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Transport characteristics of water molecules in carbon nanotubes investigated by using molecular dynamics simulation

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ABSTRACT

The transport characteristics of water molecules in carbon nanotubes (CNTs) is studied in this work using molecular dynamics simulation method. The effect of channel diameter, defects and the inter-layer spacing on the transport of water molecules is studied by subjecting the flow of water molecules through CNTs under pressure. The findings show that the efficiency of water transport in CNTs can be improved by deploying bigger SWCNTs. In addition defects in the nano-fluidic system will also reduce the transport efficiency of water molecules. Additionally, for the case of double walled CNTs (DWCNTs), it is found that the inter-layer spacing in a DWCNT has a significant influence on the rapid transport of water molecules. The transport characteristics of water molecules in CNTs have been systematically and comprehensively studied using the MD simulations and the discussions are presented in this paper.

1. Introduction

The application of carbon nanotubes (CNTs) as a medium for fluid transport is significant to understand the nano-level fluidic processes, which are important for technologies such as drug delivery [1,2], fluid separation [3,4], and biological channels [5–8]. A lot of significant research has been performed recently to investigate the role of CNTs as nano-scale flow channels for transport of water, macromolecules, ions, and protons in the field of nano-fluidics [9–11] and nano-biotechnology [12–15]. Numerous studies have been conducted to investigate the transport properties of water molecules in CNTs [16–20]. The flow characteristics of a freshly fabricated membrane consisting of aligned multi-walled carbon nanotubes (MWCNTs), with graphitic inner cores which would mimic a biological flow channel were studied by Majumder et al. [16]. The studies conducted by them showed that liquid flow through a membrane composed of an array of aligned carbon nanotubes is four to five orders of magnitude faster than the predicted values on conventional fluid-flow theory. Myers [17] studied the enhanced flow in CNTs using an analytical based approach adopting a mathematical model. It was found that no noticeable enhancement is observed in large tubes. Additionally, an enhancement in flow is observed with a decrease in radius of the CNT for smaller CNTs. Reddy and Lu [21] conducted analysis on the structural vibrational properties of the fluid conveying single walled CNTs (SWCNTs). The analysis was significant since they were able to quantify the description of mass flow rate inside the SWCNT as a function of the natural frequency of SWCNT. The interfacial friction of water molecules with graphitic surfaces of various topological features were studied by Falk et al. [22]. Their studies showed that the frictional coefficient decreases with carbon nanotube radius for water inside, but increases for water outside. However, the frictional coefficient were independent of topology for the case of graphene slab. Additionally, the frictional coefficient was also found to diminish below a threshold diameter for armchair CNTs, which results in enhanced flow rate of water molecules through CNTs. Thomas and McGaughey [23] made use of molecular dynamics (MD) simulations to investigate the pressure-driven flow enhancement of water molecules through armchair CNTs of varying diameters. The studies showed that the enhancement decreases with increasing CNT diameter and are lower than previously reported experimental results. It was also hypothesized in their investigation that the discrepancy could have arisen due to a miscalculation of the available flow area and/or the presence of an uncontrolled external driving force (such as an electric field) in the experiments. As an extension to this work, they also investigated the behavior of water near carbon surfaces and explored the nature of water flow through CNTs and carbon nanopipes [24]. The MD simulation studies also pointed out that further measurements of water flow through CNTs are required to understand the magnitude of the flow enhancement and its variation with CNT

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diameter. It was also found that since atomically smooth and defect-free CNTs were used in MD simulations, the discrepancies with experiments were to be likely caused by differences in the chemistry of the carbon surface. Recently, Walther et al. [25] made use of large scale MD simulations to study the flow of water molecules in micrometer long CNTs. The length scale of the CNT membranes used in their simulations enabled them to replicate the lengths used in the experiments. The results suggest that the reported superfast water transport rates must be attributed to effects other than hydrodynamic interactions of water with pristine CNTs.

The review of literature studies on the transport properties of water molecules through CNTs clearly indicate that the CNTs have enormous potential to be used for applications involving nano-level fluid flow. However, the transport characteristics of water molecules in a nano-fluidic flow channel with topological defects (such as vacancy defect) is not well studied in literature. Furthermore, for the case of water flow through double-walled CNTs (DWCNTs), the influence of inter-layer spacing on the transport properties remains to be investigated. Hence, the main objective of our work is to investigate the transport properties of water molecules in SWCNTs in response to the geometrical characteristics of the SWCNT. The influence of concentration and the location of defects on the transport properties of water molecules in a nano-fluidic flow channel is also investigated. We have further analyzed the transport properties of water molecules through DWCNT to understand the effect of inter-layer spacing on the flow characteristics of the water molecules through DWCNT. The investigation of defects and inter-layer spacing on the transport properties of water molecules in a nano-fluidic device presents an important and crucial design input for fabricating CNT based nano-level drug delivery and nano-fluidic NEMS devices. The transport properties of water molecules under pressure driven flow have been comprehensively studied and the results are presented in this paper.

2. Computational model

The numerical simulations described in this work is carried out by using the classical molecular dynamics simulation method in which force field equations are used to describe the inter-atomic interactions. These inter-atomic interactions can be divided into the interaction between the carbon atoms in CNT and graphene sheets, the interaction between the water molecules and the carbon atoms of CNT and graphene sheets and the interaction between the water molecules. The inter-atomic interactions of carbon atom in SWCNT are described using the Brenner's second generation reactive empirical bond order function (REBO) [26]. The REBO potential is able to accurately describe the properties of solid-state and molecular carbon nanostructures [27,28] while maintaining the accuracies of the *ab initio* and semi-empirical methods in simulating large systems [29]. The REBO function is defined mathematically as:

$$E_{\text{REBO}} = V_R(r_{ij}) - b_{ij}V_A(r_{ij}) \tag{1}$$

where the repulsive and attractive pair terms are given by V_R and V_A respectively. The b_{ij} term is used to include the reactive empirical bond order between the atoms.

The non-bonded interactions between the carbon atoms in CNT and graphene sheets and the water molecule is typically modeled using a Lennard-Jones (LJ) potential function [30–32], which accurately describes the short-range electron repulsion and long-range electron attraction between the CNT and water molecules [25]. The LJ potential is tuned using the parameters obtained from ref [33] to accurately describe the experimentally observed water–graphene contact angle. The non-bonded interactions between the carbon atoms and the water molecule is given by [33]:

$$E_{\text{non-bond}} = \sum_{i,j} 4\varepsilon\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right] \tag{2}$$

where ε_{CO} = 0.3135 kJ/mol and, ε_{CH} = 0.253 kJ/mol which are the well depth parameter, σ_{CO} = 0.319 nm, and σ_{CH} = 0.282 nm denote the collision diameter between carbon to oxygen and carbon to hydrogen respectively [33].

The interaction between the water molecules is described using the flexible fixed-point charge (FPC) water model [34]. The FPC water model is capable of accurately reproducing the properties of water for different ranges of pressure, temperature, integration time steps and system sizes. Additionally, the FPC model is the most accurate 3 site water model that makes it ideal for MD computations of biological systems involving large number of water molecules [35]. The FPC water model is described as:

$$E_{\text{FPC}} = E_{bond} + E_{bend} + E_{vdW} + E_{els} \tag{3}$$

where E_{bond} and E_{bend} are intra-molecular potential function that represents the bond strength energy and bending energy in a water molecule respectively. The terms E_{els} and E_{vdw} denote the electrostatic potential and van der Waals potential between water molecules respectively. The complete details of this potential function is described in the work by Zhang et al. [34].

2.1. Calculation of pressure and force on water molecules

The pressure on water molecules is obtained by computing the stress on entire system of water molecules. The pressure is computed by the formula [36]:

$$P = \frac{Nk_BT}{V} + \frac{\sum_i^N \vec{r}_{ij}\cdot\vec{F}_{ij}}{dV} \tag{4}$$

where N is the number of atoms in the system, K_b is the Boltzmann constant, T is the temperature, d is the dimensionality of the system (2 or 3 for 2 dimension/3 dimension), V is the system volume.

The inter-atomic force between atoms i and j, $\vec{F}_{ij}$ is defined as the gradient of potential energy which is given by [36]:

$$\vec{F}_{ij} = -\left(\frac{dE(r_{ij})}{dr_{ij}}\right) \tag{5}$$

where r_{ij} is the distance between the atoms i and j and $E(r_{ij})$ is the potential between the atoms i and j.

3. System specification

In this paper, the transport of water molecules through the CNTs is achieved by using a pressure control model [37]. The system specification is shown in Fig. 1. The system consists of a reservoir of dimensions 62.52 Å × 65.22 Å × 50 Å filled with 6300 water molecules. The water molecules are held in reservoir by two planar graphene sheets, viz. GS1 and GS2. The two sheets GS1 and GS2 are initially separated by a vertical distance of 50 Å. Pressure is applied on the water molecules by downward displacement (along z direction) of GS1 that contains a hole which has the same size as that of the diameter of the CNT. At the beginning, the rigid CNT is displaced vertically downward inside the reservoir for a distance of 30 Å with a constant velocity of 10 m/s. After this, GS1 is pushed vertically downward with a velocity of 10 m/s until it is displaced by a distance of 20 Å from its initial position. The downward displacement of GS1 increases pressure on the water molecules that enables rapid transport of water molecules through the CNT core. The length of the CNT used in our simulation is 100 Å.