

## Diffusion dynamics of water controlled by topology of potential energy surface inside carbon nanotubes

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(Received 17 December 2007; published 28 March 2008)

The effect of topology of single-walled carbon nanotubes (CNTs) on the diffusion dynamics of water confined in the armchair and zigzag CNTs was investigated. It was found that the activation energy of molecular diffusion in zigzag CNTs is greater than that in armchair ones at similar diameters, which leads to water molecules in zigzag CNT diffusing much slower than in armchair CNT. Further calculations of potential energy surfaces (PESs) of water in these two types of CNTs explain the mechanism of diffusion dynamics of confined water. This research shows that the topology of PESs inside CNT could control the diffusion behaviors of water inside it. Since topology of PESs inside CNT could be modified by various chemical and/or physical methods, this work indicates the possibility of controlling the diffusion behaviors inside the CNTs by molecular engineering approach, without changing its pore size.

DOI: [10.1103/PhysRevB.77.125438](https://doi.org/10.1103/PhysRevB.77.125438)

PACS number(s): 66.10.C-, 47.61.-k, 61.46.Fg, 31.15.xv

Carbon nanotubes (CNTs) are important building blocks for nanocomposite materials and nanomachinery due to their unique physical properties (electronic, optical, thermal, mechanical, etc.)<sup>1,2</sup> and extensively receive interest for materials, biology, and geology sciences. The unusual transport property of fluids confined in CNTs is one of these most important features and stimulates many researches and applications in these fields. Recently, many studies suggest that the CNT could serve as nanoscale pipes to deliver fluids and molecular species. This feature can be used in the nanoscale charge (proton) storage devices,<sup>3</sup> industry membrane,<sup>4</sup> and drug-delivery devices.<sup>5</sup> The mechanisms of transport for polar species such as water molecules, protons, ions, RNA, DNA, and so on through membrane channels remain one of the most interesting topics in biology research. CNTs, as a structurally simple and rigid hydrophobic channel, serve as a good model to explore fundamental aspects of the transportation in biological transmembrane channels and biological nanofluidics.<sup>6-9</sup>

In the past five years, the nanofluidic properties of water through CNTs were studied experimentally<sup>10,11</sup> and theoretically.<sup>12-14</sup> Hummer and co-workers<sup>15-17</sup> observed water conduction through CNT and showed that water confined to narrow cylindrical pores formed one-dimensional chains held together. Striolo<sup>18</sup> showed that confined water molecules diffuse through a fast ballistic motion mechanism in infinitely long CNT of 1.08 nm diameter. Kolesnikov *et al.*<sup>19</sup> anomalously revealed soft dynamics of water in CNT by a combined inelastic neutron scattering and molecular dynamics (MD) simulation. However, in most of these researches, much attention was paid to the effect of pore size to the transport behaviors of fluids in CNTs. The effects of topology, for example, the helicity of CNTs to the diffusion dynamics of polar molecules, such as water, inside the hydrophobic pore are still poorly understood. Recently, we presented MD simulations<sup>20-22</sup> of the effects of pore size and the helicity of CNTs on the transport properties and fluid structure of confined water. In our previous work, a very interesting finding is that the diffusion behavior of confined

water in zigzag- and armchair-typed CNTs is distinctly different: the diffusivity in the zigzag CNT is much lower than that in the armchair CNT at similar pore sizes, as shown in Fig. 2 of Ref. 20. Since the pore size is similar in two cases, this phenomenon indicates that the diffusion behaviors of CNT could be strongly controlled by other properties beside pore sizes, e.g., the topology of CNT. Deeper investigation of mechanism for this phenomenon is very important.

In this paper, we present our works on the mechanism of the influence of the topology of CNTs to the diffusion dynamics of confined water. The research was performed by a combination of dynamics analysis, molecular mechanics (MM), as well as quantum mechanics calculations. The armchair (14,14) CNT and zigzag (24,0) CNT with similar pore diameters (1.90 and 1.88 nm, respectively) were selected as a model to perform the potential energy surface (PES) calculations.

In this work, the details of MD simulations were the same as that described in previous works.<sup>21,22</sup> On the basis of the overall averaged diffusivity, the diffusivities and their components for different shells of water molecules in the armchair and zigzag CNTs were further analyzed in detail. Owing to the arrangement of carbon atoms, the helicity of CNTs affects the diffusion dynamics of water molecules in different shells of the fluid column (outer and inner). We observed that at various temperatures, the diffusion of the outer shell water molecules (near the tube wall) is much slower than that of the inner shell (near the central axis) in both types of CNTs, which indicates that the interaction between the tube-wall and the outer shell water molecules is much stronger than the interaction between the tube-wall and the inner shell water molecules. Figure 1 shows the diffusivity components of water molecules in the outer shell and those in the inner shell as well as the overall averaged diffusivity in armchair and zigzag CNTs as a function of the tube diameter at 298 K. The result shows that the diffusion in axial direction is dominant in two types of CNTs. However, what more important is that the diffusion of the outer shell molecules is much slower than that of the inner shell in both types of CNTs either in

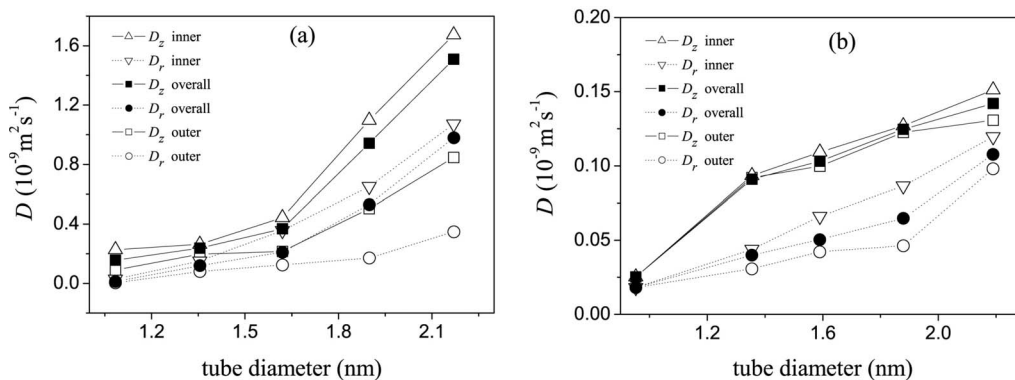


FIG. 1. Diffusivity components of water confined in (a) armchair and (b) zigzag CNTs as a function of tube diameter for the outer and inner shells at 298 K and  $1.0 \text{ g cm}^{-3}$ .

axial direction or in radial one. The water molecules in the outer shell moved much more slowly than those in the inner shell, which can be clearly observed from the trajectory animation. It indicates that the interaction between the tube-wall and the outer shell water molecules is much stronger than the interaction between the tube-wall and the inner shell water molecules. In addition, for all diffusivity components, both the diffusivities of the inner shell molecules and that of the outer shell molecules in armchair (14,14) CNT are larger than those in zigzag (24,0) CNT at different temperatures, as shown in Fig. 2. On the other hand, the overall averaged diffusivity of water confined in CNTs is also related to the fractions of water molecules in the outer and inner shells. It was found that the relationship of the overall averaged diffusivity and the diffusivities of the outer and inner shells follows  $D_i = x_{i,outer}D_{i,outer} + x_{i,inner}D_{i,inner}$  where  $x_i$  is the fractions of molecules in the outer and inner shells and  $i$  denotes the different directions in which the diffusivity has a component. Thus, the overall averaged diffusivity is determined by both the diffusivity and the fractions of molecules in the outer and inner shells, i.e., by the contribution of the product of  $x_i D_i$ . In case of small tube size, there are more water molecules in the outer shell, and the diffusivity is very small owing to the greater interaction of the tube-wall potentials. Thus, the term “outer” in the above equation is dominant,

and the overall averaged diffusivity is very small. However, with increase in the tube size, the number of water molecules in the inner shell increases and the proportion of the term “inner” in the equation goes up, and becomes dominant finally, hence the diffusivity increases in a large extent and the overall averaged diffusivity gets larger. Figure 3 shows the fractions of water molecules in the outer and inner shells confined in two types of CNTs as a function of tube size. Compared to the armchair CNT, in the zigzag CNT with larger diameter, the difference of the number of water molecules in the outer and inner shells is relatively small, and the diffusivity itself is also small, as shown in Fig. 1, so the difference of  $x_i D_i$  for the outer and inner shells is not obvious. Therefore, the variation of the overall averaged diffusivity with tube size is smooth. In conclusion, the confinement effect of zigzag CNT to water molecules is stronger, and the diffusivity of water molecules is much lower compared to that in armchair CNT.

We compared our results with the experimental ones of Mamontov *et al.*<sup>23</sup> for the diffusivity of water. We found that the experimental diffusion coefficients of water confined in armchair single-walled carbon nanotube (SWNT) with mean diameter of  $14 \pm 1 \text{ \AA}$  are  $(0.7-5.4) \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$  from 190 to 260 K, which are basically consistent with our simulation results,  $\sim 3 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$  at 298 K. However, unfor-

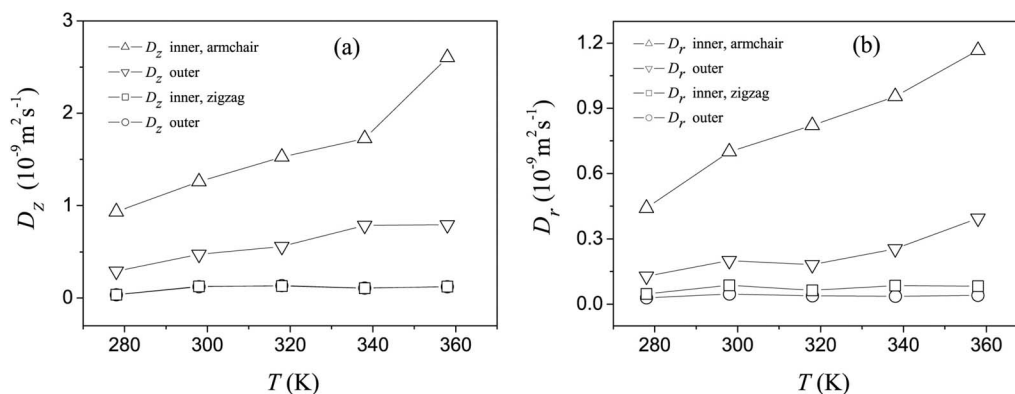


FIG. 2. Diffusivity components of water confined in armchair (14, 14) and zigzag (24, 0) CNTs as a function of temperatures for the outer and inner shells at  $1.0 \text{ g cm}^{-3}$ . (a) In the axial direction and (b) in the radial direction.

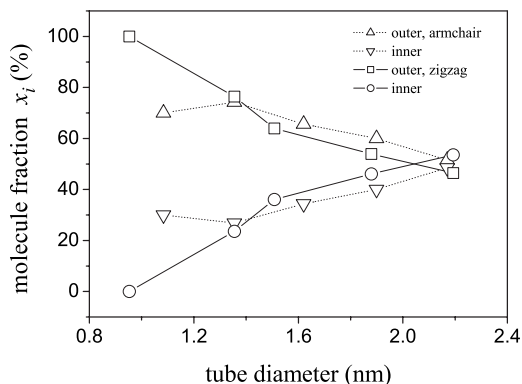


FIG. 3. Fraction of water molecules confined in armchair and zigzag CNTs as a function of tube diameter for the outer and inner shells at 298 K and  $1.0 \text{ g cm}^{-3}$ .

tunately, the authors did not report the experimental data for 298 K, therefore, to compare with the experimental result, we extrapolated the experimental data with the Arrhenius equation and the Vogel–Fulcher–Tammann (VFT) equation.<sup>24</sup> We obtained that the diffusion coefficient for water confined in (10,10) SWNT at 298 K is about  $9.2 \times 10^{-10}$  and  $6.9 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$  from the Arrhenius and the VFT equations, respectively, as shown in Fig. 4(a). As pointed out by Mamontov *et al.*,<sup>23</sup> the values of the diffusion coefficient determined from the quasielastic neutron scattering (QENS) data may be overestimated.

A character which one could use to understand the diffusion dynamics is the activation energy of molecular diffusion in the CNT. Those in armchair (14,14) and zigzag (24,0) CNTs were calculated from a series of MD simulations at different temperatures. Since the diffusivity components in axial direction are the only sensible definition in such a case with radial direction confined, only the axial diffusivity ( $D_z$ ) was taken into consideration. Based on the activation transition theory, the relationship between the diffusion coefficient and the activation energy ( $E_a$ ) could be described as  $\ln D = -E_a/RT + A$ . The logarithms of axial diffusion coefficients versus the reciprocal of temperature in two types of CNTs were plotted, as shown in Fig. 4(b). By using the least squares

fitting, one could easily get  $\ln D = 3.79409 - 1216.884/T$  in armchair CNT and  $\ln D = 4.2566 - 1939.774/T$  in zigzag CNT. Obviously, the activation energies of diffusion for these two types of CNTs could be obtained from the slope of beelines,  $E_a = 2.42 \text{ kcal mol}^{-1}$  for armchair CNT and  $E'_a = 3.86 \text{ kcal mol}^{-1}$  for zigzag CNT. The experimental observation of a dynamic crossover in water confined in double-wall carbon nanotubes (DWNTs) was also reported by Chu *et al.*<sup>25</sup> The activation energy of diffusion was estimated to be  $2.63 \text{ kcal mol}^{-1}$  in DWNT with mean inner diameter of  $16 \pm 3 \text{ \AA}$ , which is comparable with the diameter of armchair (14,14) and zigzag (24,0) CNTs we used. Hence, the activation energy we extracted on the basis of the MD simulations is in good agreement with this experimental work. One can easily find that the diffusion activation energy in zigzag CNT is  $1.44 \text{ kcal mol}^{-1}$  greater than that in armchair one, thus the translational motion, i.e., diffusion of water molecules, is much slower than that in armchair CNT. In fact, in zigzag CNT, the water molecules oscillate around their equilibrium positions, or move circlewise around the central axis in a relatively long time, which can be clearly observed from the trajectory animation.

The second character that could be used to understand the diffusion dynamics is the PESs of water inside two types of CNTs. The PESs could describe the interaction energies of the system in different geometries. Then, one could perform dynamics analysis on that. The calculation of PESs is already very common recently and proven to be critical for the understanding of dynamics on atomic scales.<sup>26</sup> However, this technique is seldom currently used on diffusion dynamics research. In this paper, in order to understand the different activation energies of molecular diffusion in CNT, a water molecule was used as a probe to calculate the PESs of water inside two types of CNTs. In the calculation of PESs, the choice of coordination system is an important question. Here, cylindrical coordinates ( $r, \theta, z$ ) were used to describe the location of a water molecule as molecular probe, where  $r$  denotes the distance of the oxygen atom of water molecule from the central axis,  $z$  is the coordinate along the central axis, and  $\theta$  is the polar angle, as shown in Fig. 5(a). In both of the CNTs, the scanning scale of the potential energy for  $\theta$  is from  $0^\circ$  to  $359^\circ$  with a step of  $1^\circ$  and for  $z$  from

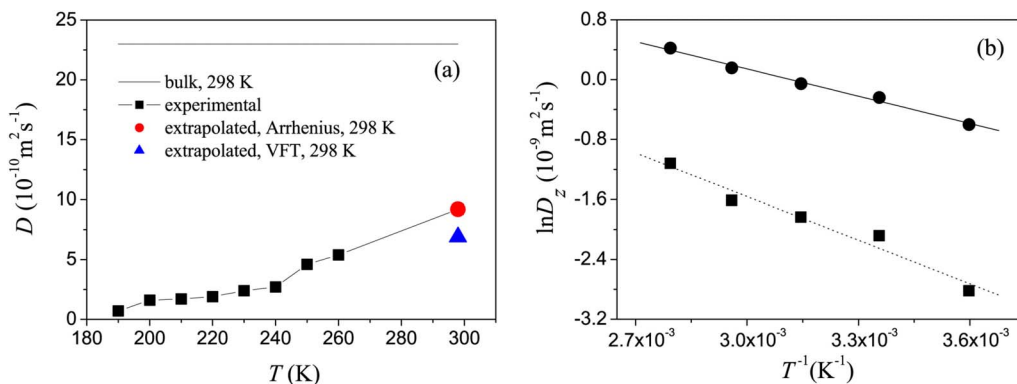


FIG. 4. (Color online) (a) Experimental and extrapolated diffusion coefficients from Ref. 23 as a function of temperature and comparison with the bulk water. (b) Logarithm of axial diffusivity as a function of the reciprocal of temperature in armchair (14, 14) and zigzag (24, 0) CNTs. (●) simulated in armchair, (—) fitted in armchair, (■) simulated in zigzag, and (·····) fitted in zigzag.

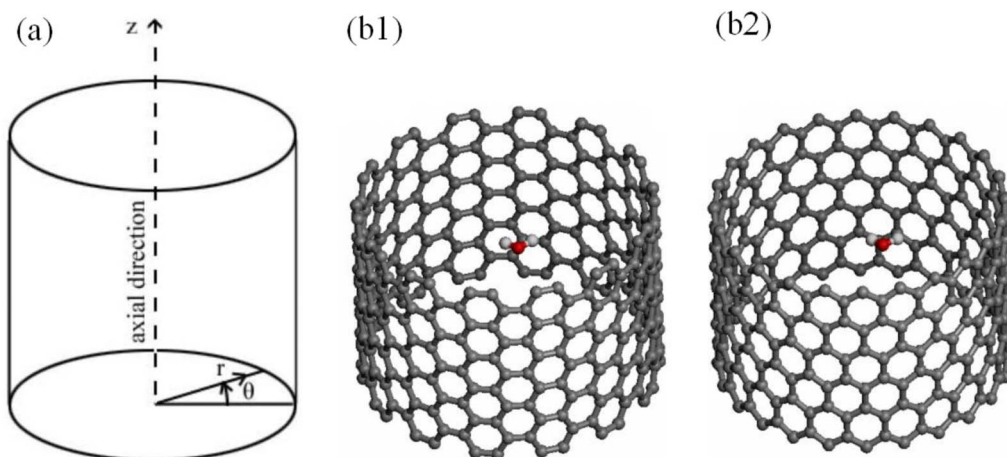


FIG. 5. (Color online) (a) Frame of the cylindrical coordinates used to describe the molecular probe in the interior surface of both armchair (14, 14) and zigzag (24, 0) CNTs. (b) Snapshot of molecular probe in interior surface of armchair (14, 14) CNT (b1) and zigzag (24, 0) CNT (b2).

1.0 to 5.5 Å with a step of 0.1 Å. Here,  $r$  was selected with the position of water molecules of highest local density (in the third shell, which is nearest to the nanotube wall) in two types of CNTs reported in our previous MD simulations, which is 6.29 Å for armchair CNT and 6.55 Å for zigzag one.<sup>20</sup> The snapshots of initial position of water probe in interior surface of armchair (14,14) and zigzag (24,0) CNTs are displayed in Fig. 5(b).

First, the PESs of MM force field were calculated with optimized potentials for liquid simulation-all atoms force

field, in order to be consistent with MD simulations. Figure 6 shows the three-dimensional (3D) and the two-dimensional (2D) plots of relative potential energy  $E(\theta, z)$  of two types of CNTs. The lowest potential energy in the scanning scale was taken to the zero. Due to the difference in helicity, the profiles of  $E(\theta, z)$  of them are obviously different.  $E(\theta, z)$  of two types of CNTs periodically changed both along the  $z$  and  $\theta$  directions. For  $E(6.29, \theta, z)$  of armchair (14,14) CNT, there are 14 local energy minima along the  $\theta$  direction when  $z$  is approximately in the positions of 1.9, 3.1, and 4.3 Å. The

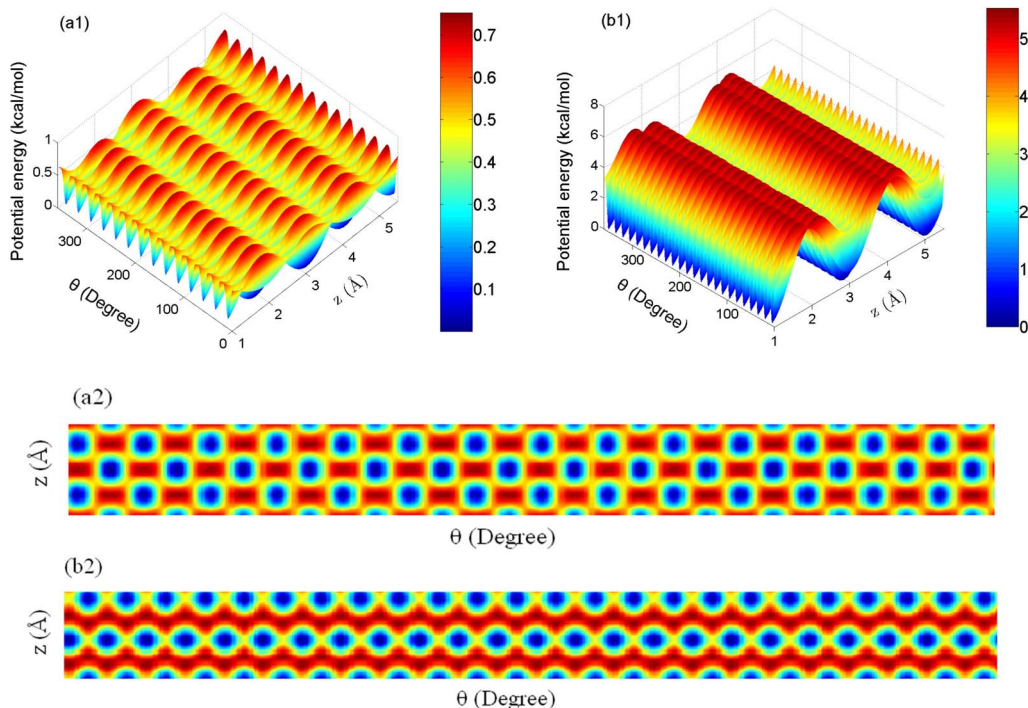


FIG. 6. (Color online) 3D and 2D plots of potential energy of armchair (14, 14) and zigzag (24, 0) CNTs by MM. The lowest potential energy in the scanning scale was taken to be zero. Blue, green, yellow, and red colors indicate the energy from low to high. (a1) 3D plot of  $E(6.29, \theta, z)$  in armchair (14, 14) CNT. (a2) 2D plot of  $E(6.29, \theta, z)$  in armchair (14, 14) CNT. (b1) 3D plot of  $E(6.55, \theta, z)$  in zigzag (24, 0) CNT. (b2) 2D plot of  $E(6.55, \theta, z)$  in zigzag (24, 0) CNT.

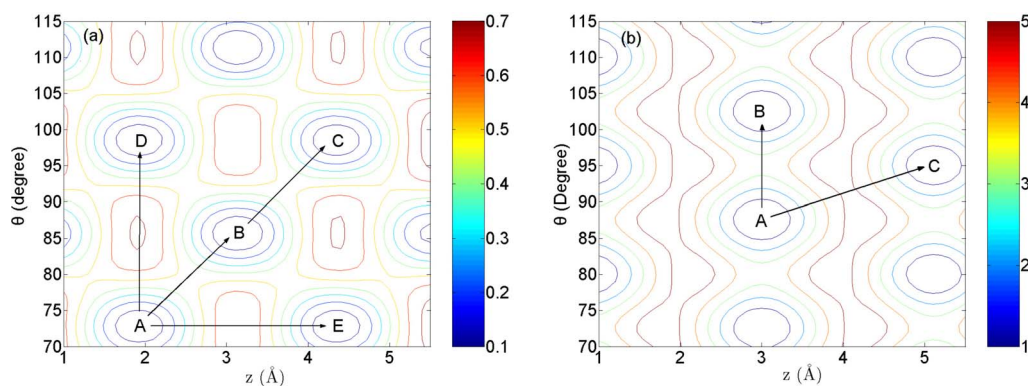


FIG. 7. (Color online) Contour plots of potential energy  $E(\theta, z)$  of (a) armchair (14, 14) CNT and (b) zigzag (24, 0) CNT by MM. Arrows indicates the possible diffusion pathway.

number of local energy minima along the  $\theta$  direction is just equal to the number of six-numbered rings in every circle that is perpendicular to the central axis. For  $E(6.55, \theta, z)$  of zigzag (24, 0), there are 24 local energy minima along the  $\theta$  direction when  $z$  is approximately in the positions of 3.0 and 5.1 Å. The number of six-numbered rings in every circle is also 24. The profiles of  $E(\theta, z)$  strongly indicate that the arrangement of carbon atoms or helicity is one of the most important factors that affect the PESs of water inside CNTs.

In order to investigate the effect of PESs of water inside CNTs on the diffusivity of confined water more clearly, the contour plots of  $E(\theta, z)$  with partial  $\theta$  scale (from 70° to 115°) were generated. Figure 7 shows the contour plots of potential energy  $E(\theta, z)$  of two CNTs. The letters marked in the contour plots denote the position of local energy minima. There are three possible diffusion pathways in armchair (14, 14) CNT deduced from the contour plot. AD is the diffusion pathway of water molecules along the  $\theta$  direction, which means that water molecules diffuse circlewise around central axis, and AE is the diffusion pathway of water molecules along the central axis. Water molecules in these two directions need to overcome an energy barrier around 0.7 kcal mol<sup>-1</sup>. For pathway AB, the diffusion route of water molecules is both along the central axis and polar angle. The energy barrier in this route is about 0.5 kcal mol<sup>-1</sup>, and it should be more favorable in contrast to pathways AD and AE. As the water molecules diffuse to B, the environment of PESs in B is as the same as that in A, and the water molecules favorably diffuse to C. In this pathway, water molecules diffuse along the cylindrical surface in a spiral path and the length of the diffusion route is more than that of pathways AD and AE. This result was supported by the work of Mao and Sinnott<sup>27</sup> for predictions of a spiral diffusion path for nonspherical organic molecules (ethane and ethylene) in CNTs. It is also supported by the experiments, which reveal the incorporation of iodine atoms in the form of helical chains inside armchair-typed CNT.<sup>28</sup> In zigzag (24, 0) CNT, pathways AB and AC are probably the diffusion paths. However, the energy barrier of AB is approximately 3.3 kcal mol<sup>-1</sup>, which is 1.8 kcal mol<sup>-1</sup> lower than the energy barrier of pathway AC. It indicates that the water molecules tend to move circlewise around the central axis rather than move in a spiral way, which is consistent with the ob-

servations by trajectory animation. This conclusion was supported by the work of Shu and Gong, in which the favorable diffusion path of adatom in zigzag CNT is moving circlewise around the central axis.<sup>29</sup> The energy barrier either in pathway AB or AC in zigzag (24, 0) CNT is much higher than that in pathways ABC, AD, and AE in armchair (14, 14) CNT, which is why the diffusion of water molecules is much slower in zigzag (24, 0) CNT than that in armchair (14, 14) CNT, as observed in our MD simulations.<sup>20</sup> Though these two types of CNTs have almost the same diameter, the difference in helicity leads to large difference in the potential energy surface profile and affects the diffusion motion of water molecules inside them.

Then, quantum mechanics was further used to calculate these PES in order to confirm the MM PES calculations with the  $r$  value and scanning scale as the same as the contour plots shown above. The  $p$  orbital of carbon atoms in CNT is very important for their physical and chemical properties. Naturally, its effect on PESs is attractive and interesting. However, this effect is missing in MM/MD simulation because of their force field bases. Considering the big size of CNTs and the large amount of points needed to generate the PESs, we select quantum mechanics in the extended Huckel level of theory, which already took  $p$  orbital into account. Figure 8 shows the 3D plots of potential energy  $E(\theta, z)$  of two types of CNTs using the extended Huckel method. The profile of PESs in the scanning scale looks similar to that of MM calculation. For  $E(6.29, \theta, z)$  of armchair (14, 14), the energy barrier of diffusion pathways AB and BC is approximately 1.0 kcal mol<sup>-1</sup>, about 0.5 kcal mol<sup>-1</sup> lower than pathways AD and AE. For  $E(6.55, \theta, z)$  in zigzag (24, 0) CNT, the energy barrier of diffusion pathway AB is approximately 3.0 kcal mol<sup>-1</sup>, about 1.8 kcal mol<sup>-1</sup> lower than pathway AC. The extended Huckel calculation also illuminates the diffusion behavior in two types of CNTs as we induced from MM calculation and MD simulation. In addition, the energy barrier of diffusion pathway ABC in armchair (14, 14) is about 2.0 kcal mol<sup>-1</sup> lower than that of pathway AB in zigzag (24, 0). It means that the water molecules will be trapped in deeper potential wells in zigzag CNT than in armchair one. This result illuminates that water molecules diffuse much slower in zigzag (24, 0) CNT than that in armchair (14, 14) one, and it is in good agreement with the MD simulation and

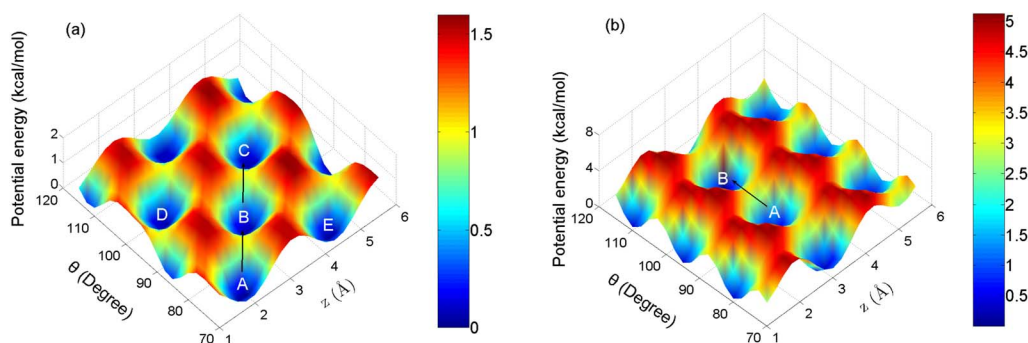


FIG. 8. (Color online) 3D plots of energy  $E(\theta, z)$  of (a) armchair (14, 14) CNT and (b) zigzag (24, 0) CNT by quantum mechanics in the extended Huckel level of theory. Arrows indicates the favorable diffusion pathway.

the MM calculation. However, it is worth pointing out that the direct comparison of the difference of the pathway energy barriers for these two types of CNTs with that of their diffusion activation energy should be carefully interpreted. In the former case, only the stronger interaction between the nanotube wall and the third shell water molecules in armchair (14, 14) and zigzag (24, 0) CNTs was considered. While in the latter, the activation energy of diffusion is the statistical average of all shells of water molecules (here, three shells). However, considering that the third shell contains most of the water molecules inside the armchair (14, 14) and zigzag (24, 0) CNTs and mostly contributed to the diffusion, as illustrated in Figs. 2 and 3, this calculation provides a workable way to describe how the interaction between the wall of CNTs and the water molecules affects the diffusion pattern of water.

Up until now, most researches in this field concern the effect of pore size to the diffusion dynamics. As recently mentioned by Holt *et al.*,<sup>5</sup> the structure of water in CNT is strongly dependent on the diameters of CNTs, thus the diameters of CNTs remarkably affect the transportation of water. In this paper, our analysis results illuminate that the helicity of CNTs also has notable effect on the diffusion dynamics of water inside them without changing of pore size of CNTs, and this effect could be well described by the PESs of water inside CNTs.

Because of the potential applications of CNTs in nanodevice, industry membrane, and drug-delivery devices, it is important to control the flow of molecules through the CNTs. However, for single-walled CNTs, the pore size is discrete and it is very hard to be adjusted, which limits the application of this feature. Recently, experimental progresses on molecular engineering already show that it is possible to modify the mechanism and electrical properties of CNTs. However, there are still few reports of molecular engineering

approach of adjusting the transfer property of CNTs. Here, our research shows that the PESs of water inside CNTs could affect the transport behavior. Since PESs inside CNTs could be adjusted by various molecular engineering approaches because of the chemical activity of carbon atoms which form CNT,<sup>2,30-34</sup> our result indicates the possibility to adjust the diffusion behavior inside CNTs by molecular engineering approach, without changing the pore size. That would greatly extend the application of the special transportation features of CNTs.

In summary, the influence of helicity of CNTs on the diffusion dynamics of water confined in the armchair and zigzag CNTs was investigated by MD simulation, molecular mechanics, and quantum mechanics calculations. The activation energy of molecular diffusion in zigzag CNT calculated by MD simulation is much larger than that in armchair CNT, which is consistent with our previous result that water diffuses much slower in zigzag CNT than in armchair CNT. In addition, the PESs of water inside armchair (14,14) and zigzag (24,0) CNTs were explored to understand the mechanism of this phenomenon. MM calculation of PESs indicate that in armchair (14,14) CNT, water molecules diffuse along the cylindrical surface in a spiral path, while the water molecules tend to move circlewise around the central axis in zigzag (24,0) CNT. This feature was also confirmed by further quantum mechanics calculation, which takes the effect of  $p$  orbital into consideration. We hope that this research could provide useful information for the molecular engineering of CNT based devices and their applications in the fields of membrane, nanoscale energy (proton) devices, nanomachinery, novel drug-delivery devices, and so on.

This work was financially supported by the National Natural Science Foundation of China (Grants No. 50576080, No. 20503025, and No. 60533050).

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