⁵, the strength and the bending angles of the hydrogen bonds are considered as discrete quantities with energy values characteristic of each state. On the other hand, the continuum models do not distinguish different species, but conceive of the structure as a continuous distribution of geometries or large distortions about an average structure^{89–91}. According to Krindel and Eliezer⁸⁵, in the continuum models, the energy of the hydrogen bond is assumed to be a continuous and a smooth function of the bending angle. In addition, less-hydrogen bonded molecules are postulated to exist and over coordinated molecules are located in rather flexible structures.

As highlighted by Smith et al.⁷⁶, interpretations based on mixture models are typical in spectroscopic studies, whereas these mixture models are not supported by molecular dynamics simulations^{92,93} (see **Figure 2.7a-b**). With the development of experimental and computational techniques, both the continuum and the mixture models had been modified and improved continuously. According to Soper and Ricci⁹⁴, in the light of current experimental data, it is proposed, for instance, that liquid water consists of low density regions, where well-ordered, ice-like structure dominates, and denser regions, which have less ordered structure, mostly having interstitial/fifth water molecules. This model is an intermediate interpretation between the mixture and continuum conceptual views of water structure.

There are several experimental methods to measure physical quantities target to characterize the hydrogen bond structure. The calorimetry is a traditional method to measure temperatures and corresponding latent heats. From measurements of latent heat of vaporization, enthalpies of formation of hydrogen bond can be deduced⁹⁵. Calorimetric measurements are often used in conjunction with other methods, providing complementary data⁹⁵. Most modern experimental methods, such as optical spectroscopy, are based on interactions of these molecules with a electromagnetic wave that acts as a probe. The measurements can be based on the absorption or scattering. Geometrical quantities may be evaluated based on three basic methods: rotational spectroscopy, X-ray or neutron diffraction, and infra-red (IR) spectroscopy⁹⁵. Dynamic quantities such as spectroscopic constants are obtained from IR spectroscopy⁹⁶, which is the most sensitive and precise method to observe hydrogen bonds⁹⁵. Similarly, microwave spectroscopy appears to be a highly precise technique that conveys considerable of fundamental data on the geometry of hydrogen bond^{97,98}. In addition, nuclear magnetic resonance (NMR) spectroscopy has become a standard method to investigate hydrogen bonds in hydrogen bonded system^{99–101}, because its ultrahigh spectral resolution and the precisely known spin-spin interaction dependence on distances. The NMR spectroscopy is sensitive to the establishment of hydrogen bond, thus it is a indirect method that allows the observation of the hydrogen bonds in solution.

Computer simulations may provide crucial information about the hydrogen bond network. These investigations are in general based on the classical and *ab initio* molecular dynamics simulations, and also Monte Carlo. A growing trend in this research area is to integrate these methods with graph theory to access the hydrogen bond network details. Graph representations have a long history in chemistry^{102,103}. According to Grabowski¹⁰⁴, early implementations of graph theory in this scientific area were generally

Figure 2.7: Hydrogen bond angle and distance distributions displayed in liquid water by molecular dynamics simulations. This figure is obtained based on the geometric criteria depicted in **Figure 2.5(a)**. Such distribution, taken from molecular dynamics simulations, reveal the continuum conceptual water’s view.

associated with covalent bonds. Such approach was essential in that time to investigate a wide array of chemical phenomena, from general chemical reactivity of Markov chains in chemical catalysis and protein folding kinetics^{105,106}. However, according to Ozkanlar and Clark¹⁷, intermolecular chemical interactions defining the graph, such as displayed in water hydrogen bond network, have received insufficient consideration in spite of the fact that such interactions determine the physical properties of liquids. Indeed, water exhibits highly complex phenomena and this is attributed to the hydrogen bond network details.

The general organization of water molecules in a hydrogen bond structure has similarities to the networks found in computer science¹⁷. Contemporary graph network analyses theory have rapidly evolved in the the development of the world wide web (WWW) and cloud computing, for instance. Such progress allies to the identification of the similarity with the hydrogen bond structure has to come fruitful in recent studies that have investigated the local organization of water in bulk system under different temperatures¹⁷. It was achieved through the graph theory which was successfully implemented in the ChemNetworks code¹⁷ to analyze the hydrogen bond network. This methodology was also used to investigate the specific organization patterns of water about a solute, and it was shown to be an effective data-mining tool for understanding widely properties^{107,108}. In addition, the topologies of molecular clusters were used to understand the physical properties related to a specific topological motif, since the local hydrogen bond network is presumed to determine the structural and dynamical properties of fluids, according to Ozkanlar and Clark¹⁷. Furthermore, the hydrogen bond topologies displayed in other solvents were also

Figure 2.8: Schematic diagram of the workflow for ChemNetworks. Adapted from reference¹⁷.

investigated to understand intermolecular chemical networks formed between water and methanol¹⁰⁹.

As depicted in **Figure 2.8**, the ChemNetworks code first reads each individual water Cartesian coordinates and some input parameters that outline the rules associated with defining the intermolecular interactions that create hydrogen bonds between water molecules (or with other molecules). If periodic boundary conditions (PBC) are present, then these are also considered, hence that the hydrogen bond structure may cross the PBC boundaries. A list contained all pairs of molecules that share an hydrogen bond is created. The entire hydrogen bond network of the simulated water is then converted into a graph object $G(V, E)$, wherein the oxygen atoms are vertices/nodes (V) and the intermolecular hydrogen bonds between water molecules are edges (E) (see **Figure 2.9a**).

A series of topological analysis can be performed based on the graph construction. This analysis covers the degree (**Figure 2.9a**), geodesic path length (**Figure 2.9b**) and also geometric patterns (see **Appendix A**). The primary graph-theoretical analyses include determination of each vertex degree within every network/graph available, e.g., each snapshot of statistical data with molecular coordinates. In graph theory terminology, the degree of a vertex is merely a count of the number of connections to that vertex. A possible degree analysis is count the number of edges per vertex, producing a histogram of the edge distribution, similarly to shown in **Figure 2.10(a)**. In the water network context, degree is equivalent to the number of hydrogen bonds per molecule as shown in **Figure 2.10(b)**.

According to Ozkanlar and Clark¹⁷, the average of the edge distribution is essentially equivalent to the integrated radial pair distribution function (RPDF) between the atoms that defines the intermolecular interaction within the graph. The authors argue that the degree distribution can be chemically important because it deconstructs the PDF into its different intrinsic components. Thus, if the average number of hydrogen bonds are modified due to an external factor, such as the addition of ions as depicting in **Figure 2.10(a)**, the changes in the degree distribution will indicate the perturbations with respect to the bulk-phase, for instance. The water degree distribution can be grouped in molecules with

Figure 2.9: a) Graph vertices (V) and edges (E) representation above a set of water molecules. Each edge represent an hydrogen bond. The number of edges is the coordination number of each water molecule. The vertices represent each Oxygen atom. b) Geodesic representation of an hydrogen bond network structure. Lines represent edges. The red line between A and B vertices is the shortest contiguous path of edges between A and B vertices (geodesic).

less than four hydrogen bonds (under coordinated), exactly four hydrogen bonds, and more than four bonds (over coordinated). The results obtained by Ozkanlar and Clark¹⁷ revealed that in bulk water at 300 K and 1 atm, the most common number of hydrogen bonds for any given water molecule is three (38.53%), with 27.27% participating in four bonds, followed by 24.4% having two hydrogen bonds. In addition, the minority of species has only one hydrogen bond (7.30%), whereas only 0.90 and 1.60% have zero and five, hydrogen bonds, respectively. Similar distribution was obtained with the SPC/Fw water model, widely employed in our calculations (see **Figure 2.10(a)**). In general, it is observed that the concentration of waters of each degree dynamically fluctuates but it is overall constant over the time¹⁷. This is a clear indicator of the equilibrated nature of the simulation data. In addition, Ozkanlar and Clark¹⁷ observed that the definition used follows very nicely the trends in the RPDFs as a function of temperature, wherein an increase in the number of degree of four waters is observed with decreasing temperature. The authors used to exemplify the population of waters with four hydrogen bonds, which increases from 24.20 to 31.20% as water is cooled from 307.7 to 278.1 K.

The knowledge of the degree distribution is important, for instance, to the interpretation of differential x-ray experiments at room temperature^{110–113}. Although the first-neighbor shell in water is expected to be tetrahedral, there are significant local defects where the coordination is either greater or less than four. Energetically accessible, local defects are necessary to describe the flow processes of liquid water¹¹⁴. In special, the fifth-coordinated water has an important interpretation in the water dynamics analysis. According to Sciortino et al.¹¹², if the mobility of the liquid was related to the local density, then one would expect the molecular mobility to increase as the density decreases. Instead, the authors observed the opposite trend: lowering the density by 10% decreases the diffusivity by a factor of two at 273 K. Furthermore, the authors observed significantly higher mobility for molecules with more than four neighbors. Therefore, the molecular mobility is enhanced in the presence of extra molecules in the first coordination shell. The authors argue that the extra molecule in the first coordination shell lowers the energy barriers for translational as well as rotational motion. In addition, the authors argue that the faster dynamics

are not necessary due to a weaker local bonding, but to a progressive reduction of the tetrahedral symmetry of the local minima in the potential-energy surface. Thus the extra molecule can enhance the restructuring of the typical hydrogen bond network when the thermal energy is much smaller than the hydrogen bond energy. The creation of increased mobility by increasing the (global) density is the well known anomalous motional behavior of water under compression¹¹⁵. Such kind of hydrogen bond can also help to explain the Mpemba effect¹¹⁶. Tao et al.¹¹⁷ explain that in warm water, the weaker hydrogen bonds with predominantly electrostatic contributions are broken, accelerating the nucleation process that leads to the hexagonal lattice of solid ice. As a consequence, warm water freezes faster than cold water.

Indeed, the hydrogen bond strength has a dependence on the local environment, where the presence of additional molecules considerably changes the potential between two molecules. Such behavior is clearer explained by Huš and Urbic⁷⁵, who have shown that the introduction of additional water molecules to the local environment linearly increases or decreases the hydrogen bond strength E_{HB} for ~ 0.7 kcal/mol per added molecule according to the equation:

$$E_{HB} = A + nB \quad (2.9)$$

where, A is the dimmer hydrogen bond energy, B is the hydrogen bond strength variation. The variable n describes the number of water molecules in the local environment and it is defined as $n = n_{AA} + n_{DD} - n_{DA} - n_{AD}$. The authors used the indices AA and DD to denote donor molecule in the environment bonded to a donor molecule in the dimmer; or acceptor molecule in the environment bonded to the acceptor molecule in the dimmer, respectively (cooperative effect). Indices AD and DA were used to designate the opposite relationship, *i.e.*, donors in the environment bonded to the acceptors in the dimmer and vice versa (anti-cooperative effect). The same authors explain that whether bond strength is increased or decreased depends on the donor or acceptor nature of the newly formed hydrogen bonds with the local environment. Furthermore, changes on the second coordination shell were found in that work to influence the hydrogen bond strength for about a third as much as on the first shell, while not impacting its length. Huš and Urbic⁷⁵ conclude that the hydrogen bond strength can vary for as much as 90% between extreme cases of cooperativity and anti-cooperativity nature of hydrogen bonding⁷⁵.

Under coordinated water molecules refer to those ones with fewer than the ideal four neighbors as in the bulk of water. They can be found at the edges of the hydrogen-bonded networks such as snowflakes, hydration shells, surface water, ice nanocrystals¹¹⁸, and ice surfaces^{119,120}. As argued by Buch¹¹⁹, this kind of hydrogen bonds is even more fascinating and, at the same time, the less known than those ones that are fully coordinated in the bulk. According to Huang et al.¹²¹, molecular under coordination may modify the local charge structuring¹²², may influence the binding energy¹²³, and non bonding electron polarization¹²⁴. Furthermore, the authors shown that molecular under coordination shortens and stiffens the H-O bond spontaneously, which extends and softens the $O \cdots H$ interactions through Coulomb repulsion¹²⁵. These systems of under coordinated molecular dominance have important physical, chemical, and biological effects, because molecular under coordination induced unusual bond behaviors¹²¹.

Even away from the surface, on average, molecules in liquid water appear to engage fewer tetrahedrally hydrogen bonds than in ice. However, such uncoordination is not really interpreted as a true dangling bond in several studies¹²⁶. The liquid's flow properties are governed by intermolecular fluctuations on femtoseconds time scales and hydrogen bonding rearrangements on ps time scale. According to Eaves et al.¹²⁶, the interpretation of many experiments and MD simulations used the concept of non-hydrogen-bond (NHB) as broken

Figure 2.10: (a) Degree distribution comparison between pure water and brine at same thermodynamic conditions. The salt ions may reduce the coordination of water molecules by substituting the hydrogen bonds by ionic interactions. (b) possible configurations of water molecules in five different coordinations.

or dangling hydrogen bonds. The NHBs do not satisfy exactly the geometric criteria for a HB but they are in the surrounding environment, influencing the electrical potential. The authors shown that NHB molecules are unstable species that appear transiently during natural fluctuations about an hydrogen bond or when molecules trade hydrogen-bonding partners. From this perspective, experimental works¹²⁶ show that the vast majority of non-hydrogen-bonded configurations return to hydrogen bonds on the time scale of water's fastest intermolecular motions (fs), suggesting that water's structure is more ordered than instantaneous measures suggest. Eaves et al.¹²⁶ argue that these results support a picture where NHB configurations are only visited transiently during large fluctuations about a hydrogen bond or during the switching of hydrogen bonding partners. In addition, the authors argue that NHB model is not consistent with the presence of stabilized dangling hydrogen bonds or a conceptual picture of water as a mixture of environments (mixture model)¹²⁷. This interpretation is confronted by other models displaying, for instance, chain structures with two strong hydrogen bonds, one donating and one accepting¹²⁸. Such structure is described by Wernet et al.¹²⁸ as formed by molecules arranged in strongly hydrogen bonded chains or rings embedded in a disordered cluster network connected mainly by weak hydrogen bonds¹²⁸. In this case, dangling hydrogen bonds could be presumably strongly bind foreign or native species, being chemical active sites.

A secondary graph theoretical analysis performed with the ChemNetworks involves the determination of the geodesic for each set of vertices present in the system. A geodesic in graph theory is the shortest edge path between two vertices. If the network is composed of hydrogen bonds, the geodesic represents the shortest contiguous hydrogen bond path between every pair of vertices. Such information is desirable in the world wide web to increase the connection velocity between two servers, for instance. A similar problem is faced by the Google PageRank algorithm to rank the giant number of websites by a search engine. The graph structure in an hydrogen bonded system displays numerous branch points along edge paths and multiple paths existing between sets of vertices¹⁷, similar to the world wide web problem. The geodesic path analysis can reveal the water branched structure and the distortion induced by the environment, as shown in **Figure 2.11(a)** and **Figure 2.11(b)**. In addition, the analysis of the geodesic path length distribution

Figure 2.11: (a) Geodesic path distribution comparison between bulk brine and pure water. (b) Schematic representation of the graph network displayed by an hydrogen bond structure in pure water and brine. Circles (vertices) represent the water molecules, while the lines (edges) represent hydrogen bonds. Geodesic (blue blurred line) is the shortest continuous path displayed between two spatially separated vertices (A and B). The path length increase in brine with respect to the pure water relies on the network discontinuity imposed by the ions.

provides informations about the system interconnectivity and enable a global view over the network topology (see **Figure 2.9b**). To perform this analysis, the ChemNetworks code converts the N system edges into the adjacency matrix $N \times N$ with elements a_{ij} being 1 or 0, according to whether or not there exist an edge between i and j vertices. Geodesic¹²⁹ path is calculated via the Floyd-Warshall algorithm^{130,131}, widely employed in such analysis.

More insight about the hydrogen bond network can be achieved through the search of geometric patterns with the ChemNetworks. There has been historically a strong interest in the presence of cyclic oligomers, and water hexamers (the bag, boat, book, cage, chair, prism, prism book, and ring configurations) in liquid water (see **Appendix A**). ChemNetworks can perform direct structural search of specific organizational patterns. The code has incorporated geometric criteria to identify these structures allowing for thermally induced angular deformations. According to Ozkanlar and Clark¹⁷, the algorithm for cyclic trimers search, for instance, first checks whether a water i is hydrogen bonded to water j . Then, it checks whether water j is hydrogen bonded to water k . If this water is hydrogen bonded to water i , then for this set of waters, it checks whether structure satisfies the vertex angle criteria set for a cyclic trimer. The set of waters that satisfies these criteria are identified as cyclic water trimers formed in the liquid. This procedure is extended to search for cyclic tetramer, pentamer, and hexamer oligomers. As the temperature decreases, the population and persistence of the geometric patterns increase, and some of them are predominated. As shown by Ozkanlar and Clark¹⁷, at 278.1 K, the square tetramer predominated with 58% of frames, followed by the boat conformation 36%, the hexamer chair (27%), the cyclic pentamer (23%), and the hexamer bag (10%).

The geometric patterns represent water clusters which can have a large number of water molecules on their periphery (see **Appendix A**). A cluster is an aggregate of molecules that are held together by hydrogen bonding network. It is intermediate in size between a molecule and a bulk solid¹³², often exhibiting quite different properties from the corresponding bulk phase¹³³. Clusters have received special attention due to their size-dependent chemical-physical properties and their geometric stability¹³⁴. The cluster investigation relies within a water model which establishes a dynamic hydrogen bond

network, in which both the number and the strength of the hydrogen bonds fluctuate continuously¹³⁵ (continuum model). The realization that water display itself as clusters may help explain many anomalous water characteristics such as its highly unusual density temperature dependence¹³². According to Chaplin¹³⁶, the clusters are resulting from the competition between maximizing van der Waals interactions (leading for higher orientation entropy, denser and individually weaker but more numerous water-water binding energies) and maximizing hydrogen bonding (leading for more ordered structuring, lower density, and fewer but stronger water-water binding energies)¹³². Thus, both of the number and orientation of HBs are seen to determine the energetics and stability of water clusters. Chaplin¹³⁶ also shows that the clusters can interchange between lower and denser forms by bending, but not breaking, some of the hydrogen bonds¹³⁶. Furthermore, structuring may also flicker between statistically and topographically equivalent clusters but involving different molecules by shifting their cluster centers¹³⁶. In addition, cluster formation and their lifetime are both increased due to the highly cooperative nature of hydrogen bonding displayed in this kind of systems¹³⁷. Water clusters play on the stabilization of certain supramolecular structures¹³⁸. Its study is also important to understand hydration phenomena at molecular level, since it contain cavities are capable of enclosing small solutes^{139–141}.

The stability of water clusters is predominantly governed by the total number of HBs present in the cluster. According to Gadre et al.¹³², for clusters having two-dimensional patterns, structures with maximum number of HBs generated from donor-acceptor (DA) arrangements of water molecules are energetically more stable. The authors conclude that the cyclic isomers (**Appendix A**) up to pentamers are energetically more favorable than their acyclic analogues. Prism clusters were predicted to be the lowest energy isomer, followed by cage, book, and cyclic isomers¹³³. The water hexamer holds a special place in the experimental and theoretical studies of water because it is the smallest water cluster in which the monomers form a fully three-dimensional structure¹³⁴. Furthermore, it represents the transition from monocyclic two-dimensional to multicyclic three-dimensional structure. According to Wang et al.¹⁴², the hexamer has thus been referred to as the “smallest drop of water”, serving as the prototypical system to understand the molecular structure and dynamics of the water hydrogen-bond network in the bulk phases¹⁴². The authors justify because of the strong directionality of the hydrogen bonds, the hexamer exhibits several low-lying isomeric forms whose structure and energetics have been the subject of extensive investigations¹⁴².

The population of clusters in the water is not constant but there can exist several factors influencing it. Wang et al.¹⁴² shown that the population of the cage isomer increases relative to the prism population as the temperature increases, with the population of the book isomer (**Appendix A**) remaining very small up to 60 K. In addition, the same authors shown that at higher temperature the book population raises and eventually becomes dominant above 150 K. The same authors argue that the temperature dependence of the isomer populations is mainly determined by the competition between energetic and entropic effects, with the latter favoring the book structure over the cage structure, and the cage structure over the prism structure. It occurs, since compact structures are preferred at low temperature. However, as temperature increases, the high entropy associated with the HB networks leads to more open structures. In addition, the authors shown that, in general, compact structures were energetically more favored¹³². In this context, the structure comprising of cyclic tetramers was found to be the most stable one.

2.4 Summary

In this chapter, we described the theoretical background of the methods belonging to our multilevel approach at molecular level: DFT, MD and NEGF. Finally, we reviewed the main studies related to water hydrogen bond structure. This review is important to understand the results obtained from the hydrogen bond network analysis based on the graph theory. It is a relatively novel methodology and it is extensively employed throughout the thesis. This methodology was implemented in the ChemNetworks code by Ozkanlar and Clark¹⁷. The code is a multipurpose tool for performing topological analyses of chemical networks defined by intermolecular interactions. Subsequent analyses include degree census, geodesics, and direct structural searches of specific network patterns. These properties can help to understand the network patterns and organization that may influence the fluid physical properties. It can be used to understand a very large range of chemical systems that include complex solutions, liquid interfaces, self-assemblies, or pure liquids undergoing phase changes.

CHAPTER 3

MULTILEVEL MOLECULAR MODELING APPROACH FOR RATIONAL DESIGN OF IONIC CURRENT SENSORS FOR NANOFLUIDICS

3.1 Introduction

Devices based on field effect were proposed to control and/or select the transport of biological and chemical species through microchannels⁷. Typical devices can be briefly described as composed by electronic transport channels, within a broad range of materials and sizes, designed to modify an input signal. Another interesting application in the transport perspective is the channels or pores for atomic/molecular manipulation. This functionality is expected to be refined in downsize scales, and it is currently explored for nanofluidics. In particular, nanofluidic devices can handle the sensing of small amounts of atoms/molecules¹⁴³, where the mass transport may influence the electronic transport at solid/liquid interface. The detection of a single atom/molecule is necessary in several applications for the lab-on-a-chip technology, such as: drug delivery, discovery and rapid diagnosis⁸. Nanofluidics systems are suitable for a single atom/molecule detection because of the confining scale involved, similar to those of molecules and in some cases even allowing single-atom channels.

In this context, carbon nanotubes¹⁴⁴ (CNTs) are promising candidates for applications, such as: field effect transistors^{145,146}, gas sensors¹⁴⁷ and nanofluidics devices^{148,149}. Ballistic transport and high current density^{150,151} are key features of CNTs for electronic transport applications. The CNT tailored endings and hydrophobic character lead to ultrafast transport of water with minimal friction^{4,152,153}. Water molecules can flow through CNTs at a rate 4–5 orders of magnitude faster than predicted by macroscopic hydrodynamics¹⁵⁴. In addition, the conductivity of CNTs is highly susceptible to changes in charge states in contact with chemical species¹⁴³. Moreover, it is expected that the high Surface-area-to-volume ratio increases their sensitivity.

The potential of CNTs in nanofluidics to separate the solute from solvent was explored in desalination applications⁶. In pressure-drive experiments, the sodium ion retention was high (99 %) in the (6,6) CNT^{155,156}. In addition, a nanopore-based platform formed by single-walled carbon nanotubes was used to demonstrate the detection of single ions crossing the tube¹⁵⁷ through measurements of ionic current traces^{157–159}. Bushmaker et al.¹⁴³ reported on the extreme sensitivity of nanoelectronic devices to single gaseous ion (N_2^+) adsorption, which was attributed to single-ion-induced charge depletion because of the significant electron transfer due to the adsorbed ion. The ability to actively detect and manipulate single ions in solution may favor several processes as the chemical synthesis and catalysis. In this context, some experimental studies were addressed to the ionic current control^{158,159}. This capability was achieved through the external electrical field and it is similar to the electrical current control in three-state field effect transistors¹⁰.

The operating principle of CNT-based sensors consists of inducing a modulation on the electrical conductivity due to charge exchange by the adsorption of chemical species, which leads to an output signal^{160,161}. Both semiconducting and metallic CNTs exhibit inherent change in the electrical conductance when exposed to certain chemical species¹⁶². As an advantage, the selection of metallic or semiconducting carbon nanotubes for sensing applications is nonessential¹⁶³. Although, free electrons in metallic nanotubes favor the charge exchange, improving the device sensitivity.

For a rational design of nanofluidic devices, a computational methodology is highly desirable. However, the emergent phenomena on these nanodevices occurs across size and time scales, where the mass flow may influence the electronic transport. This imposes several challenges from the computational perspective, where usually each method deals only with a specific scale. From the best of our knowledge, there is no single methodology capable of capturing all the complexity of these ionic and electronic transport phenomena at nanoscale. The best strategy could be to combine the methodologies within a multilevel scheme by linking the constitutive laws and physical properties through the distinct resolution levels.

In this work, we introduce a top-down multilevel approach which combines molecular dynamics simulations (MD) with electronic and transport first-principles calculations. The capability of this approach was demonstrated in a case study, where electrolyte we were able to properly investigate the aqueous solution flow inside a (6,6) CNT (see **Appendix D.1**) and the consequences on the electronic transport properties. Signatures of partially hydrated Na, Li, and Cl atoms observed on the CNT conductance revealed the potential of this system for single atom/molecule detection. This developed approach may lead to a rational design of novel nanofluidic devices.

3.2 Methodology

3.2.1 Top-Down Multilevel Approach

To model and characterize a system with potential in sensing applications, we propose a multilevel computational approach, ranging from molecular dynamics to quantum mechanics calculations. This approach imposes a high level of consistency between the methodologies to reproduce the system properties as accurate as possible over successive scales.

In the top-down approach depicted in **Figure 3.1**, we take the advantage of classical molecular dynamics simulations to handle the characteristic time and size at nanoscale and first-principles calculations for electronic and transport properties. Such a strategy requires exchange of information between the models through a link element. The connection was

Figure 3.1: Illustration of the investigated systems organized in a schematic representation of our top-down multilevel approach. We start our modeling with molecular dynamics simulations (MD) to provide representative instantaneous atomic configurations to input for successive calculations based on quantum mechanics at the electronic level. Calculations based on DFT provided the electronic structure details. The charge density difference plot (blue isosurface) suggests the electronic level of these calculations by showing the charge rearrangements resulting from the interaction between the partially hydrated ion with the CNT. The system setup at the bottom of the figure consists of a scattering region and two leads of pristine CNTs. The scattering region is represented by a CNT portion filled by a partially hydrated ion.

achieved by taking a set of snapshots obtained from the classical molecular dynamics, for a given thermodynamic condition. At the electronic level, these representative atomic configurations, within the classical potential energy surface, are passed into first-principles calculations for the electronic and further transport properties characterization.

3.2.2 Simulation Details

The case study system is composed by graphene layers, a carbon nanotube and the electrolyte aqueous solution (see **Figure 3.1**), with 59096 atoms in total. In our device model, the graphene layers are the reservoir walls and they saturate the dangling bonds at the CNT terminations¹⁶⁴. Covalent bonds between graphene layers and single-walled carbon nanotubes were already observed experimentally during the growth stage¹⁶⁵. The (6,6) CNT is the nanofluidics channel; its narrow diameter (0.8 nm) imposes a strong reduction of the ionic coordination number, favoring the interaction between the ions and the CNT inner surface. According to Beu¹⁶⁶, the more probable paths taken by the ions during their passages through larger CNT channels, i.e., (8,8), (10,10), are located in the pore center. Thus, the fully hydrated ions are expected to not influence the CNT electronic transport properties with the same intensity observed in the (6,6) nanochannels.

Water molecules were added randomly within the reservoir at a density of 1 g/cm³ with PACKMOL¹⁶⁷. Then, the initial positions were further optimized by the conjugate gradient algorithm by minimizing the forces and energy. The water+ions solution was generated by replacing water molecules by ions. Two electrolyte aqueous solutions were studied separately (LiCl at 4.9 wt % and NaCl at 6.7 wt %) therefore, leading to a comparative study about the effect of different kinds of ions on the CNT conductance.

The procedure adopted in each stage of our top-down multilevel approach is as follows:

I) MD: Molecular dynamics simulations were performed by using the Large Atomic Molecular Massively Parallel Simulator (LAMMPS) package¹⁶⁸ resulting in a total computational cost of $\sim 10^4$ core-hour¹. The water molecules are represented by a flexible potential (SPC/FH), which is known to improve the description under confinement¹⁶⁹. The classical potential for the carbon nanotube was taken from Walther et al.¹⁷⁰, and for the ions from refs¹⁷¹ and¹⁷² (**Appendix B.1** has more details about the force field). The non-bonded interactions between atoms were described by Coulomb and Lennard-Jones potential with arithmetic mixing rule. The long range electrostatic interactions were solved by PPPM⁶⁰ method. All simulations were carried out with periodic boundary conditions. The carbon atomic positions were kept “frozen” to simulate the reservoir walls and avoid spurious lattice deformations in the suspended nanotube. The production run was performed during 25 ns with a time step of 0.5 fs in NPT ensemble. We employed a Nosé-Hoover thermostat^{63,64} and barostat¹⁷³ for the temperature and pressure controlling, respectively, with a target of 300 K and 1 atm for the whole system. For $N = 59096$ atoms of the system, $N_C = 10198$ are frozen carbon atoms. Thus, the corrected temperature for the brine is given by $T = 300N/(N - N_C)$, yielding $T = 362\text{K}$, as it was observed in the simulations. An electric field with 0.4 V/Å intensity was applied on the axial direction to obtain the ionic flow within CNT channel.

II) DFT: First principles calculations based on the density functional theory (DFT)³⁶, as implemented in Siesta code³⁹, were carried out to investigate the energetic and electronic properties. Norm-conserving pseudopotentials¹⁷⁴ were adopted to describe the electron-core interaction and the exchange and correlation interactions were represented by the local density approximation functional (LDA). The LDA was employed in previous studies^{175–177} involving adatoms in graphene-based systems and it gives reasonable energetics¹⁷⁸. Localized atomic orbitals with an energy cutoff of 400 Ry and double-zeta polarized (DZP) designed the basis set¹⁷⁹. The possibility of a magnetic ordering was investigated considering the spin polarization. The Brillouin zone was sampled by using a Monkhorst and Pack⁴⁴ scheme, with equivalent of 36 k-points in the 1D Brillouin

¹Intel Xeon CPU E5-2697 v2 @ 2.7 GHz CPU

zone of the CNT primitive unit cell. We added 40 Å of empty slab in the directions perpendicular to the nanotube axis to avoid interactions between periodic images. The resulting computational cost expended to evaluate the electronic properties of the related systems is estimated to be $\sim 10^4$ core-hour² per snapshot.

III) NEGF: In order to investigate the CNT electronic transport properties, we have not considered the reservoir atoms. This is justified because one can imagine the leads located at the nanotube, and not at the reservoir. Thus, only the CNT part of the system is taken into account. Under such consideration, we were able to reduce the number of atoms from tens of thousands (60k) to hundreds (around 800). Although, the number of atoms is two orders of magnitude lower, the computational cost of the *ab initio* simulations is still much higher, as all the electrons of the system (thousands) are taken into account in a many-body fashion. We estimated a computational cost reaching $\sim 10^5$ core-hour³ per snapshot for this stage. The MD calculations were computationally around 10^1 times cheaper than first principles, which in turn was 10^1 times faster than NEGF. A typical system setup for the electronic transport investigation consists of a central scattering region connected to left and right semi-infinite metallic contacts (see **Figure 3.1**). Four and thirteen pristine CNT unit cells are taken for the leads and the scattering parts, respectively. The last one includes buffer regions inserted in order to ensure a good screening, thus avoiding perturbations on the leads Hartree potential. The electronic transport properties were calculated with the DFT³⁶ methodology coupled to the NEGF technique as implemented in Transampa code⁴⁵. The charge density was converged under self-consistent cycles and, after that, the transmittance was calculated for 256 points along a 4 eV energy window around the Fermi level.

3.3 Results and Discussion

3.3.1 Pure Water Inside CNT

We explored the effects of the pure water adsorption on the inner CNT surface, in order to isolate the specific contributions on the CNT electronic properties. According to our observations, the water molecules inside the (6,6) CNT resembles a one dimensional chain with each water molecule forming two hydrogen bonds on average⁴ (see **Figure 3.2a-b**). This is in agreement with previous studies, also based on molecular dynamics simulations¹⁸⁰. Additionally, other studies showed that only 40% of the lost energy due to dehydration is recovered through nonbonded interactions with the carbon atoms¹⁵². As a result, the hydrogen bonds between water molecules inside the tube have a lifetime near to six times greater than observed in bulk water⁴. Despite the strong interaction, water molecules can rotate freely around their aligned hydrogen bonds⁴.

The effect of the water line on CNT electronic properties was investigated here taking into account the translational symmetry, therefore, mimicking an infinite nanotube. As usual, it is necessary to have a match between the length of the water line and the carbon nanotube lattice parameter. To evaluate the water periodicity within the CNT, we calculated the axial distribution function¹⁸¹ $a(z)$. This quantity relates the number of molecules, and the cylindrical volume element, with differential width dz and diameter $D = 0.8$ nm, that constrains those water molecules at axial distance z . $a(z)$ is defined in such a way that $\int_{z=0}^{z=\pm L} a(z) \frac{\pi D^2}{4} dz = N_t - 1 \simeq N_t$, where N_t is the number of water

²AMD Opteron 6376 @ 2.1 GHz CPU

³With Blue Gene/Q machine with IBM PowerPC A2 @ 1.6 GHz CPU

Figure 3.2: a) Side and b) front views of the water line inside the carbon nanotube system. c) Axial pair distribution function. d) Electronic band structure comparison between bulk CNT and filled with water.

molecules between $z = \pm L$. In **Figure 3.2c** we show the $a(z)$ curve for $L = 2$ nm. With 12 water molecules and 13 CNT unit cells, there is a periodic structure with 0.8% lattice mismatch. This relation was found to be an optimal composition with a reasonable number of atoms. As a result, we observed that the band structure around the Fermi level (± 2 eV) remains with the same distribution in comparison to the pristine CNT (**Figure 3.2d**). This occurs because the interaction between water and the carbon nanotube reveals weak binding energy and small charge transfer¹⁸², leading to its insensitivity to H_2O exposure¹⁸³. As the water presence does not influence the band structure, we can infer that the electronic transport will also not be affected. Thus, it is reasonable to suppress the water molecules on the electrodes, simplifying these costly simulations.

3.3.2 Electrolyte Aqueous Solution Into (6,6) CNT

Based on MD simulations, we observed that ions follow the electric field direction, with positive and negative charges displacing in opposite order. We noticed the absence of more than one ion inside the tube simultaneously in the whole simulation run, being ideal to single atom/molecule sensing applications. Furthermore, the orientation of the confined water molecules is driven by the ionic character of the ions with hydrogen atoms pointing toward the anions, while oxygen atoms point toward the cations. The one-dimensional water chain is broken due to the diffusion of the ions. Thus, the number of water molecules is increased in the front and reduced in the back of the atom crossing the tube. All investigated ions are partially dehydrated inside the tube, thus they can interact directly with the inner CNT surface (**Appendix D** has more details about the effect of single ion interactions with the CNT wall).

We take a sample of 10 snapshots to evaluate consistently the effect of the electrolyte aqueous solution on the CNT electronic properties by DFT calculations. In the supercell, we include 13 nanotube primitive cells in order to minimize the interaction between the adsorbed atoms (Na, Cl, Li) in the neighboring cells. The size of the supercell is large enough to include water molecules belonging to, at least, the third hydration layer formed

Figure 3.3: Energy band structure comparison between pristine CNT (gray dashed line) and one that is exposed to Li a), Na b) and Cl c) partially hydrated atoms inside the tube. Broader color regions delimit the broadest deviations around the average (black lines) band structure calculated over the sample. In the Cl case, the variations are so large because the Cl molecular level fluctuations are in the plotted energy window. These fluctuations were attributed to the variable potential well, probably resulting from the Cl variable proximity with the water molecules within the CNT.

around the ions in the CNT axis direction. We observed the hydration loss in the radial direction of the atoms crossing the tube is compensated by rearrangements in the CNT electronic structure with significant charge exchange ($\simeq \pm 1.0e$), as noticed by the Bader charge analysis¹⁸⁴. The Cl receives, whereas Li and Na atoms donate electrons, thus the analyzed atoms manifest their ionic character during the adsorption on CNT, even if they are not exactly above some stable or metastable sites. The band shift—relative to the Fermi level—is a consequence of the charge excess or absence on the CNT (see **Figure 3.3** a-c). Such result is similar to the ones observed in the adsorption of single atoms at the CNT stable and metastable sites (see **Figure D.1**, **Table D.1**, and **Table D.2** in the **Appendix D.2**). Therefore, the effect of the remaining water molecules around the ions on the CNT electronic properties is negligible in narrow diameter tubes. Besides the charge exchange, we notice that chlorine molecular levels displayed below the Fermi level in **Figure 3.3c** may interact with the CNT band structure.

Figure 3.4: Transmittance comparison between pristine CNT (black dashed line) and one that is exposed to Li a), Na b) and Cl c) partially hydrated atoms inside the tube. Broader color region delimits the broadest deviations around the average (blue line).

3.3.3 Electronic Transport Properties

Quantum transport calculations were performed over 10 snapshots to check the CNT sensitivity with respect to the electrolyte aqueous solution within the tube⁴. In the NEGF methodology, the ballistic conductance of a perfect (pristine) system is proportional to the number of conduction channels (number of bands at a given energy). Two energy bands in the vicinity of the CNT Fermi level induce a quantum conductance of $2G_0$ for each spin, where $G_0 = e^2/h$ (see **Figure 3.4a-c**). Above 1 eV from the Fermi level, the electric conductance is higher due to the six channels per spin ($6G_0$) observed on the band structure in **Figure 3.3 a-c**).

An imperfect system displays lower conductance, since the defect acts as a scattering center. Under the electrolyte aqueous solution flow, the CNT transmittance is unaffected within the 1 eV window around the Fermi level (**Figure 3.4a-c**). However, remarkable differences between the pristine CNT and one that is exposed to electrolyte solutions are noticed around -1.2 eV of the energy spectrum for the systems with Na and Li and about 1.0 eV for the systems with Cl.

The changes on the transmittance can be understood based on the available number of

⁴We observed that a sample with ten snapshots is enough to support our discussion. To quantitatively show this, we calculate the standard error in the transmittance curve. We properly chose an energy level (at -1.25 eV) where we observed the broadest fluctuations around the transmittance average in **Figure 3.4c**. At this energy, we obtain a small standard error ($\pm 0.1G_0$), which displays similar width as the curve line in the transmittance axis (**Figure 3.4c**). The standard error calculated for other energy levels is expected to be lower.

conductance channels along the transport system, including the scattering region and the electrodes. As the adsorbed atoms alter the band structure of the CNT, the transmittance is also changed. In **Figure 3.5a–d** one can observe that the number of available states are affected in the scattering region, due to the charge transfers with the ions. For some energies, the number of channels is reduced (from 6 to 2), affecting the total transmittance. In addition, an increase in the number of available states (from 2 to 6) also occurs at some energy levels of the scattering region. Although, such increase is not observed on the transmittance, because the system is hindered by the number of available states (2) at the leads. **Figure 3.5d** shows a qualitative view on the transmittance and available states at different energy levels. In addition, a distinct effect for cations and anion is observed: there is a decrease in the number of available channels for the anion around 1.0 eV, whereas for the cation it happens at -1.0 eV. Thus, cations and anions can be distinguished based on the transmittance results.

Furthermore, the noise observed on the transmittance of the CNT exposed to partially hydrated Cl atom is attributed to the coupling between Cl molecular states — found below the Fermi level — with the CNT band structure at the same energy region (see **Figure 3.3 c**). Such interaction acts as the scattering center by lowering the transmittance.

It is important to stress that we have simulated pristine CNTs, for the leads and scattering regions. The interaction with the ions was through charge transfer, which is already enough to alter the total transmittance. For defective CNTs, the interaction with the ions would probably be enhanced, thus, possibly improving the ionic selectivity, as has been already shown in the literature^{185,186}.

3.4 Conclusion

We introduced a top-down multilevel approach that combines classical molecular dynamics simulations with electronic and transport calculations, based on first-principles, to properly model the basic functionality of nanofluidic devices with sensing properties. The operation mechanism involves electronic and dynamical aspects arising from different size and time scales that required a synergy between the methodologies. The link between resolution levels was achieved through the potential energy surface translated in the instantaneous atomic positions representative of the thermodynamical state. We demonstrate the potential of this technique by exploring the CNT sensitivity to electrolyte aqueous solution exposure. Molecular dynamics simulations at nanoscale revealed the structure of the brine inside the (6,6) CNT connected to a fluid reservoir and exposed to a pressure and electric field driving forces. The narrow diameter prevents the system from having more than one ion inside the tube simultaneously, being ideal for single atom/particle detection. Furthermore, it constrains the ionic hydration leading to they direct interaction with the carbon atoms. Sequentially, their response on the CNT transport properties was evaluated at the electronic level. We noticed a band shift as a consequence of the significant amount of charge exchange between the partially hydrated atoms and the channel. In addition, the density of states is modified on the scattering region as a response of the local charge accumulation on the CNT. The ionic signature observed on the transmittance curve allows for distinguishing the adsorption of atoms with cationic from anionic character. These results were explained based on the available number of conductance channels at specific energy level along the electronic transport system. The sensitivity enhancement should be achieved by further exploring structural defects and doping on these systems.

In summary, the study introduced here provides a platform for further advances in the

Figure 3.5: Normalized density of states distribution projected on carbon atoms along the electronic transport system. We take a representative snapshot of the sample to illustrate the effect on CNT density of states when exposed to partially hydrated Li a), Na b), and Cl c) atoms. d) Schematic explanation of the distinct effects of cations and anions on the available number of electronic states (2 or 6) in the energy spectrum along the transport system and how it affects the final transmittance.

development of nanofluidic devices by molecular computational simulations. The top-down methodology combined with our system setup can be useful in several studies that involves electrolyte aqueous solutions and their effects on nanochannels electronic and transport properties. Specially, these findings are useful to the experimentalists seeking for the rational design of new single atom/molecule sensors in nanofluidics applications.

CHAPTER 4

HYDROGEN BOND NETWORK UNDER CONFINEMENT ENVIRONMENTS: THE CASE OF CALCITE SLIT PORES

4.1 Introduction

Calcite, an anhydrous calcium carbonate polymorph, is a major component of carbonate reservoir rocks. Its interaction with fluids has important function in geological processes¹⁸⁷, such as: biomineralization¹⁸⁸, CO₂ sequestration¹⁸⁹ and oil exploration and production¹⁹⁰. To control these processes, it is necessary to consider the porous nature of carbonate rocks¹⁹¹, since it can modify the fluid-mineral interaction due to the spatial confinement, and variations on the chemical and electrostatic environment. However, the heterogeneous pore distribution, pore type, pore connectivity, and grain size^{192–195} pose challenges to investigate the system properties^{196,197}. In this context, many studies have focused on understanding the calcite/fluid interface^{198–202}, since it can influence the properties of the confined water. However, many aspects of the structure, dynamics and energetics of fluid/carbonate interaction are not fully understood and this remains a topic of active research.

Among the carbonate minerals, calcium carbonate (CaCO₃) is one of the most abundant minerals on Earth. Many studies have been focused on the calcite [10 $\bar{1}$ 4] surface, since it is the most stable one^{203–205}. In this context, several works have addressed the water/calcite interface both experimentally^{204,206–214} and theoretically^{213,215–224}. Within the experimental framework, X-ray scattering^{208,211} and X-ray reflectivity techniques were employed to determine calcite surface speciation²⁰⁹ as well as to characterize the interface²¹⁰. In particular, Fenter and Sturchio²⁰⁸ showed two distinguishable water density layers with the peaks observed at (2.14 ± 0.02) Å and (3.44 ± 0.12) Å distant from the calcite surface. Similarly, first principles calculations revealed an associative molecular adsorption type displayed by the first structured water layer^{218,220,223,225,226}. In addition, molecular dynamics simulation studies reported that water exhibits two structured layers in the vicinity of the [10 $\bar{1}$ 4] surface, with a third layer being weakly ordered^{210,216}.

The effect of calcite surface on water dynamics has been extensively investigated by evaluating physical quantities, such as: the water translational diffusion^{207,219,227}, residence time^{219,228,229} and the exchange rate²²⁷. According to these studies, the confinement interfaces retained by calcite pores have a strong effect on these properties. In particular, molecular dynamics simulation studies performed by Kerisit and Parker²¹⁹ showed that water diffusion is anisotropic near the calcite surface, similarly to observed for other fluids (methane, nitrogen and carbon dioxide)²³⁰: the calculated parallel diffusion coefficients in the first and second water layers are $0.6 \times 10^{-9} \text{ m}^2/\text{s}$ and $0.9 \times 10^{-9} \text{ m}^2/\text{s}$, respectively; the diffusion in the normal direction was $< 0.2 \times 10^{-9} \text{ m}^2/\text{s}$ in the first two layers. In this study, the diffusion at the center of the pore was twice the bulk one. However, MD simulations indicate the diffusion at the center of the pore is bulk-like²²⁷. Such a controversy is a strong indication that more studies are needed within this topic.

The exchange of water molecules adsorbed at calcite surface was predicted by molecular dynamics simulations to occur at a rate of one exchange during 10 ps²²⁷. In addition, the residence time of water molecules in the first density layer is expected to be about 6 times greater with respect to the second one²¹⁹. A recent study of structure and dynamics of water at step edges in $[10\bar{1}4]$ surfaces²²⁸ associated the wide range of residence times to two types of water, with the shorter residence times reflecting the unbounded molecules. A detailed analysis of the hydrogen bond (HB) network within confined interfaces retained by calcite pores could elucidate important aspects of such observations. In this context, we investigate the effect of the solid surface and confinement on water HB network displayed inside calcite slit pores (and hydrophilic surfaces in general). We aim to provide additional atomistically detailed analysis by combining molecular dynamics simulations with HB network analysis based on graph theory. In addition, we aim to provide a systematic evaluation of the HB network across the density layers in order to better understand the structural and dynamical properties of water within confinement interfaces. To address the effect of extreme confinement, we vary the pore size from 6–1 nm (see **Figure E.1a**).

4.2 Methodology

Classical molecular dynamics simulations were performed to access the trajectories of water within calcite slit pores. These calculations were based on the large atomic/molecular massively parallel simulated (LAMMPS) package¹⁶⁸ to take advantage of parallel computing resources. We observed a computational cost of $\sim 10^4$ core-hour¹ per investigated pore. The analyzed properties based on the trajectories include water density profile, HB network and time persistence.

The calcite atomic structure was obtained from the crystallographic data published by Markgraf and Reeder²³¹. It was cleaved to expose the $[10\bar{1}4]$ surface due to its major stability^{203–205}. The calcite slab was converged to nine layers, exposing mirror surfaces. The resulting cell dimensions were $a = 96.9 \text{ \AA}$, $b = 88.8 \text{ \AA}$ and $c = 27.2 \text{ \AA}$, with a total of 3888 CaCO_3 units. Water molecules were added randomly within the slit pores at a density of 1 g/cm^3 through the PACKMOL package¹⁶⁷.

We employed the interatomic potential derived by Raiteri et al.²¹⁶. In this force field, carbonate units and water molecules (SPC/Fw) were represented by flexible potentials²³², giving a better description of the solid/liquid interface²¹⁰ (see **Appendix B.2**). In addition, these flexible models can improve the description of confined systems, since the bond lengths and angles can be altered in such environment.

¹Using the AMD Opteron 6376 @ 2.1 GHz CPU

Figure 4.1: (a) Fluctuations in O and H atoms density profile along z axis perpendicular to the surface. Three layer can be identified with valleys positions at: 2.67 $\text{\AA}$, 3.89 $\text{\AA}$ and 5.48 $\text{\AA}$ with respect the calcite wall. Dashed line represent the density profile for the 1 nm pore size. (b) Probability distribution of water dipole moment orientation along the z direction for 1 nm calcite pore.

We started the simulation by minimizing the forces and energies through the conjugate gradient algorithm. The equilibration procedure involved first adding a Gaussian velocity distribution of 10 K (with no net linear or angular momentum) and running a 50 ps simulation in NVE ensemble, considering a timestep of 1 fs. Later, the timestep was reduced to 0.5 fs and a 500 ps simulation was performed in NVT ensemble at 400 K. The temperature increment was driven to avoid any local minimum due to a possible artificial liquid structuring from the initial configuration. Then, a 250 ps simulation run in NVE ensemble was followed by at last 1 ns NPT simulation at 300 K and 1 atm. The production run was performed for 1 ns in NVT ensemble. For the NVT simulation we have employed the Nosé-Hoover thermostat^{63,64} and for the NPT simulation, the Nosé-Hoover barostat¹⁷³ was added. Within these simulations, the potential representing non-bonded pair interactions was truncated at a cutoff distance of 9 $\text{\AA}$. In addition, the long range electrostatic interactions were solved by PPPM⁶⁰ method. All the simulations were performed under periodic boundary conditions (PBC).

4.3 Results

4.3.1 Water Structuring

The evaluation of the density profile revealed the layered aspect of water within the calcite slit pores (**Figure 4.1(a)**). For all the analyzed systems, water display three distinct peaks in the vicinity of the calcite surface due to the strong interaction between the molecules and the hydrophilic surfaces, in agreement with other studies retained on water/calcite interface^{210,219,233}. Such oscillation smooths beyond the third layer and reach bulk values at 8 $\text{\AA}$ distant from the calcite surface. Additionally, the 1 nm pore displays an atypical response, since no constant density was observed at the pore center due to the superposition of surface effects.

The water ordering was evaluated through the angle distribution of dipole moment orientations with respect to the surface normal vector, as shown in **Figure 4.1(b)**. In layer 1, we observed two preferential orientations: parallel ($\theta \approx 90^\circ$) and pointing away

from the calcite surface ($\theta \approx 50^\circ$). Dipole moments of water molecules within layer 2 are oriented towards the calcite surface, displaying an angle $\theta > 90^\circ$. The water ordering observed in this two layers is attributed to the strong directional interactions with the calcite surface²²⁷. In addition, it reveals the preferential position of the water molecules with respect to the surface ions, where the $\theta < 90^\circ$ is attributed mainly to the interaction with the calcium, while $\theta > 90^\circ$ is attributed typically to the interaction with the carbonate group through the hydrogen atom. A residual ordering remains in layer 3, probably due to the interaction with the structured water displayed by layer 2.

4.3.2 HB Network Analysis

It is well established that the HB network has significant effect on the water physical properties²³⁴. In this section, we analyze the number of HBs per molecule — the degree, in graph theory — displayed inside each structured layer. To elucidate the effect of calcite surface on this physical quantity, we distinguish the HBs established only between water molecules from these ones considering also the hydrogen-carbonate interactions. The HB network was evaluated through the ChemNetworks code under the geometrical criterion described on **Section 2.3.2**.

We observed in layer 1, each water molecule established preferentially one HB, according to the **Figure 4.2(a)**. This number increases when the carbonate groups are considered on the calculation (see **Figure 4.2(b)**). According to the **Table E.1** in **Appendix E.2** only 30% of the expected number of HBs for bulk water is attributed to the interactions between water molecules, while 53% of the HBs are established with the carbonate group. Considering also the dipole moment orientation distribution results in **Figure 4.1(b)**, these results indicate that water molecules interact with the calcium atom, but they established also HBs with the oxygen atoms belonging to the carbonate group. The adsorption energy of a single water molecule in such configuration is expected to be around 23 kcal/mol, according to the DFT calculations performed by Srinivasan et al.²³⁵. This value is more than four times greater than the HB energy established in a water dimer calculated with similar methodologies²³⁶ (≈ 5 kcal/mol). Despite the high density displayed by this layer, the average number of HBs is 17% lower than expected in bulk phase.

Moving on to layer 2, 75% and 22% of the HBs are established between water molecules and the carbonate group, respectively. In this layer, the average number of HBs is only 3% lower than expected for the bulk one. An interesting finding in this layer is that a substantial number of water molecules display four and five HBs. The tetrahedral coordinated molecules may exhibit stronger HBs, since they may stay connected in optimal geometry, resulting in its stability. In addition, the fifth-coordinated water has an important interpretation in the dynamic analysis, since the extra molecule in the first coordination shell lowers the energy barriers for translational as well as rotational motions, as discussed in **Section 2.3.2**. Layer 3 displays similar degree distribution with respect to the bulk phase, because of the absence of interactions with the calcite surface (see **Figure 4.2(b)**). Therefore, this analysis allows us to identify the limit of the calcite surface influence on water properties and the establishment of a clear separation line between the adsorption layer and the bulk-like water.

In hydrophobic pores, the layering of water near the surface also affects the HB structure^{12,237,238}. However, in hydrophilic pores, there is a partial compensation of the water-water HB by the water-surface interaction. Thus, the average number of HBs near a hydrophilic pore is higher than expected in hydrophobic pores²¹⁸. Besides the HBs, we have shown that the strong interactions with the hydrophilic calcite surface also impose the

Figure 4.2: (a) Degree distribution observed in each density layer compared with bulk water; (b) Degree distribution of water-water and water-surface HBs in each layer in comparison to bulk phase.

positions and orientations of the water molecules on the interface^{207,216,220,227}. As the pore size is increased, the contributions of the adsorption layer to the confined water properties have reduced effect on the total system, thus it tends to the bulk behavior (see **Table E.2** in **Appendix E.2**).

Connectivity extension analysis through the geodesic evaluation provides an additional information about the HB topology. Our layered analysis shown in **Figure 4.3(a)** revealed surface water displays shorter geodesic paths in comparison to the ones observed in bulk phase. In addition, layer 3 displays similar geodesic distribution to the bulk water, reinforcing the interpretation of the absence of surface effects on this region. Furthermore, pore averaging reveals a broader geodesic path distribution, specially in the 1 nm pore size system (**Figure 4.3(b)**). These results indicate a distorted network, leading to more extended paths to connect spatially separated molecules. This effect is attributed to the broken network exhibit by the system. Thus, larger geodesic paths are displayed to overcome or contour the discontinuity imposed by the calcite surface on the confined water (see explanation in **Figure 2.11**). This effect is more pronounced in small pores due to the higher surface-area-to-volume ratio. In addition, the large geodesic path length displayed by water within the calcite pores indicates the wide extension of the HB branches. Such structures may cross the confined environment, connecting low to high dynamics molecules. Such fluid is expected to exhibit overall low dynamics (rotational and translational) with respect to the bulk phase.

The evaluation of geometric patterns in confined water gives us an additional information about the HB network organization. Water may display several geometric patterns in suits of HBs as described in **Section 2.3.2**. We investigated this feature within the confinement environment. It is considered a geometric pattern, if the network shape matches with a structure criteria described in the reference¹⁷ (see **Appendix A**). According to the **Figure 4.4(a)**, calcite affects the formation of geometric patterns in the surface layer, specially these ones with larger structures, *i.e.* hexamers and cyclic pentamers. However, the small cyclic oligomers, such as cyclic tetramers, are these ones with the most stable structures, and with strong directional HBs as described in **Section 2.3.2**. However, the reduction of the local tetrahedral arrangement with respect to the bulk water, observed in **Figure 4.4(b)**, indicates the absence of a possible occurrence of crystalline ice-like

Figure 4.3: (a) Geodesic distribution in each layer compared with bulk water for equal slab width. Error bars represent standard errors; (b) Geodesic distribution comparison between bulk water and water confined in 1 nm calcite pore. Error bars are smaller than the line sizes. The bulk water layer width of were the same of confined water. Only water-water HBs were taken into account in this calculation.

Figure 4.4: (a) Geometric pattern distribution within each layer. Similar results were obtained for all the pores analyzed in this work. The number of geometric patterns was divided by the layers size in the confinement direction. To obtain the volumetric density is only divide this results by the surface area ($\approx 89 \times 97 \text{ \AA}^2$) (b) Geometric pattern distribution in each pore in comparison to bulk water. To allocate a geometric pattern to a layer, we consider these ones whose center of mass is inside the layer. Only water-water HBs were taken into account in this calculation.

ordered structures^{239–241} within the confinement environment. In addition, the bulk-like fashion is just recovery in pores larger than 5 nm.

4.3.3 Survival Probability and Bond Time Persistence

The survival probability function $P(t)$ describes the stability of water retained within a spatial region by relating the number of molecules $N(t)$ at time t with respect to the initial amount $N(0)$. $P(t)$ can be properly fitted to the function $\exp[-t/T_R]$, where T_R is the residence time. According to the **Figure 4.5(a)**, layers 2 and 3 display (4.98 ± 0.03) ps and (3.11 ± 0.03) ps residence times, respectively. These values are comparable to

Figure 4.5: (a) Residence and (b) HB persistence time for each layer in the 1 nm pore. Similar results are observed in all the pore sizes. To clarity only the first 100 ps are presented. Only water-water HBs were taken into account in this calculation.

the one observed in bulk phase²⁴². In contrast, the residence time displayed in layer 1 is (214.59 ± 0.14) ps, similar to the T_R value for the water adsorption on an isolated Ca^{2+} ion²²⁸. Therefore, layer 2 displays short residence times with respect the layer 1, since it is located outside the surface Ca^{2+} hydration shell²²⁸.

HBs are broken and reformed due to the thermal vibrations. We evaluate the network stability by relating the number of bonded molecules $N(t)$ at time t with respect to those ones $N(0)$ initially connected. The time correlation function $c(t) = \exp[-(t/t_p)^\beta]$ fits a stretched exponential decay with respect to the time, where t_p is the persistence time and $\beta = 0.8$ was chosen to properly adjust the function. In **Figure 4.5(b)** we shown the time correlation data. From our fits, we obtained the following persistence times: 0.06 ps, 0.10 ps, 0.13 ps for layers 1, 2 and 3, respectively. The sub-pico second persistence time is attributed to the libration motion, since it is the primary source of HB breaking and reforming^{82,243}. The time persistence is directly related to the average number of HBs, to obtain “mobile” water molecules. Therefore, the lower average number of HBs outside the tetrahedral optimal geometry allied to the strong interaction with the surface calcium ion leads to an increase in the librational frequency, hence the short HB persistence time. Similar results were obtained for water in contact to α -quartz surface by Ozkanlar et al.²⁴⁴.

4.3.4 Conclusion

Our layer by layer analysis revealed the effect of calcite confinement interfaces on water properties. Besides the density and dipole moment orientation significant changes were observed on the HB network. Such detailed analysis handle important contributions to the understanding of water structure and dynamics within hydrophilic nanochannels.

The structural analysis performed in this work allowed to access the details of water/calcite interface. We shown that water molecules belonging to the surface layer trade off their water-water interactions to establish water-carbonate HBs. In addition, layer 2 displays high contribution of four and five coordinated molecules, which have important consequences in the water dynamics. Furthermore, layer 3 displays similar degree distribution with respect to the bulk phase due to the absence of interactions with the calcite surface. All these analyzes together revealed the precise extent of surface effects on water properties.

Pore average properties may reach bulk-like behavior only in large pores (> 5 nm) due to the high surface-area-to-volume ratio displayed in extreme confinement environments. In addition, we demonstrated the bulk-like fashion of the network at the pore center, beyond the third structured layer. Strong confinement effects are only evident in the 1 nm pore due to the overlap of surface responses. Water within such systems displays more extended geodesic paths and lower average number of HBs. The longer geodesic paths may connect low to high dynamic molecules, resulting in a overall slow-down diffusion, as it is observed experimentally. As a consequence, such branched structure can effect also the dynamics of the bulk-like region in the pore center. Furthermore, the reduction of the local tetrahedral arrangement indicates the absence of a possible occurrence of a more concentrated crystalline ice-like ordered structures^{239–241} within the confinement environment, in comparison to the bulk system.

In summary, we characterize the network structure of confined water within calcite slit pores by combining molecular dynamics simulations with HB network analysis based on graph theory. We disentangle the interaction details at calcite/water interface and evaluate the extension of surface effects. The quantitative information provided in this work is important to understand the dynamic properties and how such pores may operated as nanochannels in nanofluidics applications.

CHAPTER 5

FRESH MOLECULAR LOOK AT CALCITE–BRINE NANOCONFINED INTERFACES

5.1 Introduction

Phase transition anomalies¹¹ and formation of icelike structures¹² are some examples of a variety of phenomena that can emerge in nanoscopic environments with water at or near a solid interface. Investigating water properties under such conditions is essential to understand the underlying molecular mechanism of porous media in geochemical, synthetic and biological crystal growth¹³. Such processes often occur in water with some salt concentration, and currently, the structures of solvent and ions at solid–solution interfaces, as well as the effect of ions on water properties under confinement, are poorly understood²⁴⁵.

Previous studies explored the effect of spatial confinement on the hydrogen bond network and the dynamics based solely on pure water^{68,246–248}. According to Dore²⁴⁷, water in a confined geometry shows significant modification on its hydrogen bond structure in comparison to the bulk phase. The author showed by neutron diffraction spectroscopy, the formation of an extended hydrogen–bonded network similar to that one observed in amorphous ice. Different experimental techniques revealed that the water viscosity increases and the diffusion coefficient decreases^{249,250}. The slowdown of water dynamics confined by narrow hydrophilic walls is a common feature in these systems.

On the other hand, the effect of salt ions on water structure and dynamics has been widely explored^{251–253}. Both experimental and theoretical studies describe the effect of ions on the hydrogen bond network in terms of making and breaking capability²⁵¹, *i.e.*, certain type of ions break and others make hydrogen bonds. The effects of ions on the hydrogen bond network translate to changes in water viscosity according to these works. Furthermore, some studies indicate that electrolyte aqueous solutions have a similar effect as of pressure on the water hydrogen bond network²⁵³.

Few authors have drawn together some aspects of the complexity found in a system, which involves the effects of ions, solid surface interface, and nanoconfinement on water properties^{212,254–259}, but many knowledge gaps still remain. Currently, it is difficult to separate these individual contributions by experimental techniques. In this context,

the progress achieved so far in this research field can be expanded or complemented by computational simulations through an atomistic perspective, contributing to a predictive understanding of some important aspects involved in pore scale processes.

In this article, we report the results of a systematic study performed with the aim of bringing a new insight into the effect of ions on the structure and dynamics of water under spatial confinement retained by calcite (CaCO_3) slit pores. The complexity found in the system required the adoption of an original approach carried out to properly understand these important aspects arising in porous media. It was achieved by combining molecular dynamics simulations with hydrogen bond network analysis based on graph theory and NMR modeling. We were able to properly isolate the contributions of the ions, surface, and confinement to the network structure of hydrogen bonds and to relate it with the dynamical properties accessed by the transverse spin relaxation time analysis. Measurements of the ^1H transverse relaxation times (T_2) enable definite assignment of water protons of different mobilities to the observed diffusion processes and, hence, can be used to identify structural changes in porous minerals. Furthermore, the water branch aspects, seen from a new perspective based on graph analysis, revealed the formation of more extended hydrogen bond geodesic paths under extreme confinement and salt ions. Substantial amount of water branches, formed by continuous hydrogen bonds, are able to cross the pore, connecting low to high dynamic molecules. The response on water dynamics was observed on the transverse spin relaxation, indicating an overall slowdown of diffusion. We also highlight the observation of an electrostatic and physical barrier near the calcite surface due to the epitaxial water. The icelike structure is characterized by slow T_2 and prevalence of highly coordinated water molecules. The spatially alternated electrostatic potential resulting from high ordering of water dictates the ionic distribution inside the pores, thus reducing the probability of desolvation and attachment of foreign chemical species. This may have significant implications and can contribute to the current understanding of the crystallization and biomineralization processes. We discuss the physical indications and potential significance of our results in crystal growth and dissolution processes.

5.2 Methodology

Classical molecular dynamics simulations were performed using the large atomic massively parallel simulator (LAMMPS)¹⁶⁸ package. The calculations were performed in the NPT ensemble with an anisotropic barostat for thermodynamic equilibration at 300 K and 1 atm, followed by a NVT production run for 5 ns with a time step of 0.5 fs. Temperature and pressure were controlled based on the Nosé–Hoover methods^{63,173}. In addition, the nonbonded pair interactions were truncated at a cutoff distance of 9 Å and the long-range electrostatic interactions were solved by the particle–particle–particle–mesh⁶⁰ method. The numbers of ions and water molecules inside each investigated pore are specified in **Table E.3**.

To describe the interatomic interactions, we used the force field developed by Raiteri et al.^{216,222} for a calcite–water interface. This force field allows flexibility of the carbonate ion, and the water molecules are described by the SPC/Fw model²³². To account for the interactions of sodium and chlorine ions in American Petroleum Institute (API)–brine, we employed the parameters extracted from the work of Grossfield et al.²⁶⁰. The Ca-O_w parameter obtained by Raiteri and co-workers^{216,222} is used here to describe its interaction with water (see **Appendix B.2**).

5.3 Results

Our calcite pore model is based on the crystalline structure with rhombohedral morphology obtained from the crystallographic data published by Markgraf and Reeder²³¹. This structure was cleaved to expose the $[10\bar{1}4]$ surface because of its major stability^{203–205}. The slit geometry is the simplest representation of a pore, and it allows us to investigate spatial confinement effects by progressively varying the surface–surface distance (see **Figure E.1a**). We considered pore sizes ranging from 6 to 1 nm to systematically investigate the confinement effects emerging in brine within nanoscopic environments. We adopt the API–brine model, which is constituted by 8 wt % NaCl and 2 wt % CaCl_2 .

5.3.1 Brine Structure within Calcite Slit Pores

The PACKMOL¹⁶⁷ package was used to add water molecules randomly within the slit pores at a density of 1 g cm^{-3} . Ions were then inserted by randomly substituting water molecules. In addition, ions were included only in the pore center, preserving each hydration shell, thus avoiding their spurious presence near the surfaces trapped in local minima²⁶¹. After the system reached thermodynamic equilibrium under fully atomistic molecular dynamics simulations, it was observed that water molecules are structured in layers near the solid surface interface, similar to the ones observed in pure water system^{68,212,219} (see **Figure 5.1 a–d**). Under ambient conditions, an adsorbed region is always present at hydrophilic surfaces, and it is attributed to the strong interaction between water and calcite. According to our previous work⁶⁸ and in agreement with experimental results²¹⁴, the water density profile exhibits three distinguishable peaks, approximating bulk values beyond $8.0 \text{ \AA}$ from the calcite surface. Water molecules belonging to layers 1 and 2 (**Figure 5.1 a–d**) interact directly with the calcite surface⁶⁸ and therefore they constitute the surface or adsorption layer. Inside layer 3, water molecules do not established hydrogen bonds with calcite surface, but their density is affected by the ordering of surface layer and the ionic steric effect. Calcite systems with slit pore sizes ranging from 6 to 2 nm display similar density profiles as shown in **Figure 5.1a**. However, the system with 1 nm pore size (**Figure 5.1c**) has an overlap of right– and left–side density profiles because of the extreme confinement. The differences, with respect to the other investigated systems, arise only in the density on layer 3 and the pore center, thus leaving layers 1 and 2 unaltered. Our layered analysis following in this work is based on the water structuring observed in the density profile. Additional layers (layers 4–6), separated by $5.0 \text{ \AA}$ as depicted in **Figure 5.1a**, were considered to investigate systematically the effect of confinement.

Besides the water molecule positions, the calcite hydrophilicity also determines the water dipole moment orientation with respect to the surface normal vector (see **Figure 5.1b** and **Figure 5.1d**). This is observed mainly on water molecules belonging to the surface layer because they interact directly with the calcite surface. Some water molecules are linked to surface calcium atoms via their oxygen atoms, whereas other ones form a hydrogen bond with the calcite surface oxygen atoms, resulting in preferential orientation angles²⁶². All investigated systems show similar dipole moment distributions for the surface layer. The ordering of water molecules revealed by dipole moment orientation analysis starts disappearing inside layer 3 and reach bulklike behavior beyond $8.0 \text{ \AA}$ from the calcite surface. These results are similar to the ones observed in pure water under the same conditions⁶⁸, showing that the investigated ions preserve the layered aspect of the water density profile and the dipole moment angle distribution.

Layered distribution appears also in the Cl^- and Na^+ density profiles (**Figure 5.1a**). However, according to our observation, the mechanism which explains this behavior is

Figure 5.1: a) Particle density profiles displayed along the 4 nm pore by the water oxygen; Na, Ca, and Cl ions in the electrolyte aqueous solution; and surface Ca and O calcite atoms. For clarity, the atomic density profiles of Na, Cl, and Ca are multiplied by a factor of 15, 15, and 40 respectively. The surface limits were defined on basis of the average positions of surface calcium atoms. The dashed lines delimit the layers. b) Normalized probability distribution of dipole moment orientations with respect the surface normal vector. The electrostatic potential (white line) emerged because of water structuring. These results are representative of the systems with pore sizes from 6 to 2 nm. c) Particle density profiles and d) normalized probability distribution of water dipole moment orientations for the 1 nm pore size system.

different from the one used to describe the epitaxial ordering of water. Although our pore model is charge-neutral, the calcite surface shows a strong local variation of charge because of the alternate arrangements between their ionic groups²¹². Water ordering in well-defined layers and orientations creates an alternation of positive and negative excess charges^{212,219} (see **Figure 5.2a**), leading to an electrostatic potential profile, as shown in **Figure 5.1b** (white line). Consequently, the ions are not structured by layers directly because of the ionic nature of the surface, as one could intuitively expect, but because of the electrostatic

potential arising from water structuring. In practice, the positions of the regions with a larger charge density exhibited by Na^+ (Cl^-) ions (see **Figure 5.2b** and **Figure 5.2c**) do not correspond to the negative (positive) charge exhibited by the CO_3^{2-} (Ca^{2+}) group on calcite surface into the (1-10) direction (y axis), but it is associated with the accumulation region of negative (positive) charge observed on the two-dimensional density distribution of the water charge (**Figure 5.2a**). Therefore, the Na^+ and Cl^- distributions are mediated by this potential, whereas Ca^{2+} ions are located more at the pore center because of their larger hydration shell²¹² (see **Figure 5.2d**). Furthermore, the systems with 6–2 nm pore sizes exhibit ionic density profiles that reach more uniform distribution beyond 8 Å from the surface, but the values differ from bulk densities because of the rearrangements of the ions excluded from the surface layer. The system with 1 nm pore size shows the largest difference in the ionic concentration with respect to the bulk system in the pore center because of extreme confinement. Nevertheless, the ions do not reach the calcite surface because substantial energetic penalty has to be overcome, as reported in experimental studies²¹².

5.3.2 Hydrogen Bond Network Analysis

Liquid water exhibits a multiform structure formed of hydrogen bonds with molecules at different degrees (number of hydrogen bonds per molecule) of connections forming a complex network¹⁷. The purpose of the hydrogen bond network analysis was the quantitative elucidation of the effect of the environment (ions, confinement, and solid surface interfaces) on this structure. To address this kind of problem, we adopt the approach on the basis of graph theory implemented in ChemNetworks code¹⁷. Hydrogen bonds were analyzed based on a set of representative instantaneous atomic configurations taken from molecular dynamics simulations. We considered a geometric criterion for the hydrogen bonds, where the $\text{O-H}\cdots\text{O}$ angle is $180^\circ > \theta > 150^\circ$ and the $\text{O}\cdots\text{H}$ distance is lower than 2.5 Å¹⁷.

We observed that hydrogen bonds formed between water molecules belonging to the surface layer are ruptured because of the discontinuity in the water system at the interface with the calcite surface. However, many of the hydrogen bonds are reformed because of the interaction with the oxygen atoms from the carbonate group⁶⁸. The network structure of hydrogen bonds in the adsorption region (see **Figure 5.3a-b**) is almost unaffected by the ions from API brine. It occurs because they are located far away from the surface (beyond 3.0 Å); consequently, the degree (number of hydrogen bonds) distribution of water molecules inside layer 1 is similar to the one observed in pure water under the same environment. Furthermore, the slight difference observed in the degree distribution of brine with respect to that of the pure water system, both placed in layer 2, is attributed to the few ions that penetrate this layer and the proximity with layer 3 (see **Figure 5.3c**): the steric effect that occurs in layer 3 reduces the number of available water molecules to form hydrogen bonds with the molecules located in layer 2. However, the degree distribution of layer 2 remains with a high contribution of four coordinated water molecules, which resembles icelike phases.

The network structure of hydrogen bonds, in the sense of the average number of hydrogen bonds, in subsequent layers is related to the relative Cl^- and Na^+ concentrations and corroborates with the interpretation retained by many studies²⁵¹ about the capability of the ions to make and break hydrogen bonds (see **Figure 5.3d-g**). Such a response is observed more clearly in layer 3, which exhibits a remarkable imbalance concentration of these two kinds of ions. We demonstrate in a previous work⁶⁸ that pure water inside

Figure 5.2: a) Normalized charge density for water inside the 3 nm pore taken over the whole molecular dynamics simulation. Calcite cleaved in the $[10\bar{1}4]$ direction exhibits CO_3^{2-} and Ca^{2+} groups placed alternatively along the y direction. The blue and red colors represent excess of positive and negative charges, respectively. b) Na^+ (green hue), c) Cl^- (red hue), and d) Ca^{2+} (blue hue) normalized charge density distributions are progressively added. Ions are accommodated in the charge accumulation regions displayed by water ordering.

layer 3 (and in subsequent layers) has similar degree distribution as observed in the bulk phase because the molecules located in this region are disconnected from the hydrophilic surface, and this result is insensitive with respect to the pore size. However, according to **Figure 5.3g**, the average number of hydrogen bonds observed in layer 3 is slightly different from the one observed in the brine system in the bulk phase. The result matches with the imbalance between Na^+ (making) compared to Cl^- (breaking) concentrations in this layer (see **Figure 5.3d** and **Figure 5.3e**). In practice, the decrease of Cl^- with respect to the Na^+ concentration enhance the number of hydrogen bonds. Furthermore, the reduction of the average number of hydrogen bonds observed in layers 4–6 is consistent with the relative increase in Cl^- with respect to the Na^+ concentration. Although Ca^{2+} ions have structure-making capability²⁵¹ (see **Figure 5.3f**), but because their low density (1 order of magnitude lower than that of Cl^-), their presence preserves the average number of hydrogen bonds.

An assembly of water molecules connected by hydrogen bonds design a network with numerous branches and multiple extensions¹⁷. Currently, such a structure can be accessed by analyzing the graph geodesic through Floyd–Warshall algorithm¹⁷. In the context of the hydrogen bond network, the graph geodesic is the shortest continuous path designed by a series of hydrogen bonds formed between two water molecules. Its analysis provides information about the interconnectivity of water molecules, and it enables a nonlocal view over the network topology of the spatially confined brine. Such calculations may be really expensive, generating large files containing the geodesic paths data. We estimate a

Figure 5.3: Degree distribution comparison between pure water and brine located inside a) layer 1, b) layer 2 and c) layer 3. Relative particle density, with respect to the bulk values, of d) Na⁺, e) Cl⁻, and f) Ca²⁺ ions inside each layer for all investigated systems. g) Layered distribution of average number of hydrogen bonds. Standard errors are too small to be represented in this graphic scale.

computational cost reaching $\sim 10^6$ core-hour¹ to perform all the calculations (brine and pure water in all pore sizes). In addition, the geodesic data amount reached at least 16 TB (tera bytes). We emphasize the computational cost was expensive, in particular, for large pore sizes (4–6 nm), since the Floyd-Warshall algorithm scales $O(V^3)$ with respect to the number of vertices.

In all analyzed pores, we observed an increase, in comparison to the pure water system, in the geodesic path length (see **Figure E.1b**) with the addition of salt ions, as shown in **Figure 5.4a** (additional results are shown in the **Appendix E, Figure E.2–Figure E.7**). This effect is enhanced under extreme confinement displayed by systems ranging from 2 to 1 nm pore sizes. In such an environment, an high percentage of geodesic paths crosses the pore in the confinement direction and connects high to low dynamics molecules (see **Figure E.6**). A layered analysis through the different regions depicted in **Figure 5.1a** was performed to evaluate the origin of this geodesic path characteristic. We observed that the absence of ions in the surface layer results in similar geodesic path properties for brine and pure water (see **Figure E.3**). Differences between water and brine appear on the path length distributions of layers 4–6. However, the property is unrelated to the pore size or layer label (see **Figure E.4a** and **Figure E.4b**). Overall, these results indicate

¹ AMD Opteron 6376 @ 2.1 GHz CPU

that larger geodesic paths connect two spatially separated water molecules to overcome or counteract the network discontinuity imposed by the salt ions and also by the calcite surface (on the surface water), this effect is more pronounced in small pores because of the higher surface-area-to-volume ratio.

Distortions generated on the hydrogen bond network are also observed through the analysis of the O–O–O triplet angle distribution (see **Figure E.5**). It is characterized by an intense and broad peak corresponding to the tetrahedral coordination of pure water²⁶³. The salty ions and confinement interface decrease the position of this peak in the angle axis. To explore this effect in more detail, we determined the average angle of the distribution calculated over the water molecules belonging to a specific geodesic path length. The average angle displayed in API brine was found to be 3° smaller than that obtained for the pure water system (see **Figure 5.4b**). As a consequence, the geodesic paths are more folded, as revealed by the tortuosity analysis shown in **Figure 5.4c**. The collective geometric distortion leads to approximately $0.25 \text{ kcal mol}^{-1}$ gain (more negative) in potential energy per water molecule (see **Figure E.7**). The main contributions to the potential energy come from modifications in the triplet angle distribution because the hydrogen bond average distance remains the same and the slight differences observed in the average hydrogen bond angle keep the energy invariable. This role is also pore-size-dependent, as observed mainly in systems with high surface-to-volume ratio, because of the contribution of surface water, which displays average triplet angles around 8° lower with respect to the remaining system. Such response represents approximately $0.4 \text{ kcal mol}^{-1}$ gain in the potential energy per water molecule (see **Figure E.7**). Taken together, the distortions generated on the hydrogen bond network revealed by the geodesic path and O–O–O triplet angle analyses can explain the gluelike mechanical properties displayed under extreme confinement^{264,265}.

5.3.3 Dynamical Properties

The hydrogen bond network discussed in the previous section evolves dynamically because of continuous dissociation and formation on time scales ranging from tens of femtoseconds to picoseconds^{96,266}. In the subsequent sections, we extend the analysis of nanoconfined API brine on the basis of water dynamics (translational and rotational), which arises as a consequence from this particular hydrogen bond network. In addition, we analyze how this influences the transverse relaxation time here accessed by NMR modeling. The work related to the dynamics properties is assigned to the cooperative interaction with Mutisya²⁶⁷, who is specialist in NMR modeling. We highlight that the dynamical analysis is not the focus of the current thesis. However, the cooperative work yielded fruitful results that justify the insertion of this part in thesis, therefore, providing additional and useful informations to the understanding of water properties within confinement interfaces. Indeed, the NMR is a standard method to investigate hydrogen bonds in hydrogen bonded system. Mutisya et al.⁶⁸ successfully implemented and applied the theoretical calculation of the transverse (T_2) spin relaxation based on a semiclassical theory developed by Bloembergen, Purcell and Pound (BPP)²⁶⁸ (see **Appendix C**). In the following subsections, we discuss the dynamical properties in the light of NMR modeling and water structural properties.

Diffusion

The diffusivity of the water molecules within the calcite slit pores was analyzed by plotting the mean square displacement (MSD) as a function of time (see **Figure E.8**). From these, the normal diffusive linear dependence in time was observed starting from

Figure 5.4: a) Evolution of geodesic path length distributions for brine and pure water confined inside pore sizes with 1, 2 and 6 nm. Comparison between pure water and brine b) average angle and c) average tortuosity calculated over each path length (see **Figure E.1** b). The results for the missing pores are shown in **Figure E.2s** a-c). Standard errors are too small to be represented in this graphic scale.

30 to 200 ps for 2–6 nm and 1 nm pores, respectively. The calculated reference of self-diffusion coefficient (D) obtained by Equation C.1 for water molecules in bulk API brine is $1.98 \pm 0.01 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, which is lower than the value obtained for bulk water ($2.35 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$)⁶⁸ using the same force field. The D value for water molecules in the API brine under confinement is significantly reduced, and it ranges from 0.23×10^{-5} to $1.46 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ from 1 to 6 nm calcite pores (**Figure 5.5a**). This trend indeed confirms that the water self-diffusion coefficient is strongly correlated to the pore surface–area–to–volume ratio,²⁶⁹ *i.e.*, the smaller the ratio, the faster the water mobility. In addition, in confined systems, the translational diffusion of water is highly dependent on the local density and ordering⁶⁸. For the confined API brine, we have shown in the previous section that the inclusion of ions enhances local and nonlocal ordering, highlighted here by the distortions in the

Figure 5.5: a) Three-dimensional self-diffusion coefficient of water molecules in the confined API brine solution as a function of pore size. b) Parallel two-dimensional self-diffusion coefficient as a function of distance from the calcite surface and pore size. Error bars from the fitting of the MSD data are smaller than the symbol sizes. c) Rotational correlation time for all of the water in API brine inside calcite slit pores. d) Rotational correlation time as a function of distance from the surface. Error bars from the exponential fitting are roughly of the same size as that of the symbols. e) T_2 relaxation time of confined water in API brine on the surface and in the bulklike region of calcite 1–6 nm pores. f) Total T_2 relaxation time as a function of pore size. The propagated errors are too small to be represented in this graph.

hydrogen bond network (**Figure 5.4a–c**). Because the diffusional motion is nonlocal,²⁷⁰ our findings shed light on the origin of the overall slowdown of translational displacement in confined aqueous solutions observed experimentally²⁴⁷.

To disentangle the influence of the surface and ions on water diffusion, we calculated the parallel self-diffusion coefficient $D_{\parallel}$ (Equation C.2) of the water molecules that remain in layers 1–6 (see **Figure 5.1a**) during a certain time interval t' . According to **Figure 5.5b**, the diffusion of water is slowest in layers 1 and 2 and very similar to that of the confined pure water⁶⁸. Because of the absence of ions in these two layers, the slowdown is attributed to the strong water–surface interactions, which induce local ordering (see **Figure 5.1b** and **Figure 5.1d**). Even though experiments have demonstrated that the self-diffusion of water around ions is dependent on structure–making/–breaking properties^{270,271}, we obtain an overall downward shift of $D_{\parallel}$ values in layers 4–6, which are in otherwise bulklike region and dominated by Cl^- structure breaking ions. These findings indicate that the hydrogen bond network distortions revealed in **Figure 5.4a–c** govern the self-diffusion behavior of water in confinement.

Although the surface dominates in slowing down the self-diffusion coefficient $D_{\parallel}$ in 6–2 nm pore size, the trend changes for a 1 nm pore; the parallel diffusion coefficients in all of the three layers are comparable. We link this ambiguous diffusion behavior to the high accumulation of the ions at the pore center (see **Figure 5.1c**). This results in enhanced overlap of the hydration shells and structural rearrangements, which inhibit translational dynamics. The calculated values of $D_{\parallel}$ as a function of distance from the hydrophilic calcite surface are lower than those of water confined in hydrophobic pores^{12,237,238}. The strong reduction of $D_{\parallel}$ near hydrophilic surfaces is associated with the high water density and structuring in contrast to those in hydrophobic surfaces where the weak slowdown has been related to the formation short-lived icelike structures¹².

Reorientational Dynamics

The longer the rotational correlation time, τ_c , the slower the molecular reorientation, thereby revealing restrictions in the rotational degrees of freedom of hydrogen bonds²⁷². According to **Figure 5.5c**, τ_c decreases with increasing pore size, with a slowdown factor of 5.3 for a 1 nm pore and 1.8 for a 6 nm pore, in comparison to those in bulk API brine. Previous studies^{68,273,274} have associated this slowdown in reorientational dynamics of confined pure water to the slightly enhanced hydrogen bond strength caused by spatial confinement. In addition, the presence of ions in our system breaks the hydrogen bond network as evidenced by the degree distribution (**Figure 5.3c**). The immediate consequence of this is the reduction of the number of accessible states for water reorientation, leading to reduced reorientations because of the steric effect²⁷⁵. Furthermore, molecular dynamics studies on aqueous solutions^{275,276} have shown that the electrostatic interaction of water oxygen with Na^+ , Cl^- , and Ca^{2+} ions is greater than that of the water–water hydrogen bond, which explains the further hindrance of the reorientational dynamics of water molecules in brine solution.

The local reorientational dynamics investigated from layer-by-layer analysis indicates that water molecules in layers 1 and 2 have the slowest reorientational dynamics, as expected for hydrophilic surfaces. Despite the absence of ions in these layers, τ_c is slightly higher than that for the confined pure water⁶⁸. This is an indication that the ions that appear in layer 3 slightly stabilize the water reorientation on the adsorption layer, highlighted here to be a direct effect of the local structuring of the water and ions (see **Figure 5.1a–d**) along the surface normal. The significance of the structure–makers (Na^+ ions) and –breakers (Cl^- ions) is evident from the τ_c values obtained in layers 3–6; high relative density of structure–makers (breakers) results in a longer (shorter) τ_c in comparison to that of bulk brine²⁷⁵. Although Ca^{2+} ions are structure–makers, their small concentration has a minor effect at the center of the pores. The uniformity of the values in layers 4–6 demonstrates that the surface has negligible effects on the rotational dynamics in this region of the pore.

For the system with 1 nm pore size, the τ_c values obtained for each layer indicate that water is highly immobile as compared with larger pores (see **Figure E.9** for the behavior of $C_{HH}(t)$ in a 1 nm pore in comparison to that in 2 and 6 nm pores). The arrangement of water and ions within the 1 nm pore (**Figure 5.1c**), shows that most of the water–water hydrogen bonds are exchanged for water–ion interactions or water–surface bonds. The resultant τ_c is longer, an implication that for a high concentration of ions the relative contribution of structure–makers and –breakers is indistinguishable and the collective effect is dominant for structure–makers. These findings are in agreement with molecular dynamics simulations of water in concentrated solutions²⁷⁵.

Transverse Spin Relaxation

As a very sensitive indicator of local mobility and the binding state of water in porous media, the transverse relaxation time (T_2) is an important parameter to characterize calcite–brine interactions. Spin relaxation can arise from translational as well as rotational dynamics²⁷⁷, and thus any fluctuations can affect the measured value of T_2 . We observed that calcite–water interaction affect mainly the surface water (layers 1 and 2) resulting in T_2 value 1 order of magnitude lower than that for bulklike water (see **Figure 5.5e**). Except for the 1 nm pore that displays high ionic concentration near surface layer, the T_2 value for the water molecules in the surface layer is similar to the value for pure water confined in calcite slit pores⁶⁸. It can be inferred from this study that for pores of at least 2 nm, the physical and electrostatic barrier created by the water molecules on the calcite

surface leads to similar T_2 on the surface for both confined pure water and brine solutions because of the absence of ions in this region. This low T_2 value observed on the surface layer of water can be viewed as a measure of the wetting character of the calcite surface by the fluid²⁷⁸. These findings are in qualitative agreement with experimental observations that surface interactions help in lowering the relaxation times^{279,280}.

In the bulklike region (formed by layers ranging from 4 to 6 nm), the relaxation of water molecules is highly dependent on the pore size. For the calcite pores studied here, the relaxation time reaches the bulk API brine T_2 relaxation time for pores with sizes ranging from 3 to 6 nm. Other than the confinement, an additional factor for the bulklike region relaxation time is the ionic concentration because in general, Na^+ and Ca^{2+} ions decrease while Cl^- ions slightly increase the NMR relaxation time^{281,282}. For the bulk API brine, the collective effect of these ions is the reduction in the NMR T_2 relaxation time to 3.48 s in comparison to 4.59 s⁶⁸ for bulk water obtained from molecular dynamics simulations. We show that for larger pores (4–6 nm), where the surface has negligible effects in the bulklike region, there is slight increase of the T_2 relaxation time which we attribute to the high density of Cl^- . This behavior correlates with the local rotational dynamics, which indicates that translational dynamics has negligible effect on the T_2 relaxation in the bulklike region. In contrast, the T_2 relaxation time in the bulklike region is relatively shorter than the bulk API brine for the smaller pores. Specifically, for the 1 nm pore, we establish a limit of the fast-exchange model, which is valid for small pores as long as separate surface and bulklike phases exist. The high concentration of ions in the 1 nm pore center leads to a spin relaxation in layer 3, which is comparable to the surface layers (layers 1 and 2) making it difficult to clearly separate the surface and bulk phases.

The total T_2 relaxation time of the confined API brine averaged over the surface and bulklike regions according to the Brownstein and Tarr model²⁸³ is shown in **Figure 5.5f**. The trend of the NMR T_2 relaxation time studied in calcite pores reflects the general sensitivity of NMR measurements to pore-size distributions, where a lower T_2 is expected for small pores, whereas large pores result in higher T_2 values. The experimental T_2 cutoff for carbonates is on the order of hundreds of milliseconds²⁸⁴, which is comparatively shorter than our calculated values. This is expected because in our theoretical model the dipolar interactions are modulated only by hindered molecular dynamics, which is not the only relaxation mechanism in natural rocks²⁸⁵. In comparison to pure water confined in calcite, the presence of ions slightly lower the T_2 relaxation time⁶⁸. The reasons for this change are 2-fold: on the one hand, spin relaxation arising from translational diffusion is attenuated as a consequence of the distortions in the hydrogen bond network (**Figure 5.4a–c**). On the other hand, the unbalanced concentration between structure-makers and -breakers observed mainly in bulklike region in the brine solution slightly increases the rotational spin relaxation. Considering that the surface dominates the observed T_2 in porous media²⁷⁷, the T_2 values measured in this kind of systems are expected to be dependent on the properties of the surface water. For small pores (as shown here for a 1 nm pore) and/or for systems with high ionic concentrations, the ions play a significant role in the obtained T_2 values.

5.4 Conclusion

We provided a fresh molecular look with significant insight into the discussion about the effect of confinement interfaces and ions from electrolyte aqueous solutions on liquid water structure and dynamics. To properly address the system properties, we adopt an original approach by combining molecular dynamics simulations with hydrogen bond network analysis based on graph theory and NMR modeling. Our main contributions are

to describe the structures of the solvent and ions at calcite–solution interfaces and we discuss the physical indications and potential significance of our work in the crystal growth and dissolution processes.

The particular ionic distribution observed inside the calcite slit pore is related to the spatially alternated electrostatic potential, which arises from the strong ordering of water molecules in contact with the solid surface interfaces (**Figure 5.2a–d**). As a consequence, the Na^+ and Cl^- ions occupy, respectively, the negative and positive accumulation regions observed in water 2D charge density profile, whereas Ca^{2+} ions are located mainly in the pore center because of their larger hydration shell. In particular, the Na^+ and Cl^- electrolyte ions occupy the available sites near the solid/brine interfaces, resulting in a screening effect²⁸⁶, thus reducing the probability of desolvation and attachment of foreign chemical species directly on the surface²⁸⁷. Such a response can influence the crystal growth and can explain the results obtained experimentally on scale formation in hardwater pipes²⁸⁸. The authors related the growth rate to the surface wettability, and they argue that hydrophilicity decreases the calcium carbonate uptake because such particles must compete with pre-existing solid–solution interactions.

We observed that the hydrogen bond structure (**Figure 5.3a–c**) and particle density (**Figure 5.1a**) of water belonging to the adsorption layer are negligibly affected by the API brine. None of the considered ions reach the calcite surface because of the 1) electrostatic potential barrier, which arise from the ordering water molecules belonging to the surface layer and 2) the physical barrier imposed by the surface icelike structure characterized by highly coordinated water molecules and slow T_2 . These results revealed an additional mechanism displayed by the calcite surface, which is able to inhibit the formation of pathways for the crystal growth; thus these results should be considered in the crystallization models. The hydrogen bond network is temperature–sensitive¹⁷ and therefore the barrier imposed by surface water can be lowered by the heating process. Temperature growth rate dependences are observed by several authors in both biogenic²⁸⁹ and inorganic²⁹⁰ crystallizations, and according to our interpretation, such a response can be related to this particular water structure.

Furthermore, the effect of ions on the branched aspect of water hydrogen bond network was properly characterized through the geodesic path analysis based on graph theory. We revealed that larger geodesic paths connect two spatially separated water molecules to overcome or counteract the network discontinuity imposed by the salty ions and the calcite surface (see **Figure 5.4a–c**). Large geodesic paths are extended across the pores and they connect surface water with high dynamics molecules at the pore center. Especially, systems with 2 and 1 nm pore sizes exhibit a high percentage of the geodesic paths connecting the two surface water regions (see **Figure E.6**). Considering the effect on the potential energy (see **Figure E.7**) due to the path folding, such water structure can explain the gluelike mechanical properties observed in the confinement environment by several authors^{264,265}. The overall slowdown in water diffusion noticed with NMR modeling (see **Figure 5.5a,b**) is attributed to this particular distortion in the hydrogen bond network. It can influence the crystal growth rate by particle attachment because the hydrated particle may take a longer time to reach an attachment site at the calcite surface²⁹¹.

Such a particular hydrogen bond network revealed in the current work has dramatic consequences on water dynamics, and they are intimately related. The translational and rotational dynamics are uncorrelated, and our results show that the faster rotation at the center of the pores is due to the high density of Cl^- ions in this region. On the contrary, the global nature of the translational motions leads to a universal low diffusion coefficient regardless of the nature of ions. Although the surface has the greatest effect on

the relaxation time, the enhanced dipolar interactions due to a more folded hydrogen bond network further slow down the calculated T_2 relaxation time of brine in confinement. Our findings obtained by NMR modeling complement the experimental measurements of aqueous solutions in nanoscopic media by providing useful measures of pertinent parameters.

CHAPTER 6

CONCLUSIONS AND OUTLOOK

The topic of this thesis approaches a recent scientific field denominated nanofluidics, which covers the study of the properties, manipulation, and control of fluids constrained within nanometer-sized environments. The discrete nature of liquids and the electrostatic interactions occurring at solid/liquid interface are key features determining the properties of nanofluidic-based systems. Within this scope, we identified an exciting research subject to be explored with the aim of bringing important results towards the understanding of the phenomena occurring in nanoscopic environments. In this context, computer simulations, within an atomistic perspective, were essential to investigate the properties of the related systems, leading to a predictive insight into underlying physical and chemical processes at nanoscale occurring there.

Currently, computational materials science comprises relatively well-established methodologies and knowledges about the basic properties of individual systems, such as the water, brine, and several other materials. In addition, the nanofluidics-based systems involves interface effects, resulting in unique properties. A single methodology mostly is not capable to disentangle all the complexity displayed in these interacting multiphase systems, which often exhibit also multiscale phenomena. Thus, the challenges imposed by the nanofluidic-based systems, within the computational modeling framework, require innovative initiatives to overcome the limits imposed by the traditional methodologies. In this thesis, we integrated and applied computational approaches aimed to design and characterize nanofluidic-based systems at atomic level. Our study was motivated by the potential of such systems for the development of the so-called nanofluidic devices, which may be designed for a broad range of applications; and the lack of suitable methodologies capable to provide a detailed quantitative elucidation of the fluid and interface properties exhibited in the spatially confinement environments.

To address the multiscale phenomena problem, we combined the methodologies within a multilevel scheme by linking the constitutive laws and physical properties through the distinct resolution levels. We explored this strategy in the nanofluidics to disentangle the properties of systems that display mass flow influencing the electronic transport. To properly investigate similar systems, we introduced in this thesis the hierarchical top-down multilevel approach by combining classical molecular dynamics simulations with first principles electronic transport calculations. The methodology integration involves, for instance, the snapshot collection, and the system isolation for the transport calculations. The introduced approach extended the applicability of these known methods at molecular

level towards nanofluidics phenomena. In addition, our developments added a new flavor to the known multilevel approaches that can be extended to another challenge problems in nanofluidics²⁹² or even in another research areas.

As an outlook for the top-down scheme introduced in our thesis, we can propose an important application of this approach to investigate the energetics and structural features of the molecular adsorption on porous media surfaces. Such research may be particularly important in the oil industry to investigate the adsorption details of hydrocarbon on calcite rocks, for instance. The adsorption of organic compounds, i.g. acetic acid, and the water structuring around these molecules occurs within the nanoscale window, whereas the energetics and charge exchanges involves effects at electronic level. In this context, a top-down multilevel approach, combining molecular dynamics simulations with first principles calculations, may be the best strategy to access the desired properties by considering the solvent explicitly.

The potential of our top-down multilevel approach was demonstrated in this thesis by investigating how the water and ionic flow through a (6,6) carbon nanotube (CNT) influences its electronic transport properties. Through the molecular dynamics simulations, we observed the ionic entrance in the nanochannel, being observed around 20 ions crossing the pore during the whole simulation time (25 ns). We showed that the confinement on the CNT favors the partially hydrated Na, Cl and Li ions to exchange charge with the nanotube. The effect of charge rearrangements could be observed on the energy band structure shift with respect to the Fermi level. This leads to a change in the electronic transmittance, allowing to distinguish cations from anions. The electrical output signal trace, revealed in our study, may serve as an indirect measurement of the ionic current recorded as a sensing output. With this case study, we were able to show the potential of this top-down multiscale approach applied on the design of novel nanofluidic devices. More important than the specific results of our case study, we presented an innovative approach that can be used to address the complexity displayed by several other nanofluidic-based systems. We anticipate the potential of defective CNTs as a suggestion to be explored in future works, since the interaction with the ions is predicted to be enhanced, thus, possibly improving the ionic selectivity.

In addition to the introduced approach, we may anticipate also the potential of CNT channels for other nanofluidics applications. The CNTs enable new electrokinetic functionalities for a accurate manipulation/separation of electrolytes in fluid devices. The same range of capabilities has the potential to be extended to another challenge problems, such as in mixture separations of gaseous systems. In this context, the multilevel strategy may be the best procedure to proper design and characterize the nanofluidics-based systems at molecular level, contribution to a predictive understanding of its basic functionality.

Currently, the properties of fluids in nanoconfinement are still far from being fully understood. In general, the properties of fluids in nanoscopic environments are expected to be quite different from the usual bulk ones because the interface effects. Considering that the fluids macroscopic properties results from the collective role of individual molecules in the system, the liquid structural features could provide important informations to the understanding of the system dynamics, for instance. In this context, the hydrogen bond network analysis within the graph theory was successfully implemented with the aim to provide the topology details of hydrogen bonded systems. However, the surface effects arising in porous media required a modified version of the existent approach to systematically access the fluids properties at solid/solution interface.

Thus, other challenge problem addressed in current thesis was the hydrogen bond network analysis of confined fluids. We implemented the layered analysis of the hydrogen

bond network to disentangle the interaction details of surface water, the effect of ions, and the extension of the surface effects on the fluid properties. In addition to the channel transport properties unveiled with our multilevel approach, the knowledge of fluid basic properties displayed under confinement is essential to the design and characterization of nanofluidic devices and for the understanding of natural bio-geological processes.

Indeed, the knowledge obtained through our layered version of the hydrogen bond network analysis may assist the development of novel nanofluidic devices, since the fluid features in confinement environments are key features permeating the basic functions of such systems. Besides this research, the expertise delineated in this work may conduce the development of further studies related to the hydrogen bond network in porous media. In this context, we can suggest several interesting problems to be elucidated in terms of hydrogen bond network, such as: the effect of surface charge, the nanochannel material and shape, distinct chemical species as solute, and the temperature. Particularly, in oil industry we may delineate some important applications of our layered approach to investigate the structural and interaction details displayed at oil/brine and the complex oil/brine/rock interfaces. As we have done with the dynamics properties, the structural features can be related to other physical quantities, such as the contact angle and the wettability. Such study may be particularly important within the enhanced oil recovery (EOR) investigation.

In addition to the cited applications, the hydrogen bond network analysis may give essential informations about the network topology that can be used as a data-mining tool, therefore, providing several features to a machine learning study. Indeed, the employment of machine learning techniques is a growing trend in material science and until now, this approach is just starting to be explored to address the nanofluidics problems²⁹³. In the same fashion, we can dare to extend the range of applications of our slab approach to other graph networks, i.g., social media interconnections in frontier conflict problems²⁹⁴.

By applying the layered hydrogen bond network analysis in a case study, we unveil the structure and dynamics of brine-calcite nanoconfined interfaces. We brought a fresh look at molecular level on the phenomena involving this compelling interface with potential significance on the processes occurring in pore scale. This study was based on fully atomistic classical molecular dynamics simulations combined with nuclear magnetic resonance modeling (NMR) and hydrogen bond network analysis stand on graph theory. The framework suggested in this thesis can shed light on the behavior of other fluids under nanoconfinement. Such knowledge is of broad interest and may give stimulating understanding on the plethora of processes within nanoconfinement environments (e.g. biomineralization, desalinization, dynamics on nanoporous media and nanofluidics).

We have exposed the particular hydrogen bond network of water under nanoscopic confinement and ions. In particular, the graph analysis of such structure revealed the formation of more extended geodesic paths capable to cross the nanopore. Such feature may explain the glue-like mechanical properties observed in confined environment. The overall slowdown in water diffusion noticed with NMR modeling is attributed to this particular distortion on the hydrogen bond network. Furthermore, it may influence the crystal growth rate by particle attachment, since the hydrated particle takes longer time to reach to an attachment site at the calcite surface. In addition, the graph analysis allowed the observation of a surface water, which is characterized by an 58% higher contribution of four coordinated water molecules with respect to the bulk phase and by one order slower NMR T_2 parameter. The electrostatic and physical barrier displayed by the surface water may inhibit the formation of pathways for the crystal growth. In addition, the ionic distribution observed inside the calcite slit pore is related with the spatially alternated electrical potential arising from the strong ordering of water molecules in contact with

the solid surface interface. In particular, the Na and Cl electrolyte ions interact with this potential, which results in a screening effect. In fact, these ions kept 4Å away from the calcite surface. Thus it may also reduce the probability of desolvation and attachment of foreign chemical species directly on the surface.

In summary, in this thesis we got important advances towards the understanding of the phenomena occurring in nanofluidics-based systems through the integration of molecular modeling methodologies (HB network analysis, NMR modeling, DFT, MD, NEGF). Such procedure in our work led to fruitful advances in nanofluidics with important publications in the area. Indeed, the solution of complex problems in science research fields makes it necessary a synergy between different approaches, in line with the multidisciplinary spirit. We believe that such approach may be the solution for other challenging problems encountered in complex systems involving multiscale phenomena. Therefore, we encourage other initiatives within the multilevel/multimethodology purpose widely used in our thesis.

In spite of the several puzzling physics problems do not explored within the topic of this study, because the limited time imposed by the PhD research project, the theoretical background can drive the development of further original studies retained in other challenger projects. Finally, the combined methodology strategy, allied to the experimental advances, allows us to glimpse a promising future of the nanofluidics research field in the upcoming years.

APPENDIX A

GEOMETRIC PATTERN DEFINITIONS

The following figures were captured from the Ozkanlar and Clark¹⁷ supplementary material. The geometric criteria are the same implemented in the ChemNetworks code.

A.1 Cyclic Oligomers

A.2 Hexamer Oligomers

Hexamer Bag

$$\begin{aligned} 80^\circ &\leq (\angle O1-O2-O3) \leq 140^\circ \\ 80^\circ &\leq (\angle O2-O3-O4) \leq 140^\circ \\ 0^\circ &\leq |\angle O1-O2-O3-O4| \leq 25^\circ \\ 60^\circ &\leq |\angle O5-O1-O4-O6| \leq 180^\circ \\ 60^\circ &\leq |\angle O6-O4-O1-O5| \leq 180^\circ \end{aligned}$$

(e)

Hexamer Boat

$$\begin{aligned} 100^\circ &\leq (\angle O1-O2-O3) \leq 130^\circ \\ 100^\circ &\leq (\angle O1-O4-O5) \leq 130^\circ \\ 100^\circ &\leq (\angle O6-O5-O4) \leq 130^\circ \\ 100^\circ &\leq (\angle O6-O3-O2) \leq 130^\circ \\ 80^\circ &\leq (\angle O3-O2-O4) \leq 100^\circ \\ 80^\circ &\leq (\angle O2-O4-O5) \leq 100^\circ \\ |\angle O2-O3-O5-O4| &\leq 15^\circ \\ 10^\circ &\leq |\angle O3-O4-O2-O1| \leq 90^\circ \\ 10^\circ &\leq |\angle O4-O3-O5-O6| \leq 90^\circ \end{aligned}$$

(f)

Hexamer Book

$$\begin{aligned} 80^\circ &< (\angle O1-O2-O3) < 100^\circ \\ 80^\circ &< (\angle O2-O3-O4) < 160^\circ \\ 80^\circ &< (\angle O3-O4-O5) < 100^\circ \\ 80^\circ &< (\angle O4-O5-O6) < 100^\circ \\ 80^\circ &< (\angle O5-O6-O1) < 160^\circ \\ |\angle O1-O2-O3-O6| &\leq 20^\circ \\ |\angle O3-O4-O5-O6| &\leq 20^\circ \end{aligned}$$

(g)

Hexamer Cage

$$\begin{aligned} (\angle O \cdots H - O) &> 130^\circ, \text{ for all waters} \\ 60^\circ &< (\angle O1-O2-O3) < 120^\circ \\ 60^\circ &< (\angle O2-O3-O4) < 120^\circ \\ 40^\circ &< |\angle O1-O2-O3-O4| < 90^\circ \\ 150^\circ &< |\angle O5-O1-O3-O6| \leq 180^\circ \\ 150^\circ &< |\angle O6-O2-O4-O5| \leq 180^\circ \end{aligned}$$

(h)

Hexamer Chair

$$\begin{aligned} 100^\circ &\leq (\angle O1-O2-O3) \leq 130^\circ \\ 100^\circ &\leq (\angle O1-O4-O5) \leq 130^\circ \\ 100^\circ &\leq (\angle O6-O5-O4) \leq 130^\circ \\ 100^\circ &\leq (\angle O6-O3-O2) \leq 130^\circ \\ 80^\circ &\leq (\angle O3-O2-O4) \leq 100^\circ \\ 80^\circ &\leq (\angle O2-O4-O5) \leq 100^\circ \\ |\angle O2-O3-O5-O4| &\leq 15^\circ \\ 10^\circ &\leq |\angle O3-O4-O2-O1| \leq 90^\circ \\ 10^\circ &\leq |\angle O4-O3-O5-O6| \leq 90^\circ \end{aligned}$$

(i)

Hexamer Prism

$$\begin{aligned} 50^\circ &< (\angle O1-O2-O3) < 70^\circ \\ 50^\circ &< (\angle O4-O5-O6) < 70^\circ \\ 80^\circ &< (\angle O2-O3-O4) < 100^\circ \\ 80^\circ &< (\angle O3-O4-O5) < 100^\circ \\ 80^\circ &< (\angle O5-O6-O2) < 100^\circ \\ (\angle O2 \cdots H - O1) &> 120^\circ \\ (\angle O3 \cdots H - O2) &> 120^\circ \\ (\angle O3 \cdots H - O1) &> 120^\circ \\ (\angle O5 \cdots H - O4) &> 120^\circ \\ (\angle O6 \cdots H - O4) &> 120^\circ \\ (\angle O5 \cdots H - O6) &> 120^\circ \\ (\angle O4 \cdots H - O3) &> 140^\circ \\ (\angle O1 \cdots H - O5) &> 140^\circ \\ (\angle O6 \cdots H - O2) &> 140^\circ \end{aligned}$$

(j)

Hexamer Prism/Book

$$\begin{aligned} 50^\circ &< (\angle O1-O2-O3) < 70^\circ \\ 80^\circ &< (\angle O2-O3-O4) < 100^\circ \\ 80^\circ &< (\angle O3-O4-O5) < 100^\circ \\ (\angle O5-O4-O6) &> 70^\circ \\ (\angle O2 \cdots H - O1) &> 120^\circ \\ (\angle O2 \cdots H - O3) &> 120^\circ \\ (\angle O1 \cdots H - O3) &> 120^\circ \\ (\angle O5 \cdots H - O4) &> 120^\circ \\ (\angle O4 \cdots H - O6) &> 120^\circ \\ (\angle O3 \cdots H - O4) &> 140^\circ \\ (\angle O1 \cdots H - O5) &> 140^\circ \\ (\angle O6 \cdots H - O2) &> 140^\circ \end{aligned}$$

(k)

Hexamer Ring

$$\begin{aligned} 110^\circ &< (\angle O1-O2-O3) < 130^\circ \\ 110^\circ &< (\angle O2-O3-O4) < 130^\circ \\ 110^\circ &< (\angle O3-O4-O5) < 130^\circ \\ 110^\circ &< (\angle O4-O5-O6) < 130^\circ \\ 110^\circ &< (\angle O5-O6-O1) < 130^\circ \\ |\angle O1-O2-O3-O4| &\leq 30^\circ \\ |\angle O1-O6-O5-O4| &\leq 30^\circ \\ |\angle O2-O1-O4-O5| &\geq 150^\circ \\ |\angle O6-O1-O4-O3| &\geq 150^\circ \end{aligned}$$

(a) This angle is used if H-bond angle, θ , is larger than this angle. Otherwise, θ is used.

(l)

APPENDIX B

FORCE FIELDS

B.1 Force Field for CNT-Brine

The carbon nanotube and graphene sheets are modeled by terms describing Morse bond, harmonic cosine of the bending angle, and a 2-fold torsion potentials as

$$U(r_{ij}, \theta_{ijk}, \phi_{ijkl}) = K_{Cr}(e^{-\gamma(r_{ij}-r_C)} - 1)^2 + \frac{1}{2}K_{C\theta}(\cos \theta_{ijk} - \cos \theta_C)^2 + \frac{1}{2}K_{C\phi}(1 - \cos 2\phi_{ijkl}), \quad (\text{B.1})$$

where θ_{ijk} and ϕ_{ijkl} are representing all the possible bending and torsion angles, and r_{ij} represents all the distances between bonded atoms. K_C , $K_{C\theta}$, and $K_{C\phi}$ are the force constants of the stretch, bend, and torsion potentials, respectively, and r_C , θ_C and ϕ_C the corresponding reference geometry parameters for graphene. In table **Table B.1** we show the values of the corresponding parameters.

Table B.1: Parameters for the bonded potential of carbon-based system¹⁷⁰.

Bond (Morse)	K_{Cr} [kJ/(molÅ ²)]	r_C [Å]	γ [Å ⁻¹]
	478.9	1.418	2.1867
Angle (Harmonic Cosine)	$K_{C\theta}$ [kJ/mol]	θ_C [°]	
	562.2	120.00	
Torsion	$K_{C\phi}$ [kJ/mol]		
	25.12		

The flexible **SPC-FH** water model is described by intramolecular harmonic stretching and bending between the hydrogen and oxygen atoms as

$$U(r_{ij}, \theta_{ijk}) = \frac{1}{2}K_{Wr}(r_{ij} - r_w)^2 + \frac{1}{2}K_{W\theta}(\theta_{ijk} - \theta_W)^2, \quad (\text{B.2})$$

where K_{Wr} and $K_{W\theta}$ are the parameters of the potential, and r_W and θ_W are the reference bond length and angle, respectively. The values of corresponding parameters are show in **Table B.2**.

Table B.2: Parameters for the flexible (**SPC-FH**) water model¹⁷¹.

Bond	K_{Wr} [kJ/(molÅ ²)]	r_W [Å]
	4637	1.0
Angle	$K_{W\theta}$ [kJ/(mol rad ²)]	θ_W [°]
	383	109.47

Non bonded interaction between charged atoms are comprised of a Coulomb potential

$$U(r_{ij}) = \frac{1}{4\pi\epsilon_0} \frac{q_i q_j}{r_{ij}}, \quad (\text{B.3})$$

where ϵ_0 is the permittivity in a vacuum, and q_i , q_j are the partial charges. The charge values for each atom are giving in **Table B.3**.

Table B.3: Atomic charge.

Element	C	O	H	Li	Na	Cl
Charge [e]	0.0	-0.8476	0.4238	1.0000	1.0000	-1.0000

A Lennard-Jones (LJ) term is added to account for the steric and van der Waals interaction:

$$U(r_{ij}) = 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right], \quad (\text{B.4})$$

where σ_{ij} is the depth of the potential well and σ_{ij} is the finite distance at which the inter-particle potential is minima. The parameter values are show in **Table B.4**.

Table B.4: Lennard-Jones parameters for the CNT-brine system. The parameters were taken from ^aReference¹⁷⁰, ^bReference¹⁷¹ and ^cReference¹⁷².

	ϵ_{ij} [kcal/mol]	σ_{ij} [Å]
C-C ^a	0.105	3.851
O-O ^b	0.155	3.188
H-H ^b	0.039	0.651
Na-Na ^b	0.047	2.45
Cl-Cl ^b	0.150	4.10
Li-Li ^c	0.165	1.506

To describe the LJ interaction between crossing atoms, σ and ϵ parameters are combined by arithmetic mixing rule

$$\sigma_{ij} = \left(\frac{\sigma_i + \sigma_j}{2} \right) \text{ and } \epsilon_{ij} = \left(\frac{\epsilon_i + \epsilon_j}{2} \right). \quad (\text{B.5})$$

B.2 Force Field for Calcite-Brine

The flexible **SPC/Fw** water model²³² and the carbonate portion of calcite are described by intramolecular harmonic stretching and bending terms between the atoms as

$$U(r_{ij}, \theta_{ijk}) = \frac{1}{2}K_r(r_{ij} - r_0)^2 + \frac{1}{2}K_\theta(\theta_{ijk} - \theta_0)^2, \quad (\text{B.6})$$

where θ_{ijk} and r_{ij} representing all the possible bending angles and distances between bonded atoms, respectively. The K_r and K_θ are the parameters of the potential depth, and r_0 and θ_0 are the reference bond length and angle, respectively. An out of plane potential was added to describe the carbonate C-O/O/O intramolecular interaction

$$U(d) = K_2d^2 + K_4d^4, \quad (\text{B.7})$$

where d is the distance between the central atom (C) and the plane formed by other ones (O); and K_2 and K_4 are polynomial multiplication factors. The values of corresponding parameters for bonded terms are show in **Table B.5**.

Table B.5: Parameters for bonded terms. The parameters are taken from reference²²². Here the symbol O refers to the oxygen of carbonate, while O_w refers to that of water.

Bond-Harmonic	Interaction	K_r [eV Å ⁻²]	r_0 [Å]
C–O	Intramolecular	35.9	1.313
O_w –H _w	Intramolecular	45.93	1.012

Angle-bending	Interaction	K_θ [eV rad ⁻²]	θ_0 [°]
O–C–O	Intramolecular	12.0	120.0
O_w –H _w – O_w	Intramolecular	3.291	113.24

Out of plane	Interaction	K_2 [eV Å ⁻²]	K_4 [eV Å ⁻⁴]
C–O/O/O	Intramolecular	20.796	360.0

The non bonded potential is composed by Buckingham, Lennard-Jones, and Coulomb terms. The Buckingham potential treats short-range interactions in a more physical way as compared to the Lennard-Jones one, by using an exponential repulsive term. Its functional form is given by

$$U(r_{ij}) = A_{ij} \exp\left(-\frac{r_{ij}}{\rho_{ij}}\right) - \frac{C_{ij}}{r_{ij}^6}, \quad (\text{B.8})$$

where r_{ij} is the particle-particle separation distance; C_{ij} represents the dispersive attraction between species, and A_{ij} the strength of the potential. The corresponding parameters are shown in **Table B.6**.

Table B.6: Buckingham parameters. All calcium and carbonate intermolecular terms are tapered to zero over the range of 6-9 Å. The parameters are taken from reference²²².

Species	Interaction	A [eV]	ρ [Å]	C [eV Å ⁶]
Ca–O	Intermolecular	3161.6335	0.27151	0.00000000
Ca–C	Intermolecular	120000000.	0.12000	0.00000000
O–O	Intermolecular	63840.199	0.19891	27.8990080
O–O _w	Intermolecular	12534.455133	0.21517	12.0900225
O–H _w	Intermolecular	396.320957	0.22300	0.00000000
Ca–O _w	Intermolecular	1186.492877	0.29700	0.00000000

The Lennard-Jones potential is more robust for solution phase simulations and it was added to account for the steric and van der Waals interaction of some kind of atoms. They functional form is given by

$$U(r_{ij}) = 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right], \quad (\text{B.9})$$

where σ_{ij} is the depth of the potential well and σ_{ij} is the finite distance at which the inter-particle potential is minima. The corresponding parameters are shown in **Table B.7**.

Table B.7: Lennard-Jones parameters taken from reference²²² for water and calcite, and reference²⁶⁰ for NaCl atoms.

Species	Interaction	ϵ_{ij} (eV)	σ_{ij} (Å)
O _w –O _w	Intermolecular	0.0070576	3.16435
Cl–Cl	Intermolecular	0.0065046	4.54
Na–Na	Intermolecular	0.002033777	2.7275
Ca–Ca	Intermolecular	0.000133902	3.534508

To describe the LJ interaction between crossing atoms, ϵ and σ parameters are combined by Lorentz-Berthelot mixing rules:

$$\epsilon_{ij} = \sqrt{\epsilon_i * \epsilon_j} \text{ and } \sigma_{ij} = \left(\frac{\sigma_i + \sigma_j}{2} \right). \quad (\text{B.10})$$

Non bonded interaction between charged atoms are comprised of a Coulomb potential

$$U(r_{ij}) = \frac{1}{4\pi\epsilon_0} \frac{q_i q_j}{r_{ij}}, \quad (\text{B.11})$$

where ϵ_0 is the permittivity in a vacuum, and q_i , q_j are the partial charges. The charge values for each atom are given in **Table B.8**.

Table B.8: Atomic charge. The values are taken from reference²²² for water and calcite, and reference²⁶⁰ for Na and Cl atoms.

Element	C	O	Ca	O _w	H _w	Na	Cl
charge [e]	+1.123	-1.041	+2.000	-0.820	+0.410	+1.000	-1.000

APPENDIX C

NMR MODELING

C.1 Self-Diffusion

The translational dynamics was quantified by calculating the self-diffusion coefficient. The self-diffusion coefficient D is a measure of the rate of displacement of water molecules from their equilibrium position. In other words, it is the slope of the mean square displacement (MSD) as a function of time. It was calculated from the mean square displacement Einstein relation²⁹⁵;

$$D = \lim_{t \rightarrow \infty} \frac{\langle |\mathbf{r}(t) - \mathbf{r}(0)|^2 \rangle}{6t} \quad (\text{C.1})$$

where $\mathbf{r}(t)$ is the position vector of the water molecule center of mass at time t . The angular brackets denote an average over time origins and all water molecules. Within the layers, parallel self-diffusion coefficient $D_{||}$ in each layer is given by:

$$D_{||}(\{z\}) = \lim_{t \rightarrow \infty} \frac{\langle \Delta \mathbf{r}(t)^2 \rangle_{\{z\}}}{4P(t)t} \quad (\text{C.2})$$

where $\{z\}$ represents the set of molecules that remain in the slab centered at a distance z from the surfaces during the interval $[0, t']$. $P(t)$ is the survival probability function ($P(t) = 1/T \sum_{t=1}^T N(t)/N(0)$), which relates the number of molecules $N(t)$ which remain in the slab in the time interval $[0, t']$ to the number of molecules $N(0)$, which were present at the initial time $t = 0$. T is the total number of time steps averaged over.

C.2 Rotational Dynamics

For the rotational dynamics, we investigate the HH intramolecular vector reorientation, which is probed by proton NMR in H_2O experiments²⁹⁶. The rotational dynamics are analyzed by computing the second order reorientation time-correlation function $C_{HH}(t)$, for the water HH-bond vector $\mathbf{u}$, which is given by:

$$C_{HH}(t) = \langle P_2[\mathbf{u}(0) \cdot \mathbf{u}(t)] \rangle \quad (\text{C.3})$$

where P_2 is the second order Legendre polynomial²⁹⁷. The relaxation time can be compared with that measured in 1H NMR experiments for a rotation about the HH vector²⁹⁸. The rotational correlation time τ_c was obtained by fitting the autocorrelation function $C_{HH}(t)$ (second order Legendre polynomial) to a stretched exponential function $a_0 e^{-(t/\tau_c)^\beta}$ for the confined water and a simple exponential function $a_0 e^{-(t/\tau_c)}$ for the bulk system. It has been used previously to fit correlation functions for supercooled water²⁹⁹.

C.3 Transverse Spin Relaxation

The determination of T_2 relaxation time of proton bearing fluids is a widely accessible experimental technique used to study the properties of porous media. However, although the NMR signal contains the contribution of all relaxing spins, it is difficult to disentangle the contributions of water in different regions of the pore and the main mechanisms leading to the relaxation. By simulating the relaxation rates in each layer, we aim to provide local variation of the spin relaxation times, which is helpful in enhancing the interpretation of the experimental NMR signal response obtained from the contribution of all molecules.

The theoretical calculation of the transverse (T_2) spin relaxation is based on a semiclassical theory developed by Bloembergen, Purcell and Pound (BPP)²⁶⁸. According to BPP theory, the transverse NMR relaxation rate of a system involving relaxation of the same nuclear species is given as:

$$\frac{1}{T_2} = \frac{3}{8} \left(\frac{\mu_0}{4\pi} \right)^2 \gamma^4 \hbar^2 I(I+1) [J(0) + 10J(\omega) + J(2\omega)] \quad (C.4)$$

where, γ , $\hbar$ and I are the gyromagnetic ratio, Planck's constant and spin of the diffusing spins, respectively. μ_0 is the permeability of free space and ω is the Larmor frequency in the applied static field. The spectral density function $J(\omega)$ is obtained from Fourier transform of the correlation function $G(t)$:

$$G(t) = \left\langle \frac{P_2(\cos \phi)}{r_0^3 r^3} \right\rangle \quad (C.5)$$

where, ϕ is the angle between the water molecule HH vectors $\mathbf{r}_0$ and $\mathbf{r}$ at the initial and later time, respectively. $P_2(\cos \phi) = \frac{1}{2}(3 \cos^2 \phi - 1)$ is a Legendre polynomial averaged over the number of spins and time origins. The pore radius dependence of the T_2 spin relaxation is calculated based on the fast-exchange model^{283,300}. In this model, the fluid confined in a pore has two distinct phases: a bulk phase, which has the same relaxation properties as the bulk liquid and a surface phase whose relaxation rate is greatly affected.

If the rotational and translational dynamics of dipolar couplings can be assumed to be stochastically independent of each other, the effective T_2 relaxation rates can be expressed as:

$$\Gamma_2 \equiv \frac{1}{T_2} \approx \frac{1}{T_2^{rot}} + \frac{1}{T_2^{trans}} \quad (C.6)$$

where T_2^{rot} and T_2^{trans} correspond to rotation and diffusion of spins respectively.

A rotating water molecule causes an intramolecular magnetic dipole-dipole interaction between the protons in a molecule, which is a function of the distance r separating the two spins. With the assumption that $\omega^2 \tau_c^2 \ll 1$, where ω is the frequency and τ_c is the rotational correlation time, the relaxation time rate is a function of the rotational correlation time

and is given by³⁰¹:

$$\Gamma_2^{rot} \equiv \frac{1}{T_2^{rot}} \approx \left(\frac{\mu_0}{4\pi} \right)^2 \frac{3}{2} \frac{\gamma^4 \hbar^2 \tau_c}{r^6} \quad (C.7)$$

where γ is the gyromagnetic ratio, μ_0 is the permeability of free space, $\hbar$ is the Planck's constant and r is the separation of spins.

In addition, diffusing water molecules cause intermolecular magnetic dipole-dipole interactions. The T_2 relaxation time rate due to diffusing spins is as follows³⁰¹:

$$\Gamma_2^{trans} \equiv \frac{1}{T_2^{trans}} \approx \frac{\pi}{5} \frac{N_s \gamma^4 \hbar^2}{aD} \quad (C.8)$$

where N_s is the density of spins per cm^3 , a is the distance of closest approach and D is the translational self-diffusion coefficient.

APPENDIX D

CARBON NANOTUBES

D.1 Structural Features

Carbon nanotubes (CNTs) are cylindrical structures with the diameter within nanometer size (10^{-9} m), while the length can reach the micrometer order (10^{-6} m). Its physical structure can be understood from a graphene “honeycomb” lattice rolled at specific angle. The rolling direction is given by the chiral vector:

$$\vec{C}_h = n\vec{a}_1 + m\vec{a}_2, \quad (\text{D.1})$$

where n and m are the projections of graphene lattice on the basis vectors ($\vec{a}_1$ and $\vec{a}_2$). The CNT nomenclature is associated with this integers: 1) if $n = m \neq 0$, the nanotube is type *armchair*; 2) if $n \neq 0$ and $m = 0$, the nanotube is type *zig-zag*; 3) if $n \neq m \neq 0$, the nanotube is type *chiral*.

The diameter of an ideal nanotube is related with the (n, m) indices:

$$d = \frac{a}{\pi} \sqrt{(n^2 + nm + m^2)}, \quad (\text{D.2})$$

where $a = 2.46$ Å is the graphene lattice parameter.

The electronic properties are also related to the (n, m) values³⁰²: *armchair*, *chiral* and *zig-zag* — with $|n - m| = 3k$ (where k is a integer) — are metallic. CNTs type *zig-zag* — with $|n - m| = 3k \pm 1$ — are semiconductors. The semiconductor CNT band gap ranges from few meV to about 1 eV depending upon the cylindrical radius³⁰³.

D.2 Single Atom Adsorption on CNT

We explored the effect of the single Na, Li and Cl atom adsorption on the carbon nanotube (CNT) walls in order to isolate the specific contributions on the tube electronic properties. The adsorption energy is an usual quantity employed to evaluate that. It was calculated through the equation:

$$E_a = E_{tot} - (E_{CNT} + E_{atom}), \quad (\text{D.3})$$

Table D.1: E_a values (in eV) for the adsorption of the Li, Na and Cl atoms on the the CNT sites.

	Inside			Outside		
	T	B	H	T	B	H
Li	–	–	-1.87	–	–	-1.73
Na	–	–	-1.68		-1.26	-1.43
Cl	–	-1.64	-1.64	-2.10	–	–

Table D.2: Charge exchange amount displayed in the CNT stable and metastable sites for the Na, Li and Cl adsorption.

	Inside			Outside		
	T	B	H	T	B	H
Li	–	–	+1.0	–	–	+1.0
Na	–	–	+1.0		+1.0	+1.0
Cl	–	-0.58	-0.58	-0.24	–	–

where E_{tot} is the total energy of the carbon nanotube with the adatom (Cl, Li or Na); E_{CNT} is the total energy of the isolated CNT and E_{atom} is the total energy of the free adatom. In the supercell, we include six nanotube primitive cells in order to minimize the interaction between the neighboring adsorbates³⁰⁴. Following other authors³⁰⁵, the total energy of the isolated atom is taken from a spin-polarized calculation.

The CNTs have potentially three adsorption sites³⁰⁶, namely top (T), bridge (B), and hollow (H). A single atom was placed on each of these adsorption sites (outside and inside the tube), followed by the full geometry optimization by first-principles calculations. Through the energy minimization by the conjugated gradient process, we observed that, outside the CNT, the most stable site for Cl atom is the T. For the Na and Li atoms, it is the H (see **Table D.1**). These results are in agreement with previous studies performed on similar system setup^{175,305,307}. In addition, we observed that the Na atom can adsorb in the B site. However, this atomic configuration displays higher adsorption energy in comparison to the most stable site (metastable). All the other analyzed outside sites are unstable for the adsorption of the investigated atoms.

Inside the CNT, the stable site for Li is the T, the same displayed on the outside region (see **Table D.1**). Furthermore, the Na most stable site still is the H, but the B site, noticed outside the CNT, is unstable on the inner region. The CNT inner surface displays two stable sites for Cl atom adsorption: H and B. Both of them display the same adsorption energy. The concave geometry inside the CNT favors the adsorption of the Na and Li atoms (with respect the outer region). However, the Cl adsorption energy is reduced in both H and B sites.

The charge exchange between the CNT and the adsorbed atoms was estimated through the Bader charge analysis^{184,308}. We observed that the CNT and the adatoms exchange a significant amount of charge. In addition, the sign of the charge transfer to the CNT has a relation with the position of the elements in the periodic table: the atoms belonging to the 17 family receive, whereas the atoms belonging the 1 family donate electrons to the CNT, according to the **Table D.2**. Therefore, the analyzed atoms manifest their ionic character during the adsorption on the carbon atoms.

Subsequently, we analyzed the effect of the charge exchange on the CNT band structure

Figure D.1: Energy band structure comparison between the CNT bulk (gray lines) and that one interacting with the Li, Na and Cl atoms (blue and red). We considered all the stable and metastable sites for the adsorption of the atoms on the CNT.

(see **Figure D.1**). We observed that the CNT electronic states are displaced with respect to the Fermi level. The band shift direction is connected to the amount and the sign of the charge transferred to the CNT^{309,310}. Furthermore, the CNT band structure is more affected with the Cl adatom on the outer region, whereas the Cl adsorption energy is lower in the inner site. Moreover, the greater transfer of charge and slice distortion in the linear character of the CNT bands around the Fermi level indicate the ionic character of the interaction prevails over the covalent¹.

¹The non-null magnetic moment displayed for the Cl atom adsorption on CNT should be further investigated.

APPENDIX E

ELECTROLYTE AQUEOUS SOLUTION WITHIN CALCITE SLIT PORES

E.1 Pore Model

Figure E.1: a) Calcite slit pore model highlighting the water at calcite surface (inset). b) Geometric quantities determined to characterize the hydrogen bond network through the graph geodesic analysis.

E.2 Pure Water Within Calcite Slit Pores

Table E.1: Average number of hydrogen Bonds values observed within the structured layers. Here, ww represents the hydrogen bonds formed between water molecules, while $ww + wc$ considers also the hydrogen bonds between the carbonate group on the calcite surface.

Interaction	Layer 1	Layer 2	Layer 3	Bulk
ww	0.871 ± 0.004	2.166 ± 0.014	2.729 ± 0.012	2.8847 ± 0.0005
ww+wc	2.384 ± 0.011	2.787 ± 0.022	2.839 ± 0.012	—

Table E.2: Average number of hydrogen bonds values observed within the calcite slit pores

1 nm	2 nm	3 nm	4 nm	5 nm	Bulk
1.89	2.34	2.48	2.56	2.60	2.88

E.3 Brine Composition

Table E.3: Number of ions and water molecules within each investigated pore.

Size (nm)	Na	Cl	Ca	H ₂ O
1	71	89	9	2595
2	143	181	19	5189
3	213	269	26	7790
4	285	361	38	10382
5	358	452	47	12976
6	428	540	56	15573

E.4 Hydrogen Bond Network Properties

Figure E.2: a) Evolution of the geodesic path length distribution for brine and pure water confined inside pore with sizes ranging from 3 to 5 nm. Comparison between pure water and brine b) average triplet O-O-O angle and c) average geodesic path tortuosity calculated over each path length. Standard errors are too small to be represented in this graphic scale.

Figure E.3: Evolution of the geodesic path distribution for brine and pure water belonging to the surface layer (layers 1 and 2). The findings are similar in all analyzed pores due to the absence of ions on this layer. Standard errors are too small to be represented in this graphic scale.

Figure E.4: a) Evolution of the geodesic path length distribution for water and b) brine cross the layers and pore sizes. The layered analysis revealed that the presence of ions of our brine model is the main factor modifying this property inside the layers away from the calcite surface. Standard errors are too small to be represented in this graphic scale.

Figure E.5: O-O-O triplet angle distribution comparison between brine and pure water for each analyzed pore. Standard errors are too small to be represented in this graphic scale.

Figure E.6: Percentage of geodesic paths crossing the pore in the confinement direction. We considered crossing paths those ones who have at least one water molecule inside each surface water layer. Standard errors are too small to be represented in this graphic scale.

Figure E.7: Evolution of the average potential energy (circles) displayed by three water molecules, connected by hydrogen bonds, with respect to the O-O-O triplet angle. This energy is calculated from the classical Lennard-Jones and Coulomb potential of our water model. We considered samples with hundred data points for each angle value. The blue line is to guide the eyes.

E.5 Dynamical Properties

Figure E.8: MSD as a function of time for brine confined in calcite slit pores of sizes 1–6 nm.

Figure E.9: Rotational correlation function, $C_{HH}(t)$, as a function of time and distance from the confining calcite surface for a) 1nm, b) 2 nm and c) 6 nm pores.

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