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Confined Water: Structure, Dynamics, and Thermodynamics

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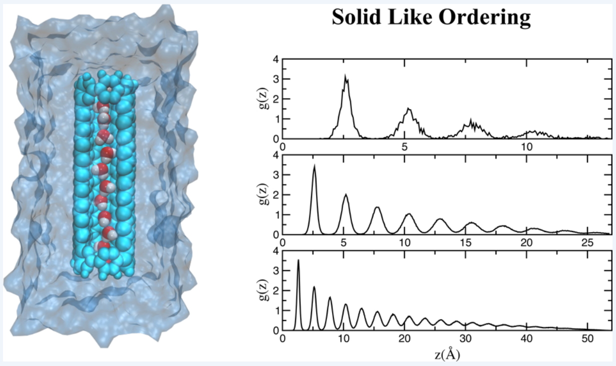

CONSPECTUS: Understanding the properties of strongly confined water is important for a variety of applications such as fast flow and desalination devices, voltage generation, flow sensing, and nanofluidics. Confined water also plays an important role in many biological processes such as flow through ion channels. Water in the bulk exhibits many unusual properties that arise primarily from the presence of a network of hydrogen bonds. Strong confinement in structures such as carbon nanotubes (CNTs) substantially modifies the structural, thermodynamic, and dynamic (both translational and orientational) properties of water by changing the structure of the hydrogen bond network. In this Account, we provide an overview of the behavior of water molecules confined inside CNTs and slit pores between graphene and graphene oxide (GO) sheets.

Water molecules confined in narrow CNTs are arranged in a single file and exhibit solidlike ordering at room temperature due to strong hydrogen bonding between nearest-neighbor molecules. Although molecules constrained to move along a line are expected to exhibit single-file diffusion in contrast to normal Fickian diffusion, we show, from a combination of molecular dynamics simulations and analytic calculations, that water molecules confined in short and narrow CNTs with open ends exhibit Fickian diffusion because of their collective motion as a single unit due to strong hydrogen bonding.

Confinement leads to strong anisotropy in the orientational relaxation of water molecules. The time scale of relaxation of the dipolar correlations of water molecules arranged in a single file becomes ultraslow, of the order of several nanoseconds, compared with the value of 2.5 ps for bulk water. In contrast, the relaxation of the vector that joins the two hydrogens in a water molecule is much faster, with a time scale of about 150 fs, which is about 10 times shorter than the corresponding time scale for bulk water. This is a rare example of confinement leading to a speedup of orientational dynamics. The orientational relaxation of confined water molecules proceeds by angular jumps between two locally stable states, making the relaxation qualitatively different from that expected in the diffusive limit.

The spontaneous entry of water inside the hydrophobic cavity of CNTs is primarily driven by an increase in the rotational entropy of water molecules inside the cavity, arising from a reduction in the average number of hydrogen bonds attached to a water molecule. From simulations using a variety of water models, we demonstrate that the relatively simple SPC/E water model yields results in close agreement with those obtained from polarizable water models.

Finally, we provide an account of the structure and thermodynamics of water confined in the slit pore between two GO sheets with both oxidized and reduced parts. We show that the potential of mean force for the oxidized part of GO sheets in the presence of water exhibits two local minima, one corresponding to a dry cavity and the other corresponding to a fully hydrated cavity. The coexistence of these two regimes provides permeation pathways for water in GO membranes.

I. INTRODUCTION

Water is the most important chemical compound on the surface of the earth and the main constituent of all living organisms.[1] The properties of bulk water have been the subject of intense investigations for many decades. However, in many technologically and biologically relevant situations, water is either confined in small cavities or in contact with a surface. The effects of confinement on the structural and dynamical properties of water can be very substantial.[2,3] Confinement may lead to the appearance of new phases[4−6] not present in the bulk under the same thermodynamic conditions, cause slowing of the dynamics of water molecules near hydrophilic protein chains,[7] and speed up the dynamics in the hydrophobic cavity of a carbon nanostructure.[8,9] The alignment of dipole moments of water molecules[10] in narrow carbon nanotubes (CNTs), liquid−liquid transitions,[11] and highly anisotropic orientational dynamics inside carbon nanostructures[12] are other examples of how the properties of liquid water are modified as a result of confinement.

The interaction of water with carbon nanostructures such as CNTs, graphene, and fullerene has attracted considerable attention in recent years. This is partly associated with the practical interest in CNTs, which have many promising

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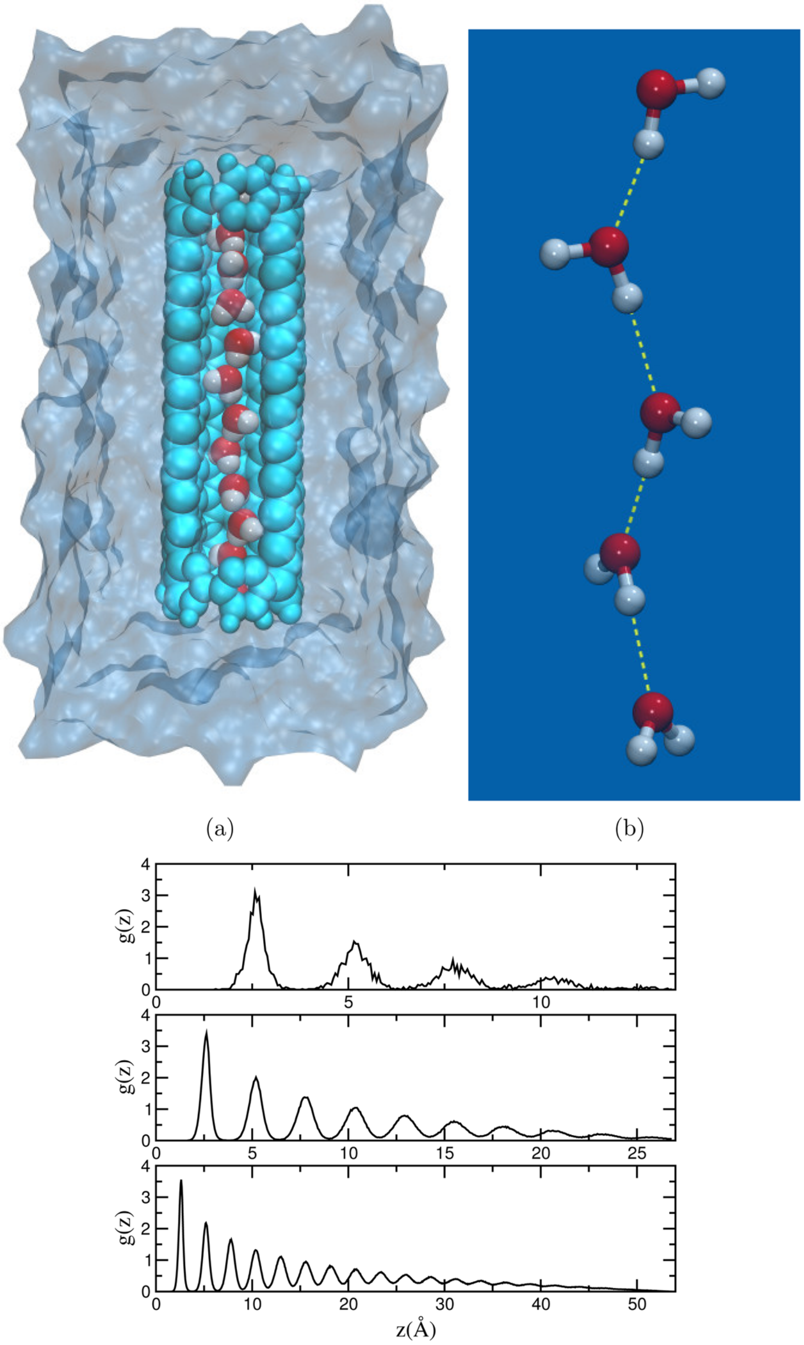

(a) (b)

(c)

Figure 1. (a) Single-file arrangement of water molecules inside a single-walled (6,6) CNT. (b) Hydrogen bond configuration in a single-file water chain. One of the hydrogen atoms of each water molecule is not hydrogen-bonded, and hence, the corresponding OH vector can rotate freely. (c) Pair correlation functions of water molecules inside (6,6) CNTs of various lengths (14, 28, and 56 Å top to bottom). The well-defined sharp peaks signify solidlike ordering of water molecules inside the CNT.

applications in energy storage, desalination, voltage generation, flow sensing, etc.[13,14] Layering of water confined between two hydrophobic surfaces has been observed in experiments, and a significant attractive force between two rough hydrophobic surfaces immersed in water has been experimentally demonstrated. Computer simulations have played an essential role in understanding the behavior of water in both interior and exterior regions of carbon nanostructures. For example, experimental investigations of water in narrow CNTs were motivated by the molecular dynamics (MD) simulation of Hummer et al.,[15] which showed that water molecules spontaneously enter a (6,6) CNT immersed in water in spite of the hydrophobic nature of the nanotube cavity.

In this Account, we summarize the results obtained mostly from our simulation studies of several important aspects of the structure, dynamics, and thermodynamics of water molecules confined inside single-walled CNTs and slit-shaped pores between graphene oxide (GO) sheets. The article is organized as follows. In the next section, we describe the structure of water inside narrow CNTs. Section III describes the dynamics

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of water molecules confined in CNTs. The thermodynamics of water entry into CNTs is discussed in section IV. The role of the water model used in a simulation of the properties of water confined inside a CNT is discussed in section V. The unusual behavior of water inside a slit-shaped pore between two GO sheets is discussed in section VI. Section VII contains a summary of the main results and a discussion of future directions.

II. STRUCTURAL PROPERTIES OF WATER CONFINED IN A CNT

Water molecules confined in narrow CNTs cannot cross each other, resulting in a single-file arrangement (Figure 1) in which each water molecule makes hydrogen bonds with only two nearest-neighbor water molecules: oxygen acts as an acceptor and one of the hydrogens from either side acts as a donor. This leads to a highly oriented hydrogen bond network inside CNTs (see Figure 1). The dipole moments of the water molecules confined in a short CNT are ordered in two equivalent directions, each of which makes a small angle with the axis of the nanotube. Flips of the chain of water molecules occur via the diffusion of orientational defects that connect ordered domains of water molecules with opposite directions of dipolar alignment.[12] As shown in Figure 2, the flipping of dipole moments occurs on a time scale of nanoseconds that depends on the length of the CNT. Köfinger et al.[16] developed a lattice model for single-file water confined in CNTs using the parameters obtained from extensive MD simulations. Using this model, they showed that water dipoles can be aligned in nanotubes with lengths of up to millimeters at ambient temperature, beyond which thermal fluctuations destroy the alignment. Many MD simulations have been performed to investigate the dependence of CNT hydration on factors such as the diameter[17] and chirality of the CNT and the carbon−water interaction.[18] Striolo et al.[19] studied the effect of the nanotube diameter on the adsorption isotherms of confined water. They observed layered water structures inside a CNT when the diameter is commensurate with the formation of a hydrogen bond network. Different reports indicate distinct types and degrees of order in the water structure inside such nanotubes. Noon et al.[20] and Liu et al.[21] reported that the water molecules are arranged in a highly ordered fashion, with layers arranged in a helical geometry forming a spiral-like chain of the molecules along the CNT axis.[20]

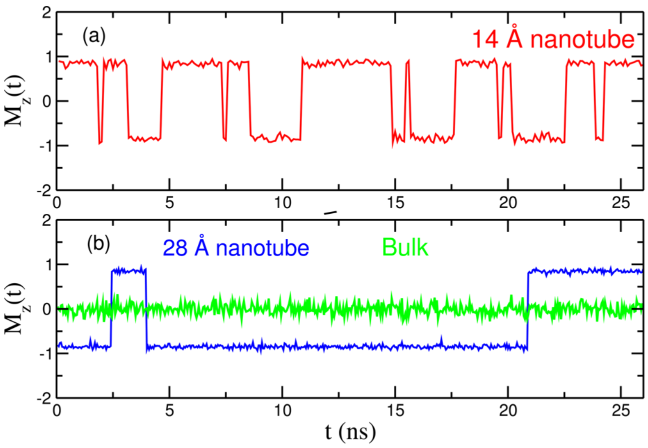

Figure 2. Time evolution of the average dipole projection along the nanotube axis. The flipping time varies depending on the length of the CNT.

The existence of a variety of new ice phases not seen in the bulk and the occurrence of a solid−liquid critical point[11,22] have also been suggested. MD studies by Koga et al.[11] suggest that confined water molecules can exhibit a first-order freezing transition to hexagonal and heptagonal ice nanotubes. Among the *n*-gonal ice nanotubes examined, the pentagonal and hexagonal ice nanotubes appear to be the most stable. Alexiadis and Kassinos[23] showed that the structure observed in a simulation may depend crucially on the choice of the water model. We recently performed a comparative study of different water models, including polarizable ones, to investigate the ordering of single-file water molecules inside narrow CNTs.[24] We found solidlike ordering for all of the water models, but the mean separation between neighboring water molecules was found to depend on the water model.

III. DYNAMICS OF WATER CONFINED IN A CNT

Translational Dynamics

As a result of changes in the structure of the hydrogen bond network, different types of transport can occur depending on the diameter of the nanopore. Inside narrow CNTs where water molecules cannot cross each other, single-file diffusion with a mean-square displacement (MSD) scaling as the square root of time is expected. Initial studies reported subdiffusive behavior of water molecules inside narrow CNTs. However, Striolo[25] reported that the translational dynamics of water molecules inside a (8,8) CNT (diameter 10.9 Å) with periodic boundary conditions in the axial direction is of the fast ballistic type on time scales up to 500 ps at room temperature. Analysis of simulation data beyond 1 ns indicates that the diffusion mechanism changes to Fickian-type diffusion with no evidence of single-file diffusion. Cui[26] observed that water diffusion along the radial direction in a cylindrical pore obeys Fick's law with a diffusion coefficient slightly lower than the bulk value. We have shown that the computation of the MSD of water molecules confined in short, open-ended (6,6) CNTs (diameter 8.1 Å) immersed in a bath of water requires extensive averaging and that the computed MSD values depend weakly on the length of the nanotube used in the simulation (see Figure 3).[10] Because of the finite length of the CNT, the MSD shows saturation at long times, with the saturation value depending on the length of the nanotube. The diffusion behavior of single-file water confined inside short, open-ended (6,6) CNTs is essentially Fickian because the molecules move collectively as a single unit as a result of the presence of strong hydrogen bonding between adjacent water molecules. The MSD as a function of time is in quantitative agreement with the analytic prediction for a simple one-dimensional diffusion model with absorbing boundary conditions (see Figure 3). The residence time of water inside the CNT depends quadratically on the length of the nanotube, again signifying Fickian diffusion. Subsequently, we demonstrated that water molecules confined in a narrow carbon nanoring with no open end exhibit single-file diffusion when the molecules form multiple clusters.[27]

Chen et al.[28] systematically studied the structure of the network of hydrogen bonds formed by water molecules inside CNTs. They showed that the hydrogen bonds between water molecules inside a narrow (6,6) CNT form a chainlike structure, whereas the hydrogen bond network in wider nanotubes exhibits locally concentrated clusters. The transla-

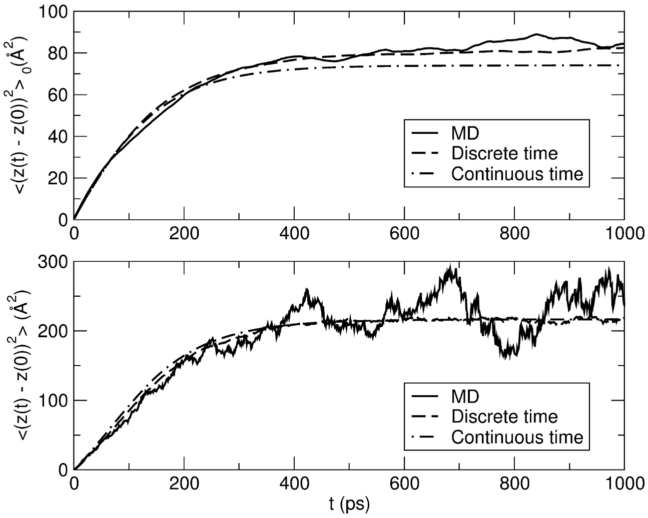

Figure 3. (top) Time-origin-averaged MSD and (bottom) fixed-time-origin MSD of water molecules inside a 14 Å long (6,6) CNT. Solid lines, MD results; dashed and dash-dotted lines, analytic results for continuous-time and discrete-time random walks.

tional dynamics in the two cases are found to be quite different. Kayal and Chandra[29] studied the effects of an orthogonal (normal to the nanotube axis) electric field on the structural and dynamic properties of single-file water inside a (6,6) CNT and showed that the CNT undergoes a filled-to-empty transition with increasing electric field strength because the electric field disrupts the chain of hydrogen bonds.

Orientational Dynamics

The water molecules confined in a (6,6) nanotube form an orientationally ordered chain with the dipole moments of the water molecules pointing either parallel or antiparallel to the axis of the tube (see Figure 1b).[10] Occasionally there are orientational defects in the chain where the dipole moment of the water molecule points perpendicular to the chain. As shown in Figure 1b, each water molecule in the chain is hydrogen-bonded to two water molecules, one in front of it and the other behind it. This arrangement of molecules leaves one hydrogen atom of each water molecule free, not participating in any hydrogen bond. The altered hydrogen bond network severely modifies the reorientational dynamics[12] of the confined water molecules. To quantify the effects of confinement on the reorientation dynamics, we calculated various reorientational correlation functions, such as the time autocorrelation functions of the dipole moment, HH vector, and OH vector of the confined water molecules. The orientational relaxation of the confined water molecules was found to occur on several different time scales and also exhibits strong directional anisotropy. The slowest relaxation is that of the collective dipole moment (time scale of several nanoseconds). This relaxation is mediated by orientational defects in the hydrogen-bonded chain: a transition from the parallel state to the antiparallel state (or vice versa) occurs when a defect is able to hop across the whole chain. Since the creation of a defect is energetically unfavorable, collective flips of the dipole moment occur rarely (on a time scale of nanoseconds). On the other hand, the relaxation of the vector joining the hydrogen atoms (the HH vector) of each confined water molecule (time scale of about 200 fs) is much faster than that of water molecules in the bulk.

In addition, the water molecules exhibit another rotational mode, where there is a fast (time scale of about 60 fs) exchange of the positions of the hydrogen atom participating in the hydrogen bonding in the chain and the one that is free, representing a dangling bond. This exchange is mediated by a nondiffusive angular jump (see Figure 4). We studied these angular jumps for water inside a single-walled (6,6) CNT.[9] For these water molecules, the mean jump angle is about 50°,[9] and the mean waiting time between successive jumps is about 1 ps.

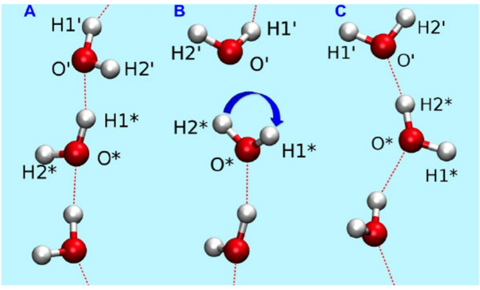

Figure 4. Illustration of the jump-mediated orientational relaxation in single-file water confined in a CNT. The central molecule performs a jump here: first H1* is hydrogen-bonded to O′, and at a later time, H2* is hydrogen-bonded to O′. Adapted from ref 9. Copyright 2009 American Chemical Society.

Spectral Density

The spectral density or power spectrum of the confined water molecules is computed from the Fourier transform of the linear or angular velocity autocorrelation function and can be associated with different vibrational and rotational processes. In 2001, Marti and Gordillo[30] reported the power spectrum of single-file water molecules confined inside CNTs. They observed shifts in the positions of low-frequency peaks and the emergence of a new peak at the high frequency of 3400 cm^{-1}. It was proposed that this peak is due to the splitting of the bulk water stretching mode into symmetric and asymmetric modes as a result of confinement. More recently, we found a sharp peak in the low-frequency part of the spectral density for narrow CNTs.[31] The peak occurs at 47 cm^{-1} for (6,6) and 121 cm^{-1} for (5,5) CNTs (see Figure 5). This peak corresponds to vibrational motion perpendicular to the CNT axis, as seen from the decomposition of the power spectra into components for motion parallel and perpendicular to the CNT axis. The peak is more blue-shifted for (5,5) CNTs because the confining potential is stronger in that case. For wider (7,7) and (8,8) nanotubes, the power spectrum is similar in shape to that of bulk water. In the case of rotational density of states, a distinct peak is observed at 146 cm^{-1} for water molecules confined in a (6,6) nanotube, whereas for the (5,5) nanotube this peak appears to have merged with the zero-frequency diffusive peak (see Figure 6). The emergence of these peaks is a result of the change in the librational motion of water molecules when they are arranged in a single-file manner. Further, it was shown that the presence of additional libration modes and restricted translational motion lead to enhanced rotational entropy and suppressed translational entropy, as discussed in the next section.

IV. THERMODYNAMICS OF WATER ENTRY INTO CNTS

Several simulations and experiments have demonstrated that water spontaneously fills the hydrophobic pore of a nanotube

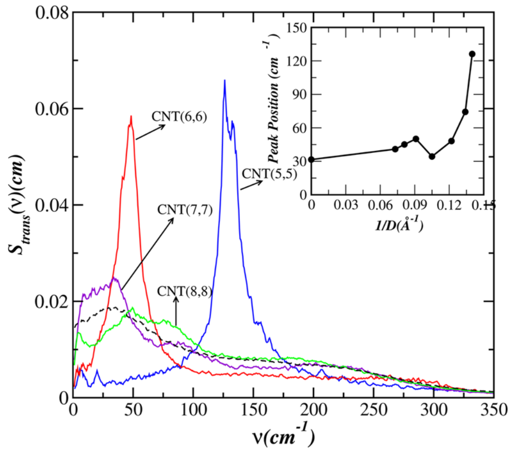

Figure 5. Translational densities of states for water molecules in the bulk (dashed line) and those confined inside (8,8), (7,7), (6,6), and (5,5) nanotubes of length 54 Å, calculated at T = 300 K. There is a gradual shift in the peak frequencies as the diameter of the tube is increased. The inset shows the variation of the peak position with the inverse of the tube diameter.

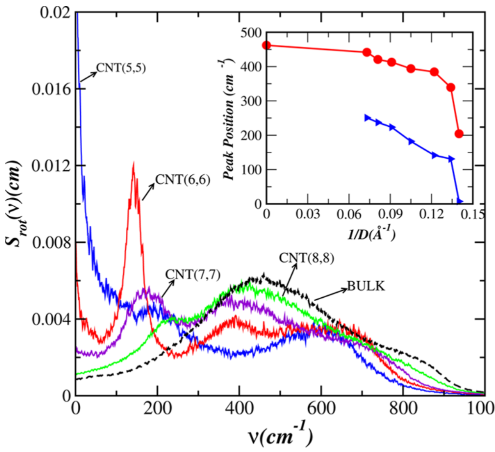

Figure 6. Comparison of the rotational density of states of water molecules in the bulk with those of water molecules confined inside (8,8), (7,7), (6,6), and (5,5) nanotubes of length 54 Å, calculated at T = 300 K. The inset shows the dependence of the peak positions on the inverse of the tube diameter. Blue triangles denote the positions of the first peak and red circles the positions of the second peak of the rotational density of states.

when it is immersed in a water bath.[15,32,33] The number of hydrogen-bonded neighbors of a water molecule inside a narrow nanotube is generally smaller than that in the bulk. This causes the hydrogen-bonding energy of water molecules inside a nanotube to be higher than that of water molecules in the bulk. Therefore, considering the energetics, it is surprising that water molecules spontaneously fill the nanotube.

To understand the thermodynamics of entry of water molecules into the hydrophobic pore of a narrow CNT, Vaitheeswaran et al.[34] used the Widom test particle insertion method to calculate the free energy of transfer of a water molecule from the bulk to the channel inside peridically repeated and closed-ended single-walled (6,6) CNTs. They used an approximate decomposition of the free energy into entropy and energy terms to obtain results suggesting that the entry of water molecules into (6,6) CNTs is driven by the energy rather than the entropy. We investigated how the orientational freedom[15] of single-file water molecules in narrow CNTs affects the thermodynamics of water occupancy.[31] Estimates of the entropy of water molecules confined in CNTs of diameters ranging from 6.9 to 10.8 Å (in standard nomenclature, (5,5) to (8,8)), where water molecules are organized in different geometrical arrangements, were made using the two-phase thermodynamics (2PT) method.[35,36] In all cases, we found that the confined water molecules have greater rotational entropy than the water molecules in the bulk, the difference being maximum for molecules inside the narrowest (5,5) nanotubes. Pascal et al.[37] also reported similar findings. Subsequently, we showed that when the free energies of both the water molecules and the CNT are properly taken into account, the entry of water molecules into the nanotube becomes energetically favorable, but the change in the energy is smaller than the entropy change, making the entropy change the main driving force for water entry.[38] We also studied the effects of changing the temperature on the thermodynamics of water entry into (6,6) CNTs.[38] Both the entropy and energy of transfer were found to decrease with increasing temperature, keeping the free energy of transfer nearly constant (see Table 1).

Table 1. Energy, Entropy, and Free Energy of Transfer per Water Molecule and Average Occupancy of the Nanotube at Different Temperatures for a 54 Å Long Open-Ended Nanotube

T (K)	ΔE (kcal/mol)	TΔS (kcal/mol)	ΔA (kcal/mol)	average occupancy
273.16	−0.96 ± 0.15	0.73 ± 0.11	−1.69 ± 0.26	19.7
285.15	−1.01 ± 0.15	0.71 ± 0.11	−1.72 ± 0.26	19.4
298.15	−1.15 ± 0.15	0.58 ± 0.14	−1.73 ± 0.29	19.1
313.15	−1.28 ± 0.15	0.47 ± 0.14	−1.75 ± 0.29	18.9
333.15	−1.43 ± 0.15	0.35 ± 0.14	−1.77 ± 0.29	18.7
353.15	−1.48 ± 0.16	0.27 ± 0.14	−1.76 ± 0.30	18.3

V. ROLE OF THE WATER MODEL IN THE SIMULATED PROPERTIES OF WATER CONFINED IN A CNT

A large number of models, often parametrized to reproduce only a few properties at ambient temperature and pressure, have been used in simulations of water. Mostly, nonpolarizable and orientation-independent water models such as TIP3P, SPC/E, and TIP4P have been used in existing simulation sudies of confined water molecules. A few simulation studies of water molecules confined in CNTs have used flexible water models,[30] polarizable water models,[39,40] or ab initio methods.[41−43] However, these studies were limited to investigations of a few spectroscopic and dynamic quantities only. We recently carried out simulations of single-file water molecules confined in narrow CNTs using five different water models and computed several structural, dynamic, and thermodynamic quantities.[24] The five different models included TIP3P[44] and SPC/E, which are three-site rigid water models; the flexible water model SPCFw;[45] TIP3PM; and the polarizable water model POL3,[46] which includes the induced dipole moment along with the permanent dipole moment. TIP3PM is a modified TIP3P model with Lennard-Jones potential interaction sites for all three atoms, thus making its interaction with the graphene/CNT surface orientation-dependent. The thermodynamic and structural properties of water molecules near a graphene surface were shown to be very sensitive to the range and orientation

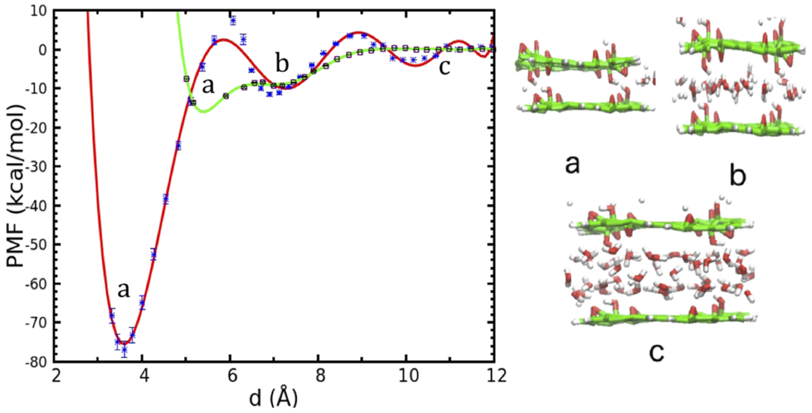

Figure 7. Potentials of mean force (PMFs) of functionalized graphene (33% oxidation) in water (green) and pristine graphene in water (red). The configurations of functionalized graphene in water corresponding to the minima at (a) 4.8 Å and (b) 7 Å and the local minimum at (c) 10 Å in water are shown at the right. The polynomial fits to the PMF profiles are guides to the eye only.

dependence of the potential used in the simulation.[47] In contrast, we found that the inclusion of anisotropic van der Waals interactions does not have any significant effect and that most of the features of the dynamics remain the same for TIP3P and TIP3PM. The results for the SPC/E and SPCFw models were found to be similar, indicating that the flexibility of the bonds does not play an important role. We also showed that the POL3 model reproduced the hydrogen bond dynamics most accurately (as compared to ab initio simulations) among these water models. The SPC family of water models leads to behavior closer to that found for the POL3 model than the TIP3P family of water models. Considering the overall ability of different water models to reproduce the structure, dynamics, and thermodynamics of confined water, it was concluded that the SPC/E water model would be the optimum choice.

VI. WATER CONFINED IN SLIT PORES

The properties of water molecules confined in a slit-pore geometry between two graphene or graphene oxide (GO) sheets (see Figure 7a–c) have also received a great deal of interest.[48−53] Using X-ray diffraction, Iiyama et al.[48] observed that the diffraction pattern of water molecules confined in a hydrophobic slit pore contains sharp peaks that are not seen in bulk water. These sharp peaks suggest that the water molecules in the slit pore have an ordered structure in directions parallel to the walls of the pore. Using MD simulations, Choudhury and Pettitt[50−52] obtained a variety of results on the structure, dynamics, and energetics of water molecules confined between two graphene sheets. From calculations of the potential of mean force (PMF), they concluded that weak attractive interactions between the sheet atoms and the water molecules influence the hydration behavior and unveiled the role of the sheet size and sheet–water interaction potential in the crossover between water-separated sheets and contact-pair sheets. In another study, Giovambattista et al.[6] analyzed the effect of thermodynamic parameters and plate separation on the phase behavior of water confined between two hydrophobic or hydrophilic plates. They observed that in the presence of hydrophobic plates the effect of pressure is to enhance the water structure and to push water molecules toward the plates, whereas for hydrophilic plates the water structure is insensitive to pressure. Hirunsit and Balbuena[53] studied the structure and dynamics of water molecules confined in slit-shaped graphite pores with widths varying from 7 to 14.5 Å at a fixed density of water. For the smallest interlayer separation, they observed the formation of a layered structure of water molecules parallel to the graphite surfaces.

We recently investigated the thermodynamics of water ordering between two graphene and GO sheets by calculating the PMF of the sheets in the presence of water molecules.[54] The PMF was calculated by integrating the force exerted by one of the sheets on the other one in the presence of the solvent. The PMF profile for graphene in water (see Figure 7) shows a strong van der Waals attraction of 180 kcal/mol at a separation of 3.4 Å. This global minimum is followed by two local minima at distances of 6.75 and 9.5 Å between the sheets. These correspond to single and double layers of water, respectively. These two minima are separated by a low energy barrier of 20 kcal/mol. For GO sheets at various oxidation levels, we found PMF profiles that contain two minima, one at 4.8 Å that corresponds to a dry cavity and another at 6.8 Å that corresponds to a fully hydrated cavity, as shown in the instantaneous snapshots shown in Figure 7. The coexistence of these two domains provides percolation pathways in multilayered GO membranes. We also calculated the entropy and free energy of the water molecules confined inside the pristine and oxidized parts of a GO sheet using the 2PT method.[35,36] Because of the stronger electrostatic interaction between the graphene oxide and water in the oxidized part of the sheet, water has lower entropy compared with that in the pristine part of the GO sheet. For various intersheet spacings, water molecules between graphene sheets show faster translational dynamics than water molecules between GO sheets because of the attractive electrostatic interactions between GO sheets and water molecules.

VII. CONCLUSIONS

In this Account, we have reviewed different aspects of the structure, dynamics, and thermodynamics of water molecules confined in carbon-based nanostructures. Strong confinement leads to a dramatically modified hydrogen bond network compared with that in bulk water. This is reflected in unusual dynamic and structural properties of confined water molecules. One of the main outcomes is the emergence of new water structures, ranging from single-file ordered chains in narrow CNTs and various *n*-gonal ice nanotubes in wider CNTs to two-dimensional ordered structures in slit-pore geometries. Despite their single-file arrangement, water molecules confined

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in short CNTs with open ends exhibit Fickian diffusion, which is attributed to strong correlations among the ordered water molecules. The orientational dynamics of water molecules confined in CNTs is strongly anisotropic, with relaxation times for different kinds of rotation differing by orders of magnitude. These molecules exhibit enhanced order along the CNT axis but are more free to rotate about the axis in comparison with water molecules in the bulk. This makes the rotational entropy of water molecules inside the cavity larger than that in the bulk. This gain in entropy makes it thermodynamically possible for water molecules to stay inside CNTs and bilayer cavities of carbon nanostructures in spite of the hydrophobic interactions. The modified hydrogen bond network also leads to the interesting phenomenon of permeation of water molecules through GO membranes while permeation of much smaller helium atoms is blocked.

In spite of the significant progress reported in this Account, experimental validation of some of the interesting phenomena observed in the computational studies is still pending. Recent successes in observing the structure of water confined between graphene layers[55] and isolating vibrational modes of water molecules confined in CNTs[56] are encouraging signs suggesting that the technological challenges associated with experimental studies will be overcome in the near future. We expect that this Account will inspire experimentalists to further investigate interesting properties of confined water molecules.

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The authors declare no competing financial interest.

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