Chemical Physics 476 (2016) 23–28

Contents lists available at ScienceDirect

Chemical Physics

journal homepage: www.elsevier.com/locate/chemphys

Water imbibition into nonpolar nanotubes with extended topological defects

Farzaneh Ramazani, Fatemeh Ebrahimi *

Physics Department, University of Birjand, Birjand 97175-615, Iran

A R T I C L E   I N F O

Article history:
Received 10 May 2016
In final form 20 July 2016
Available online 21 July 2016

Keywords:
Capillary filling
Nanotubes
Stone–Wales defects
Molecular dynamics simulations

A B S T R A C T

We use molecular dynamics simulations to investigate the kinetics of water uptake into model non-polar nano-tubes (NTs) of various opening sizes with extended Stone–Wales topological defects at ambient conditions. We observed that the rate of mass-uptake into defected NTs which is always smaller than the case of pristine NTs, depends on the size of the defected area, the radius of the NT and above all, the location of the defected zone, with respect to the tube entrance. For nano-tubes with defected area far from the entrance, the change in the dynamics is insignificant, unless the length of the defected zone is large. The effect is more pronounced for narrow tubes, where water inside NT forms a single-file structure.

1. Introduction

During the last decades, studying the dynamics of water transporting across nanochannels has attracted great attention of researchers. The intense interest to this phenomenon is due to its wide technical applications in biomolecule separation, water purification, nanofiltration, energy conversion and thermal management [1–3]. Moreover, the unique properties of water inside nonpolar nanotubes such as the ordered water structure, excellent on-off gating behavior, high permeability and fast motion of water molecules [4,5], present a strict analogy with biological and geological systems [6]. For example, it was shown previously that a possible coexistence of filled and empty states can occur, for a short narrow carbon nanotube (CNT) immersed in water with slightly modified van der Waals attraction between water molecules and carbon atoms, which can be induced from small altering of the pore polarity and solvent conditions [4,7,8].

In many real lifelike experiments such as fluid transport in living organisms and water purification, scientists usually face to the Capillary action which is one of the common ways of filling nanochannels [1,9,10]. Carbon nanotubes are one of the best promising candidates for investigating water imbibition into nonpolar nanochannels [11]. Experiments and molecular simulations have shown that the atomic-scale smoothness of the surface and the ordering of the water molecules in carbon nanotubes can lead to an almost friction-less molecular transport within them [4,7,8,12–18].

Fabricating defect free nanotubes is very difficult and existence of any kind of defects is common in practical constructed nanochannels. For example, during growth of a single wall carbon nanotube, a bending stress that may come from the nanotube's own weight, or interaction with neighbor nanotubes, or limited growing space, leads to formation of pentagon-heptagon topological defects or (5775) defect [19]. Many atomistic simulations and various experiments have shown that this kind of defects, usually referred as Stone–Wales defects, occurs in boron nitride [20,21] and silicon carbide nanotubes [22], as well. This kind of defects also plays a key role in large-scale structural rearrangements in graphitic networks [23,24]. In fact, in order to use NTs for nanoscale devices, as well, it is necessary to tune their transport properties which can often be performed by controlling the strength of the permeation of water through NTs via altering the roughness of the boundary walls [25], introducing vacancy sites, adatoms [26–28] and even strain induced structural distortion [29] and topological defects [28,29].

So far, most of theoretical works and numerical simulations have devoted on fluid flow inside perfect, pristine and defect-free carbon nanotubes and there are few researches focused on the effect of deviations from the perfect hexagonal graphene structure of the bounding walls on fluid transport inside nano-channels [27–29]. In the case of pressure driven flow, Nicholls et al. [26] have shown that increasing the concentration of defects within the surface of a (7,7) CNT leads to considerable reductions in mass flow rate and fluid velocity. Li et al. [27] modeled the permeation of

---

* Corresponding author.
E-mail address: f_ebrahimi@birjand.ac.ir (F. Ebrahimi).

http://dx.doi.org/10.1016/j.chemphys.2016.07.015
0301-0104/© 2016 Elsevier B.V. All rights reserved.

water through CNTs with Stone Wales defects by molecular dynamics simulation. They found that a low density of defects has a negligible effect on water permeation and a significant reduction in the flow rate is observed for high density of defects.

The aim of the present paper is to study the impact of the presence of extended topologically defected zones in the outcome of spontaneous imbibition of water into model nanotubes. It is well-known that the bounding wall structure can affect both the wall-fluid frictional forces, as well as the wettability of the nano-confinements [26,30–32]. Our model nonpolar nanotubes are pristine single wall carbon nanotubes in which the structure of the carbon hexagonal rings within an entire section of length H_d have been transformed to (7,5) rings (Stone–Wales defect) [33]. Although this model structure does not occur in real CNTs, however, the investigation of water permeation through such model structures, help us to understand the mechanism of capillary action in the presence of extended topological heterogeneities in bounding wall structure of any kind of nonpolar nanotubes. Also, This model can be regarded as a heterojunction of tubes with the same radius but different wall structure [34].

In the next section we describe the molecular models and the details of the MD simulations. Next, the results are presented and discussed.

2. Model description

We consider the spontaneous imbibition of water into tubular CNT-like nanotubes of different radius and fixed length $H = 100$ Å with extended topological defected zones. In our model NT, the carbon atoms have been arranged in armchair CNT sites, but, in a cylindrical area of length $H_{d,}$ all the carbon hexagonal rings has been transformed according to Stone-Wales defect topology. A Stone–Wales defect is the simplest of the topological defects in which the bond between two carbon atoms is rotated by 90° with respect to their midpoint, so the four adjacent hexagons in a region are changed into two pentagons and two heptagons [33]. The presence of periodic arrangement of bond rotational defects (similar to Stone–Wales-type transformations, where consecutive hexagons can be converted to sets of triangles and octagons) can lead to a model structure shown in Fig. 1.

At its left end, the NT is in contact with a water reservoir consisting of two graphene sheets perpendicular to its axis. The schematic of the simulation system is illustrated in Fig. 2. At the beginning of the simulations, Water molecules displaced in a simple cubic lattice arrangement in the reservoir. They were modeled by the TIP3P model [35] of water molecules and kept at a constant temperature of 300 K using a DPD thermostat [36]. The pressure in the water reservoir was kept constant at a value very close to zero. Water molecules were held rigid using the shake algorithm [37]. The left end of the CNT was capped with a plug during typically 120 ps, to prevent water from entering the tube, but, the right end remained open during the entire time. When the water reached equilibrium, the left cap was removed to allow the molecules to penetrate the CNT. Periodic boundary conditions were applied in all directions, and the carbon atoms were held fixed during the simulation. The box size along the z direction is taken large enough to ensure that the periodic images do not interact. We use the particle-particle particle-mesh (PPPM) method [38,39] for long-range Columbic interactions with a short-range cutoff value of 1.0 nm. For short-range Lennard-Jones (LJ) interactions, we use a cutoff value of 1.4 nm. For NT-water interaction, we used standard form of the LJ potential for the oxygen-carbon interaction with $\varepsilon = 0.1144$ kcal/mol and $\sigma = 3.276$ Å [12]. The simulations are performed in a NVT ensemble using molecular simulation package LAMMPS [40] for 0.5 ns with a time step of 2 fs.

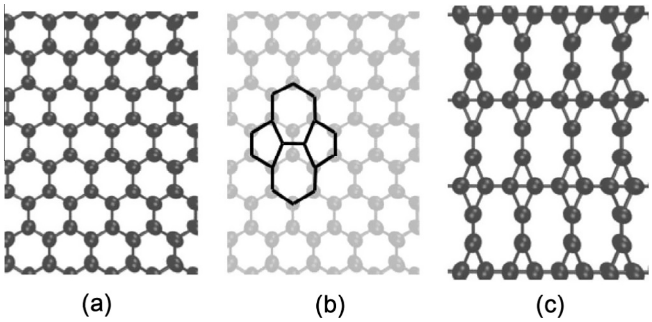

Fig. 1. Schematics of (a) perfect graphene structure, (b) Stone-Wales defect formation and (c) our proposed model.

3. Results

3.1. Water imbibition into the CNTs with transformed carbon rings

It has been demonstrated that fluids in nanoscale constrictions can be highly structured both in equilibrium and non-equilibrium processes [41]. In the case of pressure driven flow of water into CNTs, not only the liquid structure but the flow enhancement may alter due to confinement-induced changes [42]. Several types of water arrangement have been observed, based on the size of CNT opening. Water structures corresponding to disordered bulk-like water were observed in CNTs with diameter more than 1.39 nm. While, stacked hexagon rings were observed in CNTs with diameter of 1.25 nm, stacked and tilted pentagon rings for CNTs with diameters of 1.10 and 0.97 nm, respectively, and also single file molecular chains for CNT diameter of 0.83 nm. These observations suggest a transition from continuum to subcontinuum transport, from the abrupt reduction in flow enhancement between the 1.39 and 1.25 nm-diameter CNTs, which is consistent with the above mentioned changes in water structure with decreasing CNT diameter. We carried out MD simulations on pristine CNTs whose radii are between 0.41 and 2.03 nm. The results show that the aforementioned classification is valid for spontaneous imbibition of water into CNTs, as well, and one can distinguish two different flow regimes based on the size of opening: (1) The continuum flow regime in which we encounter a bulk-like liquid water within the tube, and (2) The sub-continuum flow regime in tubes whose diameters are so small that one cannot ignore the molecular structure description of water when predicting the mass and momentum transfer. Moreover, likewise the pressure-driven flow, a variety of fluid structures forms within the tube, based on the size of the opening (see Fig. 3). In fact, for wider CNTs the water structure and density have the characteristics of a disordered molecular structure, while for the sub-continuum flow we encounter ordered molecular structures of water molecules in the tube ranging from single-file molecular chains for (6,6) CNT, to tilted and stacked pentagon rings for (7,7) and (8,8) CNTs, respectively, and also stacked hexagon rings in (9,9) CNT.

The above simulations have been repeated for the model NTs with completely transformed structures (samples D with $H_d = H$ in Fig. 2). We observed that the aforementioned category is still valid for this model structure (see Fig. 3) showing that transformed carbon rings does not change the structure of water molecules inside nanotubes. However, as explained in the following paragraphs, the dynamics of the capillary filling of the nanotubes is different from that of pristine CNTs. In fact, the main difference with the pristine CNT is the slowing down of the front velocity.

In the central and right panel of Fig. 3, the radial and axial density profiles for pristine (P) and model (D) nanotubes, with