

Infiltration behaviour of water in a carbon nanotube under external pressure

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The wetting behaviour and associated pressure effect of water in single-walled carbon nanotubes (SWCNTs) are investigated through molecular dynamics (MD) simulations. It is found that water molecules can enter SWCNTs via surface diffusion, and the effective infiltration rate increases with pressure. The effect of pressure on infiltration rate is highly non-linear, exhibiting characteristics of both hydrophilic and hydrophobic surfaces. There exists a nominal infiltration pressure that is dependent on the SWCNT size, above which the water flux is significantly increased.

Keywords: carbon nanotube; water infiltration; simulation

Owing to their excellent combinations of mechanical, electrical and chemical properties, carbon nanotubes (CNTs) have been subjected to intensive research. Among many potential applications, the control of nanofluidic behaviour by CNTs is a particularly interesting area. On account of their small length scale, large specific surface area and smooth surfaces, they are excellent candidates of nano-conduits in nanofluidic devices as well as channels for molecular transport. Nanoporous materials including CNTs are regarded as a key technology for biomedical applications such as molecular sieves for DNA sequencing applications, nanopipets [1], biomolecule separation [2], molecule detection [3], biocatalysis [4] and encapsulation media for storage and transport [5], as well as energy-related applications such as energy absorption and damping [6–12].

In order to fulfill these promises, the interaction between CNT and fluid must be adequately understood. One of the most fundamental issues to explore is the wetting behaviour of the inner surface of the nanotubes. CNTs might be considered as non-wettable nanopores, since a large graphite surface is usually hydrophobic [13] and CNTs cannot be dissolved in water [14]; that is, nominally water should not infiltrate into CNTs under ambient condition. However, Dujardin et al. [15] found in

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their experiments that CNT bundles can be wetted by liquids of surface tensions $< 130\text{--}170\text{ mNm}^{-1}$, including water whose surface tension is 72.8 mNm^{-1} at room temperature. Rossi et al. [16] used an environmental scanning electron microscopy to study the wetting behaviour of water in CNTs, and found that CNTs produced by chemical vapour deposition with disordered tube walls were actually hydrophilic, and the contact angles of CNTs with water were in the range from 5 to 20° . Recently, in an energy-absorption experiment [9], in order to achieve pressure-induced infiltration in CNTs, non-aqueous liquids had to be employed. Although these experimental results showed that the inner surface of CNTs can be hydrophilic, such behaviour is strongly dependent on surface quality. Particularly, impurities and defects may make a hydrophobic surface hydrophilic-like. Therefore, in order to understand the above experimental results and to explore the intrinsic infiltration and wetting behaviour of water versus CNT, theoretical and numerical studies are necessary.

Over recent years, a large number of molecular dynamics (MD) simulations have been carried out for the transport behaviour of liquid molecules inside CNTs [17–22]. For instance, Hummer et al. [23] reported that an initially empty single-walled carbon nanotube (SWCNT) can be filled instantaneously by surrounding water molecules. In their computation, a short (6, 6) CNT (of length $\sim 1.3\text{ nm}$) with both ends open is immersed in a reservoir with 1000 water molecules. In such a system, however, several issues may affect the observed spontaneous infiltration behaviour: (1) the water molecules diffused into the tube from different ends may interact with each other since the distance between them may be shorter than the cut-off distance in classic MD simulation; (2) a (6, 6) tube may be too small to avoid strong interactions between the tube and the water molecules; (3) the interaction between the water molecules and the tube's inner surface is affected by the existence of water molecules outside the tube. In engineering applications, especially when CNT bundles or multi-walled CNT (MWCNT) are used, the wetting behaviour of the inner surface is of interest, and the mechanisms of which are still quite unclear.

Another MD study by Werder et al. [24] has led to the determination of the effective contact angles of water droplets inside an SWCNT, which were found to lie in the range $104.8\text{--}136.4^\circ$ when the tube diameter varies between 0.82 and 1.63 nm. We caution that such a result may not directly imply that the water molecules wet CNTs, since the contact angle is a parameter defined at the macroscopic scale, and the results derived from a small cluster of water molecules confined in a CNT may not be conclusive. A more reliable measure of wettability (or “hydrophobicity”) at the nanoscale should be based on the details of the entrance process as well as on the changes in free energy of water molecules, as will be discussed shortly.

Currently, most computational works focus on the transport behaviour of water inside CNTs. The infiltration behaviour, i.e. the entrance of water molecules into a CNT from an external reservoir and the wetting behaviour of the CNT inner surface, has been less studied. Research into pressure-induced infiltration is also lacking, which has led to tremendous challenges in developing advanced energy-absorption systems and volume-memory liquids [6]. In this article, we use MD simulations to explore the pressurized water infiltration into a CNT at a constant temperature. We attempt to address the following questions: (1) Is the inner surface of a CNT wettable by water molecules under ambient condition? (2) What is the wetting mechanism? (3) How does the external pressure affect the wetting behaviour and the infiltration mechanism?

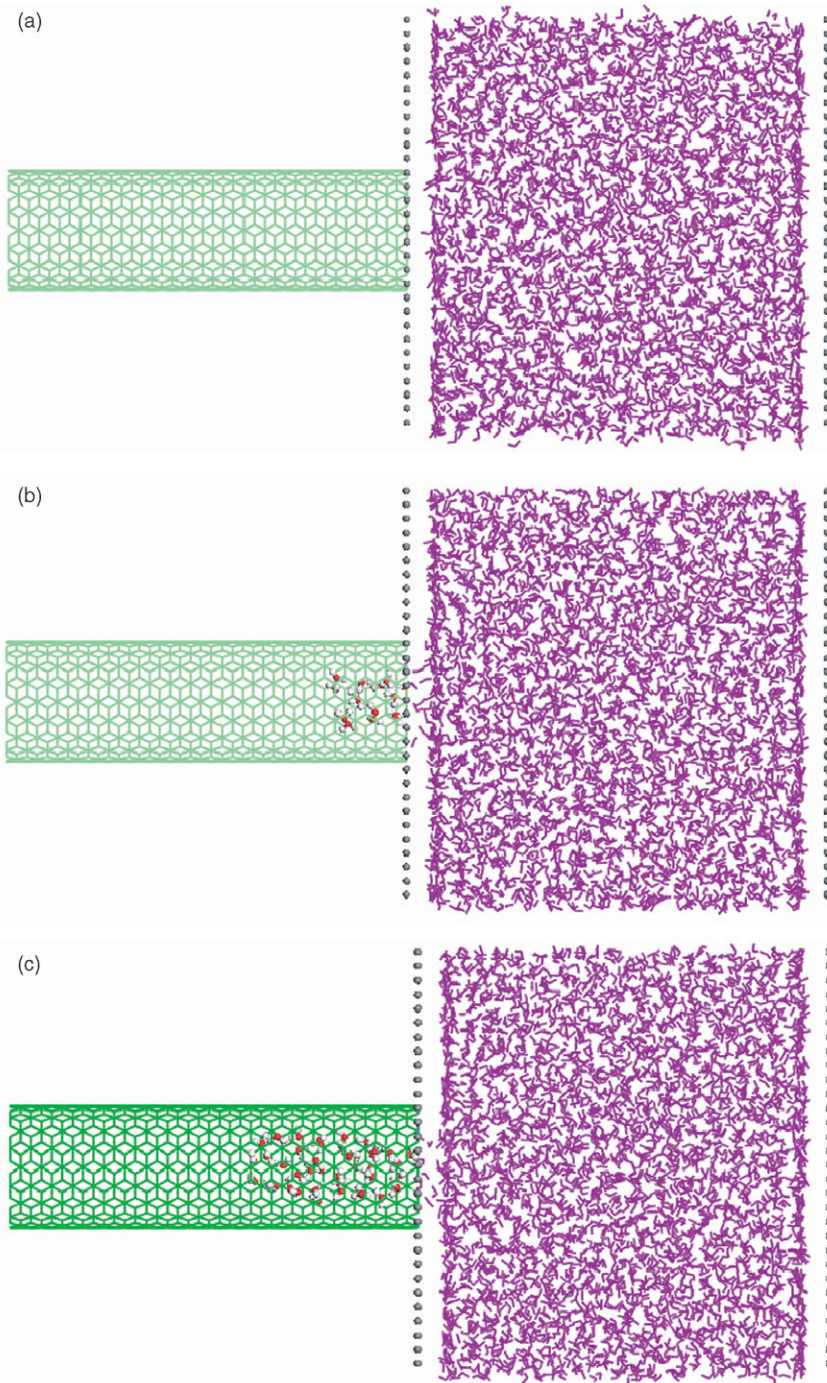


Figure 1. (a) Snapshot of the initial structure before water infiltration into the CNT. (b) Snapshot of water infiltration under about 0.1 MPa and at 300 K (after 30 ps). (c) The snapshot of water infiltration under 130 MPa and at 300 K (after 30 ps).

With reference to Figure 1a, the computational cell includes a rigid SWCNT segment of length about 5 nm, and a “reservoir” which is bounded by two parallel rigid carbon atom planes (along the axial z -direction of the tube). A total of 3376 water molecules are inside the “reservoir” which maintains the normal density of water at 300 K and 1 atm. The cell size is $4.65 \times 4.65 \times 11.0 \text{ nm}^3$ with periodic boundary conditions applied in the lateral directions (x - and y -directions), and there is no periodic boundary condition along the z -direction. The infiltrated water molecules can interact only with the inner surface of the CNT and the remaining water molecules cannot interact with the outer surface of the CNT. In addition, the water molecules can only infiltrate into CNT from one end (the opening on the right side in Figure 1). In order to study the size effect of infiltration, we select three different CNT segments, (20, 20), (15, 15) and (10, 10), which have diameters of 2.7, 2.0 and 1.35 nm, respectively. With the current setting of the computational cell, the aforementioned constraints in reference [23] are alleviated.

The MD simulations were carried out in the canonical (NVT) ensemble by using the condensed-phase optimized molecular potentials for atomistic simulation studies (COMPASS) force field, which was derived from *ab initio* calculations [25] in which the intermolecular potential energy of water molecule is described by both the short-range Lennard–Jones potential and the Ewald summation of the long-range Coulombic potential. The Berendsen thermostat is used to keep the temperature constant and a fixed time increment of 1 fs is used in the current MD simulations. Initially, the right end of the CNT is closed with a cover of rigid carbon atoms, and the water molecules in the reservoir are equilibrated for about 50 ps; the cover is then removed and the system behaviour monitored for another 30 ps.¹ Such a procedure is repeated for the same system under different pressures, p . The initial structure is shown in Figure 1(a). The water pressure is varied by changing the volume of the reservoir.

Figures 1b and c show snapshots of the system configurations under 0.1 and 130 MPa after 30 ps, respectively. Figure 1b shows that water molecules can infiltrate into the CNT even under ambient condition, whereas more water molecules may infiltrate under higher pressures (Figure 1c). The relationship between the normalized infiltrated water volume and the system pressure is shown in Figure 2. Here, for each tube size, as the pressure varies the infiltrated water volume (which is proportional to the infiltrated molecule number) is normalized by that at 1 atm; the infiltrated water volume at 1 atm is also shown in Figure 3 by the triangular symbols. The error bar in Figure 2 represents the variation of infiltrated water volume within 5 ps due to thermal fluctuations. According to Figure 2, the infiltrated water volume gradually increases with pressure when the pressure, p , is relatively low, and its increasing rate sharply rises when p exceeds a critical value (e.g. 50 MPa for the (10, 10) tube), after which the slope decreases rapidly and the volume–pressure curve becomes relatively flat again. These phenomena cannot be explained by conventional fluid mechanics: for example, conventional fluid mechanics predicts that no water can enter a hydrophobic tube under ambient conditions and that at a critical pressure the capillary force can be overcome and water can infiltrate the tube without the need to supply any additional pressure. Such conventional theory at macroscopic scales does not agree with the simulations at nanoscale dimensions.

In ambient conditions (e.g. Figure 1b), MD simulations show that the water molecules can spontaneously wet the inner surface of a CNT, consistent with the literature (see, for example, [23]). In other words, the inner surface of a CNT does not appear as “hydrophobic” as say graphite at the continuum scale. This can probably be attributed to

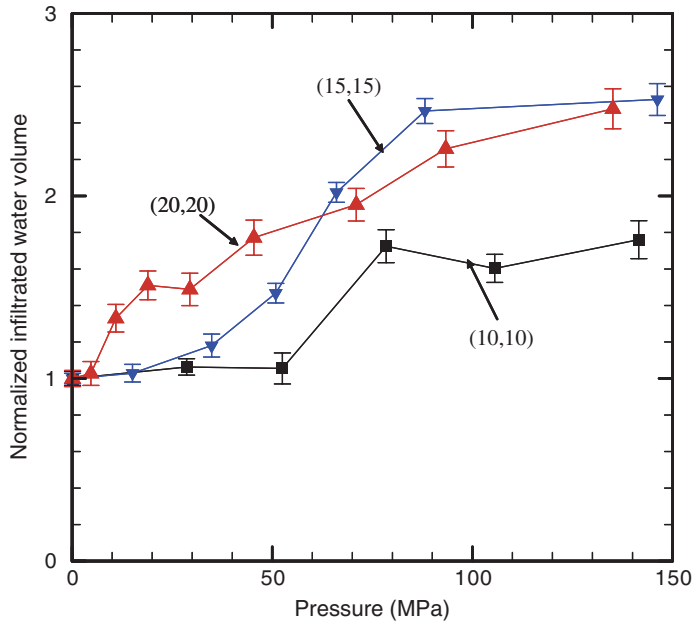


Figure 2. Relationship between external pressure and normalized infiltration water volume for three different tube radii. The infiltrated water volume is normalized by that under 1 atm for tubes with different radii (Figure 3).

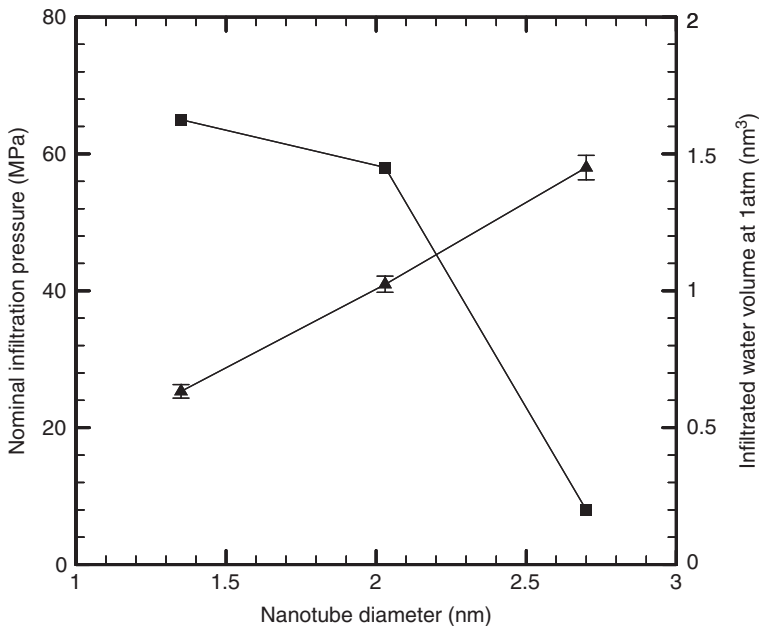


Figure 3. Relationship between nominal infiltration pressure and nanotube diameter (squares), and between nanotube size and infiltrated water volume at 1 atm (triangles).

the nanoscale size and an associated confinement effect. Consider the state of water confined inside the CNT and that of water outside it. For a time-average approximation, the free-energy difference between these can be expressed as $\Delta U = \Delta\gamma d(2\pi r) + \Delta E n$, where $\Delta\gamma$ is the effective solid–liquid interfacial tension, d is the infiltration depth along the wall of the SWCNT, r is the radius of the SWCNT, n is the number of infiltrated water molecules and ΔE is the change in free energy after infiltration (which is related with the creation of a “surface” and also the change of the environment of the infiltrated water molecules). In bulk water, both van der Waals and electrostatic interactions (hydrogen bonds) exist among water molecules. If water molecules enter a CNT, they need to first overcome the energy barrier (i.e. the non-bonded attraction exerted by others and lose at least two of their four hydrogen bonds). Such an energy barrier is usually quite high for bulk water molecules.

In MD simulation, under ambient conditions, we noticed that water molecules enter the CNT primarily via surface diffusion; that is, instead of directly entering the CNT, the reservoir water molecules that are close to the CNT inner surface (termed *surface water molecules* in the following discussion) which have already established “interaction” with carbon atoms, can be first “pumped” into the CNT and stay near the CNT wall. Then, these infiltrated molecules can attract another layer of water molecules into the CNT, which is thus gradually filled along the radial direction from the boundary to the centre. The volumes of infiltrated water for tubes with different radii (under ambient conditions) are shown in Figure 3 (as triangles). It shows that the infiltrated water volume varies linearly with the tube diameter, and thus linearly with the number of carbon atoms on the tube edge, but varies non-linearly with the cross-sectional area of the tube.

There are two mechanisms associated with the observed surface diffusion. First, due to the smaller coordination number, the surface water molecules have higher energies than the bulk water molecules, and thus their energy barrier for infiltration is lowered. Thermal fluctuations provide one possible source for these molecules to enter a CNT at ambient temperature and pressure. In addition, the van der Waals attraction between the carbon atoms and the surface water molecules can further reduce the energy barrier. In order to verify such a mechanism, we removed the CNT and exposed the reservoir of water molecules to a “vacuum” half-space, and found that no water molecules could diffuse into the vacuum within the same period of simulation time. This clearly shows that the van der Waals interaction between the water molecules, and CNT is necessary for the surface water molecules to overcome the energy barrier. Note that although the fraction of water molecules exposed to the open end of a CNT (surface water molecules) is very small compared with that of the bulk liquid phase, the CNT inner surface becomes nominally wettable by water, since the CNT interior volume is also small. In other words, the wetting behaviour under ambient condition relies on surface diffusion of surface water molecules, since most of the bulk water molecules are yet incapable of overcoming the energy barrier to directly infiltrate into the tube. After the surface water molecules enter the CNT, the CNT inner surface and the infiltrated water molecules are in a metastable state.

Since the CNT in the current simulation is rigid, an external pressure field does not affect the water inside the CNT. With an increase of external pressure, the free energy of water molecules in the bulk liquid phase rises accordingly. Thus, an additional driving force is involved to release the quasi-hydrostatic pressure of the reservoir water, i.e. the energy barrier of water infiltration is lowered as the pressure is increased, not only for the surface water molecules but also for the bulk water molecules. It is

remarkable that the relationship between infiltration rate and pressure is highly non-linear. When the pressure is relatively low, the surface diffusion mechanism dominates, and the variation of infiltration rate is quite insensitive to pressure, especially for smaller tubes. However, a nominal infiltration pressure exists, above which the infiltration rate significantly increases: with the assistance of external pressure, the energy barrier is reduced to a critical level, at which water molecules (besides the surface water molecules) can overcome it and enter the CNTs without the help of the tube wall (surface attraction), causing the large increase in infiltration volume. After the nominal infiltration pressure is reached, further increase of external pressure does not have a pronounced effect on the infiltration flux since there is no other primary energy barrier. This phenomenon is different from the capillary effect at the macroscale. For a conventional hydrophilic surface, the capillary pressure will spontaneously drive the liquid into the tube without the requirement of additional external pressure; for a conventional hydrophobic surface, the liquid should first overcome the capillary effect. In the case of CNTs under investigation, it shows a mixed characteristic of both; that is, the CNT should be regarded as neither hydrophobic nor hydrophilic owing to the unique confinement at nanoscale. Such unique behaviour of nanofluids cannot be fully described by conventional theories established at the macroscopic scale, and further studies are required to model effectively such behaviour.

The nominal infiltration pressure is size dependent. Figure 3 shows the relationship between the nominal infiltration pressure and the CNT radius. The nominal infiltration pressure is obtained from the average pressure that corresponds to the largest variation of infiltrated water volume on the pressure-infiltrated water volume relationship (Figure 2). With increase of tube size, the infiltration pressure decreases slightly for tubes with larger radii, and the reduction is more obvious when the CNT size becomes even larger. When the tube diameter increases to ~ 2.7 nm, the nominal infiltration pressure reduces to ~ 8 MPa. For a tube with larger radius (and also smaller surface area per volume), the free-energy difference between water molecules inside and outside CNT is smaller on account of the larger infiltrated volume and weaker CNT confinement effect, which lead to a reduced infiltration energy barrier. Therefore, a smaller perturbation is required for water infiltration, resulting in a lower nominal infiltration pressure.

In summary, through MD simulations, we have investigated the following issues: (1) the wetting behaviour of water on the inner surface of CNTs under ambient conditions; (2) the wetting mechanism under ambient conditions; (3) the effect of external pressure on the infiltration behaviour. It is found that water molecules can wet the inner surface of a CNT under ambient pressure by surface diffusion, which can be attributed to the surface water molecules having higher energies. Random thermal fluctuations and van der Waals attraction forces exerted by CNT atoms can help the surface water molecules to overcome the energy barrier. When the applied external pressure is below a critical value, the infiltrated water flux is relatively insensitive to pressure. As a critical pressure is reached, the energy of the bulk water molecules is sufficiently high and they can enter the tube without have to rely on the surface diffusion mechanism. Thus, beyond the critical pressure, the infiltrated water volume significantly increases and eventually approaches a steady state. The nominal infiltration pressure decreases with increase of tube diameter.

Acknowledgement

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Note

1. Using MD simulations, Hummer et al. [23] reported that it takes only a few ps for water molecules to infiltrate a CNT under ambient conditions. In the present work, not only is the tube radius much larger than that used in reference [23] but also an external pressure is applied; thus the water molecules are able to penetrate the tube within a few ps.

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