ABSTRACT: We compared the diffusion of water confined in armchair and zigzag carbon nanotubes for rigid and flexible water models. Using one rigid model, TIP4P/2005, and two flexible models, SPC/Fw and SPC/FH, we found that the number of the hydrogen bonds that water forms depends on the structure of the nanotube, directly affecting the diffusion of water. The simulation results reveal that, due to the hydrophobic nature of carbon nanotubes and the degrees of freedom imposed by the water force fields, water molecules tend to avoid the surface of the carbon nanotube. This junction of variables plays a central role in the diffusion of water, mainly in narrow and/or deformed nanotubes, governing the mobility of confined water in a nontrivial way, where the greater the degree of freedom of the water force field, the smaller mobility it will have in confinement as we limit the competition between area and volume and it no longer plays the unique role in changing water diffusivity.

INTRODUCTION

Water permeates almost everything in Nature. It is present in all living organisms. It is hard to find a system which is not in contact with this curious substance directly or indirectly. Water can be found as vapor, liquid, or solid since its triple point lies in a range of temperatures and pressures naturally present on Earth’s surface. Water also presents itself in any length scale, from thousands of kilometers in bulky oceans down to a few nanometers as inside carbon nanotubes. Undoubtedly, any attempt to understand how this planet works includes the study of water and how their properties interfere in virtually every single aspect of our lives.

Most physical quantities are affected by environmental variables, specially those related to length scales. Macroscopic systems do not necessarily work in the same way as they do at the nanoscale level. For example, measurements and computational simulations showed that water confined in carbon nanotubes (CNTs) is expected to have structural, transport, and dynamical properties different from those observed in the bulk liquid.1–12

The water behavior in the nanoscale realm is of crucial interest to all of the scientific community, specially those related to nanofluidic properties, due to its importance in nonporous systems with a wide range of applications based on nanotube membranes. Examples include water treatment technologies, energy storage systems, nanosyringes, drug delivery, intracellular solute transport, and cancer therapy.2,13–24

Diffusion is a crucial transport property reflecting the dynamic behavior of fluids. Water in the bulk phase presents Fickian diffusion, when the mean square displacement (MSD) is linear with time.4,25

When confined in CNTs, water diffusivity depends on the physical characteristics of the confining tube.4,26 For example, if the confinement prevents the water molecules from passing each other, the diffusion can occur in a single-file mode, e.g., MSD $\sim t^{1/2}$.1,27 In the case where the water molecules move coordinated, their diffusion can occur in a ballistic mode, e.g., MSD $\sim t^2$.1,26 Furthermore, when the water molecules can pass through each other, the diffusion is of the Fickian type as in the case of the bulk phase.28,29

Theoretical studies using molecular dynamics (MD) simulations of water molecules confined in CNTs of different diameters observed that the diffusion coefficient of the confined water is nonmonotonic as a function of the diameter, which can be ascribed to the surface effect and the size effect of CNTs.9,30,31 In addition, the faster diffusivity of water in CNTs could be attributed to the ordered hydrogen bonds formed between water molecules within the confined channels of

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CNTs and the weak interaction between water and the CNTs. In addition to this already complex scenario, the diffusion coefficient obtained by MD simulations depends on the details of the models used.

Water is a complex substance to model, because of the competing effects of hydrogen bonding and van der Waals interactions. In the literature, there are several models to describe water. These models are constructed to fit a set of experimental data, and their success depends on being able to reproduce additional experimental properties both in the bulk and in confined water.

TIP4P/2005 is one of the most used rigid models. It is composed by four points: the oxygen with mass, two hydrogens with positive charges, and a fictitious location between the oxygen and the hydrogen to represent the displaced charge of the oxygen. This model was parametrized using experimental data such as the maximum density temperature, the enthalpy of vaporization, and the density of liquid water at ambient conditions. It can reproduce thermodynamic properties of water in a wide range of temperatures but is not able to reproduce processes involving chemical bond formation and dissociation.

In order to circumvent this limitation, flexible models were created. They represent the O–H bond lengths and angles by harmonic functions and are better equipped to reproduce flexibility transport properties. The flexible models, SPC/Fw and SPC/FH, were fitted from the SPC to describe dynamic properties.

From the experimental point of view, a great number of methods, such as infrared spectroscopy, neutron scattering, X-ray diffraction, X-ray Compton scattering, and nuclear magnetic resonance, are suitable to study the structure and dynamics of confined water inside CNTs. However, to the best of our knowledge, no experimental work fully explains how water organizes and diffuses when confined. Interpreting experimental data is challenging because nanotubes are far from being perfect in the real world (a fact that is commonly abstracted in theoretical models along with their internal degrees of freedom), presenting defects, vacancies, and structural distortions, which may affect several water properties.

Losey et al. studied the flow of water in CNTs using several water models. They observed that the flux of water through a carbon nanotube depends on the diameter of the carbon nanotube and the quantitative value of the flow depends on the models used in the MD simulation, which was also reported in the works of Liu et al. In addition, they reported that the flexible SPC/Fw model is very efficient to describe the viscosity at 298.15 K and 0.1 MPa.

In this context, the main objective of this study is to determine how flexible water models differ from the rigid ones when simulating water diffusion in carbon nanotubes and also how water molecules organize under severe confinement. We considered different nanotube chirality structures, in cases where tubes are perfect, kinked, and wrinkled.

We examine the structural and dynamic properties of confined water affected by chirality and nonuniform deformations in nanotubes. Furthermore, we considered perfect, kinked, and wrinkled tubes with zigzag and armchair chirality types. Internal degrees of freedom of carbon nanotubes were modeled by Morse, harmonic, and Lennard-Jones potentials. For water, we considered three simulation models. The rigid TIP4P/2005 model and two flexible ones, which are SPC/E variants: the SPC/FH and SPC/Fw. The SPC/Fw and SPC/FH models, unlike the TIP4P/2005, allow the variation of both the angles and the equilibrium bonding distances of the water molecule. The influence of the introduction of these degrees of freedom in the system and the different parameters adopted in each force field alter the structural and dynamic behavior of the water, and our objective is to analyze this phenomenon when we confine the water molecules in carbon nanotubes with two types of deformation.

The paper is organized as follows. In Models and Simulation Details, computational details are presented. Results and Discussion are next followed by the Conclusions.

**MODELS AND SIMULATION DETAILS**

We performed molecular dynamics simulations with a constant number of particles, volume, and temperature to analyze how different water models affect the results for the diffusion coefficient of confined water. For water, we used the rigid model TIP4P/2005, which reproduces several thermodynamic water properties and the flexible SPC/Fw and SPC/FH models, which reproduce water dynamic properties.

The TIP4P/2005 model represents water by a rigid four point structure where there is one point at the oxygen, which has no charge, two points in the hydrogen, and another point M where the oxygen charge is located. The water–water interaction is modeled by oxygen–oxygen Lennard-Jones plus coulomb for the hydrogen and M-point interactions. The parameters are shown in Table 1. The SPC/Fw and SPC/FH models are inspired in the SPC rigid model, which has three points: one for the oxygen with Lennard-Jones and coulomb interactions and two for hydrogen with coulomb interactions.

In addition to the Lennard-Jones and coulomb interactions, the SPC/Fw and SPC/FH models have additional interaction terms. The SPC/Fw and the SPC/FH parameters are shown in Table 1. The SPC/FH model places a negative charge at a point M at a distance from the oxygen along the H–O–H bisector. The distance between the oxygen and hydrogen sites is . The angle formed between hydrogen, oxygen, and another hydrogen atom is given by . For flexible models (SPC/Fw and SPC/FH), and are the potential depth parameters, and are the reference bond length and angle, respectively.

![Table 1. Force Field Parameters Used for Each of the Water Models](https://doi.org/10.1021/acs.jpc.c300490)
are illustrated in Table 1. The comparison between the models indicates that the SPC/FH is more rigid with larger spring constants than the SPC/Fw. The SPC/FH includes a Lennard-Jones hydrogen–hydrogen interaction, allowing a stronger interaction with neighboring molecules.

The study of the impact of introducing these degrees of freedom in the system, as well as the different parameters adopted in each force field, provides a necessary overview to determine the most suitable model to study the systems adopted in each force field, provides a necessary overview to determine the most suitable model to study the systems analyzed in this work.

Water molecules were confined in carbon nanotubes (CNTs) with different diameters, chirality, and two types of deformation: kneaded K and wrinkled W (See Figure 1).

Table 2. Parameters for the Perfect Carbon Nanotubes

<table>
<thead>
<tr>
<th>CNT</th>
<th>(d_i) (nm)</th>
<th>(L_z) (nm)</th>
<th>(\rho) (g/cm(^3))</th>
<th>(\text{H}_2\text{O})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(7,7)</td>
<td>0.95</td>
<td>123.4</td>
<td>0.90</td>
<td>901</td>
</tr>
<tr>
<td>(12,0)</td>
<td>0.94</td>
<td>123.0</td>
<td>0.91</td>
<td>901</td>
</tr>
<tr>
<td>(9,9)</td>
<td>1.22</td>
<td>50.5</td>
<td>0.92</td>
<td>908</td>
</tr>
<tr>
<td>(16,0)</td>
<td>1.25</td>
<td>50.5</td>
<td>0.80</td>
<td>908</td>
</tr>
<tr>
<td>(12,12)</td>
<td>1.63</td>
<td>22.5</td>
<td>0.94</td>
<td>901</td>
</tr>
<tr>
<td>(21,0)</td>
<td>1.64</td>
<td>22.9</td>
<td>0.86</td>
<td>901</td>
</tr>
</tbody>
</table>

**Figure 1.** Snapshot of the perfect \(P(n, m)\), wrinkled \(W(n, m)\), and kneaded \(K(n, m)\) simulated carbon nanotubes.

Following the notation \((n, m)\) to characterize the chirality of CNTs, we use three armchair nanotubes \((n = m)\), namely, \((7,7)\), \((9,9)\) and \((12,12)\), and three zigzag nanotubes \((m = 0)\), namely, \((12,0)\), \((16,0)\) and \((21,0)\). The diameter of the CNTs can be given as a function of the indices \(n\) and \(m\) as
\[
d = (\sqrt{3}/\pi)a\sqrt{n^2 + m^2 + nm},
\]
where \(a = 1.42\) Å is the C–C bond length.

In order to investigate the effects of radial asymmetry on the diffusion of confined water, we uniformly deformed the nanotubes to different degrees. The kneaded nanotubes were produced by taking a perfect nanotube and uniformly kneading it in the \(y\) direction until nonuniform wrinkles are formed. Wrinkles were created in a disorderly fashion, but as the number of wrinkles is small, the size distribution of the segments between two wrinkles were the same for nanotubes of the same diameter. On average, each nanotube was compressed at five different positions on the \(z\) axis, with eccentricity values ranging between 0.0 and 0.8.

Furthermore, for comparison purposes, perfectly structured nanotubes were also produced. Perfectly symmetrical nanotubes are characterized by an eccentricity of 0.0. We defined the three types of nanotubes used, both armchairs and zigzags, as perfect \(P(n, m)\), kneaded \(K(n, m)\), and wrinkled \(W(n, m)\).

The carbon–carbon and carbon–water interactions were modeled using the Lennard-Jones potential (14). The classical potential for the interaction between carbon atoms has been described with an energy of \(\epsilon_{CC} = 0.086\) kcal·mol\(^{-1}\) and an effective diameter of \(\sigma_{CC} = 3.4\) Å\(^{-1}\). The carbon–oxygen energy \(\epsilon_{CO} = 0.11831\) kcal·mol\(^{-1}\) and the effective carbon–oxygen diameter \(\sigma_{CO} = 3.28218\) Å\(^{-1}\). The parameters considered for the water models were defined and are shown in Table 1.

The water density was determined considering the excluded volume due to the LJ interaction between the carbon and oxygen atoms and the pressure varying around 1 atm in all simulations. Thus, the density is determined by
\[
\rho = 4M/\pi(d_i - \sigma_{CO})^2L_z,
\]
where \(M\) is the total mass of water in the tubes and \(L_z\) is the length of the nanotube. The CNT diameters \(d_i\) range from 0.94 to 1.64 nm; the lengths \(L_z\) range from 22.5 to 123.4 nm, and the amount of water confined in each nanotube varies from 901 to 908 molecules, as shown in Table 2. Deformed nanotubes were simulated with the same length as well as the same total mass of confined water if they are the equivalent, perfect nanotubes.

Simulations were performed with the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) package. Periodic boundary conditions were imposed in all spatial directions to comply with the Particle–Particle Particle–Mesh (PPPM) method to calculate long-range Coulomb interactions. This method handles the long-range interactions and the Coulomb field of real charges in a way that could interfere with their own images. We got around this problem by creating an \(xy\) simulation box around 100 nm for all the nanotubes, preventing the carbon nanotube from interacting with its own images and avoiding the overlapping of virtual images with real images, minimizing possible errors in the application of the method.

Water temperature was maintained at 300 K through a Nose–Hoover thermostat with a damping time of 100 fs and a time step of 1 fs for the TIP4P/2005 model and a time step of 0.5 fs for the SPC/Fw and SPC/FH models. In all simulations, we kept the nanotubes rigid without out-of-plane displacements. This procedure was employed in several similar simulations, which showed that considering the nanotube as a rigid system is a very reasonable approximation when compared to the case where the thermostat is applied throughout the system. All systems for TIP4P/2005 were balanced to 5 ns, and properties were stored every 0.01 ns for 5 ns, giving a total simulation time of 10 ns. For the SPC/Fw and SPC/FH models, all systems were balanced to 15 ns, and properties were stored every 0.01 ns for 15 ns, giving a total simulation time of 30 ns.

Due to the dimensions of the system, diffusion is minimal in the radial direction and only axial diffusion is considered.
Diffusion is determined using the one-dimensional Einstein relation:

\[
D_z = \lim_{t \to \infty} \frac{1}{2 \cdot d} \langle z^2(\tau) \rangle
\]

where \(\langle z^2(\tau) \rangle = \langle [z(t_0 - \tau) - z(t_\tau)]^2 \rangle\) is the mean-squared displacement (MSD) in the axial direction of the system.

For characterizing the structure of water, we calculated the number of hydrogen bonds (HBs) and also made density maps for the occurrence of oxygen in the \(xy\) plane. The hydrogen bonds were calculated if both of the following geometric criteria were satisfied: \(\alpha \leq 30^\circ\) and \(|r_{O|O}| \leq 3.50\) Å, where \(\alpha\) is the angle \(\text{OH}--\text{O}\) and \(|r_{O|O}|\) is the distance between two oxygens.\(^{67}\) Oxygen occurrence density maps were obtained by dividing the corresponding plane \(xy\) into square boxes 0.1 Å in length and counting the number of oxygen in each box. Higher oxygen densities are represented in red, while low densities tend to darker blue tones. Each result is composed of three sets of simulations with different random distributions of initial thermal velocity. Averages are obtained in each simulation, and the statistical error margin found was smaller than the point itself.

**RESULTS AND DISCUSSION**

Thermodynamic and dynamic quantities of bulk water when modeled by the TIP4P/2005 and the SPC/Fw models have shown good agreement with experimental results.\(^{43,45,59,60}\) The SPC/FH also shows an ability to validate studies carried out, compared with the experimental result.\(^{39}\)

First, we compared the experimental diffusion coefficient for bulk water with the results of molecular dynamics simulations for the TIP4P/2005, SPC/Fw, and SPC/FH models for 298.15 K. The experimental diffusion coefficient of bulk water is about \(23 \times 10^{-10}\) m\(^2\)/s and for the TIP4P/2005 model is \(20.8 \times 10^{-10}\) m\(^2\)/s, which agrees with several molecular dynamics simulations using the same model.\(^{43,68}\) For the flexible models (SPC/Fw and SPC/FH), the diffusion coefficients found were \(23.59 \times 10^{-10}\) and \(21.89 \times 10^{-10}\) m\(^2\)/s, respectively.\(^{69}\) The diffusion coefficient for the SPC/FH model, computed in this simulation, is lower than the values obtained by SPC/Fw. This is consistent with SPC/FH being more structured than the SPC/Fw model. The SPC/Fw diffusion is closer to the experimental value.

Next, we compared the simulations with experimental results for the diffusion coefficient of confined water. In the case of bulk water, the diffusion coefficient of the TIP4P/2005 water coincides with the experimental results.\(^{71}\) Figure 2 shows \(D\) versus temperature of water confined in a perfect armchair nanotube with size \(P(10,10)\). The black squares illustrate the experiment-derived estimates,\(^{49}\) generated by a fitting function to experimental neutron scattering spectra. It is important to emphasize that, according to the authors, the temperature dependence of diffusivity is difficult to access experimentally. In the author’s own words, the method “may be unable to capture the entire range of diffusivity, thus missing a slower fraction and yielding an artificially enlarged effective diffusion coefficient”\(^{49}\) and “Because of the overestimate of the diffusion coefficient (and, therefore, mean jump length) is likely temperature dependent, the true temperature dependence of these parameters are difficult to assess.”\(^{49}\) The experimental value of the diffusion of confined water is much larger than the value in the bulk,\(^{71}\) which is not the case for the simulations.

We calculated the diffusion coefficient of confined water in the same system and temperature range using the TIP4P/2005, SPC/Fw, and SPC/FH water models. The results of these calculations are also shown in Figure 2 as red, green, and blue circles, respectively. The figure shows that, consistent with the comments in ref 49, in the 190–230 K temperature range, the experimentally estimated \(D\) values are considerably larger than all the three calculated values, indicating that these experimentally estimated values might indeed be artificially enlarged. Moreover, as also predicted in ref 49, the apparent overestimate of the experiment-derived values is strongly temperature dependent, up to a point, at a temperature of 250 K, where both calculated values and the experimental estimate of \(D\) have the same order of magnitude.

The mobility of water inside the CNTs is highly dependent on the diameter and length of the nanotubes. The formation of hydrogen bonds decreased with decreasing diameter.\(^{72}\) In this context, the water diffusion coefficient in CNTs does not decrease monotonically with the diameter of the nanotube. However, the diffusion coefficient has a minimum for the diameters \((9,9)\) (see Figure 3), \((7,7)\), and \((8,8)\).\(^{72}\) The diffusion coefficients for the more structured systems, the rigid TIP4P/2005 and flexible SPC/FH models, are quite similar, while the SPC/Fw presents higher values that are closer to the experimental results and, in confinement, the flexibility of the SPC/Fw becomes even more relevant.

Then, we analyzed how the diffusion coefficient depends on the chirality by computing it for \(P(n, m)\) armchair and zigzag nanotubes for different diameters and water models. Figure 3 shows that water mobility is not strongly affected by CNT chirality for different diameters, except CNT's \(P(9,9)\) and \(P(16,0)\). These diameters are distinct when compared to smaller and larger nanotubes, because only a layer of water close to the wall is formed. This water layer presents a different water–wall interaction depending on the chirality.\(^{50,73}\) Water is frozen within the CNT \(P(9,9)\) for the TIP4P/2005 and SPC/FH models, while a nonzero diffusion is observed for the SPC/Fw model. In the case of CNT \(P(16,0)\), a larger mobility was found for the SPC/Fw followed by the TIP4P/2005, while a low diffusion was observed for the SPC/FH case, close to that observed in the CNT \(P(9,9)\).

For the case of \(P(n, m)\) nanotubes, armchairs, and zigzags, the TIP4P/2005 and SPC/Fw water mobilities are higher than...
that for SPC/FH, which is expected since in this model water is more structured. In the cases of TIP4P/2005 and SPC/Fw, water is frozen in the CNT P(9,9), but not in CNT P(16,0), despite both having the same diameter. The water melt in these two water models can be attributed to the spiral and ring-shaped structure water forms inside the armchair and zigzag tubes.\textsuperscript{10} SPC/FH water remains frozen for both CNT P(9,9) and P(16,0), which suggests that the more structured water might be less affected by the water–wall interaction.

Next, we addressed the question of how the deformations of CNTs affect the diffusion coefficient of water. In particular, we analyzed the difference in water diffusion for the armchair and zigzag CNTs when they change the structure from perfect P(n, m) to wrinkled W(n, m) and kneaded K(n, m) for water models TIP4P/2005, SPC/Fw, and SPC/FH at T = 300 K.
two diameters of CNTs for each chirality, (9,9) and (12,12) for armchairs and (16,0) and (21,0) for zigzags. The diameter selection was made to test how compression affects the number of layers and the distinct mobility between the two chiralities depending on the chosen force field.

Figure 4a shows that water mobility in the CNT (9,9) increases with both kinds of applied strain only for the TIP4P/2005 model. For the SPC/Fw model, the mobility depends on the type of topological static deformation applied, decreasing for wrinkled and increasing for kneaded. For the SPC/FH model, the water mobility is very small in comparison to those of the other models, regardless of the strain. The behavior of the diffusion is consistent with the number of hydrogen bonds formed. Figure 4b for the TIP4P/2005 and SPC/Fw where the increase (decrease) of the mobility is related to the decrease (increase) of the number of hydrogen bonds as it would be

Figure 5. Density maps in the $xy$ direction for the carbon nanotubes (9,9) and (16,0) perfect $P(n,m)$, wrinkled $W(n,m)$, and kneaded $K(n,m)$, and the comparison of the TIP4P/2005, SPC/Fw, and SPC/FH water models. Dark blue regions have a low probability of finding water molecules, while red regions have a high probability of finding water molecules.
expected. For the SPC/FH, however, the diffusion is almost zero and the number of the hydrogen bonds decreases with the strain. Even though distorting the nanotube disrupts the hydrogen bonds, this is not enough to melt the immobile water, which seems to find distinct “ice-like” structures as the system is compressed.

For the CNT (16,0), water diffusion, illustrated in Figure 4c, is less affected by the change from CNT by distortion for the TIP4P/2005 and SPC/Fw models while the SPC/Fw presents the same increase followed by the decrease observed in the CNT (9,9). The decrease (increase) of the number of hydrogen bonds, shown in Figure 4d, is consistent with the increase (decrease) of the mobility for TIP4P/2005 and SPC/Fw but not for the SPC/FH.

The behavior of the diffusion coefficients of the water confined in the nanotubes \( P(n,m) \) and \( W(n,m) \) of the CNTs (9,9) and (16,0) are quite different for TIP4P/2005 and SPC/Fw, indicating for this small diameter that the surface effects are really relevant. However, for the SPC/FH model, the water forms a frozen-like structure which does not depend strongly on the chirality as it will be shown by the density maps.

Finally, in order to understand the differences and similarities in CNT with distinct chirality and distortions, we analyzed the density maps shown in Figure 5. For the perfect CNT P(9,9) in all water models analyzed, the water molecules are uniformly distributed in the vicinity of the nanotube wall, forming a “frozen-like” structure. This led us to conclude that the flexibility of the models was not able to thaw the water molecules and that the effect of the tube structure on the water molecules prevails. The variation of the diffusion coefficient, therefore, is only due to the effect of the degrees of freedom of the water molecule. This phenomenon is repeated for perfect CNT P(16,0) for TIP4P/2005 and SPC/Fw models, where water molecules assume a hexagonal distribution following the wall–boundary interaction. The color maps show that in the perfect nanotube water forms a spiral while the zigzag flows in a circular shape.\(^{10}\) This behavior survives upon mild distortion.

Water rearranging itself in the two types of CNTs is due to differences in wall structures combined with the hydrophobic nature of the carbon–water interaction, where water molecules form hydrogen bonds avoiding proximity to the wall of CNTs in a region where water interaction between carbon atoms is strongly repulsive.\(^{10}\) In this case, different from the CNT P(9,9) for TIP4P/2005 and SPC/Fw, the variation of the diffusion coefficient is not only due to the effect of the degrees of freedom of the water molecules but also due to the effect of the chirality of the CNT “breaking” the structuring of water molecules, that is, being a barrier in the process of breaking and forming hydrogen bonds, acting directly in the increase of diffusion.

For the SPC/FH model at the perfect CNT (9,9) and (16,0) illustrated in Figure 5, water forms a helical structure regardless of the wall. The model adapts to form the arrangement, which gives the more immobile structure. Figure 5 also shows that the strain leads to a disorganization of the helical structure in the (9,9) case and of the hexagonal structure in the (16,0) case for the TIP4P/2005 and SPC/Fw
models, resulting in different structures. In the case of the SPC/FH model, the distortion melts the helical structure present in both cases, generating organized lines, which are independent of the chirality.

One last question is if the chirality independence observed in the SPC/FH model is present for larger diameters. Figure 6 shows the diffusion coefficient versus the deformation for all the three models and the two chiralities. Figure 5a,c indicates that with the deformation of the CNT (12,12) there was a decrease in axial diffusion and there was an increase in the number of hydrogen bonds. The same behavior is observed in Figure 5b,d for the CNT (21,0).

In general, nonuniform deformations, as in \( W(n, m) \) CNTs, bring water molecules closer together, favoring the formation of hydrogen bonds. This effect is even greater in \( K(n, m) \) CNTs, in which the deformation and the decrease in the distance between the molecules are more uniform. Changes in water diffusion due to deformations in nanotubes (12,12) and (21,0) are very similar, and chirality seems to play a minor role in this case. For these CNTs, the water models, the TIP4P/2005, the SCP/Fw, and the SPC/FH, did not show relevant differences in mobility, because as the CNTs were deformed, the same behavior prevailed, decreasing the water diffusivity. Therefore, the diffusive behavior of water is more strongly affected due to structural deformations, making the degrees of freedom of water molecules play a secondary role.

\section*{CONCLUSIONS}

In this work, we analyzed the diffusion coefficient of water under confinement in carbon nanotubes. Different nanotube sizes, topology, and deformation were considered, as well as different theoretical models of water.

We observed that the choice of force field and the structure of CNTs directly affect the dynamic behavior of water. In addition, the diffusion coefficient for water confined in CNTs with different degrees of deformation showed a nontrivial behavior; with this, we verified that the water will be dependent on the sum of the variation of the confining structure, the hydrophobic nature of the carbon nanotubes, and the degrees of freedom of water molecules imposed by the force fields.

The SPC/FH is a model that favors the water structure and suffers less impact from the wall structure for CNTs with smaller diameters. For larger CNTs, the influence of the walls becomes less relevant. In general, deformation suppresses mobility for large-sized CNTs and favors it for small-sized ones. These processes govern the mobility of confined water in a way that highlights the importance of choosing the force field of water in determining the transport properties of water.

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