Diffusion of Water Inside Carbon Nanotubes Studied by Pulsed Field Gradient NMR Spectroscopy

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Supporting Information

ABSTRACT: Diffusion dynamics of guest molecules in nanopores has been studied intensively because diffusion is critical to a number of research fields such as separation, drug delivery, chemical reactions, and sensing. In the present work, we report an experimental investigation of the self-diffusion of water inside carbon nanotube (CNT) channels using a pulsed field gradient (PFG) NMR method. The dispersion of CNTs homogeneously in water and cooling to temperatures below the melting point of bulk water allow us to probe the translational motion of confined water molecules. The results demonstrate that the self-diffusion coefficient of water in CNTs is highly dependent on the diffusion time and CNT diameter. In particular, the diffusivity of water in double-walled carbon nanotubes (DWNTs) with an average inner diameter of 2.3 ± 0.3 nm is twice that in multiwalled carbon nanotubes (MWNTs) with an average inner diameter of 6.7 ± 0.8 nm in the temperature range of 263–223 K. In addition, the effective self-diffusion coefficient in DWNTs is 1 order of magnitude higher than that reported for mesoporous silica materials with a similar pore size. The faster diffusivity of water in CNTs could be attributed to the ordered hydrogen bonds formed between water molecules within the confined channels of CNTs and the weak interaction between water and the CNT walls.

1. INTRODUCTION

Over the last few decades, carbon nanotubes (CNTs) have attracted considerable attention in the field of nanofluidics because various molecules, e.g., water and gaseous molecules, have been theoretically predicted to exhibit significantly enhanced diffusivity in CNTs than in other nanoporous materials. This has driven significant interest in assembling CNTs into membranes for separation applications. For example, the pressure-driven flow of different fluids through the multiwalled (MWNT) and double-walled (DWNT) membranes was found to be enhanced by 3 to 5 orders of magnitude with respect to the prediction from continuum hydrodynamics and Knudsen diffusion models. The enhancement in diffusivity has been attributed to the inherent atomic smoothness, chemical inertness of the nanotubes, and small amount of friction at the surface. In particular, within subnanometer CNT channels, water forms an ordered 1D chain held by tight hydrogen bonds, which leads to the spontaneous and continuous filling of hydrophobic CNT channels with a flow rate comparable to those observed in protein channels such as aquaporin. Thus, CNTs are frequently used to model biological channels and demonstrate potential applications for drug delivery, nanosyringes, and biological separations. Meanwhile, the self-diffusion inside channels with dimensions close to that of guest molecules may become a rate-determining step in chemical reactions and may affect the reaction rate or selectivities. It is thus essential to obtain a deep understanding of the diffusion behavior of molecules in CNTs in order to optimize the chemical reactivity. Despite its importance, only a few reports have been focused on the experimental studies of self-diffusion confined in CNTs. Kondratyuk et al. employed isotopically labeled molecules to measure the long-range self-diffusion coefficient of heptane in single-walled carbon nanotubes (SWNTs) via observing the displacement kinetics of heptane with 1-deuterohexane. Das et al. reported the observation of the single-file diffusion of water inside SWNTs with a diameter of 1.4 nm by an NMR method. In this study, we set out investigation of the self-diffusion dynamics of molecules within the confined CNT channels.

Pulsed field gradient (PFG) NMR is a powerful tool for studying the translational dynamics of guest molecules in porous materials and has been widely used in studies of zeolites. We employed this technique to study the self-diffusion of molecules in CNTs, and water was chosen as a probe molecule. In order to

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HNO₃ treatment. This led to open DWNTs with an average tube length of 10 μm. The resulting sample was designated as O-DWNT. Both O-DWNT and O-MWNT-H₂O suspensions, we measured their zeta potentials on a Malvern Zetasizer instrument at room temperature (Supporting Information SI-2). As an external lock solvent, CD₃CN (99.96% purity, Sigma-Aldrich), was placed in a coaxial inner tube. All samples were kept at room temperature for more than 2 days before NMR measurements.

2. EXPERIMENTAL SECTION

2.1. Carbon Nanotube Samples. MWNTs with an average inner diameter of about 2 to 3 nm (Chengdu Organic Chemicals Co., Ltd) were stepwise purified by acid washing and sonication for 4 h, resulting in inklike suspensions with CNTs well dispersed in water. The detailed preparation information on the above-mentioned four NMR samples is listed in Table 1. To verify the stability of O-DWNT-H₂O and O-MWNT-H₂O suspensions, we measured their zeta potentials on a Malvern Zetasizer instrument at room temperature (Supporting Information SI-2). As an external lock solvent, CD₃CN (99.96% purity, Sigma-Aldrich), was placed in a coaxial inner tube. All samples were kept at room temperature for more than 2 days before NMR measurements.

2.3. NMR Measurements. The ¹H NMR experiments were performed on a Bruker Avance III 400 MHz spectrometer, and the spectra were acquired with a π/6 pulse length of 4.3 μs with a recycle delay time of 10 s by accumulating 16 scans. ¹H NMR spectra were processed using an exponential line broadening of 10 Hz. The spin–lattice relaxation times (T₁) and spin–spin relaxation times (T₂) were measured by standard 180°–τ–90° inversion recovery and Carr–Purcell–Meiboom–Gill (CPMG) sequences, respectively. The self-diffusion of water in CNTs was investigated on a Bruker QNP probe, which is capable of producing magnetic field gradients with a maximum amplitude of 56 G/cm. To avoid the influence of background gradients induced by magnetic susceptibility differences in heterogeneous porous samples, as is the case for CNTs, a bipolar 13-interval pulse sequence was used in our diffusion experiments, shown schematically in Figure 1. It is composed of a standard stimulated echo sequence with the previous single gradient pulse split into a pair of two pulses with opposite polarity enclosing a π pulse. The self-diffusion coefficient was obtained by recording a series of ¹H NMR spectra in which the gradient field strength (g) was gradually increased with all other pulse sequence parameters remained constant until high spin-echo attenuation (E(g)) was achieved. In the case of unrestricted diffusion in isotropic systems, this echo attenuation can be expressed as

\[ E(g) = \exp(-D_{eff} g^2 T^2) \]

where D_eff is the effective self-diffusion coefficient of water.

Table 1. Preparation Information of NMR Samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>CNT tip</th>
<th>Quantity of CNT (mg)</th>
<th>Volume of water (μL)</th>
<th>Schematic diagram of prepared sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-MWNT-H₂O</td>
<td>closed MWNT</td>
<td>70</td>
<td>180</td>
<td></td>
</tr>
<tr>
<td>O-MWNT-H₂O-1</td>
<td>open MWNT</td>
<td>70</td>
<td>180</td>
<td></td>
</tr>
<tr>
<td>O-MWNT-H₂O</td>
<td>open MWNT</td>
<td>1</td>
<td>300</td>
<td></td>
</tr>
<tr>
<td>O-DWNT-H₂O</td>
<td>open DWNT</td>
<td>1</td>
<td>300</td>
<td></td>
</tr>
</tbody>
</table>

Figure 1. Thirteen-interval pulse sequence used in the PFG experiments.
where \( q = 2\gamma g\delta \), \( E(0) \) corresponds to the integral intensity of the NMR signal in the absence of a gradient, \( \gamma \) is the gyromagnetic ratio, \( \delta \) is the duration of a single gradient pulse, and \( \langle z^2(t) \rangle \) is the mean-square displacement (MSD). For isotropic diffusion, \( \langle z^2(t) \rangle \) can be obtained from the slope of the linear plot of the echo attenuation versus \( q^2/2 \) on the log–linear scale. The diffusion coefficient \( D \) can be calculated through the Einstein equation

\[
\langle z^2(t) \rangle = 2Dt_{\text{eff}}
\]

where \( t_{\text{eff}} = \Delta - \tau/2 - \delta/6 \), \( t_{\text{eff}} \) is the effective diffusion time, \( \Delta \) is the interval between the leading edges of the gradient pulses (observation time), and \( \tau \) is the distance between 90°–180° radio frequency pulses (echo time). The diffusion coefficient in the bulk \( (D_0) \) is independent of

Figure 2. TEM images of O-MWNT (a, b), C-MWNT (c, d), and O-DWNT (e, f). The insets in (b) and (f) are the inner diameter distributions of O-MWNT and O-DWNT. The arrows in (b) and (f) indicate the open tips of O-MWNT and O-DWNT.
the observation time. In comparison, in the case of diffusion within a restricted space such as in heterogeneous porous samples, the presence of boundaries for the diffusing molecules leads to a decrease in diffusivity with increasing observation time or root-mean-square displacement. Therefore, the measured diffusion coefficient is an effective diffusion coefficient \(D_{eff}\). The observation time was chosen to ensure that the diffusion distance during \(t_0\) is shorter than the CNT channels.

In contrast, for the diffusion confined in randomly oriented unidirectional channels, the echo attenuation follows the equation\(^ {28−31}\)

\[
\frac{E(q)}{E(0)} = \frac{1}{2} \int_{-1}^{1} \exp \left[ -q^2 x^2 \frac{\langle \Delta x^2(t) \rangle}{2} \right] dx
\]

where the integral over parameter \(x\) involves the consideration of the random orientation of the channels. In unidirectional diffusion, eq 3 results in a nonlinear plot of the signal attenuation versus \(q^2/2\) on the log–linear scale. By comparison of the fits of eqs 1 and 3 to the PFG echo attenuation, the features for isotropic or unidirectional diffusion can be distinguished.

In our PFG experiments, the maximum gradient duration was set to 3 ms, with the observation time varying between 10 and 300 ms to investigate diffusivity over a broad range of MSD. The \(\pi/2\) pulse length was 13 \(\mu\)s. The echo time was set to about 4 ms. Under these conditions, signals from the background of the NMR probe and the surface oxygenated groups of nanotubes can be filtered by the transverse relaxation of the PFG pulse sequence. The sample temperature was controlled by a stream of nitrogen within the range of 298−223 K with an accuracy of ±0.5 K. Samples were kept at each temperature at least for an hour before recording data. The gradient strength was calibrated at 25 °C using the standard water sample (1% \(\text{H}_2\text{O}\) in \(\text{D}_2\text{O}\) with 0.1 mg/mL \(\text{CdCl}_2\)).

3. RESULTS AND DISCUSSION

3.1. Pore Morphology and Structure of CNTs. Figure 2 shows TEM images of O-MWNT, C-MWNT, and O-DWNT. No significant carbonaceous or metallic impurities are observed in these three samples. Figure 2b shows that O-MWNTs have open tips at both ends (as highlighted by the arrows in (b)), indicating that both interior and exterior spaces of CNTs are available for the adsorption and diffusion of water molecules. In comparison, C-MWNTs exhibit a bamboolike structure with both ends closed (Figure 2c,d), and thus water can adsorb only on the outside of tubes. Figure 2e,f illustrates that O-DWNTs are usually in the form of bundles with open tips at the ends (as highlighted by the arrows in (f)). Note that the nanotubes of all three samples are obviously curved to different extents on the nanoscale length, deviating from the ideal shape of straight and 1D channels.

We examined further the distributions of the inner diameter and tube length of O-DWNT and O-MWNT by TEM, as shown in the inset of Figure 2 and Figure SI-1. By measuring over 300 tubes, we found that O-DWNT has a narrow inner diameter distribution, with most values falling in the range of 2−3 nm with an average diameter of 2.3 ± 0.3 nm and a narrow length distribution of 12−18 \(\mu\)m (Figure SI-1e). The inner diameter of O-MWNT is obviously larger than that of O-DWNT, approximately 5−8 nm (average diameter: 6.7 ± 0.8 nm). The length of O-MWNT is distributed in the range of 8−14 \(\mu\)m (Figure SI-1d).

The BET specific surface areas of these samples were measured by nitrogen adsorption−desorption experiments (Figure 3). C-MWNT and O-MWNT have BET surface areas of 54.7 and 288.0 m\(^2\) g\(^{-1}\), respectively. The significantly higher surface area of O-MWNT suggests that their tips have been opened, and hence the interior channels also become accessible to nitrogen molecules in addition to the exterior walls of O-MWNT with respect to C-MWNT. In comparison, the surface area of O-DWNT is 783.1 m\(^2\) g\(^{-1}\), which is in agreement with typical values reported for DWNTs with opened tips and a similar diameter.\(^ {2,33}\)

3.2. Static NMR. Since there are two possible locations for water, i.e., inside and outside of CNT channels, we need distinguish first the signal of confined water inside CNTs from that of water outside CNTs. It is known that protons of solid ice have an extremely short spin−spin relaxation time (~6 \(\mu\)s).\(^ {34}\) Therefore, the phase transition from water to solid ice leads to extreme broadening of the peak (approximately 53 kHz for the width) and thus the disappearance of the \(^1\)H NMR signal from our spectra. It was reported that the melting point of water shifts to lower temperature when confined in nanotubes\(^ {21,34−36}\) or nanopores,\(^ {35}\) and this melting-point depression is inversely proportional to the pore diameter.\(^ {37}\) Thus, one has to lower the temperature to below 273 K (the melting point of bulk water) to freeze water in the bulk and to keep water inside CNT channels mobile in order to allow NMR to monitor the dynamics of confined water.

Both C-MWNT-\(\text{H}_2\text{O}\) and O-MWNT-\(\text{H}_2\text{O}\)-1 samples were prepared using a conventional method for PFG NMR measurements, in which water and carbon nanotubes are dispersed unevenly in the whole packing region, as indicated in Table 1. The \(^1\)H NMR spectra of C-MWNT-\(\text{H}_2\text{O}\) as a function of temperature are shown in Figure 4a. At 298 K, a signal at 4.0 ppm arises, which is attributed to outside water since the tips of C-MWNT are closed. As the temperature decreases to 275 K, the signal intensity slightly increases because of the Curie effect,\(^ {38}\) and the peak moves slightly downfield (4.1 ppm) due to an increase in the density of water. However, at 263 K the signal is barely observable with the residual broad background signal from the probe, indicating the complete freezing of water in C-MWNT-\(\text{H}_2\text{O}\) and ruling out the contribution of the outside water to the NMR signal below 263 K. Figure 4b shows the \(^1\)H NMR spectra of O-MWNT-\(\text{H}_2\text{O}\)-1. Between 298 and 275 K, a trend is observed for O-MWNT-\(\text{H}_2\text{O}\)-1 that is similar to that for C-MWNT-\(\text{H}_2\text{O}\). However, the intensity of the spectrum shows a significant drop, and the line moves to ~0.1 ppm with a larger line width when the temperature reaches 263 K. Since water has frozen on the outside of nanotubes, this signal can be attributed only to the water confined inside nanotubes.
As indicated by the scaling in Figure 4b, the integral intensity of the signal at 263 K was reduced to about 3.3% of that at 298 K, implying that about 3.3% of the water is inside the nanotubes. In addition, considering the volume fraction of O-MWNT channels in the entire sample, we can estimate the percentage of endohedral water (θ) using the following equation

\[ \theta = \frac{V_m \times m_{\text{CNT}}}{V_{H_2O}} \]

where \( V_m \) is the channel volume of O-MWNT per unit mass (0.17 cm\(^3\) g\(^{-1}\), calculated from the N\(_2\) adsorption–desorption isotherm of O-MWNT), \( m_{\text{CNT}} \) is the weight of O-MWNT, and \( V_{H_2O} \) is the volume of water added. Thus, endohedral water takes up 6.6% of the totally added volume of water, which is in reasonable agreement with that estimated from NMR considering the experimental errors.

CNTs are composed of graphitic walls and thus exhibit high diamagnetic susceptibility. The magnitude of their diamagnetic susceptibility depends on the relative orientations between the magnetic field and nanotubes, the diameters and the wall thickness of nanotubes, and the defects on the nanotubes. The heterogeneity of CNT samples\(^{39,40}\) has also caused the samples to exhibit strong anisotropy of the diamagnetic susceptibility. In addition, the large susceptibility differences between nanotubes and water would induce the internal magnetic field gradients between the unevenly spread nanotubes and water. Because of the extremely short relaxation times of endohedral water (especially short \( T_2 \)), PFG NMR studies of water self-diffusion inside CNTs became impossible under the measurement conditions employed. In order to circumvent the problem, we prepared the sample in a different way by dispersing a smaller amount of CNTs homogeneously in a relatively larger amount of water (O-DWNT-H\(_2\)O, O-MWNT-H\(_2\)O) to increase the relaxation times, especially \( T_2 \).

Figure 5a shows the \(^1\)H NMR spectra of O-DWNT-H\(_2\)O as a function of temperature. Similar to O-MWNT-H\(_2\)O-1, the signal intensity also exhibits a significant decrease at 263 K compared to the bulk signal at 298 K. Thus, the signal below 263 K is and the effects would become more significant as the nonuniformity of the samples increases\(^{27,41}\). The spin–lattice relaxation time (\( T_1 \)) and the spin–spin relaxation time (\( T_2 \)) of endohedral water of O-MWNT-H\(_2\)O-1 at 263 K in Figure 4b were measured to be only 59 ms and 60 \( \mu \)s, respectively. The short relaxation times, considered to be evidence of endohedral species\(^{42-44}\), may mainly result from the strong diamagnetic susceptibility anisotropy\(^{27,40}\) of nanotubes and the large internal magnetic field gradients\(^{27,41}\) induced by susceptibility differences between the unevenly spread nanotubes and water. Because of the extremely short relaxation times of endohedral water (especially short \( T_2 \)), PFG NMR studies of water self-diffusion inside CNTs became impossible under the measurement conditions employed. In order to circumvent the problem, we prepared the sample in a different way by dispersing a smaller amount of CNTs homogeneously in a relatively larger amount of water (O-DWNT-H\(_2\)O, O-MWNT-H\(_2\)O) to increase the relaxation times, especially \( T_2 \).
attributed to endohedral mobile water according to the above analysis. The spectrum intensity decreases continuously while the line width increases upon cooling from 263 to 223 K. The corresponding spin–lattice relaxation time and the spin–spin relaxation time were measured at each temperature. The results in Figure 5b indicate that both $T_1$ and $T_2$ values decrease significantly as the temperature is lowered to 263 K and finally become constant below 243 K. These results provide further support that the outside water freezes at 263 K. As we used a well-dispersed CNT suspension with a small amount of nanotubes, the measured $T_1$ values range from 637 to 251 ms, and $T_2$ values range from 40 to 9 ms between 263 and 223 K. An increased $T_1$ ensures measurements over a wide range of diffusion time and hence the accessibility of the mean-square displacement during the experiments, while an increased $T_2$ enhances the PFG NMR signal intensity and allows us to use lower gradients with a longer duration time. The similar trends in $^1$H NMR spectra and relaxation times were also observed for O-MWNT-H$_2$O (Supporting Information SI-3). Thus, O-DWNT-H$_2$O and O-MWNT-H$_2$O samples were employed in the following PFG experiments.

Note that the tubes used in our diffusion study contain oxygenated groups, and the surface oxygen concentrations of O-MWNT and O-DWNT determined by XPS analysis are 8.9 and 13.2%, respectively (Supporting Information SI-4). A small fraction of water molecules may be adsorbed near these oxygenated sites and thus contributed to the static NMR signal. However, the contribution of these water molecules to the PFG NMR signal can be excluded because of the limited mobility and especially short relaxation times ($T_2 \approx 10^{-5}$ s), which would first be filtered by the transverse relaxation of the PFG pulse sequence. Therefore, at temperatures below 273 K the signals in our diffusion experiments are only from the mobile water inside carbon nanotubes.

3.3. Diffusion Dynamics inside CNTs. PFG experiments have been carried out in the temperature range of 263–223 K. Figure 6a shows several typical PFG NMR spectra of confined water in DWNTs at 263 K for $\Delta = 50$ ms with increasing gradient strengths (g). The attenuation of the normalized integrated areas is displayed in Figure 6b as a function of $q^2/2$ on a log–linear scale. Under the PFG NMR conditions, we observe the movement of water molecules only in the direction of the magnetic field gradient (vertical). Since CNTs are randomly oriented in our samples, we are not measuring the displacement in one specific direction (relative to the tube axis) but a value averaged over all orientations. We tried the 1D diffusion model$^{23,30,31}$ (eq 3) but got significantly poor fitting results (highlighted by the red line in Figure 6b). This indicates that 1D model is not an appropriate description for the molecular diffusion in CNTs. The probable reason may arise from the morphology of CNTs. As indicated in Figure 2, the tubes are obviously curved, deviating from the ideal straight, long 1D channels. A similar situation was also encountered when investigating molecular diffusion in some MCM-41 materials with curved pores.$^{35,46}$ Therefore, we took the normal (Stejskal–Tanner) diffusion model (eq 1). Figure 6b demonstrates that the measured PFG NMR attenuation curve can be satisfactorily fitted (the black fitting line), resulting in a straight line in the semilogarithmic plot.

The mean-square displacements ($\langle z^2(t)\rangle$) of water in DWNTs at 263 K with 50 ms observation time was measured to be $(4.0 \pm 0.2) \times 10^{-11}$ m$^2$. The corresponding effective self-diffusion coefficient ($D_{eff}$) is $(4.1 \pm 0.2) \times 10^{-10}$ m$^2$ s$^{-1}$, as calculated with the Einstein equation (eq 2), which is almost 1 order of magnitude higher than that of water diffusivity in MCM-41 (a mesoporous silica with 1D channels of about 3 nm pore size) reported in a previous study$^{25}$ $(5.7 \times 10^{-12}$ m$^2$ s$^{-1}$). Moreover, this diffusivity of water inside DWNTs is comparable to that of bulk supercooled water of $7.0 \times 10^{-10}$ m$^2$ s$^{-1}$ at 263 K reported by Hoch and colleagues.$^{47}$ It has been frequently reported that confined water in CNTs exhibited structures and dynamics properties quite different from those in the bulk. Molecular dynamics and grand canonical Monte Carlo simulations predicted ordered water configuration inside CNTs.$^{11}$ The number of hydrogen bonds was greatly reduced, and water formed a quasi-1D chain structure inside (6, 6) CNTs with spontaneous and continuous filling of the empty channels,$^{11}$ while a typical layered structure was formed when water was confined in much larger (20, 20) CNTs.$^{48,49}$ Sholl et al.$^{1,3}$ demonstrated via molecular dynamics simulations that due to the inherent smoothness of CNT walls the transport or self-diffusion of fluids in nanotubes is orders of magnitude faster than that in other microporous materials with comparable pore sizes.
Furthermore, the flow rates of pressure-driven water through membranes of MWNTs and DWNTs were experimentally demonstrated to be 3–5 orders of magnitude faster than the non-slip, continuum hydrodynamic flow through conventional macroscopic pores according to the Hagen–Poiseuille equation. The remarkably long slip length of water inside CNTs can significantly enhance the flow rate. This rapid diffusivity of water in CNTs is considered to arise from the ordered hydrogen bonding between water molecules in the well-defined nano-channels and the weak attraction between water and smooth CNTs.

On the basis of the data in Figure 6b, the mean-square displacements \(\langle z^2(t)\rangle\) for water in DWNT and MWNT at 263 K are plotted in Figure 7 as a function of diffusion time (t). As can be seen, the MSD \(\langle z^2(t)\rangle\) increases almost linearly with t, and this time dependence could be described by eq 2, as expected for normal diffusion. However, the data at longer diffusion times show some deviation from linearity. This finding suggests some confinements. It may be attributed to the fact that the molecular propagator of confined water is retarded over longer times, caused by the restricted translational motion inside CNT channels. In addition, it is noteworthy that the MSD \(\langle z^2(t)\rangle\) in DWNT is about 2 times that in MWNT, suggesting a much faster self-diffusivity in DWNT than in MWNT. This is further confirmed by the data in Table 2.

For PFG diffusion experiments have been carried out in the temperature range of 263–223 K within a broad range of observation time. The diffusivity of water in DWNT and in MWNT shows a pronounced dependence on the temperature and diffusion distance. Figure 8a presents a complete survey of the effective self-diffusion coefficients and their dependence on the root-mean-square displacements \(\langle z^2(t)\rangle^{1/2}\) for water in DWNT at five different temperatures. The data are plotted on a log–linear scale. It can be seen from Figure 8a that at all temperatures the diffusivities decrease with increasing root-mean-square displacements. This behavior can be attributed to the spatial confinement of the CNT walls on the diffusion of water molecules, with an increase in transport resistance with increasing displacement. The exact reduction of the diffusion coefficient at long distances (or observation time) is likely related to the tortuosity of CNT channels. In addition, we found that the diffusivity in DWNTs first decreases as the temperature decreases (Figure 8a), as expected. However, with further decreases in the temperature below 243 K, it remains almost steady. We speculate that the facilitated diffusion at low temperatures may benefit from the ordered water structure.

![Figure 7](image1.png)

**Figure 7.** Mean-square displacements \(\langle z^2(t)\rangle\) of water in DWNT (denoted as D-263 K) and in MWNT (denoted as M-263 K) as a function of diffusion time \(t\) at 263 K. The solid lines are the linear best fits to the experimental data using eq 2. The error bars are based on the standard error of the fitting results of the type shown in Figure 6b.

![Figure 8](image2.png)

**Figure 8.** Dependence of the effective self-diffusion coefficients on the root-mean-square displacements for water in DWNT (a) and in MWNT (b) at different temperatures.

<table>
<thead>
<tr>
<th>temperature (K)</th>
<th>DWNT</th>
<th>MWNT</th>
</tr>
</thead>
<tbody>
<tr>
<td>263</td>
<td>((4.1 \pm 0.2) \times 10^{-10})</td>
<td>((2.3 \pm 0.1) \times 10^{-10})</td>
</tr>
<tr>
<td>253</td>
<td>((2.1 \pm 0.1) \times 10^{-10})</td>
<td>((1.4 \pm 0.2) \times 10^{-10})</td>
</tr>
<tr>
<td>243</td>
<td>((1.4 \pm 0.2) \times 10^{-10})</td>
<td>((9.5 \pm 1.5) \times 10^{-11})</td>
</tr>
<tr>
<td>233</td>
<td>((1.5 \pm 0.2) \times 10^{-10})</td>
<td>((5.1 \pm 1.1) \times 10^{-11})</td>
</tr>
<tr>
<td>223</td>
<td>((1.6 \pm 0.3) \times 10^{-10})</td>
<td>((3.0 \pm 1.0) \times 10^{-11})</td>
</tr>
</tbody>
</table>

**Table 2.** Comparison of the Effective Self-Diffusion Coefficient (m$^2$s$^{-1}$) of Water in DWNT and in MWNT at a Diffusion Time of 50 ms within the Temperature Interval of 263–223 K

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formed in the well-defined confinement environment of CNTs. This ordered hydrogen-bonding network appears to be stabilized below 243 K, as evidenced by the constant values of $T_1$ and $T_2$ in this temperature interval (Figure 5b).

As shown in Figure 5b, a similar displacement dependence was observed for MWNT, and the effective self-diffusivities also decrease with increasing displacement. The diffusion behaviors of confined water in MWNTs were determined at several relatively shorter observation times (also shorter root-mean-square displacements) because at a longer times PFG NMR signals were too poor to record 16 values of the gradient field strength.

To investigate the diffusion dynamics of water in CNTs of different diameters, we compared the diffusivities in DWNTs and in MWNTs at a diffusion time of 50 ms under different temperatures, as shown in Table 2. Interestingly, the diffusivity within DWNTs is 1-fold higher than that in MWNTs under the same experimental conditions in the whole temperature range, although the latter has a much larger diameter. There were some theoretical studies on the water diffusion behaviors in CNT with different diameters using molecular dynamics simulations.\textsuperscript{49,53–55} Taking into consideration the effect of confinement and the CNT wall on diffusion, Farimani et al.\textsuperscript{54} recently investigated the variation of self-diffusion coefficients ($D$) of water in the CNTs with different diameters ranging from 0.95 to 6.8 nm. They found that the diffusivity was enhanced in CNTs with a diameter of between 2.2 and 6.8 nm and in the CNT with a diameter of 2.7 nm the enhancement was strongest. This supported our results that diffusion in 2.3 ± 0.3-nm-diameter DWNTs is faster than that in 6.7 ± 0.8-nm-diameter MWNTs. The studies by Alexiadis et al.\textsuperscript{49,55} showed that the properties of water molecules may vary with the model, which may lead to different values or trends in self-diffusion coefficients as a function of the CNT diameter. However, the relationship between diffusivity and CNT diameter in a broader range remains to be studied further experimentally, which will rely on the availability of CNTs with a variety of diameters but with similar structural integrity and surface properties.

Previous reports\textsuperscript{66–69} have suggested that the functionalization of CNTs with oxygen groups would significantly reduce the water diffusion coefficient due to the preferential interaction between oxygenated sites and water molecules. Consequently, water diffusion in DWNT should be slower than that in MWNT because DWNT contains more oxygen groups and also is smaller in diameter than MWNT. However, our study demonstrates that this does not offset the faster diffusion of water inside DWNT with respect to that in MWNT. Much more work is necessary to elucidate the effects of oxygen groups on the diffusion, which particularly relies on the availability of CNTs with the same morphology but varying concentrations of oxygen groups.

4. CONCLUSIONS

The self-diffusion of water within the channels of DWNTs and MWNTs has been studied by PFG NMR using the 13-interval pulse sequence. By using samples containing homogeneously dispersed CNTs in water with greatly enhanced relaxation times, the translational motion of confined water is directly probed below the melting point of bulk water. The obtained PFG NMR attenuation curves can be well described by the normal diffusion model. $D_{eff}$ of water in CNTs shows a significant dependence on root-mean-square displacements because of the confinement by CNT walls. Furthermore, the measured effective self-diffusion coefficient of water in DWNTs is close to that of bulk water but 1 order of magnitude higher than that reported for MCM-41, which has a similar pore size to DWNTs. The fast diffusivity in DWNTs could be attributed to the ordered hydrogen bonds formed between confined water molecules and the weak interaction between water and the CNT walls. In particular, the diffusivity in DWNTs with an average diameter of 2.3 ± 0.3 nm is 1-fold faster than that in MWNTs with an average diameter of 6.7 ± 0.8 nm within the studied temperature range. However, the underlying mechanism needs further systematic investigation, which relies on the availability of CNTs of different diameters but with similar structural integrity and surface properties.

ASSOCIATED CONTENT

Supporting Information

Outer diameter and length distributions of CNTs, zeta potential measurements, $^1$H NMR spectra of O-MWNT-H$_2$O, and XPS data of O-DWNT and O-MWNT. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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