



# Structure and dynamics of water inside hydrophobic and hydrophilic nanotubes



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## HIGHLIGHTS

- Water structure and dynamics are strongly influenced by polarity.
- The influence is negligible for wider nanotubes.
- At low density, water present smaller diffusion than at higher densities.

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## ABSTRACT

We have used Molecular Dynamics simulations to investigate the structure and dynamics of TIP4P/2005 water confined inside nanotubes. The nanotubes have distinct sizes and were built with hydrophilic or hydrophobic sites, and we compare the water behavior inside each nanotube. Our results shows that the structure and dynamics are strongly influenced by polarity inside narrow nanotubes, where water layers were observed, and the influence is negligible for wider nanotubes, where the water has a bulk-like density profile. As well, we show that water at low density can have a smaller diffusion inside nanotubes than water at higher densities. This result is a consequence of water diffusion anomaly.

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## 1. Introduction

Since its discovery [1], carbon nanotubes (CNTs) has emerged as promising model systems for nanoconfinement studies of fluids. In this respect, it has been used in a wide range of applications such as water filtration [2], single-molecule sensors [3], ion selectivity [4], and energy conversion and storage [5]. In the case of nanoconfined water solutions the efficiency of the system is determined by the water–CNT interaction. This assumption can be tested by applying electric fields [6], decorating CNT walls [7], adding surfactants [8] and many others synthetization procedures.

Although not expected, the hydrophobic inner of a pristine CNT allows the water molecules not just to enter the nanotube cavity [9] but also to present a flow rate that exceeds by three orders of magnitude the values predicted by the continuum hydrodynamics theory [10,11]. Tuning the water–CNT interaction, by making it more hydrophilic or hydrophobic, is important either to achieve higher water permeation or to induce it to experience structural and dynamical transitions [12]. However, the impact of hydrophobicity over water structure and dynamics is also under debate and may lead to significant

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changes in its behavior [13–15]. The synthesis of chemically functionalized nanotubes with hydrophobic and hydrophilic sites [16], as in biological channels [17], adds even more complexity to this picture and presents an opportunity to study the effect of polarity heterogeneity over confined water properties.

By providing site-specific details of water properties, molecular dynamics (MD) simulations has been proved useful in the study of local structuration and quantification of water flux inside heterogeneous nanotubes [18–21]. Moskowitz and colleagues [22] has found that both the occupancy and the water flux are more sensitive to the fraction of hydrophilic atoms than to its arrangement. However, when located in the tube entrance, the hydrophobic atoms can play some role, lowering the filling rate [19]. Recently, by tuning the strength of water–nanotube attractions, Xu and his group [18] has found a maximal flow when empty states are present in the inner of the nanotube, which is unexpected since in this situation the wired hydrogen-bonding network (prerequisite for high water permeability) is broken.

In the present study we use MD simulations to examine the impact of nanotube polarity over the mobility and structure of the confined water molecules at different density regimes. Hydrophobic and hydrophilic atoms were distributed in a honeycomb lattice to form the model tubular nanochannel. The size effect is also evaluated by varying the nanotube diameter. The paper is organized as follows. In Section 2, the computational details and the methods are described, in Section 3 the main results of the dynamic and structural properties of the confined water are discussed. Conclusions are presented in Section 4.

## 2. Methods

### 2.1. Water and nanotube models

Molecular dynamics were performed using the LAMMPS package [23] for simulations of TIP4P/2005 water [24] confined inside nanotubes. The nanotube atoms are arranged on a honeycomb lattice. Two different atom types were used to build the nanotube. These two atom types differ only by their Lennard-Jones (LJ) parameters of interaction with water, and correspond to  $sp^2$ -hybridized carbon with  $\epsilon_{CO} = 0.478$  kJ/mol and  $\sigma_{CO} = 0.328$  nm (labeled hydrophilic due to water attractive character) and reduced carbon–water interaction strength with  $\epsilon_{CO} = 0.27$  kJ/mol and  $\sigma_{CO} = 0.341$  (namely hydrophobic), as done in previous works [12,22]. We considered ( $n, n$ ) nanotubes, with  $n = 10, 16$  and  $30$ . The choice of TIP4P/2005 over many other models available in the literature was due to its accuracy in calculating transport properties of water at ambient conditions [24,25]. Particularly for the diffusion coefficient, we have found  $2.32 \times 10^9$  m<sup>2</sup>/s, which is in close agreement to previous theoretical [26] and experimental works [27].

Periodic boundary conditions were applied to simulate isolated infinite nanotubes. Cutoff distances for LJ and Coulomb interactions are 1.0 and 1.2 nm, respectively. Long-range Coulomb interactions was handled using particle–particle particle–mesh method [28]. The simulations were conducted in the NVT ensemble at temperature 300 K fixed by a Nosé–Hoover thermostat [29,30]. The system was equilibrated with a 15 ns simulation, followed by 15 ns of data accumulation. The timestep is 1 fs. In all simulations the geometry of water molecules was constrained by the SHAKE algorithm [31].

### 2.2. Simulational details

The water radial density profile was evaluated by dividing the inner of the nanotube in concentric cylindrical shells and averaging the number of oxygen atoms in each shell along the simulation.

The diffusion mechanism of a fluid can be reflected by the scaling behavior between the mean squared displacement (MSD) and time [32]:

$$\langle |\vec{r}(t) - \vec{r}(0)|^2 \rangle \propto Dt^\alpha \quad (1)$$

where  $\langle |\vec{r}(t) - \vec{r}(0)|^2 \rangle$  is referred as the MSD,  $\langle \rangle$  denotes an average over all the molecules and  $\vec{r}(t)$  is the displacement of a molecule during the time interval  $t$ . The  $\alpha$  exponent refers to the diffusion regime:  $\alpha = 1$  for the linear Fickian diffusion,  $\alpha > 1$  for superdiffusive and  $\alpha < 1$  for subdiffusive regime. In the bulk phase, the water molecules diffuse as the Fickian type while for the water confined in CNTs, the diffusion behavior becomes extraordinary due to the nanoscale confinement [20,33].

For a fluid, the statistical error could be reduced by averaging over all the MSD components. But the nanopore confinement in the  $x$  and  $y$  directions hinders the radial displacement of the molecules. Therefore, The radial MSD is almost zero for all cases studied here and only the axial MSD will be considered.

We use the effective diameter [34]

$$d_{\text{eff}} = d - \sigma_{CO},$$

where  $d$  is the nominal diameter and  $\sigma_{CO}$  is the Lennard-Jones (LJ) parameter for carbon–oxygen interaction. to calculate the water density inside the nanotube. In terms of  $d_{\text{eff}}$ , the effective density is then given by

$$\rho_{\text{eff}} = \frac{M}{\pi \cdot \ell \cdot \left(\frac{d_{\text{eff}}}{2}\right)^2}, \quad (2)$$

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