

# 1. Introduction

## 1.1. Clean Water and Energy: (Still) Plenty of Room at the Bottom

Water and the existence of life are tightly associated. Water is the main component of living organisms: as an example, the human body is composed by 60 to 75% in weight by water. The greater part of this water (about 60%) lies in the cells, while the rest flows in the blood and below the tissues [1]. The majority of living beings can only survive a few days in absence of water, because water is involved in most of the biological processes related to the standard metabolism [1]. As a few examples, proteins have to be solvated in order to adopt their characteristic three dimensional structure, which allows to carry out their typical functions; water is involved in the elimination of cellular metabolic residues and it is by means of water that oxygen and nutrients can be delivered throughout the body.

However, an explanation why water should be the only liquid whereby life forms and survives on Earth is still unclear and debated. In 1913 L.J. Henderson first wondered if there was a relation between the physicochemical anomalies of water and its suitability as life broth [2]. Arguably, water is the strangest liquid in the universe with many peculiar counterintuitive and anomalous properties with respect to other fluids, which are pivotal to the existence of life. This evidence has puzzled and intrigued generations of scientists, engineers, biologist, philosophers, theologians and thinkers of any kind, since Thales (VII century B.C.) and Empedocles (V century B.C.) first suggested that water is the most important among the four constituting elements (i.e. water, fire, earth and air) of the Universe.

"*Water, water, everywhere, nor any drop to drink*" declares the ancient mariner in the Coleridge's rime [3]. In that sentence, two main features of water are enclosed. First, water is ubiquitous: approximately 70% of the

Earth's surface is covered with it. Second, water is nearly a universal solvent, so that the oceans are impossibly salty. The latter paradox is rapidly becoming one of the main global problems that humanity has to face in the near future. As a matter of fact, the global community is witnessing the impact of extreme climates in floods and drought conditions often in crowded and indigent urban surroundings. In this context, drinkable water is an increasingly scarce and precious resource [4].

Hence, during their daily research activities, scientists and engineers have to be inspired by a few policy guidelines when dealing with clean water issues. Taking inspiration from the "World Water Assessment Programme" by the United Nation [4], the following manifesto should be adopted for driving basic and applied research on water:

1. Access to clean water is a fundamental right. According to the United Nations, "sufficient, affordable, physically accessible, safe and acceptable water for personal and domestic uses" is a fundamental human right and a pre-requisite to the realization of all other human rights. In other words, drinkable water should be accessible everywhere, every time by everyone on Earth.
2. Poverty remains the biggest problem facing the world today. Inadequate drinking water and sanitation services are key aspects of poverty with serious implications, such as death, disease and delayed development in the populations immediately affected.
3. Climate change with increased variability exacerbates the spatial and temporal variability of water resources and intensifies the urgent need for the proper management of water resources. Given the finite quantity of freshwater, the current business-as-usual approach to development can only limit usable water resources as a result of continual and widespread physical and chemical pollution.
4. Sectorally and geographically, water problems and challenges are neither independent nor isolated. Their solutions thus need to be addressed in a comprehensive and holistic manner, taking into account a variety of circumstances with solutions tailored to the situation.
5. Healthy ecosystems have importance far beyond their amenity or biodiversity preservation value. Healthy ecosystems are integral to the proper functioning of the hydrological cycle, thus environmental preservation must be at the heart of any action devoted to increase the preservation of drinkable water.

6. With growing demand and decreasing supply, competition among different sectors and users is increasing, requiring greater wisdom in the allocation of the resource and greater efficiency of water use. More efficient water use must be accomplished not only through the adoption of a variety of new technologies and the application of proven traditional knowledge, but also through better water governance.

Other fundamental questions are waiting for scientific and technological innovations to achieve an overall sustainability of the future global development. Complementary to the clean water issues discussed so far, sustainable energy is the other global issue linked with the activities illustrated in this thesis. As a matter of fact, climate change, increasing dependence on fossil fuels and rising energy costs are making our societies and economies vulnerable. These challenges call for a comprehensive and ambitious response, both from a sociopolitical and scientific point of view [5].

In the articulate framework of energy policy, renewable energy is a sector standing out in terms of possibilities to reduce pollution and greenhouse gas emissions, exploit decentralized and local energy sources and stimulate the development of innovative researches and industries. In 2007, the European Commission outlined some requirements for an effective control of energy consumption, use of energy from renewable sources and increase in energy efficiency [5]. If a few updates and modifications are introduced, some strategic indications for the researchers active in this field can be listed:

1. Boost technological innovation and provide opportunities for employment, with a positive impact on export prospects, social cohesion and employment opportunities, in particular as it concerns small-medium enterprises;
2. Reduce the dependence on imported oil and gas, in which the security of energy supply problem is most acute;
3. Cut the greenhouse gas emissions and environmental impact by reducing the combustion of fossil fuels;
4. Develop democratic and inexpensive energy technologies, which drastically decrease the initial investments for complex power plants without affecting the production efficiency and safety;
5. Support the commercialization of decentralized renewable energy technologies, enhance the utilization of local energy sources, shorten

transport distances and reduce energy transmission losses. Such decentralization also fosters community development and cohesion by providing income sources and creating jobs locally.

In such a context, developing efficient, costless, democratic and environmentally friendly technologies for clean water and energy purposes is fundamental to achieve the so-called *3E objectives*, namely clean Environment, sustainable Energy policy and solid Economy and social development [6]. To this purpose, the current boost in discoveries related to the behavior of fluids and materials at the nanoscale can represent a massive reservoir of opportunities for developing such sustainable novel devices.

With his famous talk "*There's plenty of room at the bottom*" [7], in 1959 Richard Feynman officially announced an upcoming scientific breakthrough. The Feynman perspective, i.e. the possibility for scientists to manipulate matter at atomistic level, was later named "Nanotechnology". This name inspired countless investigations among scientists of almost every field of science and industry: from biology to electronics, from clean water to energy. Since then, with 30 years of research and development, nanotechnology is still bringing new promises and pushing the boundaries in each field of application. Many of these nanoscale studies have already important commercial applications, while other are yet investigated from a more fundamental point of view. Still, due to its complexity, distance from everyday experience and interdisciplinarity, the pervasive feeling is that only the surface of nanotechnology has been scratched so far.

In this thesis, the interesting properties of water concerning the heat and mass transfer at solid-liquid nanoscale interfaces is detailed. The latter basic investigations are a solid starting point for more applied researches, in order to develop clean water (e.g. desalinators, molecular sieves) and renewable energy (e.g. nanofluids coolant, thermal batteries) technologies, which could help to answer the global needs for a more sustainable future of Earth.

## 1.2. Mass transfer of water at the nanoscale

The flotation of solid water (i.e. ice) on liquid water, which is due to the creation of a perfect tetrahedrally coordinated network of hydrogen bonds in turn generating six-membered rings with much empty space between the molecules, is probably the most known anomalous property of water [1]. The maximum density of water at 4°C and the particularly high thermal

capacity are also familiar anomalies. However, water is characterized by many other peculiar properties, which are mainly due to the preponderance of hydrogen bonds compared to other chemically similar substances [8]. Hence, despite thousand of years of interest and research, water properties are still far from being completely understood and exploited in technology applications.

In particular, the advances in nanotechnology research require a better understanding of the behavior of water molecules in the proximity of nanoscale interfaces. In this Section, the fundamental quantities for the mass transfer of water in nanoscale environments are defined. Then, two among the many characteristic mass transfer phenomena of water at the nanoscale are detailed, namely supercooled and nanoconfined regimes. The latter are the main properties of water which are involved in the studies of this thesis.

### 1.2.1. Mass transfer coefficients at the nanoscale

Atoms and molecules follow a perpetual random movement (i.e. Brownian motion), which can be quantified by characteristic diffusion coefficients [9, 10]. Diffusion is essential for both the existence of living organisms [11] and for the effectiveness of many technologies, such as the manufacture of electronics [9] or plastics [12], the functioning of desalination membranes [13] or thermal batteries [6] and the theranostic properties of biomedical molecules or nanoparticles [14]. Three diffusion quantities are here presented, namely  $D_T$  (i.e. Fick's - or transport - diffusion coefficient),  $D$  (i.e. self-diffusion coefficient) and  $\alpha$  (surface permeability).

The transport diffusion coefficient  $D_T$  is defined by Fick's first law as the proportionality factor between a flux of molecules  $j$  and their concentration gradient  $\partial c/\partial x$  (Figure 1.1a) [15].

Self-diffusion coefficient  $D$  of a species, as deepened in Chapter 2, characterizes the molecular mobility under equilibrium conditions, i.e. uniform concentrations. In statistical mechanics, self-diffusivity is defined by the Einstein relation between the mean square displacement of diffusing molecules and the observation time [16]. Alternatively, Karger and colleagues suggest a related and completely equivalent definition for  $D$ . It is based on a "thought experiment", in which the molecules of the same species become distinguishable (for example, by means of isotope tracers) thus undergo Fick's first law of diffusion (Figure 1.1b) [15]. Hence, once

again, it is possible to consider  $D$  as a factor of proportionality between the concentration gradients  $\partial c^*/\partial x$  of either the differently labeled molecules and their fluxes  $j^*$ . Referring to different physical situations, the coefficients of transport and self-diffusion cannot be expected to coincide [15]. In Chapter 4, the analytical relations between self- and transport diffusivities will be deepened.

Finally, when mass flows through planes of dramatically reduced permeability (e.g. a nanoporous membrane such as zeolite), the surface permeability  $\alpha$  of such barriers is defined as the factor of proportionality between the flux  $j$  and the difference in concentrations ( $c_l - c_r$ ) on either sides of the barrier (Figure 1.1c). Correspondingly, in case of transport resistances on the outer surfaces of nanoporous membranes (the so-called "surface barriers"), the difference between the actual boundary concentration and the concentration in equilibrium with the gas phase has to be considered in the definition of  $\alpha$  [15].

### 1.2.2. Supercooled regime

As seen in previous Sections, many anomalous properties are associated with water. Their relevance for biological and engineering processes sometimes cannot be straightforwardly identified; however, one of them is clearly evident: liquid water can exist at temperatures far lower than the freezing temperature [1]. At these temperatures, liquid water is said to be in the supercooled phase. The latter is a metastable phase, meaning that, sooner or later, it tends to transform into ice. In fact, the liquid state of supercooled water is definitively unusual, because it behaves as if there exists a singular temperature toward which its thermodynamic properties diverge [17].

Very briefly, in the presence of heterogeneities (e.g. in contact with foreign substances or surfaces) water freezes at atmospheric pressure at the melting temperature  $T_M \approx 273.15$  K. However, pure bulk water can be supercooled below its melting temperature down to the homogeneous nucleation temperature  $T_H \approx 235$  K, below which it inevitably crystallizes (Figure 1.2). In the range between the melting temperature and the homogeneous nucleation temperature, liquid water exists in a supercooled metastable state, which is characterized by anomalies in its thermodynamic properties [17]. There is a growing interest in the prediction of properties of supercooled water. In particular, in applied atmospheric science, it is commonly accepted that the uncertainties in numerical weather

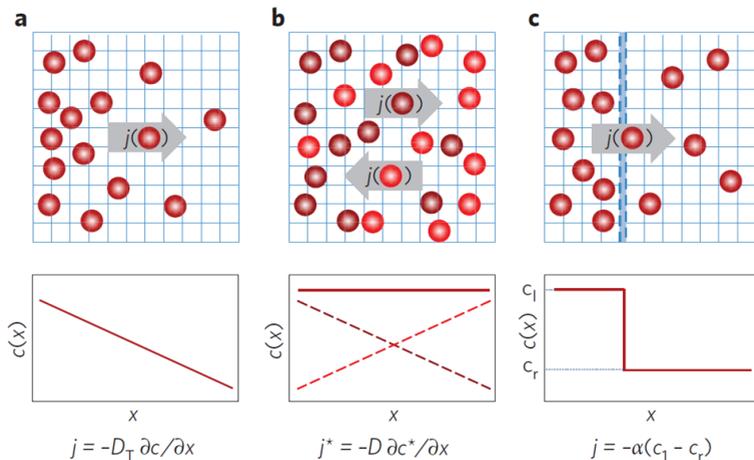


Figure 1.1.: Diffusion phenomena at the nanoscale. (a) Molecular distribution (top), concentration  $c(x)$  profiles (middle) and definition of the transport diffusion coefficient  $D_T$ . (b) Molecular distribution (top), concentration  $c(x)$  profiles (middle) and definition of the self-diffusion coefficient  $D$ .  $j$  and  $j^*$  denote the molar flux of unlabeled and labeled particles, respectively. (c) Molecular distribution (top), concentration  $c(x)$  profiles (middle) and definition of the surface permeability  $\alpha$ .  $c_l$  and  $c_r$  indicate the molecule concentrations on the left and right sides of the barrier, respectively. Figure adapted from Reference [15].

prediction and climate models are mainly caused by poor understanding of properties of water in tropospheric and stratospheric clouds, where liquid water can exist in a deeply supercooled state [18]. In particular, thermodynamic properties of supercooled water diverge toward a singular temperature  $T_C = 228$  K [17]. In 1992, Poole *et al.* suggested that the anomalous properties of supercooled water may be caused by a critical point, which terminates a line of liquid–liquid separation of lower-density (LDL) and higher-density liquid (HDL) [19] (solid blue line in Figure 1.2). This assumption was provocative because liquid water states under normal conditions are inaccessible below the homogenous nucleation temperature. For this reason, the range of temperatures between  $T_H$  and  $T_X \approx 150$  K, where low density amorphous ice melts into a highly viscous fluid, is

usually named *no-man's-land* for liquid water (Figure 1.2). On the other hand, the assumption by Poole *et al.* led to the notion of virtual critical point of liquid–liquid coexistence (LLCP), which is still used nowadays to formulate accurate equations of states for supercooled water [18]. It is worth to point out that some insights into phases of liquid water can be obtained by alternative interpretations, for example based on the order-disorder transition scenario [20].

As a matter of fact, there are at least two methods to explore the *no-man's-land* for liquid water, namely the liquid states at temperature below  $T_H$ . One possibility is to use molecular solutions rich in water (e.g. bio-nanofluids) [20]. Another one, which is receiving a growing attention because of the practical implications in nanotechnology, is to study water in nanoscopic confinement. Water near surfaces often does not crystallize upon cooling, but only recently the properties of such water have been measured [20]. For example, when confined in nanopores made of porous hydrophilic silica glass (Vycor), water does not crystallize and can be supercooled well below  $T_H$  [17]. Nanoconfinement seems to confirm the assumption of a second critical point scenario. In fact, the existence of a peak in the specific heat capacity (Widom line) and a dynamic crossover in the self-diffusion properties of water at  $T \approx 225$  K are clearly revealed by water nanoconfinement. The Widom line separates the two dynamical behaviors of water known as fragile and strong, which are due to a change in the hydrogen bond structure of liquid water [17, 22]. Clearly, this situation resembles the pseudo-critical temperature in supercritical fluids [23]. Nanoconfinement seems to damp out, rather than to exaggerate, the peaks in heat capacity of real water [20] (see, for example, Figure 1 in Reference [22]). Some authors attribute this smoothing to the confinement length scale effects [24]. Alternatively, one could interpret the results by imaging that nanoconfinement acts as a pressure [20]. This would be consistent with the concept of spreading pressure, which is popular in the thermodynamics of adsorption and, more generally, in the non-equilibrium thermodynamics of heterogeneous systems [25].

### 1.2.3. Nanoconfined conditions

A fluid is considered in a nanoconfined regime when its bulk properties are strongly altered by the presence of a solid interface at the nanoscale. The study of nanoconfined liquids, both from a theoretical and from an

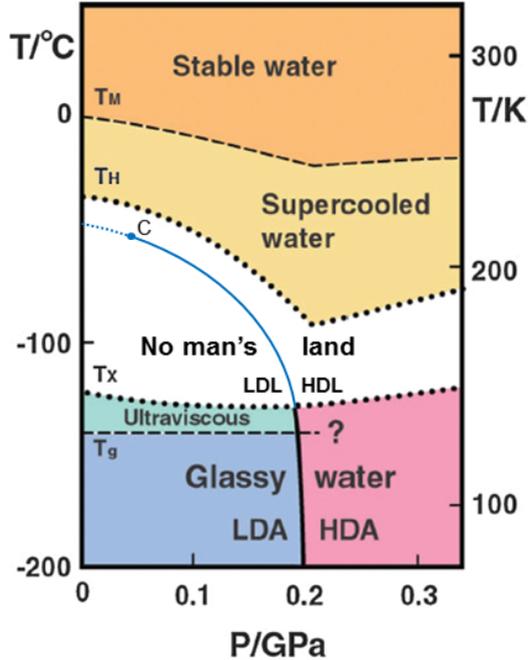


Figure 1.2.: Sketch of the "phase diagram" for non-crystalline water.  $T_M$ : melting temperature;  $T_H$ : homogeneous nucleation temperature;  $T_X$ : crystallization temperature;  $T_g$ : glass-to-liquid transition temperature. The solid blue line represents the liquid-liquid coexistence curve, whereas the dashed blue line is its extension into the one-phase region, namely the Widom line [18]. Below  $T_H$ , there may exist a liquid-liquid critical point, here marked by "C", which terminates the liquid-liquid coexistence curve. Note that it is not clear yet what the value of  $T_g$  is at high pressure (horizontal dashed black line). Figure adapted from Reference [21].

experimental point of view, is relevant to a broad variety of scientific topics, spanning from biology to energy fields [26–30]. In particular, most of the experimental studies focus on systems in which the nanoconfined geometry and the chemical structure of the solid interface can be easily controlled, such as porous hydrophilic glasses and reverse micelles [1].

Molecular simulations, e.g. Molecular Dynamics (MD) techniques, are also effective tools for investigating the properties of nanoconfined fluids and validate theoretical considerations [27, 31–34].

The nonbonded interactions between a solid and a liquid produce local modifications on the properties of both media. In particular, a liquid is considered under nanoconfined conditions when solid-liquid interaction forces - negligible at the macroscale - tend to have prominent effects on the fluid properties at the nanoscale. The latter condition manifests when the fluid lies within approximately a few nanometers from a solid interface [31]. Under nanoconfined regime, water molecules undergo dynamic and structural alterations that imply non-trivial changes of the fundamental chemical-physical properties of the fluid. These differences from the bulk properties are mainly associated with the modification of the hydrogen bond network and the impact of solid-liquid interactions on molecular mobility. Hence, nanoconfined water shows peculiar dynamical, structural, mechanical and electrokinetic properties, which are different from those of the bulk. Among other effects, phase changes, local density, diffusion and viscosity of water are strongly influenced by solid-liquid interactions in case of spatial nanoconfinement [26, 35, 36].

First, nanoconfinement conditions prevent water freezing and make possible the experimental investigation of the supercooled phase at low temperatures [26]. However, the water crystallization is avoided only in case of strong nanoconfinement, i.e. while reaching nanometric length scales. For example, the nanoconfinement of water in silica nanopores of 10 nm diameter induces a lowering of the melting temperature of about 15 degrees; whereas a confinement of about 1.5 nm is required in order to keep water liquid if temperatures close to  $T_H$  are approached. Furthermore, water remains in a liquid-like phase also below the singularity temperature if pores of diameter  $\leq 1$  nm are considered [26].

Second, under nanoconfined conditions liquid molecules form a structured solid-like layer (also known as nanolayer), which drives to a local densification of the liquid in the proximity of the solid interface, as it will be deepened in Chapter 2 [32, 37]. In particular, the nanolayer phenomenon is crucial for interpreting the characteristic properties of nanofluids, namely colloidal suspensions of nanoparticles. In fact, nanofluids can be modeled as a three-phase system consisting of a liquid phase (base fluid), a solid phase (nanoparticles) and an interfacial phase (nanolayer). Due to the increased liquid ordering and modified hydrogen bond network, the thermal conductivity of the water nanolayer is higher than the bulk one

thus acting as a thermal bridge between contiguous nanoparticles [38, 39]. The nanolayer effect has been experimentally observed by NMR (Nuclear Magnetic Resonance) approaches and, in case of silica nanoparticles, the nanolayer thickness has been estimated as approximately equal to a few molecular layers of water around the solid surface [40, 41].

Third, self-diffusivity of water is strongly reduced under nanoconfined conditions, whereas it may not be the case for transport diffusivity [42, 43]. In fact, while  $D$  of bulk water is usually dictated by the local temperature and pressure conditions, the mobility of nanoconfined water molecules is altered by the van der Waals and Coulomb interactions arising at the solid-liquid interface [27]. In Chapter 2, a scaling law for predicting the self-diffusion of water under nanoconfined conditions will be extensively discussed. However, transport diffusivity can attain quite large values even though self-diffusivity is strongly reduced by nanoconfinement, because of the slip flow conditions of water within hydrophobic nanopores. The latter phenomenon is governed by the liquid structure and collective molecular motion induced by both mechanical and electrical smoothness of the nanopore walls, and it will be further discussed in Chapter 4 [15, 43].

Finally, nanoconfined fluids may also show a dramatically increased viscosity, especially in case of gaps below a few nanometers [35, 44, 45]. Experimental and theoretical studies have both demonstrated that the viscosity of water in the proximity of hydrophilic surfaces is enhanced while increasing the nanoconfinement degree, reaching values even orders of magnitude larger than in bulk conditions [35, 44, 45]. The latter behavior is due to the strong solid-liquid interaction forces at the nanoscale, and it has been modeled by Fractional Stokes-Einstein relations [17, 46]. Moreover, it is also consolidated that usual no-slip boundary conditions, i.e. zero fluid velocity at the motionless surface, can not be considered as universal at the nanoscale. Experiments and simulations agree that liquid molecules can slip and have a non-zero velocity at a still solid surface, depending on the morphological and chemical features of the solid surface [47–51]. However, no direct experiments have clearly elucidated the relation between the viscosity of nanoconfined water, the wettability of the confining surfaces and the interface slippage [26]. In Chapter 6, an indirect evidence of the increased viscosity of nanoconfined water is found, and the related anomalous behavior modeled by a Fractional Stokes-Einstein relation [17].

### 1.3. Heat transfer phenomena at the nanoscale

Heat transfer at the nanoscale shows a few differences from the macroscopic behavior described by classical laws [52]. A better understanding of the characteristics of nanoscale heat transfer is important to improve solutions for the thermal management of electronic, optical, automotive components, and to design novel materials with tailored thermal transport properties for energy conversion, storage and utilization [53]. Here, the discussion is focused on thermal transport in nonmetallic systems, where the phononic contribution to heat conduction is predominant [54].

Phonons are collective excitations in elastic and periodic arrangements of atoms, which exist both in liquid and in solid matter. Phonons are often referred as "quasiparticles", being excited states in the quantum mechanical quantization of the vibrational modes of interacting particles or structures. Phonons strongly influence thermal and electrical conductivities of condensed matter, and they are characterized by a wide variation in both frequencies and peculiar mean-free-paths [54]. In bulk materials, most of the heat conduction is carried by phonons of large wave vector, which have typical mean-free-paths of 1–100 nm at room temperature [54]. Hence, nanostructures have the same scale of the usual mean-free-path of the phonons and, sometimes, they have dimensions comparable with the phonon wavelength. The latter evidences clearly state that a comprehension of heat transport beyond that achievable at the continuum level is needed when the nanoscale is approached. So far, no analytical theories have been able to accurately model phononic heat conduction at these scales, especially when solid-liquid interfaces are considered [54]. However, numerical and experimental studies have observed interesting phenomena related to nanoscale heat transfer, throughout both solid and liquid media [53].

First, nanoscale solid materials are characterized by the largest thermal conductivities ever observed in nature. For example, single-walled carbon nanotubes experimentally show 3500 W/mK at room temperature [55], which is almost double than the largest thermal conductivity observed for the best known heat conductor in bulk form (diamond). Even for polymers, which are usually considered as thermal insulators in the amorphous phase (about 0.3 W/mK), atomistic simulations suggest that thermal conductivity is high along a single molecular chain (up to 100 W/mK) [56]. However, anomalously reduced thermal conductivities have also been observed in nanoscale materials such as silicon nanowires, which

may find applications as thermoelectric materials [57–59]. Second, remarkable nanoscale heat transfer phenomena are also observed at solid-liquid interfaces. For instance, nanofluids display enhanced thermal conductivity, whose value is beyond the prediction of traditional effective medium theory (see Chapter 3 for a more comprehensive discussion) [60–64].

Classical molecular dynamics is a valuable tool that scientists exploit for a mechanistic understanding of the anomalies of nanoscale heat transfer. To this purpose, both equilibrium (EMD) and non-equilibrium (NEMD) MD simulations are extensively used in this thesis. Before going into the details of the performed simulations, a general introduction to heat transfer phenomena across either solid-solid or solid-liquid nanoscale interfaces is presented.

### 1.3.1. Solid-solid heat transfer

Thermal boundary resistance  $R_k$ , also known as Kapitza resistance, is a thermal resistance due to phonon scattering at the interface. The latter is due to the difference in electronic and vibrational properties between different materials, which alters the phonon propagation. Thermal boundary resistance is related to the probability of transmission after scattering, which in turn depends on the available energy states on both sides of the interface. As the sizes of structures approach nanometer dimensions, thermal boundary resistance becomes a fundamental actor in the heat transfer due to the large density of interfaces [54].

Despite decades of interest, a theoretical prediction of  $R_k$  is far from being formulated [53]. A few semi-empirical models, such as the acoustic-mismatch model (AMM) and the diffusive-mismatch model (DMM), have been suggested in the literature. Although both AMM and DMM lack in accuracy and sometimes show orders of magnitude discrepancies from experimental results, they are usually considered as rough upper and lower limits for the experimentally measured  $R_k$  [65]. In detail, the different density and sound speed between the two sides of the interface induce a mismatch in the acoustic impedances. The latter phenomenon can be considered as analogous to the mismatch between the refractive indices of optically different materials, and it is the theoretical consideration underpinning the AMM. On the contrary, the DMM considers that phonons encountering an interface have no memory of the previous trajectory. Hence, the probability that a phonon is scattered to one side of the interface or the other is only related to the phonon density of states [54]. The main

limitation of both AMM and DMM is the fact that the fraction of energy (i.e. phonons) transmitted across the interface depends neither on the interface morphology nor on the nonbonded interactions acting at the interface [65].

As widely discussed in Chapter 3, recent works have demonstrated that interfacial structure and surface chemistry strongly regulate  $R_k$  in case of both solid-solid and solid-liquid interfaces [53]. Here, a brief review of roughness, bounding, defect concentration, finite-size and grain boundary effects on thermal boundary resistance at solid-solid interfaces is presented. First, for defect-free and highly coherent interfaces, thermal boundary resistance linearly decreases with total interfacial area, which can be in turn modified by interface roughening [66]. Second,  $R_k$  can be exponentially reduced by introducing a few covalent bonds between the sides of unbounded solid-solid interfaces [67]. Equivalently, a third material characterized by strong interaction strength with both the neighboring materials of the interface can be introduced, in order to reduce the temperature jump (i.e. reduce  $R_k$ ) and become a sort of vibrational bridge [68]. Third, the presence of defects also influences heat transport at the interface, due to increased  $R_k$ . Graphene sheets are the ideal platform for evaluating the reduction of thermal conductivity by introducing a wide variety of defects (e.g. point vacancies, Stone-Wales defects or bi-vacancies) in the pristine structure. For example, a limited 0.25% defect concentration already leads to 50% reduction in thermal conductivity, because of localized thermal boundary resistances [69]. Fourth, finite-size effect, which is due to phonon scattering at the boundaries of the considered materials, is another significant source of localized temperature drop:  $R_k$  has been observed to decrease with increased specimen sizes [70, 71]. Finally, grain boundaries at solid-solid interfaces are also obstacles for phonon propagation thus sources of thermal boundary resistances [72].

### 1.3.2. Solid-liquid heat transfer

Theory and experiments for thermal boundary conductance at solid-solid interfaces are more advanced than in the case of solid-liquid ones. However, a few analyses about the relationship between the surface properties and the resulting thermal boundary conductance have been performed by several groups [72]. Here, a brief summary of roughness and wettability effects on thermal boundary resistance at solid-liquid interfaces is presented.

First, MD results suggest that the surface roughness at the solid-liquid interface reduces the temperature jump, thus it increases thermal boundary conductance [73]. In fact, roughness (i.e. increased fractal dimension of the surface) reduces the mobility of liquid molecules on the solid surface. Therefore, the latter molecules are in contact with the surface for a longer time, thus increasing the energy transfer between solid and liquid. Second, hydrophilic surface functionalizations help to reduce  $R_k$  at solid-(polar) liquid interfaces. In other words, an increased wettability, which is influenced by nonbonded interactions, reduces the temperature jump at the interface [74–76]. As an example, a few studies found that thermal boundary conductance at solid-liquid interfaces is 2-3 times larger in case of hydrophilic functionalizations respect to hydrophobic ones, because the hydrophilic surface enhances the interfacial interaction between solid and liquid and thus facilitates thermal transport [77, 78]. Similar considerations can be also formulated in case of liquid-liquid or liquid-soft matter interfaces [79, 80]. The latter observations are important to understand thermal conductivity experiments in nanofluids, because a reduction in thermal boundary conductance have an impact on their effective thermal conductance.

Thermal boundary conductance is not the only thermal parameter influenced by solid-liquid interactions at the nanoscale. Other peculiar properties of liquids related to interactions with solid surfaces at the nanoscale are mentioned in the followings, namely the effect of Brownian motion on thermal properties of nanofluids, the boiling and the thermophoresis phenomena.

Concerning nanoparticle suspensions, the Brownian motion of the nanoparticles is one of the heat conduction mechanisms proposed for understanding the particular features of nanofluids. However, while the comparison between the characteristic particle and heat diffusion time scales excludes a significant contribution to energy transport by micro-convection, Brownian motion could have important effects on the agglomeration of nanoparticles [81]. The latter effect favorites the creation of percolation paths in the nanofluid, which can lead to enhanced overall thermal transmittance [82]. Second, both surface wettability and curvature influence the boiling behavior of water in the proximity of solid interfaces. In fact, researchers have observed that fluid ordering around nanoparticles (i.e. nanoconfinement) strongly modifies the phase change behavior of the surrounding liquid; in other words, bubble nucleation and vapor film formation are related to surface hydrophilicity [83, 84]. Moreover, the liquid next to a nanoparticle can be heated above its boiling point without inducing a phase change. Unlike

the case of flat interfaces, where a critical heat flux is observed followed by the creation of a vapor layer and heat flux drop, in case of large curvatures heat flux saturates at a fixed temperature, even if the temperature of the nanoparticle is further increased. These differences in heat transfer are explained by the curvature-induced pressure close to the nanoparticle, which inhibits boiling [85, 86]. Finally, a temperature gradient can also work as a driving force for mass diffusion in Brownian mixtures of two or more species. The latter phenomenon is called thermophoresis and, generally, the motion of the molecules follows the direction of the heat flux [87].

## 1.4. Outline of the thesis

The thesis is organized in Chapters as follows:

- Chapter 1
  - The first Chapter contains the motivations of the research activities carried out in this thesis. In particular, current energy, environmental and biomedical issues are raised, and recent advances in nanotechnology are suggested as potential source of radical innovation in those sectors. To this purpose, a brief review of the most promising and interesting heat and mass transfer phenomena at the nanoscale is presented.
- Chapter 2
  - In this Chapter, a broad variety of configurations with nanoconfined water are analyzed by molecular dynamics simulations. The resulting self-diffusion coefficients are then compared by means of a dimensionless parameter, which takes into account both the confining geometry and the peculiar solid-liquid interaction energies. Finally, a scaling law for the self-diffusivity of water under nanoconfined condition is found, based on thermodynamics of supercooled water and the mechanism of Brownian motion.
- Chapter 3
  - In this Chapter, the characteristic thermal fluid properties of nanofluids are reviewed, with particular attention to the relation between the occurring nanoscale phenomena and the resulting macroscale properties. Then, non-equilibrium molecular

dynamics is used for assessing the effects of surface wettability, curvature and coating density on the thermal boundary conductance of solvated nanoparticles.

- Chapter 4
  - Here, the scaling law for the self-diffusivity of nanoconfined water is exploited for predicting the mass transport properties of membranes made out of carbon nanotube arrays. As a result, design guidelines for novel molecular sieves are proposed, allowing both a static and a dynamic control of the characteristic mass transport properties.
- Chapter 5
  - In this Chapter, simulations are used to guide the design of next generation thermal storage devices based on zeolite materials. First, equilibrium molecular dynamics simulations are used to predict the mass transport properties of water within defected zeolite membranes. Then, non-equilibrium molecular dynamics simulations are performed for evaluating the thermal transmittance of carbon nanotube networks, which can be introduced in the zeolite matrix in order to enhance its thermal conduction performances.
- Chapter 6
  - In this Chapter, the novel scaling law for the self-diffusion behavior of nanoconfined water is exploited for interpreting the relaxivity enhancement in both  $T_1$  (i.e. Gd(DOTA) bonded to silicon mesoporous particles) and  $T_2$  (i.e. super paramagnetic iron oxides nanoparticles confined in silicon mesoporous particles) contrast agents for Magnetic Resonance Imaging. Experiments are compared with modeling results and a few guidelines for a more rational design of imaging nanoparticles are outlined.
- Chapter 7
  - In this Chapter, the conclusions of the thesis are drawn, and possible future continuations and technological implications of the present work are suggested.
- Appendix

- In the five Appendices, a detailed list and description of the experimental and numerical results discussed in the thesis are presented. Moreover, two novel software developed for pre- or post-processing the simulation results are shared.

Finally, in Figure 1.3 the topics covered in this thesis are graphically summarized: different nanoscale heat and mass transfer phenomena are investigated, with broad implications in the clean water, energy and biomedical fields.

	PHYSICS	APPLICATIONS			SOFTWARE TOOLS
		CLEAN WATER	ENERGY	BIOMED	
NANOSCALE MASS TRANSPORT	Scaling self-diffusivity <i>Chapter 2</i>	CNT membranes <i>Chapter 4</i>	Zeolite-based thermal storage <i>Chapter 5</i>	MRI contrast agents <i>Chapter 7</i>	WANA <i>Appendix C</i>
	Introduction <i>Chapter 1</i>	Zeolite RO membranes <i>Chapter 5</i>	Nanofluids for heat transfer <i>Chapter 3</i>		
NANOSCALE HEAT TRANSPORT	Scaling thermal conductance <i>Chapter 3</i>		CNT fillers for thermal storage materials <i>Chapter 5</i>	Nanofluids for hyperthermia <i>Chapter 3</i>	

Figure 1.3.: Graphical representation of the topics covered in this thesis.