Heat and mass transfer of water at nanoscale solid-liquid interfaces

7. Conclusions and outlook

In this thesis, current issues from energy (i.e. cooling fluids and thermal storage), environmental (i.e. water purification) and biomedical (i.e. better imaging technologies for early detection) fields are all reviewed and discussed in the light of the nanoscale properties of water.

To this end, a hybrid methodology is adopted, which involves the use of atomistic simulations, experiments and theoretical considerations at the same time. First, Molecular Dynamics (MD) simulations are used to perform extensive sensitivity analyses on the most important effects (e.g. geometrical, chemical and physical parameters) affecting the quantities under investigation (e.g. mass diffusivity, thermal conduction parameters). Second, experimental evidences are used for validating numerical results and protocols. Third, in the light of *in silico* and *in vitro* experiments, theoretical considerations are discussed, in order to generalize the observed phenomena and better understand the physics underlying the considered problems. Finally, the resulting theory is used to provide predictions and experimental guidelines for innovative technologies, which may contribute to address some aspects involved in the energy, environmental and biomedical issues initially raised.

It turns out that the transport of water in nanoconfined geometries is different from bulk phase, and MD is used to compute the self-diffusion coefficient D of water within nanopores, around nanoparticles, carbon nanotubes and proteins. For almost sixty different cases, D is found to scale linearly with the sole dimensionless parameter θ, which is primarily influenced by geometry and represents the ratio between the confined and total water volumes. A relation between θ and D is then found by considering the thermodynamics of supercooled water. Concerning a possible environmental application, the latter relation is used for suggesting the design of a membrane with static (by means of pore distribution size) and dynamic (by means of a switchable electrostatic voltage) control of transport properties. Such membrane is made out of carbon nanotube arrays and it can be adopted for desalination, sieving or molecular sensing purposes. The $D(\theta)$ relation is also shown to accurately predict the relaxometric response

of both T_1 (i.e. Gd(DOTA)) and T_2 (i.e. super paramagnetic iron oxides nanoparticles) MRI contrast agents confined in mesoporous particles.

Moreover, the nanoscale effects influencing heat and mass transfer properties of sustainable energy and water nanotechnology-based applications are investigated. First, nanofluids, which are the next generation coolants and solar energy collectors, are studied by non-equilibrium molecular dynamics. Results confirm that thermal boundary conductance at the solid-liquid interface increases with wettability, whereas it decreases with surface density of coating. Second, zeolite membranes, which are promising materials for either thermal storage or fluid filtration purposes, are analyzed by both equilibrium and non-equilibrium molecular dynamics. Concerning mass transfer properties, infiltration isotherms and self-diffusivity of water in zeolites is tuned by introducing hydrophilic defects in the hydrophobic framework of silicalite-I. Dubinin-Astakhov model is then applied for interpreting the numerical results with a minimal number of physical parameters, whereas zeolite-water and water-water interaction energies are shown to correlate material characteristics with water transport behavior. Heat transport properties of carbon networks are finally investigated, and a few experimental guidelines are suggested for a more rational design of composite materials for either thermal storage or water filtration technologies.

Despite the hundreds of thousands of scientific publications and patents that have been pushing forward nanotechnology in the last two decades, a better comprehension of the physics of nanoscale matter is advancing at a slower rate, in particular when solid-liquid interfaces are involved. As in the past (e.g. Thomas Newcomen made the first industrial steam engine in 1705, whereas Nicolas Carnot theorized the ideal cycle only in 1823 and William Rankine operated in 1850s [597]), technological advances have been overcoming a comprehensive understanding of the exploited phenomena. However, a better knowledge of the latter phenomena is not just scientifically relevant, but it is also fundamental for decreasing the investment and time to market needed for developing novel devices. Consistently with this vision, the main results of this thesis are both the scaling law for the water diffusion under nanoconfined conditions and the experimental guidelines for a simulation-driven development of nanotechnology-based devices. Implications of the $D(\theta)$ relationship and of the R_k behavior at solid-solid and solid-liquid interfaces can help in tailoring nanostructures with precise modulation of water mobility and thermal conduction, such in the case of desalinators, molecular sieves or sensors, nanofluids, thermal accumulators or nanovectors for theranostic purposes.

However, due to the intrinsic multiscale nature of these technologies, a better comprehension of nanoscale phenomena should be coupled with the well-consolidated continuum physics, which are not discussed in this thesis and may involve nontrivial relations. For example, despite nanoscale effects are potentially predictable by means of atomistic simulations, the *a priori* determination of the effective thermal conductance of nanofluids is also strongly dependent by mesoscale phenomena (e.g. nanoparticle agglomeration and percolation), which should be analyzed with different simulation techniques and theoretical frameworks. An even more complex example concerns theranostic nanoparticles. If the final purpose is to early detect diseases by means of clearer MRI images, the relaxivity enhancement by water nanoconfinement is just the last part of a long chain of biophysical phenomena to be understood and optimized. In fact, multistage nanocarriers have to be first introduced in the body and to be neither cleared by the immune system nor cytotoxic; then, nanocarriers have to specifically target the diseased tissue and deliver the theranostic nanoparticles. The latter should be in turn able to cross the vascular barriers and to diffuse within the target tissue. Only at this stage, nanoscale physics are fundamental for predicting relaxivity or thermal ablation performances. Hence, the phenomena discussed in this thesis are just small links in a long chain of complex phenomena, which should be further deepened and coupled by a multidisciplinary approach and a cross-fertilization between the particular results obtained in each discipline.

Finally, the work discussed in this thesis have implications and perspectives along three directions, namely further molecular simulations, complementary multiscale approaches and technological implementation of the discovered phenomena. First, after thirty years of scientific interest and refinement of the methods and algorithms, it is now time for molecular simulations to become a consolidated discovery-driven research and development tool in a broad variety of industries [598]. Starting from the methods and results discussed in this thesis, other nanoscale physical phenomena relevant to the development of innovative technologies can be studied by atomistic simulations, both in the engineering (e.g. nanoengines, viscosity reduction by surface functionalization, molecular sensing, molecular sieve, nanoboiling, enhanced solar energy collection and so on) and in the biomedical field (e.g. protein folding, DNA transcription or - at the extreme - *in silico* reconstruction of the cell functioning and mechanistic exploration of life). Second, the nanoscale physics studied in this thesis should be coupled and integrated with multiscale approaches, in order to have a more comprehensive overview of the whole phenomena. For

instance, nanoscale thermal and diffusion coefficients should be used as input parameters in mesoscale simulations (e.g. Coarse-Grained, Lattice-Boltzmann or Finite Elements methods) for investigating the overall properties of nanofluids, self-assembling materials or biological networks. Last, the experimental guidelines here indicated can contribute towards a rational development of innovative devices, both company- and people-driven. In fact, while complex technologies related to the Health sector need billion Euros of investments to translate from benchmark to bedside, the rapid development of inexpensive additive manufacturing processes is drastically reducing the entry barriers in many engineering fields. From my personal perspective, the improvement of such production techniques in terms of both precision and variety of manageable materials will soon allow millions of engineers to design and test novel products based on nanotechnology materials, without the need of large initial budgets. The latter devices could be then locally produced by distributed 3D printing centers, thus allowing a more democratic diffusion of technologies aiming to rationalize and exploit in a more sustainable way Earth resources, such as food, water and energy.

8. Nomenclature

Notation

Symbol	Explanation	
a	activity	$-$
A	hyperfine coupling constant	J
b	length of the DOTA-silica bond	m
b_{GdH}	distance of closest approach of the water molecules to the paramagnetic ion	m
$\mathbf{B}_0$	magnetic field	T
c	molar concentration	$mol \cdot m^{-3}$
c_p	specific heat capacity at constant pressure	$J \cdot mol^{-1} \cdot K^{-1}$
c_{sat}	saturation molar capacity	$mol \cdot m^{-3}$
C	electrical capacitance	F
$C(t)$	autocorrelation function	$-$
d	normal distance between silica surface and Gd(DOTA) barycenter	m
$\mathbf{d}$	driving force for diffusion	m^{-1}
d_D	particle-wall distance at which D_{eff} is measured for water molecules	m

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Symbol (cont.)	Explanation (cont.)	
d_{min}	average minimum distance between silica wall and Gd(DOTA) atoms	m
D	self-diffusivity	$m^2 \cdot s^{-1}$
D_B	self-diffusivity of bulk fluid	$m^2 \cdot s^{-1}$
D_C	self-diffusivity of totally nanoconfined fluid	$m^2 \cdot s^{-1}$
D_{eff}	effective self-diffusivity of water experienced by a particle close to a solid wall	$m^2 \cdot s^{-1}$
D_R	rotational diffusion coefficient	$rad^2 \cdot s^{-1}$
D_T	transport (Fick's) diffusivity	$m^2 \cdot s^{-1}$
$Đ_i$	M-S diffusivity of species i	$m^2 \cdot s^{-1}$
$Đ_i\,(0)$	zero-loading M-S diffusivity of species i	$m^2 \cdot s^{-1}$
$Đ_{ii}$	self-exchange coefficient of species i	$m^2 \cdot s^{-1}$
E	energy	J
$\mathbf{E}$	electrical field	$V \cdot m^{-1}$
E_{DA}	Dubinin-Astakhov energy	$J \cdot mol^{-1}$
En	relaxivity enhancement	$-$
f	fluid phase fugacity	Pa
f_{12}	proportionality factor in the derivation of M-S equations (drag coefficient-like)	$kg \cdot m^{-3} \cdot s^{-1}$
F	total electron spin	$-$
$\mathbf{F}$	force	N
$\mathbf{F}_V$	force per unit volume	$N \cdot m^{-3}$
g	electronic g-factor	$-$

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Symbol (cont.)	Explanation (cont.)	
$g(r)$	radial distribution function	$-$
G	specific thermal conductance (transmittance)	$W \cdot m^{-2} \cdot K^{-1}$
G_k	thermal boundary conductance	$W \cdot m^{-2} \cdot K^{-1}$
h	molar enthalpy	$J \cdot mol^{-1}$
$\hbar$	reduced Planck constant	$1.054 \times 10^{-34} J \cdot s$
j	molar diffusion flux	$mol \cdot m^{-2} \cdot s^{-1}$
$\mathbf{J}$	molar diffusion flux relative to the molar average velocity	$mol \cdot m^{-2} \cdot s^{-1}$
k	wavenumber	cm^{-1}
k_{ij}^{b}	force constant for harmonic stretch potential	$kJ \cdot mol^{-1} \cdot nm^{-2}$
k_B	Boltzmann constant	$1.38 \times 10^{-23} J \cdot K^{-1}$
k_{ijk}^{ϑ}	force constant for harmonic angle potential	$kJ \cdot mol^{-1} \cdot rad^{-2}$
l_k	Kapitza length	m
l_{nano}	nanolayer thickness	m
L	length	m
m	mass	kg
$\mathbf{M}$	magnetization	$A \cdot m^{-1}$
$\mathbf{M}_s$	saturation magnetization	$A \cdot m^{-1}$
n	number of molecules	$-$
n_{DA}	Dubinin-Astakhov exponent	$-$
n_s	shape factor	$-$
N	number of solvent molecules	$-$
N_A	Avogadro number	$6.022 \times 10^{23} mol^{-1}$
N_n	nearest neighbors of an atom	$-$
$\mathbf{N}$	molar flux	$mol \cdot m^{-2} \cdot s^{-1}$
p	partial pressure	Pa

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Symbol (cont.)	Explanation (cont.)	
P	system pressure	Pa
P_M	mole fraction of metal ions in solution	$-$
q	partial charge	C
q_ι	density weighted scaling parameter θ	$-$
r_{ij}	relative distance between i-th and j-th atoms	m
r_1	longitudinal relaxivity	$mM^{-1} \cdot s^{-1}$
r_2	transverse relaxivity	$mM^{-1} \cdot s^{-1}$
$\mathbf{r}_{l,i}(t)$	position vector for molecule l of species i at any time t	m
r_p	particle radius	m
R	gas constant	$8.314\ J \cdot mol^{-1} \cdot K^{-1}$
R	specific thermal resistance	$m^2 \cdot K \cdot W^{-1}$
R_k	thermal boundary resistance (Kapitza resistance)	$m^2 \cdot K \cdot W^{-1}$
S	surface	m^2
S_m	membrane solubility	$cm^3_{STP} \cdot cm^{-3} \cdot kPa^{-1}$
S^2	order parameter	$-$
S_{loc}	specific SAS	m^2
S_{tot}	total SAS	m^2
t	time	s
T	temperature	K
T_1	spin-lattice relaxation time	s
T_2	spin-spin relaxation time	s
T_C	liquid-liquid critical temperature	K

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Symbol (cont.)	Explanation (cont.)	
T_g	glass-to-liquid transition temperature	K
T_H	homogeneous nucleation temperature	K
T_M	melting temperature	K
T_X	crystallization temperature	K
$\mathbf{u}$	molar velocity	$m \cdot s^{-1}$
U_c	Coulomb potential	$kJ \cdot mol^{-1}$
U_{eff}	effective potential	$kJ \cdot mol^{-1}$
U_{vdw}	van der Waals potential	$kJ \cdot mol^{-1}$
$\mathbf{v}$	velocity	$m \cdot s^{-1}$
V	volume	m^3
x	mole fraction	$-$
α	surface permeability	$-$
γ	activity coefficient	$-$
γ_I	gyromagnetic constant for protons	$2.675 \times 10^8 T^{-1} \cdot s^{-1}$
Γ	thermodynamic factor	$-$
δ	characteristic length of nanoconfinement	m
Δ^2	mean square zero field splitting energy	s^{-2}
$1/\Delta\omega_r$	angular phase shift	s
ε	Lennard-Jones potential well	$kJ \cdot mol^{-1}$
ε_0	permittivity in a vacuum	$F \cdot m^{-1}$
ε_r	relative permittivity	$-$
ζ	zeta potential	V
$\eta_{c,\%}$	percent coating coverage of nanoparticle surface	$-$

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Symbol (cont.)	Explanation (cont.)	
ϑ_{ijk}	relative angle between i-th, j-th and k-th atoms	$^\circ$
ϑ_M	pore hydration	$-$
θ	scaling parameter for self-diffusivity of nanoconfined water	$-$
θ_c	contact angle	rad
κ_{eff}	thermal conductivity enhancement	$-$
λ	thermal conductivity	$W \cdot m^{-1} \cdot K^{-1}$
μ	dynamic viscosity	$Pa \cdot s$
μ^0	reference molar chemical potential	$J \cdot mol^{-1}$
μ_B	dynamic viscosity of bulk water	$Pa \cdot s$
μ_{B^*}	Bohr magneton	$9.274 \times 10^{-24} J \cdot T^{-1}$
μ_c	molar chemical potential	$J \cdot mol^{-1}$
μ_w	water dipole moment	$C \cdot m$
ν	frequency	Hz
ϱ	porosity	$-$
ρ	mass density	$kg \cdot m^{-3}$
ρ_n	number density	m^{-3}
ρ_s	surface density	m^{-2}
σ	Lennard-Jones radius	nm
τ_D	translational diffusion time	s
τ_E	extra correlation time	s
τ_m	residence lifetime of the inner sphere water molecules	s
τ_M	molecular correlation time	s
τ_R	rotational correlation (tumbling) time	s

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Symbol (cont.)	Explanation (cont.)	
τ_T	total correlation time	s
τ_v	correlation time for splitting	s
φ_q	specific heat flux	$W \cdot m^{-2}$
ϕ	particle diameter	m
ϕ_a	fugacity coefficient	$-$
ϕ_V	volume fraction	$-$
Φ	pore diameter	m
Φ_q	heat flux	W
ψ	sphericity	$-$
ω	angular frequency	$rad \cdot s^{-1}$
ω	water uptake	$-$
ACF	autocorrelation function	
AMM	acoustic-mismatch model	
CA	contrast agent	
CD	central step distribution of defects	
CNA	carbon nanotube array	
CNT	carbon nanotube	
CPT	continuum percolation theory	
D-A	Dubinin-Astakhov	
DMM	diffusive-mismatch model	
DOTA	1,4,7,10-tetraazacyclododecane-1,4,7,10-tetraacetic acid	
DWCNT	double-walled carbon nanotube	
EDX	energy-dispersive X-ray spectroscopy	
EMD	equilibrium molecular dynamics	
EMT	effective media theory	
GUI	graphical user interface	

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Symbol (cont.)	Explanation (cont.)
HDL	higher-density liquid
IOn	iron oxide nanoparticle
LDL	lower-density liquid
LJ	Lennard-Jones
LLCP	liquid-liquid coexistence point
MAR	motional averaging regime
MD	molecular dynamics
MNP	magnetic nanoparticle
MRI	magnetic resonance imaging
MSD	mean square displacement
NEMD	non-equilibrium molecular dynamics
NMR	nuclear magnetic resonance
NMRD	nuclear magnetic relaxation dispersion
NP	nanoparticle
NPT	isothermal-isobaric ensemble
NVE	microcanonical ensemble
NVT	canonical ensemble
PCM	phase change material
PEG	polyethylene glycol
PRE	paramagnetic relaxation enhancement
RACF	rotational autocorrelation function
SAS	solvent accessible surface
SBM	Solomon-Bloembergen-Morgan theory

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Symbol (cont.)	Explanation (cont.)
SEM	scanning electron microscopy
SiMP	silicon mesoporous particle
SiP	silicon nonporous particle
SPIO	super paramagnetic iron oxide
SWCNT	single-walled carbon nanotube
TEM	transmission electron microscopy
VDOS	vibrational density of states

9. Curriculum Vitae

Matteo Fasano

Personal Data

Date of birth:	14^{th} June 1987
Sex:	male
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Citizen of:	Italy

Education

- **PhD in Energetics (2012-2014)**
  - Thesis title: Heat and Mass Transfer of Water at Nanoscale Solid-Liquid Interfaces
  - Advisors: Pietro Asinari, Eliodoro Chiavazzo
  - Place: Department of Energy, Politecnico di Torino
- **Master degree in Mechanical Engineering (2009-2011)**
  - Thesis title: Generalized thermodynamics description of complex biological systems
  - Advisor: Pietro Asinari, Eliodoro Chiavazzo
  - Place: Politecnico di Torino and Politecnico di Milano
  - Final evaluation: 110/110 and Honors
- **Bachelor degree in Mechanical Engineering (2006-2009)**

  - Thesis title: Experimental analysis of a bio-hydrogen and biomethane anaerobic production plant for energy production
  - Advisor: Romano Borchiellini, Massimo Santarelli
  - Place: Politecnico di Torino
  - Final evaluation: 110/110 and Honors

Work experience

- **Visiting scholar (07-08/2014)**
  - Place: Mechanical Engineering Department, Massachusetts Institute of Technology, Boston (MA, USA)
- **Research fellow (01-12/2013)**
  - Place: Translational Imaging Department, Houston Methodist, Houston (TX, USA)

Teaching experience

- **Teaching assistant (2012-2014, two semesters)**
  - Course: Advanced topics in Engineering Thermodynamics
  - Place: Politecnico di Torino

Publications in scientific journals

- E. Chiavazzo*, M. Fasano*, P. Asinari and P. Decuzzi, *Scaling behaviour for the water transport in nanoconfined geometries*, Nature Communications, 5:3565, 2014 (*equal contributors)
- A. Gizzatov, J. Key, S. Aryal, J. Ananta, A. Cervadoro, A.L. Palange, M. Fasano, C. Stigliano, M. Zhong, D. Di Mascolo, A. Guven, E. Chiavazzo, P. Asinari, X. Liu, M. Ferrari, L.J. Wilson and P. Decuzzi, *Hierarchically Structured Magnetic Nanoconstructs with Enhanced Relaxivity and Cooperative Tumor Accumulation*, Advanced Functional Materials, 24:4584, 2014

- M. Fasano, M.B. Bigdeli, M.R.V. Sereshk, E. Chiavazzo and P. Asinari, *Thermal transmittance of carbon nanotube networks: Guidelines for novel thermal storage systems and polymeric material of thermal interest*, Renewable and Sustainable Energy Reviews, 41:1028, 2015

- M. Fasano, E. Chiavazzo and P. Asinari, *Water transport control in carbon nanotube arrays*, Nanoscale Research Letters, 9:559, 2014

- E. Chiavazzo, M. Fasano and P. Asinari, *Inference of analytical thermodynamic models for biological networks*, Physica A, 392:1122, 2013

Publications in conference proceedings

- M. Fasano, M.B. Bigdeli, M.R.V. Sereshk, E. Chiavazzo and P. Asinari, *Overall thermal transmittance in carbon nanotube networks for thermal storage systems and composite materials*, Proceedings of the Eurotherm Seminar #99, 2:126, 2014

- A. Cardellini, M. Fasano, E. Chiavazzo and P. Asinari, *Heat and mass transfer phenomena at solid-liquid nanoscale interface in theranostic applications*, Panminerva Medica, 56:43, 2014

- M. Fasano, M.B. Bigdeli, M.R.V. Sereshk, E. Chiavazzo and P. Asinari, *Molecular dynamics simulation of carbon nano-binders into zeolite thermal storage*, Proceedings of the 12th Joint European Thermodynamics Conference, 188, 2013

Awards and achievements

- "Scuola Interpolitecnica di Dottorato" admission (2013-2014)
- "Best doctoral presentation", Department of Energy, Politecnico di Torino (2013 and 2014)
- "Working Capital" seed funding (2012)
- "Optime" award (2012)
- "Alta Scuola Politecnica" diploma (2010)
- "Roberto Rocca" scholarship (2010)

- "Accenture" scholarship (2010)