

# Molecular Dynamics Simulation Study of the Structural Characteristics of Water Molecules Confined in Functionalized Carbon Nanotubes

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Molecular dynamics (MD) simulations were performed to study the structural properties of water molecules confined in functionalized carbon nanotubes (CNTs). Four CNTs, two armchair-type (6, 6), (7, 7) and two zigzag-type (10, 0), (12, 0) CNTs, representing different helicities and different diameters, were chosen and functionalized at their open ends by the hydrophilic  $-\text{COOH}$  and the hydrophobic  $-\text{CH}_3$  groups. The structural properties of water molecules inside the functionalized CNTs, including the orientation distributions of dipole moment and O–H bonds, the length of the single-file water chain, and the average number of hydrogen bonds, were analyzed during a process of simulations. MD simulation results in this work showed that the  $-\text{CH}_3$  functional groups exert little special effects on the structural properties of water molecules. It is mainly due to the relatively small size of the  $-\text{CH}_3$  group and its hydrophobic nature, which is consistent with hydrophobic CNTs. For CNTs functionalized by  $-\text{COOH}$  groups, the configurations of  $-\text{COOH}$  groups, incurvature or excurvature, determine whether water molecules can enter the CNTs. The incurvature or excurvature configurations of  $-\text{COOH}$  groups are the results of synergy effects of the CNTs' helicity and diameter and control the flow direction of water molecules in CNTs.

## I. Introduction

Carbon nanotubes (CNTs) represent a material that has been extensively studied in both theory and experimental practice ever since their discovery.<sup>1</sup> The popularity is due, in large part, to their remarkable structural, mechanical, and electromechanical properties that make them promising candidates for components in molecular-scale devices. The hydrophobic interior of CNTs is also considered as a model for fundamental studies aimed at exploring the structural and phase behavior of water molecules within one-dimensional (1-D) nanochannels,<sup>2–6</sup> which has long been recognized as the key for both theory and practice with various applications, such as gas storage,<sup>7,8</sup> nanoelectronics,<sup>9</sup> molecular detection,<sup>10,11</sup> drug delivery,<sup>12,13</sup> and membrane separation.<sup>14,15</sup>

Nevertheless, CNTs are generally insoluble in common solvents,<sup>16,17</sup> which impede the separation and manipulation of CNTs for specific applications. It is therefore a general belief that chemical functionalization of CNTs is desirable to improve their solubility and processability<sup>18,19</sup> and lead to a significant enhancement in the properties relevant to their practical applications.<sup>20,21</sup> As a result, the study of CNT functionalization is growing rapidly and has been the subject of recent research efforts.<sup>22–24</sup> Successful approaches that have been reported for

CNT chemical functionalization can be achieved at the open ends and the inner and outer sidewalls.<sup>25,26</sup>

However, chemical functionalizations also alter the structural and electronic properties of CNTs, which in turn deserve theoretical investigations before conducting purposeful experimental functionalizations to CNTs. As for the water–CNT system, molecular dynamics (MD) simulations have been used. For example, Soseph et al.<sup>27</sup> used MD simulations to study ionic flow in CNTs functionalized by  $-\text{COOH}$  groups at both ends. Their results showed that selectivity between cations and anions could be obtained by symmetrical placement of the functional groups. Zheng and co-workers<sup>28</sup> anchored  $-\text{COOH}$  groups onto the inner wall of a CNT to change the hydrophobic surface into a hydrophilic one and carried out dual-control-volume grand canonical MD simulations to study the transport of water and methanol mixtures through those modified CNTs. Their results showed that, although the diffusion of a mixture of water and methanol inside hydrophilic CNTs is slower than that in hydrophobic CNTs (due to a hydrogen network), the transport of the mixture through hydrophilic tubes is faster than that through hydrophobic CNTs. Halicioglu and Jaffe<sup>29</sup> investigated the effect exerted by aqueous solutions on the equilibrium structure and configuration of functional groups attached to CNTs and found that the polar functional groups are energetically more stable in extended configurations. Nonpolar functional groups, on the other hand, prefer to remain folded. Our previous MD simulations results<sup>30</sup> showed that, because of the helicity difference between (6, 6) and (10, 0) CNTs, the functionalization by hydrophilic  $-\text{COOH}$  groups at one end of the CNT results in a different response to the CNTs, which in

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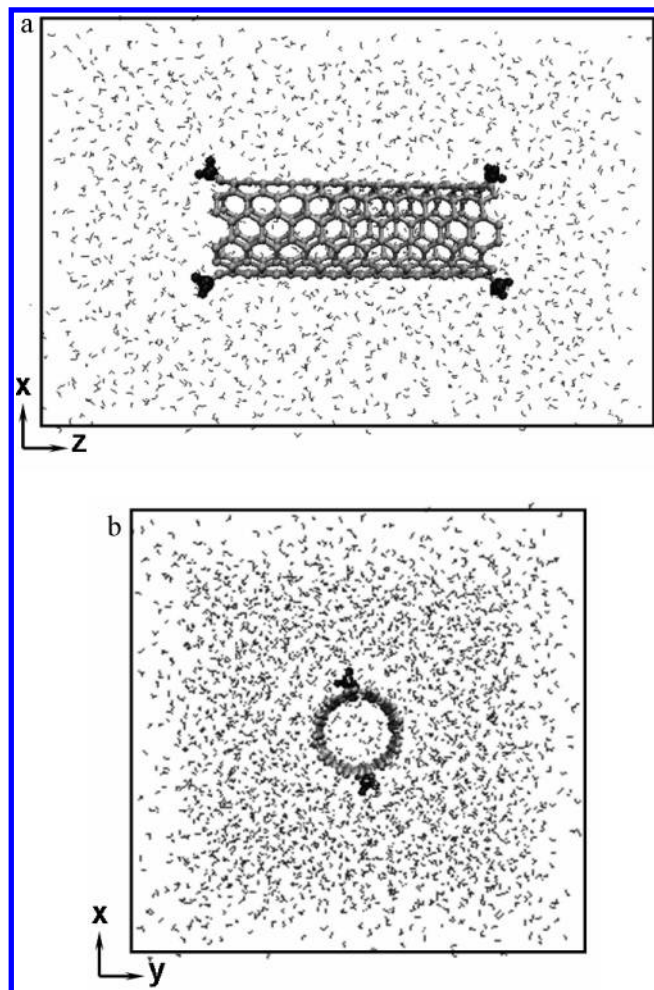
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**Figure 1.** A sketch of a  $-\text{CH}_3$  functionalized-(6, 6) CNT periodic simulation system: (a) lateral view; (b) side view. Some of the water molecules in the simulation box were removed for clarity.

turn controls the flow direction of water molecules in those functionalized CNTs.

However, the nanoscale behavior of water molecules in such functionalized CNTs is not yet well understood in those studies. For example, in the functionalized CNTs with open ends, there exist several unsolved questions: (a) Does it make any difference in the structural characteristics of water molecules if the open ends of the CNTs are functionalized by hydrophobic methyl groups ( $-\text{CH}_3$ )? (b) If the interesting results in the previous work<sup>30</sup> are brought forth by the functionalization to just one end of the CNTs, then what happens if both ends of the CNTs are functionalized by  $-\text{COOH}$  groups? (c) As pointed out in the literature,<sup>31</sup> the nanoscale confinement phenomena are dominated by tube diameter, so does a larger functionalized zigzag CNT have the ability to control the flow direction of water, as the functionalized (10, 0) CNT reported in previous work?

To shed light on these questions, we performed a series of MD simulations on the water and functionalized CNT systems. Different functional groups (hydrophilic  $-\text{COOH}$  or hydrophobic  $-\text{CH}_3$ ), different functional styles (one end functionalized or both ends modified), and the diameter, together with the helicity effects (armchair (6, 6), (7, 7) and zigzag (10, 0), (12, 0) CNTs), were investigated to study the structural characteristics of water molecules confined inside functionalized CNTs.

## II. Simulation Model and Method

The water–CNT system was modeled using classical MD simulations in the NVT ensemble, subject to periodic boundary conditions in all spatial directions. MD simulations were performed by a modification of the TINKER molecular modeling package (version 4.2).<sup>32</sup> The simulation system (with bulk water) was made up of a periodic water box,  $4 \times 4 \times 6$  nm, and a CNT(2.53–2.61 nm in length). The CNT was immersed in bulk water and placed along the  $z$ -axis in the center of the box with initially no single water molecule inside. The distance between one end of the CNT and the mirror image of the other end is about 3.5 nm, so the end-effects induced by the open ends of the CNT are neglected. Because of the large length-to-diameter ratio of CNTs, this approximation is expected to have an insignificant effect on the simulation results. The density of the bulk water was set to be  $997 \text{ kg}\cdot\text{m}^{-3}$ . Figure 1 shows a sketch of the periodic simulation system. The outer solid lines represent the boundaries of the simulation box.

Since the initial placement of water molecules does not allow an accurate predetermination of the bulk water density in the vicinity of the CNT, the volume of the computational box is preadjusted in the equilibration phase to match the density of the bulk water. The regulation of the volume was performed by repositioning the periodic boundary in the  $xy$ -planes while keeping the length of the box along the  $z$ -axis (the long axis of the CNT) fixed. It was shown that this procedure can prevent any deformation of the CNT during the volume adjustment.

The OPLS all-atom force field<sup>33</sup> was applied in which the CNT, the  $-\text{COOH}$  group, and the  $-\text{CH}_3$  group were taken to be the Lennard-Jones forms. The SPC/E model for water<sup>34</sup> was employed. Long-range Coulombic interactions were calculated by the Ewald sum method, and the nonbonded cutoff was set to 10 Å. The total interaction potentials between water molecules and carbon atoms in CNTs were calculated by the site–site interaction method:

$$U_{\text{wc}} = 4\epsilon_{\text{wc}} \sum_{i=1}^{N_{\text{w}}} \sum_{j=1}^{N_{\text{c}}} \left[ \left( \frac{\sigma_{\text{wc}}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{\text{wc}}}{r_{ij}} \right)^6 \right] \quad (1)$$

where  $N_{\text{w}}$  is the total number of atoms in water molecules,  $N_{\text{c}}$  is the total number of carbon atoms in a CNT, and  $r_{ij}$  is the center-to-center distance between an atom in a water molecule and a carbon atom in the CNT. The subscripts “w” and “c” denote a water molecule and a carbon atom of the CNT, respectively. The cross terms for the energy and size parameters,  $\epsilon$  and  $\sigma$ , were obtained by Lorentz–Berthlot combination rules, that is,  $\sigma_{ij} = (\sigma_i + \sigma_j)/2$  and  $\epsilon_{ij} = \sqrt{\epsilon_i \epsilon_j}$ . Table 1 summarizes detailed force field parameters for the Lennard-Jones interactions and the Coulombic interactions.

During MD simulations, all carbon atoms in CNTs were fixed, while the functional groups ( $-\text{COOH}$  or  $-\text{CH}_3$ ) were allowed to relax and water molecules could move freely in the simulation box. At atmospheric pressure, the variation of temperature, from 275 to 370 K, seems to exert little effect on the static properties of water molecules confined in functionalized CNTs, as shown in our previous work.<sup>30</sup> So the temperature in this study was selected to be 300 K. A time step of 2.0 fs proved sufficient for the stability of the trajectory and the conservation of total energy (the stability of total energies was better than 0.01%) and thus was used throughout. A total MD time of 1.2 ns was carried out for every MD run. The ensemble properties were averaged over the last 0.2 ns (i.e., between 1.0 and 1.2 ns). The standard deviation is estimated to be 1%.

**TABLE 1: Detailed Force-Field Parameters Used for the Lennard-Jones Interactions and the Coulombic Interactions for Water, CNTs, the  $-\text{COOH}$  Group, and the  $-\text{CH}_3$  Group**

site	$\sigma$ (nm)	$\epsilon$ (Kcal $\cdot\text{mol}^{-1}$ )	$q$ (e)
<b>H<sub>2</sub>O</b>			
O	0.317	0.155	-0.848
H	0.000	0.000	0.424
<b><math>-\text{COOH}</math></b>			
C	0.375	0.105	0.550
=O	0.296	0.210	-0.500
O	0.300	0.170	-0.580
H	0.000	0.000	0.450
<b><math>-\text{CH}_3</math></b>			
C	0.350	0.066	-0.180
H	0.250	0.030	0.060
<b>CNT</b>			
C <sup>a</sup>	0.355	0.070	0.080
C	0.355	0.070	0.000

<sup>a</sup> Anchored carbon atom on the CNTs; the charge value was taken from ref 28.

**TABLE 2: Simulation Cases for CNT–Water Systems, Where  $(m, n)$  are the CNT's Indices,  $D$  is the CNT's Diameter, and  $L$  is the CNT's Length**

case	$(m, n)$	$D/\text{nm}$	$L/\text{nm}$	functional group	
				type	number
1-1	(6, 6)	0.81	2.53	$-\text{COOH}$	4
1-2	(10, 0)	0.71	2.61	$-\text{COOH}$	4
2-1	(7, 7)	0.95	2.54	$-\text{COOH}$	2
2-2	(12, 0)	0.94	2.61	$-\text{COOH}$	2
3-1	(6, 6)	0.81	2.53	$-\text{CH}_3$	2
3-2	(7, 7)	0.95	2.54	$-\text{CH}_3$	2
3-3	(10, 0)	0.71	2.61	$-\text{CH}_3$	2
3-4	(12, 0)	0.94	2.61	$-\text{CH}_3$	2
4-1	(6, 6)	0.81	2.53		
4-2	(7, 7)	0.95	2.54		
4-3	(10, 0)	0.71	2.61		
4-4	(12, 0)	0.94	2.61		

### III. Results and Discussion

MD simulation trajectories were computed for pristine and functionalized armchair-type (6, 6), (7, 7) and zigzag-type (10, 0), (12, 0) CNTs in a water box. Four cases (12 MD runs in total) were investigated and compared with our previous work:<sup>30</sup>

**Case 1.** To investigate the functional style effect, both ends of the armchair (6, 6) and zigzag (10, 0) CNTs were symmetrically functionalized by  $-\text{COOH}$  groups, two groups at each end.

**Case 2.** To investigate the diameter and helicity effects, one end of the armchair (7, 7) and zigzag (12, 0) CNTs were symmetrically functionalized by two  $-\text{COOH}$  groups.

**Case 3.** To investigate the differences brought forward by different functional groups (hydrophilic  $-\text{COOH}$  and hydrophobic  $-\text{CH}_3$ ), one end of the armchair (6, 6), (7, 7) and zigzag (10, 0), (12, 0) CNTs was symmetrically modified by two  $-\text{CH}_3$  groups.

**Case 4.** Pristine armchair (6, 6), (7, 7) and zigzag (10, 0), (12, 0) CNTs were simulated for comparison.

The characteristics of all the MD runs are given in Table 2.

**1. Orientation of Water Molecules Inside CNTs.** The structure of water molecules confined in CNTs is first presented in terms of the orientation distributions of dipole moment (ODDM) and O–H bonds (ODOH). Two angles,  $\alpha$  and  $\beta$ , are defined as the direction of the dipole moment of a water molecule and the O–H bond in a water molecule with respect

to the  $z$ -axis of the CNTs (axial direction), respectively. The positive values of the two angles indicate the positive  $z$ -axis.

In general, as shown in Figure 2, the fluctuations of ODDM and ODOH are small with time for water molecules in various CNTs. This is a typical feature of a strongly hydrogen-bonded single-file water chain, as also pointed out by Mann and Halls.<sup>35</sup> This means that neither the functional groups nor the functional styles change the ability of water molecules to form hydrogen-bonded single-file water chains inside 1-D nanochannels.

From Figure 2 it was also found that the shapes of ODDM and ODOH are different for the cases investigated. The ODDMs for (6, 6) and (10, 0) CNTs functionalized by  $-\text{COOH}$  at both ends and by  $-\text{CH}_3$  at one end, have two distinct peaks at about  $\alpha = 15^\circ$  and  $\alpha = 165^\circ$ , while the ODDMs for the pristine (6, 6) and (10, 0) CNTs have solo corresponding peaks at  $\alpha = 30^\circ$  and  $\alpha = 150^\circ$ , respectively. The existence of two peaks for ODDM, which is also observed by Wang et al.<sup>31</sup> in their research of much larger pristine CNTs, indicates the more disordered water structures inside these functionalized CNTs.

As for the (7, 7) and (12, 0) CNTs, even if the height of peaks are slightly different, it is difficult to observe differences in corresponding angles  $\alpha$  and  $\beta$  for profiles of ODDM and ODOH among the pristine, the  $-\text{COOH}$  functionalized, and the  $-\text{CH}_3$  functionalized CNTs. Also, from Figure 2, we can observe that the peak differences for the pristine, the  $-\text{COOH}$  functionalized, and the  $-\text{CH}_3$  functionalized (7, 7) CNTs, as well as the three cases for the (12, 0) CNTs, are much smaller than corresponding peak differences of the (6, 6) and (10, 0) CNTs. It means that, compared with the pristine CNTs, the functionalizations to (7, 7) and (12, 0) CNTs do have effects on the structural characteristics of inside water molecules, because the corresponding peaks have different heights for the three cases of (7, 7) CNTs and the three cases of (12, 0) CNTs. It could be due to the fact that, in  $-\text{COOH}$  functionalized (7, 7) CNTs and in  $-\text{CH}_3$  functionalized (12, 0) CNTs, more water molecules are orientated in one direction than in the other two cases. But on the other hand, such effects are small when compared with the cases of the (6, 6) and (10, 0) CNTs.

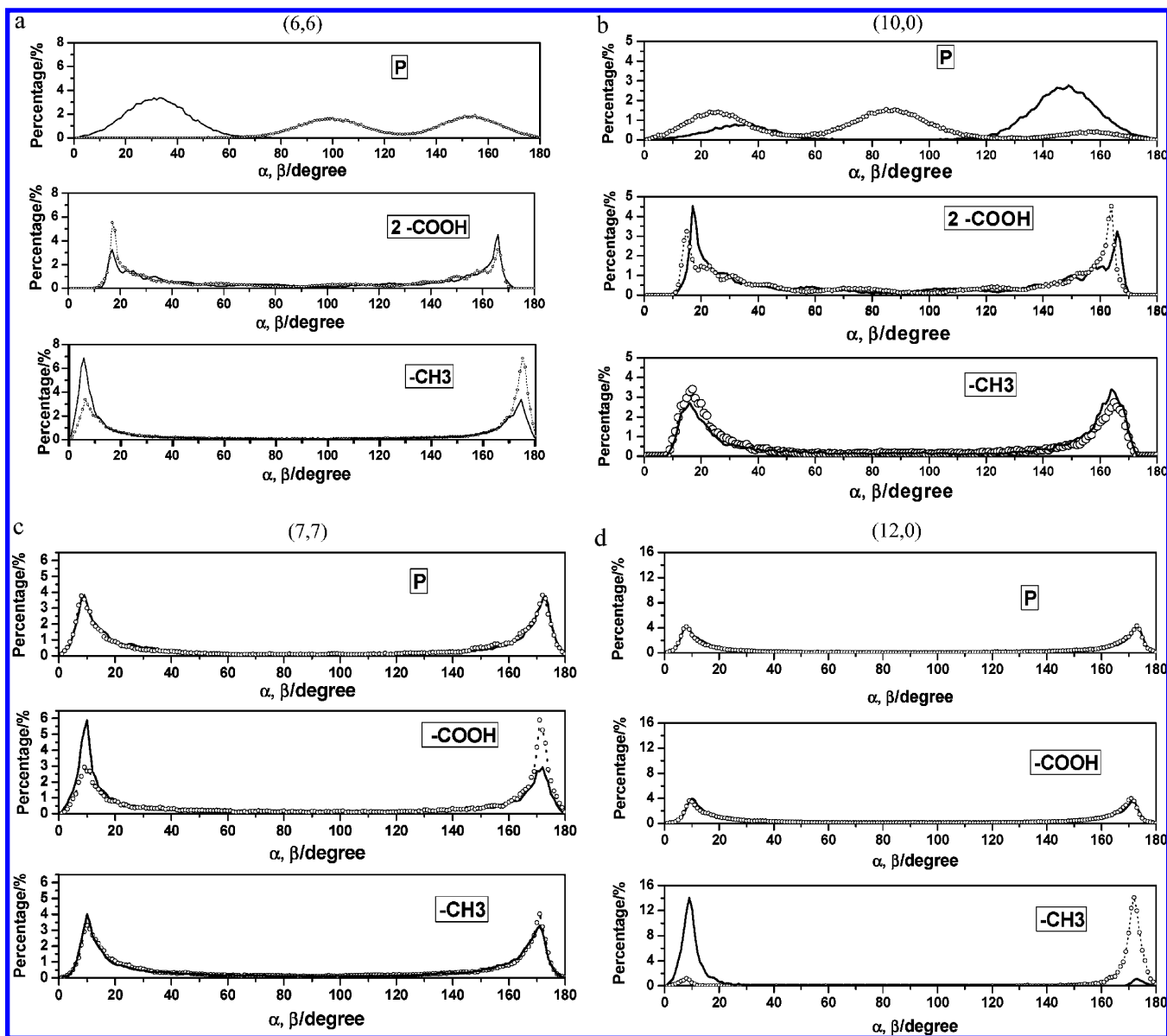
Furthermore, as shown in Figure 2, the corresponding peaks of ODDM and ODOH overlap each other, which means the “single-file” water chains have specific orientations in the interior of these CNTs.

**2. Length of the Single-File Water Chain and the Hydrogen Bonds inside CNTs.** Hydrogen bonds play a crucial role in the behavior of water; their spatial patterns and fluctuations characterize the structure and dynamics of water molecules.<sup>36</sup> The hydrogen-bond structure in this work is given in terms of the average number of hydrogen bonds per water molecule ( $n_{\text{HB}}$ ) and is determined by a geometrical criterion, similar to that of Marti et al.'s work.<sup>37</sup> Two water molecules are considered hydrogen-bonded if all of the following three conditions are satisfied:

- The distance between the oxygen atoms of both molecules is smaller than 3.75 Å;
- The distance between the oxygen of the acceptor molecule and the hydrogen of the donor is less than 2.46 Å;
- The bond angle between the oxygen–oxygen direction and the molecular oxygen–hydrogen bond of the donor is less than  $30^\circ$ .

The ensemble properties were averaged over the last 0.2 ns for the total number of water molecules that once entered the CNT ( $n_T$ ), the average length of single-file water chain ( $\langle n \rangle$ ), and the average number of hydrogen bonds per water molecule





**Figure 2.** ODDMs (solid line) and ODOHs (dotted line with open circles) of water molecules inside pristine and functionalized (6, 6), (7, 7), (10, 0), and (12, 0) CNTs. The “P”, “-COOH”, “2 -COOH”, and “-CH<sub>3</sub>” stand for pristine, -COOH functionalized at one end, -COOH functionalized at both ends, and -CH<sub>3</sub> functionalized at one end, respectively.

**TABLE 3: Water Molecules Inside CNTs, Where  $n_T$  is the Total Number of Water Molecules that Enter the CNT during the Last 200 ps,  $\langle n \rangle$  is the Average Length of the Single-File Water Chains, and  $\langle n_{HB} \rangle$  is the Average Number of Hydrogen Bonds Per Water Molecule Inside the CNTs<sup>a</sup>**

(m, n)	(6, 6)			(10, 0)			(7, 7)			(12, 0)		
functional style	P	2-C	CH <sub>3</sub>	P	2-C	CH <sub>3</sub>	P	C	CH <sub>3</sub>	P	C	CH <sub>3</sub>
$n_T$	17	32	19	15	26	15	31	<b>13</b>	32	29	48	27
$\langle n \rangle$	9.8	10.6	8.9	8.7	10.2	8.9	12.2	<b>5.1</b>	12.3	12.5	20.4	12.6
$\langle n_{HB} \rangle$	2.8	2.9	2.6	1.7	1.9	1.8	3.0	<b>0.9</b>	3.0	2.1	2.1	2.2

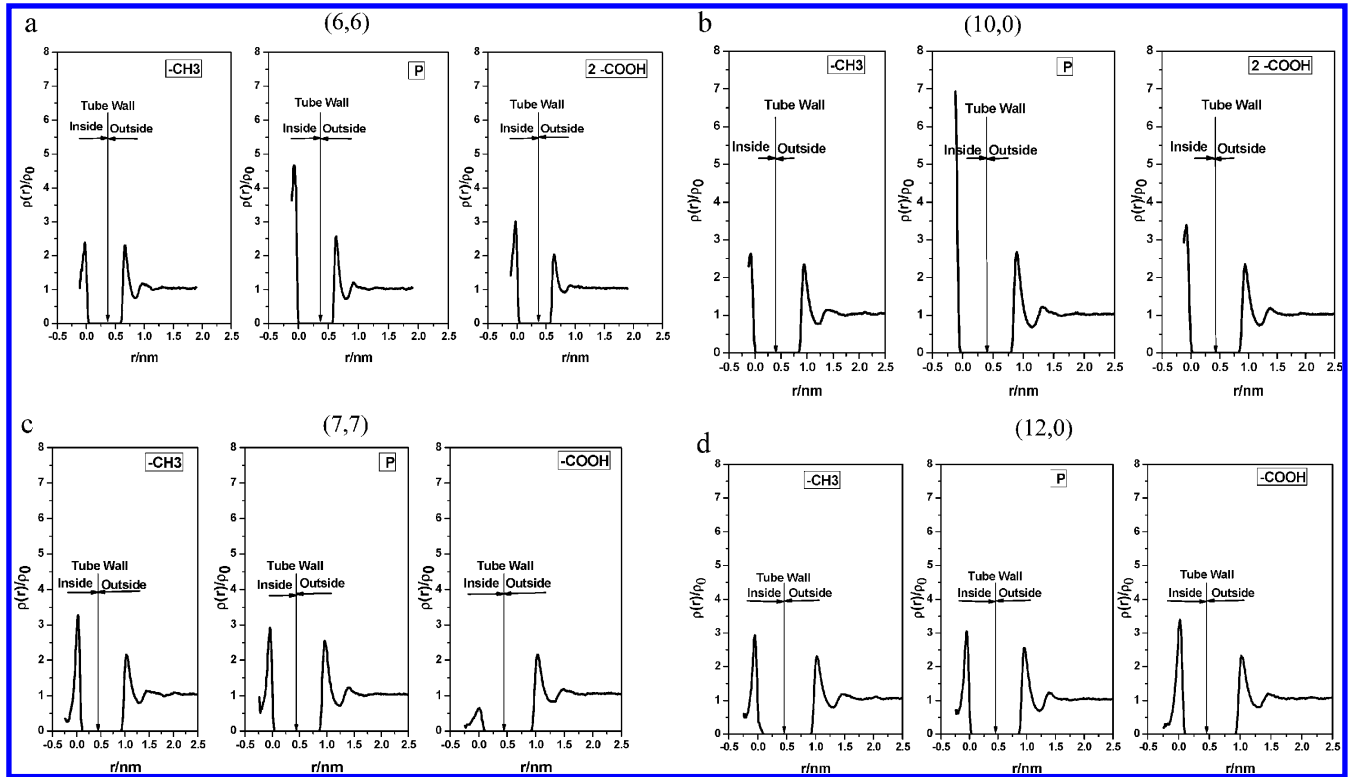
<sup>a</sup> The “P”, “C”, “2-C” and “CH<sub>3</sub>” stand for pristine, functionalized by -COOH groups at one end, functionalized by -COOH groups at both ends, and functionalized by -CH<sub>3</sub> groups at one end, respectively.

inside the CNTs ( $\langle n_{HB} \rangle$ ). The detailed information from MD runs is provided in Table 3.

We could summarize two interesting results from Table 3. One is that, except for the (7, 7) CNT, all three of the properties analyzed for the (6, 6), (10, 0) and (12, 0) CNTs change in this order: in -COOH functionalized CNT > in pristine CNT  $\approx$  in -CH<sub>3</sub> functionalized CNT. And although the -CH<sub>3</sub> functionalized (7, 7) CNT shows little difference from the pristine (7, 7) CNT as far as these properties are concerned, once the (7, 7)

CNT is modified by the -COOH groups at one end, the number of water molecules that are able to enter the interior observably decreases to a much smaller number, and this may in turn contribute to the small average number of hydrogen bonds of the water molecules inside the -COOH functionalized (7, 7) CNT.

In our previous work,<sup>30</sup> the as-functionalized (10, 0) CNT only allows water molecules to enter the interior from the unfunctionalized end because the -COOH groups at the other



**Figure 3.** RDPOs of water molecules inside various CNTs at 300 K. The “P”, “-CH<sub>3</sub>”, “-COOH”, and “2 -COOH” stand for pristine, one-end functionalization by -CH<sub>3</sub> groups, one-end functionalization by -COOH groups, and two-end functionalization by -COOH groups, respectively. The lower peak height indicates that water molecules are less ordered.

end block the way for water molecules. In that work, we attributed that phenomena to the helicity effects exerted by the zigzag (10, 0) CNT. The simulation results here indicate that the water molecules have difficulty entering the -COOH group-functionalized armchair (7, 7) CNT. Studies in search of the actual reasons for this phenomena of the -COOH functionalized (7, 7) CNT are still underway.

**3. Radial Density Profile of Oxygen Atoms (RDPO).** Nanoscale confinement is known to have significant effects on the structural properties of water molecules. The confinement by CNTs results in heterogeneous density distributions of water molecules, mainly in the direction of confinement. The radial density profile, in units of the bulk density  $\rho_0$ , was averaged over cylindrical shells ( $\Delta r = 0.13$  Å) centered at the axis of the CNT and was plotted against the cylindrical radius  $r$ . Since the oxygen atom is quite near the center of mass of a water molecule, the RDPO could logically be taken as the radial density profile of water molecules. The RDPOs of water molecules in the various CNTs are shown in Figure 3.

The peak inside the CNT ( $H_1$ ) reflects the ordered structure of water molecules inside the CNT. The narrow diameter and the hydrophobic nature of CNTs determine that the relatively stable structure of water molecules could only exist near the center of the CNTs, in the form of single-file water chains, as reported by Hummer et al.<sup>38</sup> The peak outside the CNT ( $H_2$ ) is typical for such water-CNT systems; its position and height have close relationships with the Lennard-Jones interaction parameter between the oxygen atom of a water molecule and the carbon atom of CNT( $\sigma_{CO}$ ). The heights for the two peaks ( $H_1$  and  $H_2$ ) are listed in Table 4.

The most impressive result from Figure 3 and Table 5 is that the peak height ( $H_1$ ) inside the -COOH functionalized (7, 7) CNT is extremely small. It is in accord with the water density observed for the functionalized (7, 7) CNT in the previous section: the small number of water molecules diminishes the

**TABLE 4: Heights of the Two Peaks in the RDPO in Figure 6**

( <i>m</i> , <i>n</i> )	(6, 6)			(10, 0)			(7, 7)			(12, 0)		
functional style	P	2-C	CH <sub>3</sub>	P	2-C	CH <sub>3</sub>	P	C	CH <sub>3</sub>	P	C	CH <sub>3</sub>
$H_1$	4.6	3.0	2.4	6.9	3.4	2.6	2.9	0.6	3.2	3.0	3.4	3.0
$H_2$	2.5	2.0	2.3	2.6	2.3	2.4	2.2	2.2	2.3	2.5	2.3	2.3

<sup>a</sup> The “P”, “C”, “2-C” and “CH<sub>3</sub>” stand for pristine and the functionalizations by -COOH groups at one end, -COOH groups at both ends, and -CH<sub>3</sub> groups at one end, respectively.  $H_1$  is the height for the peak inside the CNT, and  $H_2$  is that for the outer peak.

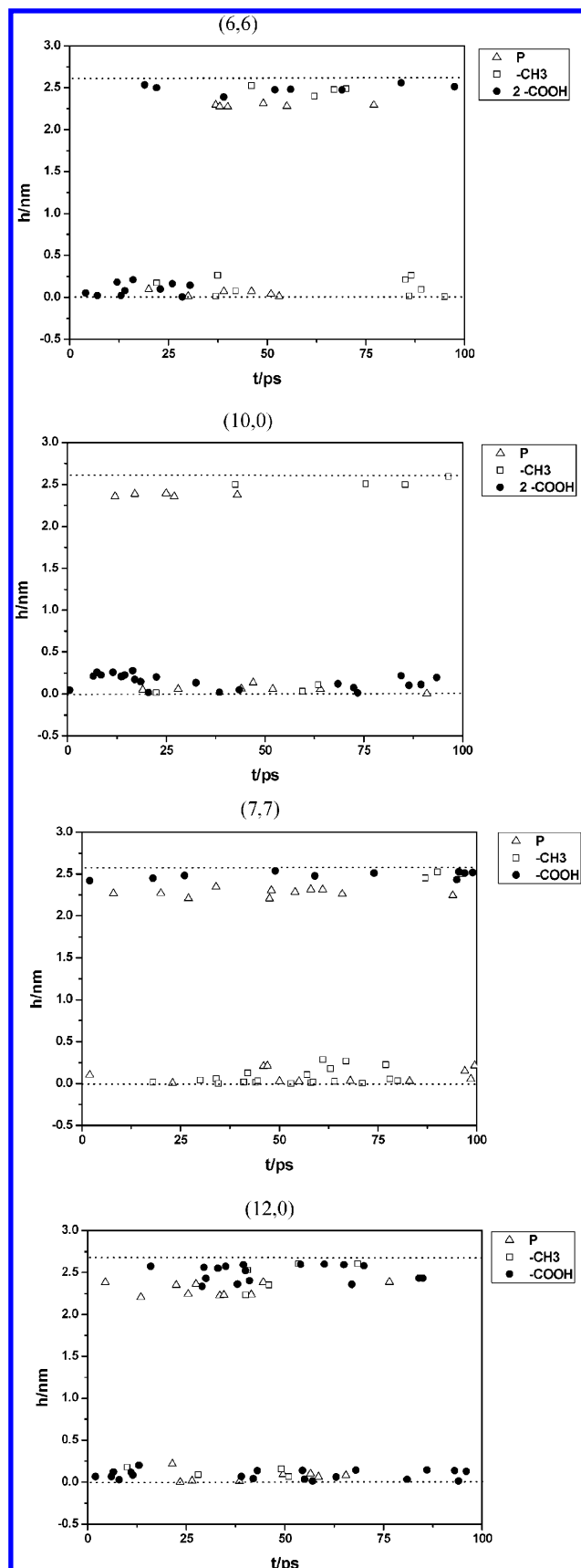
**TABLE 5: The Number of Water Molecules Entering the CNTs from Two Ends**

( <i>m</i> , <i>n</i> )	(6, 6)			(10, 0)			(7, 7)			(12, 0)		
functional style	P	CH <sub>3</sub>	2-C	P	CH <sub>3</sub>	2-C	P	CH <sub>3</sub>	C	P	CH <sub>3</sub>	C
$n_{1/h=0.0}$	6	9	10	7	3	23	11	20	0	8	4	20
$n_{2/h=2.5}$	6	4	8	5	4	0	11	3	9	10	5	17
$n_1 + n_2$	12	13	18	12	7	23	22	23	9	18	9	37

<sup>a</sup> The “P”, “-CH<sub>3</sub>”, “-COOH” and “2 -COOH” stand for pristine, one-end functionalization by -CH<sub>3</sub> groups, two-end functionalization by -COOH groups, and one-end functionalization by -COOH groups, respectively.

height value of  $H_1$ . On the other hand, the -CH<sub>3</sub> functionalized (7, 7) CNT exhibits the same characteristics as the pristine one. Table 4 also shows that once the CNTs are modified, no matter what functional groups are used and what functional styles are adopted, peak heights inside (6, 6) and (10, 0) CNTs are greatly reduced, while they hardly change for the (12, 0) CNT. In other words, the functional groups, -COOH or -CH<sub>3</sub>, exert little effect on the structural properties of water molecules inside the (12, 0) CNT.

As for the outer peak ( $H_2$ ), while the height is closely related to the force field parameter  $\sigma_{CO}$ , as shown in Table 2, it remains unchanged for all CNTs studied. This feature is also in good



**Figure 4.** Position of water molecules when entering the CNTs at 300 K. The “P”, “-CH<sub>3</sub>”, “-COOH”, and “2 -COOH” stand for pristine, -CH<sub>3</sub> groups at one end, -COOH groups at one end, and -COOH groups at both ends, respectively. The CNT is along the  $h$  axis, and the positions  $h = 0.0$  and  $h = 2.5$  are corresponding to the two ends of the CNTs. If the CNTs are functionalized at one end, that end is placed at  $h = 0.0$ .

agreement with Walther et al.’s results on the structural properties of water molecules surrounding pristine CNTs.<sup>39</sup> In addition, our results for the density profiles of pristine CNTs are generally in good agreement with the those found in the literature.<sup>31,39,40</sup>

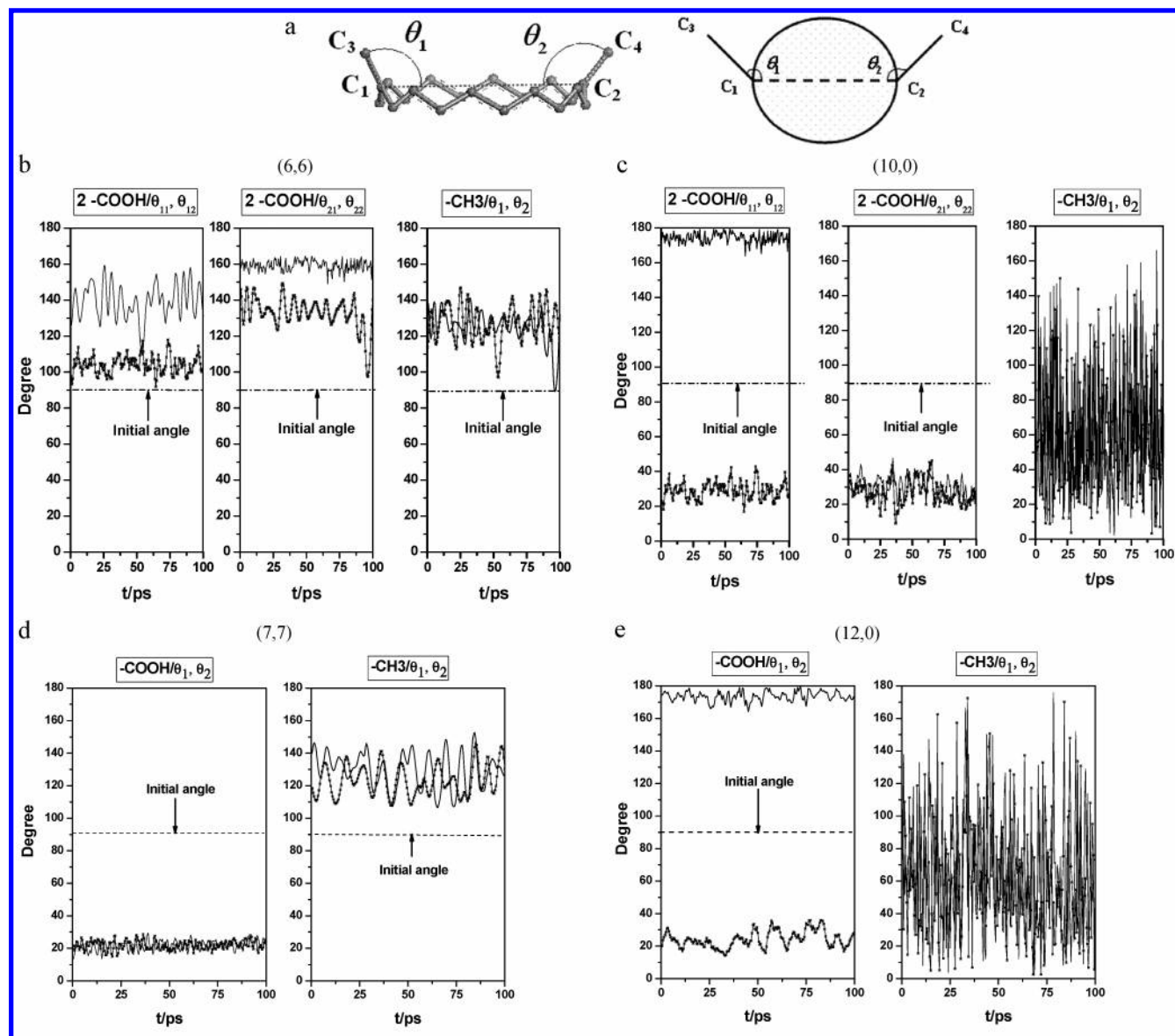
**4. Positions of Water Molecules when First Entering the CNTs and Fluctuations of the Functional Groups.** In order to have a better understanding of how the functional groups -COOH and CH<sub>3</sub> affect the behavior of water molecules, all water molecules that had entered the CNTs were tracked to find out how they entered the CNTs. The fluctuations of the functional groups were analyzed to reveal the roles they play during that process. The positions of water molecules were recorded, as shown in Figure 4 for the last 100 ps of simulation time, to show where water molecules were and when they entered the CNTs for the first time. The  $h$  axis (axial direction of CNTs) is along the  $z$ -axis. If the CNT is functionalized at one end, the modified end is placed at the origin of the  $h$  axis. The positions of the functional groups are defined by two angles, as shown in Figure 5a. C<sub>1</sub> and C<sub>2</sub> are the carbon atoms in the CNT, and C<sub>3</sub> and C<sub>4</sub> are the carbon atoms in the -COOH and -CH<sub>3</sub> groups. The fluctuations of angles C<sub>3</sub>C<sub>1</sub>C<sub>2</sub> and C<sub>4</sub>C<sub>2</sub>C<sub>1</sub> are plotted in Figure 5b.

It is observed from Figure 4 that, in general, water molecules can enter the CNTs from both ends with almost equal probabilities, but three functionalized CNTs—(7, 7) functionalized by -COOH groups at one end, (7, 7) functionalized by -CH<sub>3</sub> groups at one end, and (10, 0) functionalized by -COOH groups at both ends—display some abnormalities. We may get direct and clear information from Table 5. Once the (7, 7) CNT is functionalized by -COOH groups at its one end, it only opens the unmodified end for water molecules, behaving exactly the same as the functionalized (10, 0) CNT reported in our previous work.<sup>30</sup> In addition, it is worth pointing out that, once the (7, 7) CNT is functionalized by -CH<sub>3</sub> groups at one end, the water molecules prefer to enter the (7, 7) CNT from the functionalized end. As shown in Figure 4 and Table 5, for example, 20 enter from that modified end and only 3 from the other.

Although the (10, 0) CNT is symmetrically modified by -COOH groups at both ends, water molecules can only enter the interior from just one functionalized open end. The differences between the two functionalized ends can be clearly seen from the following analysis.

Figure 5 shows that, the angles of -COOH groups at the functionalized end of the (7, 7) CNT seem to be fixed at about 20°, indicating that the -COOH groups at the modified end of the (7, 7) CNT cover that end and block the way for water molecules. The exceptional fluctuations of the -COOH groups of the (7, 7) CNT also account for all the abnormalities of the properties analyzed above for that (7, 7) CNT. But, for the -CH<sub>3</sub>-functionalized (7, 7) CNT, the two angles are around 130° and are more stable than the angle distributions of the -CH<sub>3</sub>-functionalized (12, 0) CNT, as seen from Figure 5. And the real causes of the phenomenon that water molecules prefer to enter the (7, 7) CNT from the -CH<sub>3</sub> functionalized end deserve further investigation.

As far as the modified (10, 0) CNT is concerned, the functional groups at the two ends behave differently. The values for two angles at one end ( $h = 2.5$ ) are both around 30°, which indicates that the two functional groups cover that end and prevent water molecules from entering the interior. So the water molecules can only enter that (10, 0) CNT at the other modified end ( $h = 0.0$ ), where the two angles are about 30° and 175°. From our previous work on functionalized CNTs,<sup>30</sup> it is obvious



**Figure 5.** Definition (a) and distribution (b–e) of angle  $\theta_1$  and angle  $\theta_2$ , which reflect the position fluctuation of the functional groups of the CNTs at 300 K. The label on top of each picture, for example,  $-\text{CH}_3/\theta_1, \theta_2$ , denotes the functional groups and the two angles at that end.

that the helicity and the diameter differences are responsible for the phenomenon observed for the  $-\text{COOH}$ -functionalized CNTs. For other cases where the CNTs were modified by  $-\text{CH}_3$  groups, simulations do not show any remarkable differences. It confirms the conclusion that the introduction of hydrophobic  $-\text{CH}_3$  groups does not in turn change the structural characteristics of the water molecules confined in these CNTs. However, to control the flow direction of water molecules and make functionalized CNTs proper candidates for a water molecular switch, it still deserves further study to fully understand the phenomenon observed in these MD simulations.

#### IV. Summary and Conclusions

MD simulations have been performed to investigate the structural characteristics of water molecules confined in open-end-functionalized CNTs. The hydrophilic  $-\text{COOH}$  group and the hydrophobic  $-\text{CH}_3$  group are chosen as the functional groups. Four CNTs, two armchair types (6, 6), (7, 7) and two zigzag types (10, 0), (12, 0), representing different helicities and diameters, were chosen and functionalized. Two styles of functionalization have been tested. One is the symmetrical

functionalization to one end of the CNT, and the other is where both ends are symmetrically modified. Unexpected results were revealed by the water molecules inside the  $-\text{COOH}$ -functionalized CNTs, whereas the ones in the  $-\text{CH}_3$ -functionalized CNTs remained identical to the water molecules inside the pristine CNTs as to the structural properties analyzed in this work, including the ODDM and ODOH of water molecules, the length of the single-file water chain, and the average number of hydrogen bonds for water molecules inside the modified CNTs. This is probably because of the relatively small size of the  $-\text{CH}_3$  group and its hydrophobic nature, which is consistent with hydrophobic CNTs.

The incurvature configurations of the  $-\text{COOH}$  groups of the (7, 7) CNT block off all water molecules at the modified end, whereas the functionalized (12, 0) CNT, with a diameter similar to that of the (7, 7) CNT, enables the coexistence of the incurvature and incurvature configurations of  $-\text{COOH}$  and therefore allows water molecules to enter from the modified end. As far as the (6, 6) and (10, 0) CNTs are concerned, they are functionalized by the  $-\text{COOH}$  groups at both ends. The incurvature configurations for all four  $-\text{COOH}$  groups of the



(6, 6) CNT are responsible for the behavior differences of the water molecules compared with the water molecules confined in the functionalized (10, 0) CNT. This is because, of the four functional  $\text{—COOH}$  groups of the (10, 0) CNT, only one group takes the excurvature configuration, and the incurvature configurations of the two  $\text{—COOH}$  groups on the other end block off water molecules. Since there are no distinct differences between (6, 6) and (10, 0) CNTs or (7, 7) and (12, 0) CNTs, the phenomena observed in this work is undoubtedly attributed to the helicity effects. The helicity of CNTs determines the fluctuations of the  $\text{—COOH}$  groups, which in turn bring forth the nonuniform distribution of the CNT's electric field and alters the water conduction process. Similar conclusions were also summarized by Zimmerli et al.<sup>41</sup> in their simulation work about the curvature effects of CNTs on the conduction process of water molecules.

Once the underlying mechanisms are fully understood and the functionalizations to CNTs are conducted purposely, we may finally be able to completely control a fluid's behavior at the nanoscale confinement, and further design molecular devices with various applications.

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