

Chapter 2

Confined Water in Carbon Nanotubes and Its Applications

Seul Ki Youn, Jakob Buchheim, and Hyung Gyu Park

Abstract Unique nanoscale transport properties of carbon nanotubes (CNTs) have inspired researchers for over a decade, initially with their analogies to various biological pores and later with the potential impact on water purification. Water can permeate through a nanometer-wide pipe of the CNT interior at rates far exceeding those predicted by Hagen-Poiseuille formulation and measured in nano conduits of different material, attributed to nano confinement, hydrophobicity, and smooth potential energy landscape. Also, chemical addition to the nanotube ends was found effective in electrostatic exclusion of ions without much loss of water permeability, suggesting the emergence of CNT membranes for desalination and purification of water resources. This article introduces *Carbon Nanotube Nanofluidics* by capturing important findings and progresses made in the early developments of the area.

2.1 Introduction

Limited access to clean water defines one of the global sustainability issues facing humanity today. Growing concerns of freshwater feeding to a significant portion of the world population are calling for immediate attention from science and technology [1, 2], pertaining to efficient seawater desalination and wastewater purification. Membrane-based water purification is a popular, promising and widely spread technological option today. Nanofiltration, reverse osmosis, and forward osmosis using polymer membranes have been considered actively as a means for clean water supply. Recent advances in nanotechnology and nanomaterial synthesis

S.K. Youn • J. Buchheim • H.G. Park (✉)

Nanoscience for Energy Technology and Sustainability, Department of Mechanical and Process Engineering, Swiss Federal Institute of Technology Zurich (ETH Zurich), Sonneggstrasse 3, Zurich CH-8092, Switzerland
e-mail: parkh@ethz.ch

have allowed us to approach to scales comparable with individual membrane pore, thereby enabling rational design and manufacturing of membranes and opening up new avenues to processing water energy- and cost-efficiently.

Carbon nanotubes provide unique structures in studying nanoscale mass transport and flow phenomena that can be employed in a variety of important applications. Having nanometer-scale diameters of innermost walls whose graphitic surface is atomically smooth, they give rise to newly discovered phenomena of ultra-efficient transport of water through these ultra-narrow molecular pipes [3]. These findings lead to a vision of permeable membranes incorporating carbon nanotube pores for a filtration that could possibly address the global water stress issue. Important findings and progresses in the emerging field of so called “*Carbon Nanotube Nanofluidics*” are presented in this article.

2.2 Predictions of Water Transport in Carbon Nanotube

The task of observing and understanding water flows in CNT pores raises a set of unique fundamental questions. First, it is surprising that polar liquids such as water can fill narrow hydrophobic CNTs. Two arguments against water infilling of the CNT interior are based on considerations of energetics and capillarity. In order for a water molecule to move from bulk water to such a narrow CNT permitting only a single-file water configuration, it should be given average energy of approximately two hydrogen bonds. This unfavorable energetics was expected to prohibit the entrance of water in narrow CNTs. The capillarity argument is based on the Young-Laplace equation [4], which predicts that a very large pressure force would be needed to fill the narrow CNT pore with water. However, counterarguments can also exist. At a given temperature, water molecules share hydrogen bonding energy as a statistical distribution. It is unclear whether this energy distribution will take the same shape in bulk water and under extreme confinement, so called nanoconfinement. In addition, the capillarity argument is based on a continuum assumption in a way that a single contact angle value can be defined between water and CNT mouth. Nevertheless, it is possible that thermal fluctuation of a confined system would increase the variation in the contact angle values statistically, complicating the applicability of the continuum-based prediction. The first answer to this debate was presented by a molecular dynamics (MD) simulation. Hummer and colleagues [5] used MD simulations to observe the infilling of an extremely narrow CNT (0.81 nm in diameter and 1.34 nm in length) with water molecules. According to their simulation result it is surprising that water molecules filled the empty cavity in a CNT within a few tens of picoseconds and resided there for the entire simulation time of 66 ns. More importantly, the water molecules under such a high degree of nanoconfinement formed a single-file configuration, unseen in bulk water but observed in some biological channels [5]. The simulation allowed for comparison between binding energy distributions of water at bulk and under nanoconfinement of CNT (*i.e.*, nanotube water). Average binding energy is favorable for bulk water,

but it is the weakly bound states that are reportedly less populated in nanotube water owing to the narrowed distribution of water molecules in the binding energy space under the nanoconfinement. As the result chemical potential of the nanotube water is lowered, and the probability of finding water molecules in the open CNT interior increases. This counterintuitive result could yet be a possible one partly because CNT is hydrophobic but not superhydrophobic [6]. For example, a slight (25 %) increase in hydrophobicity in the carbon-water interaction potential could turn the stable water infiltration to bi-stability between water-filled and empty states, while 40 % more hydrophobic interaction completely emptied the CNT.

The second fundamental question is regarding the dynamics of water under the CNT nanoconfinement. If water molecules can reside preferably in the CNT interior, how would they diffuse along the nanotube? This question about dynamics could be addressed by considering the shearing interaction between water molecules and graphitic channels. Driven in an axial direction, each water molecule atop the CNT wall would experience an energy landscape set by the overall potential interaction between water molecules and carbon graphitic crystals. It has been shown that the energy landscape can be smoothed if the graphitic surface takes a positive curvature, as known as an egg carton analogy, like in the case of water confined in a CNT [7]. Each water molecule right near the CNT wall could then experience less energy consumption to overcome the energy hills and valleys, hinting that atomic-scale smoothness of the wall may help water reduce the friction. Each rolling event of a water molecule over a pair of the potential hill and valley can then be modeled as a chemical reaction process. Babu and Sathian [8] has modeled this process by the transition state theory to suggest that wall shear stress, or dynamic friction, of water that shears the CNT channel can be expressed as a hyper sine function of the axial transport velocity, which suggests that the water transport rate will increase in proportion to the applied pressure drop, linearly for moderate flow rates and nonlinearly for high speed flows.

The single-file water wire is unique in that they move collectively. When mechanically biased by applied pressure drop in an MD domain the water wire showed a fast conduction through the nanotube, a speed comparable to the transport rate in aquaporins (4–6 $\text{H}_2\text{O}/\text{ns}$) [9]. In a hydrophilic channel as narrow as these CNTs, in contrast, water molecules cannot diffuse very fast because of a strongly attractive interaction with the constituent atoms of the channel wall, causing a strong friction mechanism. As the CNT dimension enlarges and the confinement is relaxed it becomes possible that the nanotube interior accommodates more “water wires,” and at large diameters, the confinement-induced hydrogen bond ordering disappears. As the result, the water hydrogen bond network takes a bulk configuration at the core part of the nanotube while remaining somewhat ordered in the very vicinity of the wall [6].

Obviously, dynamics of the water transport in CNTs will hinge primarily on the hydrogen bond configurations at various graphitic nanoconfinements. MD simulations have attempted to provide an insight of the enhancement of water transport with reference to continuum flow formalism, or Hagen-Poiseuille flow [7, 10]. These models agree qualitatively to each other in that the enhancement factor,

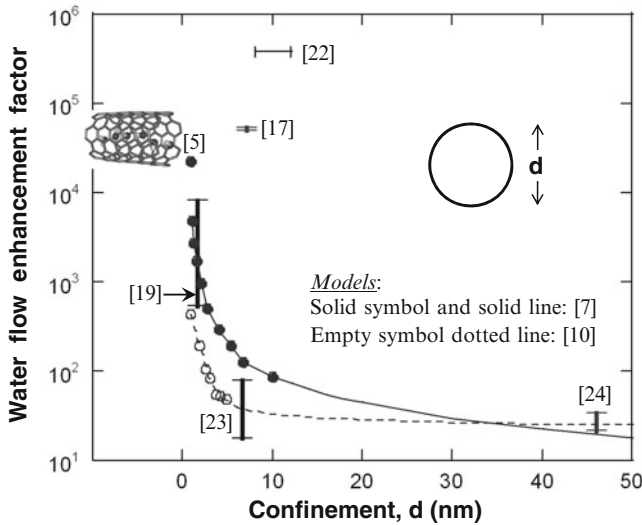


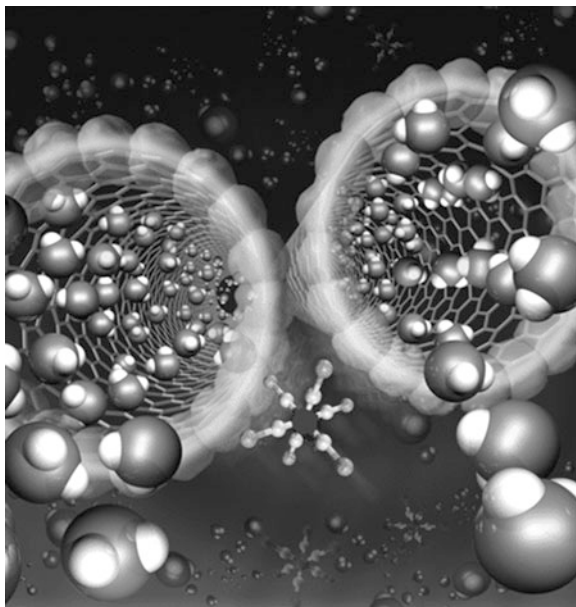
Fig. 2.1 Water flow enhancement over the Hagen-Poiseuille flow with respect to the CNT diameter. Comparison among different models and experiments

defined as the ratio of a water flow rate in a CNT to that of Hagen-Poiseuille formula at the identical tube diameter, varies from quite high values of 10^2 – 10^3 orders of magnitude at sub- to few nanometers of the CNT diameter to nearly unity at large diameters. For the detailed relationship between the enhancement and the nanotube diameter, nevertheless, they do not agree by exhibiting quantitatively distinct functions (Fig. 2.1). Such disparity between models hints that, although much progress has been made, the clear understanding of the water transport in CNTs is not yet achieved completely. For example, detailed friction mechanism demands careful investigations from experimental and theoretical ends. In the current understanding the water transport enhancement in CNTs is attributed to the nanotube properties including atomic level smoothness and hydrophobicity [11], as well as smoothening of the potential energy landscape related to nanotube curvature [7]. According to this frame of understanding, water transport in a strong nanoconfinement of the CNT is described as parallel trains of several hydrogen-bonded molecular wires traveling quite concertedly aloof from the wall (Fig. 2.2). This picture may allow drawing a plug-like velocity profile for water flows in a CNT [12].

2.3 Experimental Verifications

Despite a number of efforts to verify the aforementioned predictions with some breakthrough achievements, the field of *Carbon Nanotube Nanofluidics* today is still featured by imbalance between many simulations and rare experiments. The absence

Fig. 2.2 Trains of hydrogen-bonded water wires transporting in CNTs

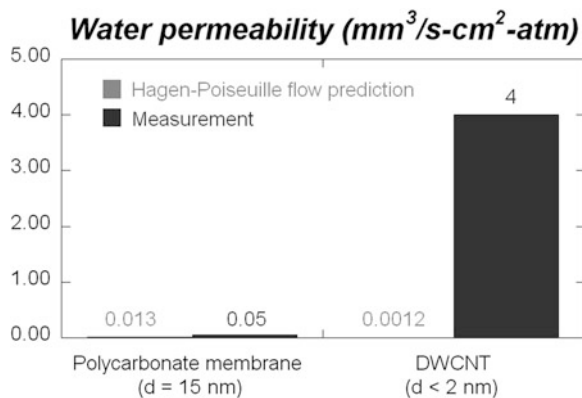


of sufficient experimental data has hampered our detailed and comprehensive understanding of the water transport under graphitic nanoconfinement. Nonetheless, there exist several outstanding achievements worthy of notice.

Most of the early experimental investigations of CNT fluid structure and transport have been inspired by Hummer and colleagues' MD modeling studies. The first experimental evidence of water infiltration of the CNT interior was obtained by Kolesnikov et al. [13] and Gogotsi et al. [14, 15] Using neutron scattering methods, Kolesnikov et al. have probed the structure of water in 1.4-nm-diameter, single-walled CNTs to confirm the residence of water molecules inside the CNTs. At cryogenic temperatures they could observe a single-file water wire surrounded by a water nanotube of square lattices. Later, Gogotsi and colleagues observed liquid molecules trapped in CNTs by transmission electron microscopy, which provides direct evidence that liquid water can favorably reside inside CNTs at room temperature.

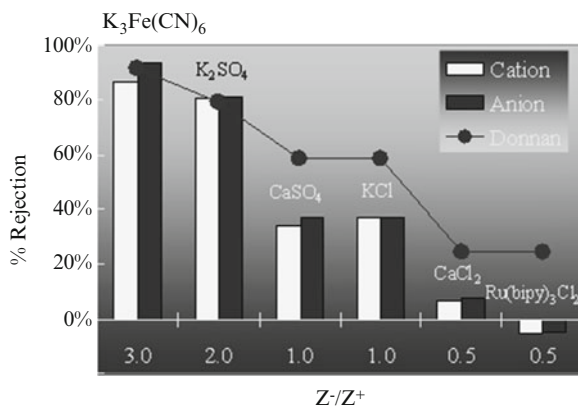
The next experimental task was to measure directly the water transport dynamics in CNTs. The challenge of the direct counting of water molecules is evident. Currently available direct flow measurement techniques may find limited applicability to molecular transport through a single CNT, illustrated by the range of flow rates predicted by MD simulations. For instance, Kalra et al.'s prediction [9] of *ca.* 6 H₂O/ns per 0.8-nm-diameter CNT at around 430 atm converts to *ca.* 12 H₂O/ns-nm². Assuming the bulk density of liquid water, this water flux is converted to a volume flow rate lower than one attoliter per second, extremely small for the present liquid flow measurement techniques.

Fig. 2.3 Water permeation through sub-2-nm double-walled CNTs (DWCNT) and a 15-nm-diameter polycarbonate membrane relative to Hagen-Poiseuille flow prediction



One strategy of overcoming this challenge is to manufacture a manifold device out of a large number of aligned CNTs, called a CNT membrane. The manufacturing strategy is rather simple. First, CNTs are grown in a vertically aligned way with the end tip of each being capped. Gap space among these aligned CNTs is filled with a matrix material such as polymer or ceramic. Finally, the nanocomposite film embedded with aligned CNTs spanning across the film is etched to cut open the hollow interior of CNTs. Thus obtained structure is a thin film porous membrane where the hollow interior of CNTs serves as graphitic pores. Two groups have pioneered this membrane manufacturing avenue. Hinds and colleagues [16, 17] have fabricated a CNT membrane out of vertically-aligned multiwalled CNTs of 6–7 nm inner diameters spanning a polystyrene thin film. They have reported orders of magnitude rapid water transport relative to classical hydrodynamics predictions. This membrane was later used to take a biomimetic approach of “gate keeping” applied to macromolecules separation *via* hindered diffusion [18]. Water transport under a stronger graphitic nanoconfinement was measured by another type of CNT membrane employing narrow (1.6-nm-diameter) CNTs. Bakajin and colleagues adopted a MEMS-compatible microfabrication process to produce this CNT membrane [19]. This membrane allowed a closer comparison to the MD simulation results. Indeed they obtained two-to-three orders of magnitude enhanced water permeation rates relative to the continuum hydrodynamics prediction (Fig. 2.3), in great agreement with MD predictions [9]. Later, Fornasiero et al. [20] attached electrostatic charge to the membrane pore by tethering carboxyl groups at the CNT pore entrance. At pH values of the membrane feed side higher than the carboxylic pKa value (*ca.* 4.8), the deprotonated carboxyl groups generated a negatively charged electric double layer that could screen the CNT pore from anions entrance at feed concentrations around those of brackish water (a few tens of millimolar) [21]. It is then the feed-side electroneutrality requirement that could also impede the permeation of cations, thereby completing the charge exclusion mechanism. It was turned out that difference in ionic strength and mobility between anion and cation determines the ion exclusion or permeation by the CNT

Fig. 2.4 Rejection coefficients measured for two CNT membranes and six salt solutions with the same equivalent concentration but different ion valence (Z)



membrane: Donnan equilibrium mechanism (Fig. 2.4). For example, KCl rejection by laboratory manufactured CNT membranes is around 40 % [20, 21], rather small but posing huge room for improvement by further studies.

2.4 Perspective

The technological impact of such rapid water flows established above involves a concept of an ultrapermeable membrane. This is a membrane that can be operational at far smaller pumping power than a few hundred bars in usual membrane applications including seawater desalination of a reverse osmosis type. For instance, water permeation through sub-2-nm CNT membranes has excelled the performance of commercial membranes [19]. Additionally established, Coulombic exclusion of ions in aqueous solutions suggests the use of the CNT membrane in water desalination, purification, waste water treatments, and extra-purification for special purposes.

Findings from MD simulations suggest that CNTs can be used in applications in which single-file water conduction is useful. For example, aquaporins almost exclusively permeate water molecules (and no ions) at speeds not low at all. Hence, one could envision seawater desalination and wastewater purification by membranes to which highly narrow CNTs serve as pores.

2.5 Conclusion

Nanoscale confinement by molecularly smooth hydrophobic graphitic walls gives rise to the unique phenomenon of ultra-efficient water transport, by some orders of magnitude faster than through other pores of comparable size. MD simulations and experimental measurements of water transport and ion exclusion are underscoring

the great promise of CNT membranes in water desalination, water purification, and nanofiltration. It is a rare combination of transport efficiency and selectivity that makes CNT membranes a powerful platform for the next generation water technology.

References

1. Schwarzenbach RP et al (2006) The challenge of micropollutants in aquatic systems. *Science* 313:1072–1077
2. Shannon MA et al (2008) Science and technology for water purification in the coming decades. *Nature* 452:301–310
3. Noy A, Park HG, Fornasiero F, Holt JK, Grigoropoulos CP, Bakajin O (2007) Slippery nanopipes: nanofluidics in nanotubes. *Nano Today* 2:22–29
4. Whitby M, Quirke N (2007) Fluid flow in carbon nanotubes and nanopipes. *Nat Nanotechnol* 2:87–94
5. Hummer G, Rasaiah JC, Noworyta JP (2001) Water conduction through the hydrophobic channel of a carbon nanotube. *Nature* 414:188–190
6. Werder T, Walther JH, Jaffe RL, Halicioglu T, Koumoutsakos P (2003) On the water-carbon interaction for use in molecular dynamics simulations of graphite and carbon nanotubes. *J Phys Chem B* 107:1345–1352
7. Falk K, Sedlmeier F, Joyl L, Bocquet L (2010) Molecular origin of fast water transport in carbon nanotube membranes: superlubricity versus curvature dependent friction. *Nano Lett* 10:4067–4073
8. Babu JS, Sathian SP (2012) Combining molecular dynamics simulation and transition state theory to evaluate solid-liquid interfacial friction in carbon nanotube membranes. *Phys Rev E* 85:051205
9. Kalra A, Garde S, Hummer G (2003) Osmotic water transport through carbon nanotube membranes. *Proc Natl Acad Sci U S A* 100:10175–10180
10. Thomas JA, McGaughey AJH (2008) Reassessing fast water transport through carbon nanotubes. *Nano Lett* 8:2788–2793
11. Joseph S, Aluru NR (2008) Why are carbon nanotubes fast transporters of water? *Nano Lett* 8:452–458
12. Hanasaki I, Nakatani A (2006) Structure and stability of water chain in a carbon nanotube. *J Chem Phys* 124:144708
13. Kolesnikov AI et al (2004) Anomalously soft dynamics of water in a nanotube: a revelation of nanoscale confinement. *Phys Rev Lett* 93:035503
14. Naguib N et al (2004) Observation of water confined in nanometer channels of closed carbon nanotubes. *Nano Lett* 4:2237–2243
15. Maniwa Y et al (2007) Water-filled single-wall carbon nanotubes as molecular nanovalves. *Nat Mater* 6:135–141
16. Hinds BJ, Chopra N, Rantell T, Andrews R, Gavalas V, Bachas LG (2004) Aligned multiwalled carbon nanotube membranes. *Science* 303:62–65
17. Majumder M, Chopra N, Andrews R, Hinds BJ (2005) Nanoscale hydrodynamics: enhanced flow in carbon nanotubes. *Nature* 438:44
18. Majumder M, Chopra N, Hinds BJ (2005) Effect of tip functionalization on transport through vertically oriented carbon nanotube membranes. *J Am Chem Soc* 127:9062–9070
19. Holt JK, Park HG, Wang YM, Stadermann M, Artyukhin AB, Grigoropoulos CP, Noy A, Bakajin O (2006) Fast mass transport through sub-2-nanometer carbon nanotubes. *Science* 312:1034–1037

20. Fornasiero F, Park HG, Holt JK, Stadermann M, Grigoropoulos CP, Noy A, Bakajin O (2008) Ion exclusion by sub-2-nm carbon nanotube pores. *Proc Natl Acad Sci U S A* 105:17250–17255
21. Fornasiero F et al (2010) pH-tunable ion selectivity in carbon nanotube pores. *Langmuir* 26:14848–14853
22. Du F, Qu L, Xia Z, Feng L, Dai L (2011) Membranes of vertically aligned superlong carbon nanotubes. *Langmuir* 27:8437–8443
23. Park HG (2007) Mass transport through carbon nanotubes. PhD dissertation, University of California Berkeley
24. Whitby M, Cagnon L, Thanou M, Quirke N (2008) Enhanced fluid flow through nanoscale carbon pipes. *Nano Lett* 8:2632–2637