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Structure and stability of water chain in a carbon nanotube

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Abstract

Water molecules form a single-file chain structure in a (6, 6) carbon nanotube (CNT), and this stability is different from that of water molecules confined in CNTs with larger diameters, let alone the bulk. Using the molecular dynamics (MD) method and quantum mechanical (QM) calculations, we investigate the characteristics in the context of density dependence of the collective structure and hydrogen bond behavior. The results obtained from MD show that high water density leads to substantially longer hydrogen bond lifetimes. On the other hand, the hydrogen bond lifetime does not noticeably decrease with decreasing density but remains roughly the same when the density is lower than a certain critical value. The mean molecular orientation angle of the water molecule, defined by the angle that comprises the water dipole moment and the CNT axis, is smaller for higher densities, and asymptotically approaches 33° on the low density side. Such an asymptotic nature of the structure and stability stems from non-uniform distribution of water molecules. The mean orientation angle obtained from QM calculations using density functional theory coincides with the MD result. QM analysis also suggests that the charge distribution of water in the CNT originates from the molecular configuration due to spatial confinement rather than strong electronic interaction between water and the CNT.

1. Introduction

When confined in small spaces, fluid molecules can act differently compared to under macroscopic conditions, due to the emergence of molecular discrete nature. A special but realistic example is water confined in carbon nanotubes (CNTs). CNTs themselves are molecules comprised of carbon atoms in a hexagonal lattice rolled up into cylindrical shapes with diameters of nanometers. These unique geometrical characteristics endow the CNTs with various interesting properties that can be used for engineering applications [1]. The mechanical, electrical, and thermal properties of CNTs have been extensively investigated so far, and interactions between other molecules have started to attract attention [2–31].

The expected applications of carbon nanotubes from a nanofluidic viewpoint include molecular filtration membranes [32], nanoflow sensors and energy conversion devices [33]. While the number is not so many yet, experiments on such targets have already been con-

ducted [2–6, 7–13, 32, 33]. Such challenging experimental reports validate and materialize the idea of CNTs as molecular nanofluidic devices. However, it is difficult in these experiments to shed light on the dynamics of atomistic details due to the measurement techniques used. Computational studies can consequently play a complementary role in the development of such nanodevices [16, 34–39, 29, 30].

In spite of the fact that CNTs have structures analogous to graphite, which is known to be hydrophobic, molecular dynamics (MD) simulations have shown the spontaneous entrance of water molecules into CNTs in equilibrium when a CNT is immersed in bulk water [15]. Ever since such single-file transport of a water molecular chain was found using MD [15], much attention has been paid to this specific diameter of CNTs [40–45].

The water molecules confined in CNTs can have collective structures that are specific to the tube diameters. For example, CNTs with structures uniquely defined via chiral vectors of (12, 12), (10, 10), (8, 8), and (6, 6) have diameters of 1.62, 1.35, 1.08, and 0.81 nm, respectively, and water molecules

form double cylindrical layers, a molecular chain in a cylindrical water layer, a cylinder, and a single-file chain inside the CNTs with these diameters, respectively (cf [19, 20, 29]). Measures of these static structures are the density distribution and the number of hydrogen bonds per molecule as a function of the radial position in the CNTs.

Considering dynamic properties, we have studied the stability of such collective structures of confined water molecules using hydrogen bond dynamics as the measure [29]. Hydrogen bond dynamics is important to understand the behavior of water in CNTs, which will help make full use of the nanoreactors and the above-mentioned nanofluidic devices made of CNTs. It will also help elucidate the mechanism of biological channels due to its physical similarity [46]. It was found that water in CNTs with diameters ranging from 1 to 2 nm show shorter hydrogen bond lifetimes than bulk water; however, the hydrogen bond lifetime for the (6, 6) CNT, which has a diameter of 0.81 nm, has a much larger value [29]. Furthermore, it shows high sensitivity to the density, which is not the case for other CNTs. The single-file water chain in the (6, 6) CNT has peculiar properties that cannot be directly deduced from the tube diameter dependence using the concept of diameter as a continuous variable. To put it simply, this is because the molecular size and shape of the water molecule is not negligible compared to the tube diameter. The (6, 6) CNT is currently the smallest CNT that is capable of accommodating water molecules [15], as far as we know.

In this study, we have investigated the structure and hydrogen bond dynamics of water confined in a (6, 6) CNT as well as its density dependence. We have used quantum mechanical (QM) calculations as well as MD. The QM study is used as a complementary method for classical MD, wherein the former focuses on structural information in conjunction with charge distribution and the latter focuses on dynamical aspects at a finite temperature.

2. Details of computation

2.1. Molecular dynamics

The (6, 6) CNT is treated as a rigid body fixed in space, and we used the SPC/E model [47] for the water molecules. The SPC/E is a rigid water model consisting of a total of three intermolecular interaction sites, i.e., for an oxygen and two hydrogen atoms for each molecule. The non-bonded interactions consist of two parts,

$$\phi_{\text{SPC/E}}(r_{ij}) = \phi_{\text{LJ}}(r_{ij}) + \phi_{\text{E}}(r_{ij}), \quad (1)$$

where the first term on the right-hand side is the Lennard-Jones potential between oxygen–carbon and oxygen–oxygen,

$$\phi_{\text{LJ}}(r_{ij}) = 4\epsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right], \quad (2)$$

and the second term is the Coulomb potential between oxygen–oxygen, hydrogen–hydrogen, and oxygen–hydrogen,

$$\phi_{\text{E}}(r_{ij}) = \frac{1}{4\pi\epsilon_0} \left[\frac{q_i q_j}{r_{ij}} - E_s(r_{ij}) \right], \quad (3)$$

$$E_s(r_{ij}) = \frac{q_i q_j}{r_c} - (r_{ij} - r_c) \frac{q_i q_j}{r_c^2}, \quad (4)$$

where r_{ij} is the distance between atom i and j , and ϵ_0 is the permittivity in vacuum. The partial charges of oxygen and hydrogen atoms in this model are $-0.8476e$ and $+0.4238e$, respectively. The bond distance between oxygen and hydrogen is 0.1 nm, and the intramolecular angle is 109.47° . These non-bonded interactions are cut off at $r_c = 1$ nm. The Coulomb interactions are modified to be smoothly truncated for the appropriate use of truncation without an unrealistic effect. A more detailed explanation of potential model parameters and its validity is described in [29] and [48].

The model CNT has a length of 18.42 nm, and various numbers of water molecules are placed in the system to examine the density dependence of hydrogen bond dynamics in detail. The cases considered are 50–81 molecules in the unit length of the CNT, which corresponds to 157 to 254 kg m^{-3} when based on a volume calculated from the conventional diameter definition of a CNT [29]. Note that an ‘inner’ volume bounded by a nanometer-scale object cannot be uniquely defined due to the impossibility of defining the surface positions of an atom. An investigation and discussion on this topic is described in [31]. This density definition is not really intuitively comprehensible, and the number of molecules per unit length of the CNT is clearer because the water forms a single-file chain structure in the tube axis direction of (6, 6) CNT. The above density corresponds to 2.71–4.40 nm^{-1} , respectively. In reality, the water density in the CNT can be considered to be dominated by the tube edge conditions, where water molecules in bulk are aligned to enter the CNT. Therefore, we do not mention the correspondence between the macroscopic pressure and the water density in the CNT, which cannot be uniquely determined without such an effect.

The hydrogen bond dynamics can be described using two correlation functions, $C_{\text{HB}}(t)$ and $N_{\text{HB}}(t)$, as follows [49]:

$$-\frac{dC_{\text{HB}}(t)}{dt} = kC_{\text{HB}}(t) - k'N_{\text{HB}}(t). \quad (5)$$

We use the hydrogen bond definition using geometric criteria, as has been used in previous reports [14, 17, 29, 30]. If the following conditions are simultaneously satisfied, a pair of water molecules is interpreted to be hydrogen bonded.

- The inter-oxygen distance R_{OO} is less than 0.36 nm.
- The distance R_{OH} between acceptor oxygen and donor hydrogen is less than 0.24 nm.
- The angle ϕ_{HB} between the line connecting the two oxygen atoms and the line connecting the donor oxygen and hydrogen atoms is less than 30° .

The consequent hydrogen bond lifetime is defined by $1/k$ [49]. The intermittent hydrogen bond correlation function $C_{\text{HB}}(t)$ represents a fraction of the hydrogen bonds preserved at time t among the original existing hydrogen bonds of tagged pairs of water molecules in the initial state. $C_{\text{HB}}(t)$ is defined to include the hydrogen bonds that were broken one or more times and reformed before or at time t . Thus, it is called ‘intermittent’. Another correlation function $N_{\text{HB}}(t)$ represents the fraction of molecular pairs that remain in the vicinity of each other while

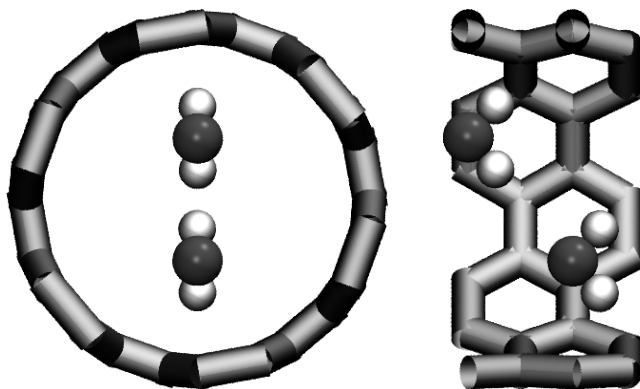


Figure 1. Initial configuration of the model for quantum mechanical calculations.

the hydrogen bond itself is broken. The samples for $C_{\text{HB}}(t)$ and $N_{\text{HB}}(t)$ are extracted every 10 fs, and the period of a sampling sequence is 15 ps. The total sampling time is 1800 ps, leading to 120 sets of 15 ps-sequences. The conditions and procedures used are based on our previous study [29].

2.2. Quantum mechanical calculation

Quantum mechanical calculations are conducted in order to account for the static structural information that is not covered by the rigid water model with fixed partial charges. GAUSSIAN03 [50] is used for structure optimization from initial configurations and the calculation of related physical quantities.

First, we consider the (6, 6) CNT with a unit length of 0.493 nm, corresponding to 48 carbon atoms. Two water molecules are located inside the CNT, and a periodic boundary condition is applied along the tube axis direction. The initial configuration is shown in figure 1. This is decided based on the results of the previous study [29] wherein each water molecule has hydrogen bonds with two neighboring molecules. One hydrogen atom of each water molecule is located on the line that connects the two oxygen atoms, and the orientation of the water molecules is set so that the angle of the dipole moment and the CNT axis are parallel. The distance between oxygen atoms is 0.246 nm, which leads to the same spacing between infinitely aligned water molecules. The distance of the oxygen atom from the central axis of the CNT is 0.147 nm. Two water molecules in the unit length of 0.493 nm corresponds to 4.06 nm^{-1} , and will be compared with one of the cases of the MD study.

The structures of the water molecules are optimized such that the positions of carbon atoms are fixed to save computational cost. The first stage of the optimization is conducted by restricted Hartree–Fock with a basis set of STO-3G. After the optimization with Hartree–Fock, the second stage is conducted using density functional theory with the B3LYP model and the 3-21G(d) basis set. For comparison, the same procedure is executed for systems of (i) one water molecule in vacuum, (ii) a pair of water molecules in vacuum, and (iii) a water chain in vacuum. Cases (i) and (ii) are for the examination of the effects of interaction between multiple

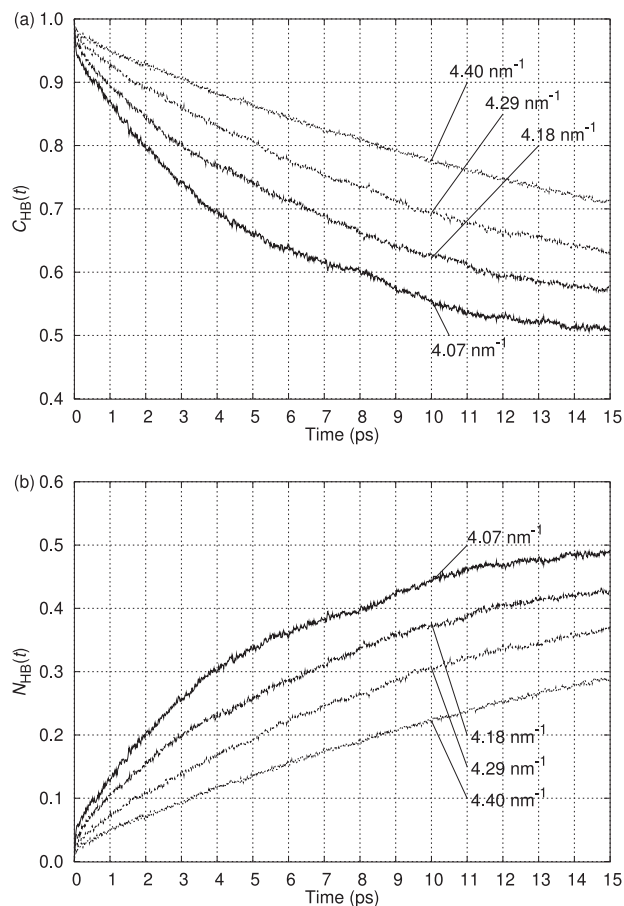


Figure 2. Water density dependence of correlation functions: (a) $C_{\text{HB}}(t)$ and (b) $N_{\text{HB}}(t)$. Not all the cases, but just typical cases, are plotted for readability.

water molecules, and (iii) is conducted to examine whether the water chain in the CNT is strongly influenced by the CNT. Cases (ii) and (iii) have the same relative configurations of molecules in the initial state as the CNT-confined case. The difference between the pair molecule and the chain in a vacuum is that a periodic boundary condition is not applied to the former whereas it is applied to the latter. The basis set for the cases of one molecule and a chain in a vacuum is 3-21G.

3. Results and discussion

The hydrogen bonds of water molecules in CNTs show long-preserving $C_{\text{HB}}(t)$ compared to the bulk case [29], and this property is more prominent for CNTs with smaller diameters [29]. This holds true for the (6, 6) CNT; however, the combination of $C_{\text{HB}}(t)$ and $N_{\text{HB}}(t)$ results in a much longer hydrogen bond lifetime than those for other CNTs. In fact, it is more than 1.5 times longer than those for other CNTs [29].

Such a peculiarity is closely related to the mobility of water molecules in conjunction with the characteristic collective structure due to the confinement. In order to examine the effects of confinement in more detail, the dependence of the correlation functions $C_{\text{HB}}(t)$ and $N_{\text{HB}}(t)$ on the water density was investigated and is shown in figure 2. The results

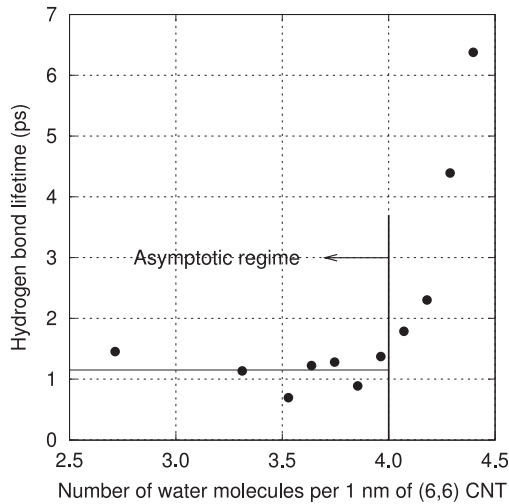


Figure 3. Water density dependence of hydrogen bond lifetimes. The thick horizontal line indicates the mean value of the points with densities less than 4 nm^{-1} .

with densities higher than 4 nm^{-1} are plotted since the cases of lower densities showed a greater spread of the results. From figure 2, we can see that the changes in $C_{\text{HB}}(t)$ and $N_{\text{HB}}(t)$ are consistent. When $C_{\text{HB}}(t)$ is long preserved (fast decreasing), the corresponding $N_{\text{HB}}(t)$ is slow growing (fast growing). Furthermore, for the four cases shown, the relation $C_{\text{HB}}(t) + N_{\text{HB}}(t) = 1.00$ holds at $t = 15 \text{ ps}$. Whereas $C_{\text{HB}}(t)$ indicates the probability that the hydrogen bonds are preserved at time t , $N_{\text{HB}}(t)$ does not simply mean all the rest but only those for which the inter-oxygen distance of a tagged pair of molecules satisfies the hydrogen bond criterion although the bond is broken. Therefore, in general, $C_{\text{HB}}(t) + N_{\text{HB}}(t)$ is less than unity, and the rest of the molecular pairs are those diffused away from each other. Here, $C_{\text{HB}}(t) + N_{\text{HB}}(t) = 1.00$ means that water molecules whose hydrogen bonds are broken cannot diffuse away from each other within 15 ps because of the closely packed configuration of the water molecules. The water molecules just rotate from the hydrogen-bonded orientation by thermal fluctuation.

The consequent hydrogen bond lifetimes as a function of water density are shown in figure 3. The density dependence

drastically changes at around 4 nm^{-1} . Densities larger than this lead to much longer hydrogen bond lifetimes. On the other hand, the hydrogen bond lifetime does not change noticeably on the lower density side. When the water is closely packed in the CNT, the molecular mobility substantially decreases. Consequently, it is less easy for the hydrogen bonds to break under higher densities. It should also be noted that this is not a matter of course. Smaller mobility is not a sufficient condition of longer hydrogen bond lifetime. If the water molecules are constrained to the configuration wherein hydrogen bonded structures are less stable, i.e. if the intermolecular orientation angle of the most stable structure is away from the angle of hydrogen bond criterion, it leads to a shorter hydrogen bond lifetime. We consider that this is the case for larger CNTs for which the hydrogen bond lifetime is shorter for higher density [29]. The hydrogen bond lifetimes in the lower density regime are asymptotic values around 1 ps. The hydrogen bond lifetime of bulk water is 0.80 ps with this model [29]. The hydrogen bonded state is more stable in the (6, 6) CNT than in the bulk state over the whole range investigated here. The velocity of a water molecule at ambient temperature is several hundred m s^{-1} , and the criterion for the hydrogen bonded state is based on the space scale of several 10^{-10} m . Thus, the timescale of the hydrogen bond lifetime is 1 ps.

The reason for these asymptotic properties in the lower density regime can be understood from the distribution of water molecules in the (6, 6) CNT, schematically shown in figure 4. The water molecules with a low density at 300 K are not uniformly distributed in the CNT but form a chain whose constituent molecules are connected by hydrogen bonds. Thus, the overall density does not indicate the effective local density, and the effective local density does not vary substantially under low density conditions. The hydrogen bond lifetime in the (6, 6) CNT should therefore be dominated by the (relative) rotational motion of water molecules from the potential energy minimum by thermal fluctuations.

The distribution of the molecular orientation angle can be considered to be another measure for the collective water structure. Figure 5 shows it with a domain of definition from 0° to 90° , where the angle is comprised of the CNT axis and the water dipole moment. The distribution shown in figure 5 is like a Gaussian in the vicinity of the peak; however, it

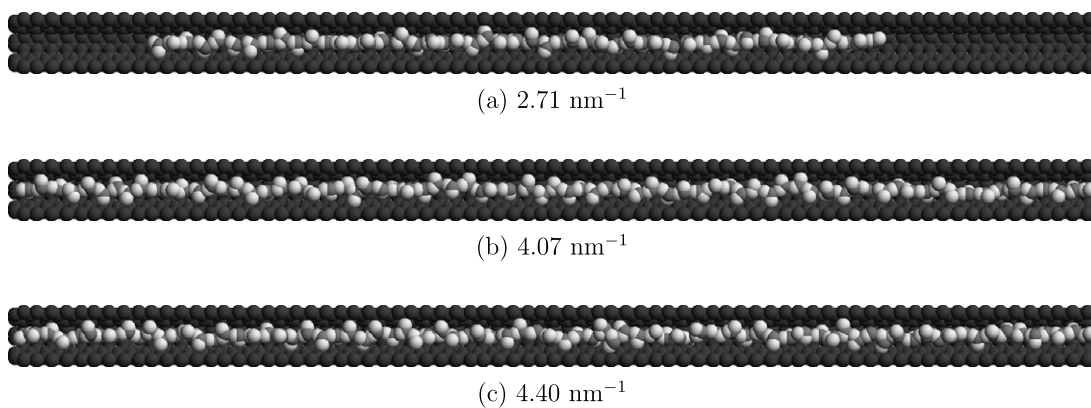


Figure 4. Snapshots of water in (6, 6) CNT for densities of (a) 2.71, (b) 4.07, and (c) 4.40 nm^{-1} .

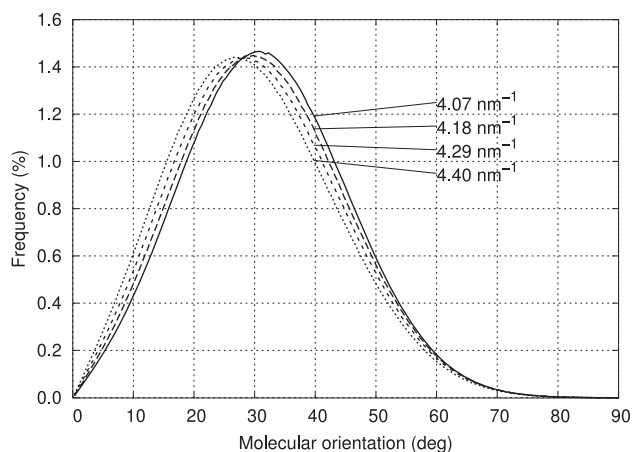


Figure 5. Distribution of water orientation angle. Not all the cases, but only typical cases, are plotted for readability.

is not symmetric in the lower frequency parts. The water angle with a domain of angle $[0, 180)$ also has essentially the same unimodal distribution in these cases (not shown). The water orientation is randomly assigned at the beginning of the simulation; however, 100 ps equilibration leads the system to these equilibrium states. Since the system is symmetric in the direction of the tube axis, one can imagine that it could also have an equilibrium state that has two peaks with the same height for the angle distribution in the domain of $[0, 180)$. However, simulation results do not show this. A water chain defect, wherein the hydrogen bond is broken, is too unstable to be preserved, compared to the configuration where one water molecule has a total of two hydrogen bonds.

The mean orientation angles and the corresponding standard deviations are plotted in figure 6. The mean orientation angle approaches 33° asymptotically with decreasing water density, and the angle decreases with increasing density from around the point where the hydrogen bond lifetimes changes substantially. The mean angle is roughly a monotonic function of the water density, and the asymptotic limit of the molecular orientation angle can be regarded as the inherent structure of the water chain in the CNT. The mean value and the standard deviation used here do not represent a ‘true value’ and its ‘uncertainty’, rather, the former represents the most stable point, and the latter is a measure of the shape of a free energy surface because the probability distribution plotted in figure 5 reflects the free energy as a function of the angle as a reaction coordinate. Indeed, the certainty of the values can be inferred from the smoothness of the line in figure 5. Although the standard deviation of the molecular angle distribution is roughly independent of the density, the hydrogen bond lifetime varies with density. In other words, the broadness of the orientation distribution does not change, but the mean orientation, i.e. the most stable structure, changes with density. The difference of several degrees of the orientation angle results in a difference of several times of the hydrogen bond lifetime.

The dynamical properties of the water chain in a (6, 6) CNT and its structural information, including dynamical effects, have been obtained from the MD. However, the potential model considered here does not account for the

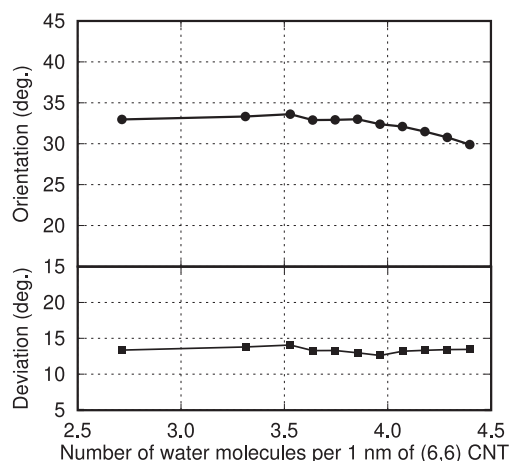


Figure 6. Water density dependence of the water molecular orientation.

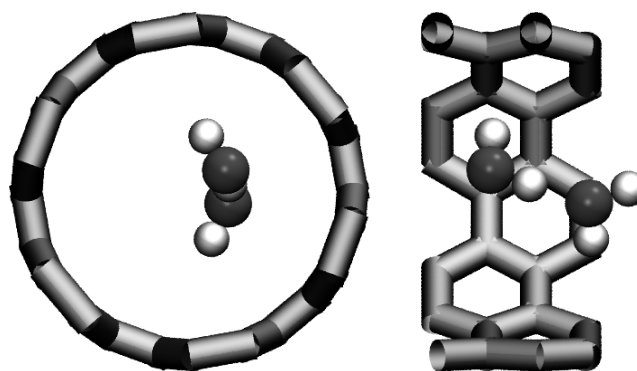


Figure 7. Water molecules inside a (6, 6) CNT whose structure is optimized by quantum mechanical calculations.

picture of a hydrogen atom belonging to more than one oxygen atom, and the water is always in a distinct state of H_2O . The SPC/E water model never changes the intramolecular atomic distances or the angle comprising the three constituent atoms, and the charge distribution is always fixed. To account for these aspects, we compare the charge distribution and atomistic configuration of water under different conditions including a single molecule in a vacuum, two molecules in a vacuum, a molecular chain in a vacuum, and a molecular chain in the (6, 6) CNT. The schematic diagram of the results for water in a (6, 6) CNT is illustrated in figure 7, and the data obtained are summarized in table 1.

The Mulliken charge for the oxygen atom of a pair of water molecules in a vacuum is larger for the hydrogen-donor side and is smaller for the acceptor side, and both are larger than that for a single-molecule state. The charge of all hydrogen atoms in a water pair is larger than that for the single-molecule state, and the largest is that of the hydrogen atom donated to form a hydrogen bond. Thus, the polarization of the water molecule is enhanced by the hydrogen bond. The atomic charge of the oxygen of water in the CNT is $-0.71e$ for both of the atoms in the unit CNT length. Similarly, the two hydrogen atoms have a charge of $+0.38e$ and the other two hydrogen atoms have a charge of $+0.34e$, where the former pertains to

Table 1. Properties of water molecules obtained from quantum mechanical calculations: q_O is the charge of the oxygen atoms and q_H is the charge of the hydrogen-bonded or that of the smaller inter-oxygen-atomic-distance side. Values in brackets are those of atoms of hydrogen donor molecules. The unit is elementary charge e . ϕ_{HOH} is the average of the intramolecular angle (degrees), d_{OO} is the inter-oxygen distance (nm), d_{OH1} is the bond distance between the oxygen and hydrogen that pertain to the hydrogen bond, d_{OH2} is the distance of donor hydrogen from acceptor oxygen, and $\theta_{\text{H}_2\text{O-CNT}}$ is the averaged value of the two values of the angle that is comprised of the CNT axis and the line that connects the oxygen atom and the center of two hydrogen atoms.

	q_O	q_H	ϕ_{HOH}	d_{OO}	d_{OH1}	d_{OH2}	$\theta_{\text{H}_2\text{O-CNT}}$
One in a vacuum	(-0.64)	(0.32)	103.9	—	0.10	—	—
Two in a vacuum	-0.83 (-0.77)	0.42 (0.37)	104.4	0.29	0.10	0.19	—
Chain in a vacuum	-0.71	0.38 (0.33)	108.2	0.25	0.11	0.14	—
Inside CNT at 4.06 nm^{-1}	-0.71	0.38 (0.34)	106.6	0.26	0.10	0.16	32.00

the hydrogen bonds. The atomic charge distribution of the water molecules in the (6, 6) CNT is equivalent for different water molecules, and the magnitude is larger than that for the single-molecule state and smaller than that for an isolated pair in vacuum.

To examine if such charge distribution is due to purely geometric constraints due to the CNT or due to the electronic interactions with it, we calculated the charge distribution of two water molecules with a periodic boundary condition in one direction, which corresponds to the water chain in vacuum. As a result, the unit length of the cell became 0.422 nm after optimization, which is shorter than that for the CNT model. As shown in the table, the charge distribution of the water chain in vacuum and that in the CNT is roughly the same. In addition, although carbon atoms have small positive and negative charges depending on the location, the average value per carbon atom is $-3.3 \times 10^{-4}e$, which is much smaller than the charges of oxygen and hydrogen atoms. Therefore, within the range investigated here, the charge distribution of the water chain in the CNT is not directly affected by the carbon atoms of the CNT, but is due to the geometric constraints due to the CNT.

Oxygen atoms in the optimized structure of water in the (6, 6) CNT are located not at the center of the CNT but at some distance from the tube axis, as shown in figure 7, which corresponds to the previous classical MD results [29]. One hydrogen atom in each molecule is located between the oxygen atoms, and the other hydrogen atom of each molecule is located on the opposite side of the ‘backbone’ formed by the oxygen atoms. The distances $R_{\text{OO}} = 0.26 \text{ nm}$, $R_{\text{OH}} = 0.16 \text{ nm}$, and the angle $\phi_{\text{HB}} = 4^\circ$ satisfy the geometric criteria of the hydrogen bond mentioned earlier. All the cases of multiple molecules are hydrogen bonded with adjacent molecules including the periodic image.

The average orientation angle of water to the CNT axis is 32° , which is in surprisingly good agreement with the MD result for the same density condition. This is remarkable correspondence, considering the limitation of the model and also the fact that we applied smooth truncation of the Coulomb interactions leading to smaller electrostatic forces between atoms. Although the degree of agreement seems to be partly due to some accidental combination of the modeling factors, the result shows that the classical potential model with such treatment of long-range interaction can still reproduce some of the properties far from the bulk conditions.

The distance between oxygen atoms in the CNT is shorter than for a pair in vacuum due to the confinement. The O–H bond distance pertaining to the hydrogen bond is larger, and the non-bonded O–H distance related to it is shorter, than that for an isolated pair. This means that the distinctive H₂O structure is less clear for the water chain. The structural difference between vacuum and CNT confinement is seen slightly in the HOH angle and the inter-oxygen distance; however, the water chain in a vacuum is a kind of thought experiment because water in reality is not likely to preserve a chain structure in vacuum; rather, it forms aggregated clusters, vapor, or bulk structures. The chain structure can exist only in a confined space.

4. Concluding remarks

We have investigated the density dependence of the collective structure and hydrogen bond dynamics of water molecules in a (6, 6) CNT using the molecular dynamics (MD) method and quantum mechanical (QM) calculations. The results obtained from MD show that the density dependence of the hydrogen bond lifetime drastically changes at around four molecules per nanometer of the (6, 6) CNT. Water densities higher than this lead to substantially longer hydrogen bond lifetimes. On the other hand, the hydrogen bond lifetime does not noticeably decrease with decreasing density but remains roughly the same in the lower density regime. The mean molecular orientation angle of water molecules is smaller for a higher density, and it asymptotically approaches 33° on the lower density side. This asymptotic nature stems from the non-uniform distribution of water molecules, i.e. they aggregate to form a chain structure at low densities.

The mean orientation angle under a moderate density condition obtained from QM calculation using density functional theory coincides with the MD result of the SPC/E model with smooth truncation. Within the range investigated here, strong electronic interaction between water and the CNT is not observed. The charge distribution of water in the CNT originates from the molecular configuration due to spatial confinement. Higher precision calculations for dispersion interaction might result in stronger interaction between CNT and water, but these are computationally too expensive at the moment.

In summary, the collective structure and stability of a molecular water chain in the (6, 6) CNT varies substantially at high densities, but has a kind of intrinsic property at

low densities. When considering proton transport or electric current of the system studied here, such a density dependence will be important. The tuning of the properties would be possible by modifying the tube edge conditions as well as the surrounding macroscopic conditions. The manipulation of the collective molecular properties of water can lead to new functionalities of molecular devices.

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