Phase transition of nanotube-confined water driven by electric field

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The effects of electric field on the phase behaviors of water encapsulated in a thick single-walled carbon nanotube (SWCNT) (diameter = 1.2 nm) have been studied by performing extensive molecular dynamics simulations at atmospheric pressure. We found that liquid water can freeze continuously into either pentagonal or helical solidlike ice nanotube in SWCNT, depending on the strengths of the external electric field applied along the tube axis. Remarkably, the helical one is new ice phase which was not observed previously in the same size of SWCNT in the absence of electric field. Furthermore, a discontinuous solid–solid phase transition is observed between pentagonal and helical ice nanotubes as the strengths of the external electric field changes. The mechanism of electric-field-induced phase transition is discussed. The dependence of ice structures on the chiralities of SWCNTs is also investigated. Finally, we present a phase diagram of confined water in the electric field–temperature plane. © 2011 American Institute of Physics. [doi:10.1063/1.3579482]

I. INTRODUCTION

Confined water within restricted spaces is expected to display unusual properties dramatically different from bulk water.¹ Single-walled carbon nanotubes (SWCNTs) have a wide range of very precisely defined diameters and chiral structures, uniquely described by their chiral indices (n, m),² thus they provide an ideal model system for the study of water in extremely confined spaces. In spite of the hydrophobic nature of the SWCNT wall, it has been demonstrated experimentally^{3–6} and computationally^{7–11} that water can fill the inner space of open-ended SWCNTs at atmospheric pressure. Those water-filled SWCNTs might be expected to play a central role in future nanoscale devices and proton storage.^{12–14} The confined water is also highly relevant to properties and functions of some biological systems, such as ion channels.^{9,15,16}

Experimental studies using vibrational spectroscopy,⁷ x-ray diffraction,¹⁷ solution NMR,¹⁸ and neutron diffraction¹⁹ have shown that the encapsulated water in SWCNTs can form different sizes of ice nanotubes (NTs), ranging from pentagonal to nanogonol nanotubes. The phase behavior of confined water has also been investigated by molecular dynamics (MD) simulations under different pressure (P), temperature (T), and tube diameter (d).^{8,20–24} In the presence of axial pressure of 50 to 500 MPa, in SWCNTs with diameters ranging from 1.1 to 1.4 nm, it was found²³ that water can exhibit a continuous phase transformation into solidlike square or pentagonal ice NTs and a discontinuous freezing transition to hexagonal or heptagonal ice NTs. At higher axial pressure of 500 MPa to 4 GPa, in SWCNTs with larger d ranging from 1.35 to 1.9 nm, multilayer polygonal and helical ice NTs were

observed.²¹ At atmospheric pressure and room temperature, it was shown⁸ that water in SWCNT can also organize themselves into a solid-like hydrogen-bonded ice sheets. More recently, Takaiwa *et al.*²⁰ proposed a phase diagram of water in SWCNT at atmospheric pressure as a function of temperature (100–300 K) and tube diameter (0.9–1.7 nm). They found that, in SWCNT with a given diameter, water only exhibited a single type of ice NT. For example, in a SWCNT with $d = 1.2$ nm, only pentagonal ice NT was observed in their MD simulations at T below 275 K. In spite of extensive studies, the effects of external electric field (E) on the phase behavior of ice NTs formed in SWCNT have not been reported.

In this study, using all-atom MD simulations, we have examined the structure and phase transition of confined water inside a SWCNT with $d = 1.2$ nm (corresponding to chiral (4,13) SWCNT) at atmospheric pressure under electric field applied along the tube axis (z -axis). Extensive MD simulations have been performed in wide ranges of E (0–4 V/nm) and T (230–350 K). Our simulations show that water can freeze into new ice NTs ((5,1) and (5,2)) through a continuous phase transition in the presence of electric field and exhibit a discontinuous ice–ice transition at low temperature as the strengths of electric field change. These results reveal that electric field can induce a rich phase behavior of water confined in a nanopore.

II. METHODS

All MD simulations are performed in the isothermal–isobaric (NPT) ensemble using the GROMACS 3.3.1.²⁵ The SWCNT is immersed in a cubic box of TIP4P²⁶ water and the minimum distance between the fixed SWCNT and the water box wall is 1.0 nm. The SWCNTs used in this study are 3.1 nm long, similar to the length of SWCNT used in a recent

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FIG. 1. Snapshots of three different ice NTs in (4,13) SWCNT: pentagonal (5,0), helical (5,1) and (5,2) formed, respectively, under $E = 0, 2$, and 3 V/nm at $T = 250$ K. The angle θ between a H-bond vector and the z -axis is shown in (5,1) ice NT. Each ice NTs can be characterized by $\langle\theta\rangle$, here the angular brackets indicate averaging over all H-bonds in a water configuration. The $\Theta = 0^\circ, 11^\circ$, and 22° represent the structure characteristic angle for (5,0), (5,1), and (5,2) ice NTs, respectively. Oxygen atoms are in red and hydrogen atoms are in white.

MD study.²⁰ There are about 65 water molecules inside the SWCNT. To avoid the perturbation by both interfacial sides, we only consider the 46 water molecules located in the middle body of the nanotube for all the analysis of phase transition. The carbon-carbon interaction parameters are adopted from a previous work of Hummer.⁹ The van der Waals interactions between SWCNT and water oxygen are described by Lennard-Jones potential. The particle-mesh Ewald method (PME)²⁷ with a real space cutoff of 1.0 nm is used to calculate the long-range electrostatic interactions and a cutoff of 1.4 nm is applied to the van der Waals interactions. The temperature and pressure of the system are maintained respectively constant by a Nose-Hoover thermostat²⁸ and 1 bar using an anisotropic Parrinello-Rahman barostat.²⁹ Periodic boundary conditions are applied in all directions.

III. RESULTS AND DISCUSSION

Formation of ice NTs from disordered liquid water in the absence and presence of electric field is monitored in the process of decreasing T from 350 to 230 K. We reverse the cooling process from the lower T to examine melting behavior and hysteresis. Phase transition of confined water at low and high temperatures is investigated by increasing the electric field from 0 to 4 V/nm and a reverse process (decreasing the electric field from 3.5 to 0 V/nm) is performed to examine the polarization hysteresis.

We specify each ice NT observed in our MD simulations by an index (n, m) by following the denotation of ice NTs by Koga et al.²³ In the analysis, a hydrogen bond (H-bond) is defined by a geometric criterion of oxygen-oxygen distance ≤ 2.8 Å. We have checked that an alternative potential energy criterion does not change the results. The angle between a H-bond vector and the z -axis is labeled as θ . For each water configuration, we calculate the average of all θ which is smaller than 45° (labeled as $\langle\theta\rangle$) and use the value of $\langle\theta\rangle$ to determine the structural feature of confined water.

Figure 1 shows the snapshots of three distinct ice NTs inside (4,13) SWCNT at $T = 250$ K under different strengths of

FIG. 2. Probabilities of (5,0), (5,1), (5,2) ice NTs inside (4,13) SWCNT vs temperature (a)–(c) in the absence and presence of external electric field, and versus E (d)–(f) at low temperature (250 K), room temperature (300 K), and high (350 K) temperature. The $P_{(5,0)}$, $P_{(5,1)}$, $P_{(5,2)}$, $P_{\text{disordered}}$ represents, respectively, the probability of (5,0), (5,1), (5,2) ice NTs and disordered liquid water. The blue, red, and green curves in (d)–(f) panel represent the probability of (5,0), (5,1), (5,2) ice NTs, respectively.

the electric field. They are pentagonal (5,0), helical (5,1) and (5,2) ice NTs formed, respectively, at $E = 0, 2$, and 3 V/nm. By calculating the probability distribution of $\langle\theta\rangle$ for all water configurations generated in the last 20 ns of four independent 50 -ns MD runs at each E , we found that the average of $\langle\theta\rangle$ over all water configurations is approximately $0^\circ, 11^\circ$, and 22° , respectively, for (5,0), (5,1), and (5,2) ice NTs. We use a symbol Θ to represent the structure characteristics angle for the three ice NTs. An (5,0), (5,1), or (5,2) ice NT is considered to be formed if the $\langle\theta\rangle$ value of a water configuration is in the range of $(\Theta - 1.5^\circ, \Theta + 1.5^\circ; \Theta = 0^\circ)$, $(\Theta - 3^\circ, \Theta + 3^\circ; \Theta = 11^\circ)$, or $(\Theta - 1.5^\circ, \Theta + 1.5^\circ; \Theta = 22^\circ)$, respectively. It is noted that the helical (5,1) and (5,2) ice NTs are new ice phases that were not observed previously in a SWCNT with the same diameter as used here by solely freezing the water,²⁰ indicating the important role of electric field on the structures of confined water.

The probabilities of (5,0), (5,1), and (5,2) ice NTs, labeled as, respectively, $P_{(5,0)}$, $P_{(5,1)}$, and $P_{(5,2)}$, as a function of T and E are given in Fig. 2. The $P_{\text{disordered}}$ represents the probability of disordered liquid water, where, $P_{\text{disordered}} = 1 - P_{(5,0)} - P_{(5,1)} - P_{(5,2)}$. It can be seen from Figs. 2(a)–2(c) that in the absence and presence of electric field, the probability curves all display a continuous phase transition behavior with the decrease of temperature. This liquid-solid transition behavior is in good agreement with that observed in the enthalpy-temperature plot reported previously in the absence of electric field.²⁰ The transition temperatures from disordered liquid water to ordered ice NTs can be obtained from the cross point of their probability curves, which are approximately $280, 295$, and 295 K for (5,0), (5,1), and (5,2) ice NTs, respectively. This estimated transition temperature of 280 K for (5,0) ice NT is in good agreement with that of 275 K obtained from the enthalpy-temperature plot in a recent MD study²⁰ and is consistent with the freezing temperature of 300 K obtained in a x-ray diffraction study.¹⁷ The different

FIG. 3. Analysis of physical properties of water confined in (4,13) SWCNT as a function of T and E . (a) dipole moment D_z per water molecule and (b) water density fluctuation $\langle \Delta \rho^2 \rangle$ vs T in the absence (0 V/nm) and presence (2 V/nm) of E ; (c) $\langle \Delta \rho^2 \rangle$ and (d) D_z vs E at low (250 K) and high (350 K) temperatures. $\langle \Delta \rho^2 \rangle$ at each point is an average of the last 20 ns of four independent 50-ns MD runs, the same for D_z .

freezing temperatures for pentagonal (5,0) and helical (5,1) and (5,2) ice NTs obtained in this study reveal that electric field can increase the liquid–solid transition temperature. Figures 2(d)–(f) gives the probabilities of (5,0), (5,1), (5,2) ice NTs as a function of E at low temperature (250 K), room temperature (300 K), and high temperature (350 K). At 250 K, water exhibits three different phases at different E . Transitions from (5,0) to (5,1) and from (5,1) to (5,2) ice NTs occur, respectively, at E around 1.25 and 2.5 V/nm. This solid–solid phase transition occurs discontinuously through a first-order transition, as seen in Fig. 2(d). However, at $T = 300$ and 350 K, the probabilities of the three ice NTs are less than 0.5 at all E indicating that the disordered liquid state is dominant. The finding of water adopting disordered liquid state at 300 and 350 K in the presence of electric field suggests that the ordering effects of electric field and nanoconfinement on the structure of confined water at high temperature are suppressed by thermal fluctuations.

The phase behavior of water in (4,13) SWCNT as a function of T and E is also analyzed using another two parameters: the component of dipole moment per water molecule along z -axis (D_z) and water density fluctuation $\langle \Delta \rho^2 \rangle$ ($= \langle \rho^2 \rangle - \langle \rho \rangle^2$, here, the angular brackets indicate averaging over time). Figures 3(a) and 3(b) give the temperature dependence of D_z and $\langle \Delta \rho^2 \rangle$ in the absence (0 V/nm) and presence (2 V/nm) of electric field. In the absence of electric field, D_z has a constant nonzero value and water freezes into (5,0) ice NT at $T \leq 280$ K. The deviation of D_z from zero at $E = 0$ V/nm is attributed to the ordered (5,0) ice NT induced by low T and nanoconfinement. D_z starts to decrease from $T = 280$ K and reaches to zero at $T = 290$ K. The vanishing of D_z at $T \geq 290$ K is consistent with the observation of water adopting a disordered liquid state. At $E = 2.0$ V/nm, D_z becomes much larger than that in the absence of electric field and remains almost constant at all temperatures [Fig. 3(a)]. The invariance of D_z at all temperatures in-

dicates that D_z cannot be used to characterize the liquid–solid phase transition induced by electric field. However, this transition behavior can be clearly seen from the plot of the variation of $\langle \Delta \rho^2 \rangle$ vs T [Fig. 3(b)]. The $\langle \Delta \rho^2 \rangle$ decreases smoothly with a distinct change between 270 and 310 K on cooling both at $E = 0$ and 2 V/nm. During the cooling process, liquid water undergoes a continuous transition into solid pentagonal (5,0) and helical (5,1) ice NTs, respectively, at $E = 0$ and 2.0 V/nm. This continuous liquid–solid transition is similar to that observed in the probability–temperature plot shown in Figs. 2(a) and 2(b). The freezing temperature of water at $E = 0$ and 2.0 V/nm can be estimated from the T value at the inflection point of $\langle \Delta \rho^2 \rangle$ vs T curve, which are, respectively, ~ 280 and ~ 295 K, in good agreement with the transition temperature obtained from the probability–temperature plot. It should be noted that hysteresis does not appear in the heating and cooling process, consistent an earlier MD study on water inside a SWCNT of $d = 1.2$ nm at $P = 1$ bar in the absence of electric field.²⁰

The variation of density fluctuation $\langle \Delta \rho^2 \rangle$ with respect to electric field (0–4 V/nm) at low (250 K) and high (350 K) temperatures is plotted in Fig. 3(c). At both temperatures, the $\langle \Delta \rho^2 \rangle$ decreases with an increase of E and reaches a plateau at $E \geq 1.5$ V/nm, implying that the presence of electric field reduces the structure fluctuation of confined water. Figure 3(c) also shows that $\langle \Delta \rho^2 \rangle$ is much smaller at low T than at high T , consistent with the finding of water adopting ordered ice NTs at low T and disordered liquid state at high T . However, the curve of $\langle \Delta \rho^2 \rangle$ vs E in Fig. 3(c) does not display any phase transition behavior of water. To explore this, we plot in Fig. 3(d) the dipole moment D_z versus E at low (250 K) and high (350 K) temperatures. Figure 3(d) shows that D_z increases with an increase of E , indicating that electric field can induce the ordering of water dipoles. This is consistent with the ordering effect of electric field on single-file water chain inside a thinner (6,6) SWCNT ($d = 0.8$ nm) reported in an earlier Monte Carlo study.³⁰ It can also be seen from

FIG. 4. (a) The interaction energy of water molecules forming ice NT as a function of the electric field strength at $T = 250$ K. Here the energy is averaged over all water molecules in ice NT. (b) The potential energy U of three distinct ice NTs (5,0), (5,1), and (5,2) at $T = 250$ K under three given electric fields: $E = 0.5$, 2, and 4 V/nm. Here, the potential energy consists of the interaction energy of water molecules and the polarization energy $(-\mathbf{D} \cdot \mathbf{E})$. $\mathbf{D}$ is the dipole moment per water molecule.

Fig. 3(d) that the D_z curve at 250 K shows three steps at $E = 0$ –1.0, 1.5–2.25, and 2.5–4.0 V/nm. These steps correspond to the formation of three different solid phases: (5, 0), (5, 1), and (5, 2) ice NTs, respectively. The abrupt changes of D_z at 250 K at $E = 1.0$ –1.5 and 2.25–2.5 V/nm correspond, respectively, to (5, 0) $\rightarrow$ (5, 1) and (5, 1) $\rightarrow$ (5, 2) ice phase transitions with the increase of E . The stepwise feature of D_z vs E demonstrates that these two phase transitions are discontinuous (first-order). Differently, at 350 K, water remains in its liquid phase and D_z increases gradually with an increase of E .

To further demonstrate the role of electric field in a phase transition-like behavior of confined water, we plot in Fig. 4(a) the interaction energy U_{int} (the polarization energy is not included) of water molecules forming ice NT at 250 K as a function of electric field strength. Similar to the stepwise feature of D_z curve versus E in Fig. 3(d), the U_{int} curve in Fig. 4(a) displays three steps at $E = 0$ –1.0, 1.5–2.25, and 2.5–4.0 V/nm. These steps correspond to the formation of three different ice NTs: (5, 0), (5, 1), and (5, 2), respectively. The abrupt changes of U_{int} at $E = 1.0$ –1.5 and 2.25–2.5 V/nm reflect, respectively, to the phase transition from (5, 0) to (5, 1) and from (5, 1) to (5, 2) ice NTs through a first-order transition. This phase transition is energetically favorable when the polarization energy $(-\mathbf{D} \cdot \mathbf{E})$ of water molecule is considered, as seen in Fig. 4(b) which gives the potential energy $U (= U_{\text{int}} + (-\mathbf{D} \cdot \mathbf{E}))$ of three different ice NTs (5,0), (5,1), and (5,2) at a given electric field ($E = 0.5$, 2, or 4 V/nm). It is noted that $\mathbf{D}$ is the dipole moment per water molecule. The upper, middle, and lower panels in Fig. 4(b) clearly show that the (5,0), (5,1), and (5,2) ice NTs have the lowest potential energy U under $E = 0.5$, 2, and 4 V/nm, respectively. These results reveal that the phase transition behavior observed in Fig. 4(a) is induced by the change of electric field.

A recent MD study shows that hysteresis loops of polarization exist for water inside (9,8), (9,9), and (10,10) SWCNTs at 225 K, wherein the polarization along z -axis was

taken as a time-average for 0.1 ns after annealed for 0.4 ns at each E (in the range of 0–3 V/nm).³¹ In contrast, polarization hysteresis is not observed in Fig. 3(d) in the process of increasing and decreasing E . Here, D_z is averaged over the last 20 ns of four independent 50-ns MD simulations. To examine whether the existence of hysteresis depends on simulation time, we have calculated D_z for a time-average of the last 1-ns of four independent 2-ns MD runs (see Fig. 5). It can be seen from Fig. 5 that hysteresis loops appear. Therefore, the hysteresis loop observed in Ref. 31 might result from the short simulation time used therein.

An important part of the mechanism of solid–solid phase transition is the role of water dipole moment induced by electric field. As water molecule has a permanent dipole moment, in the presence of electric field, water molecules realign and orient collectively along the electric field due to strong electrostatic interactions between water dipoles and electric field. For a type of ice phase, water molecules arrange themselves

FIG. 5. Hysteresis loops of dipole moment D_z per water molecule inside (4,13) SWCNT at 250 K, obtained from a 2-ns MD simulations. D_z at each point is an average of the last 1-ns of four independent 2-ns MD runs.

along an orientation that favors the formation of H-bond network. The formation of H-bond network can be facilitated by the presence of an electric field with appropriate strength. When the strength of electric field becomes greater/smaller, water molecules will realign themselves along electric field and this alignment may disrupt the preformed H-bond network and favor the formation of a new H-bond network (corresponding to a new ice phase). Therefore, E -induced ice NT formation in SWCNT may result from the interplay between strong intermolecular H-bond interactions and collective water dipole orientation along electric field.

Based on the features of P vs T and P vs E curves in Fig. 2, $\langle \Delta \rho^2 \rangle$ vs T curves in Fig. 3(b) and D_z vs E curves in Fig. 3(d), and U_{int} vs E in Fig. 4(a), we can classify the phase transitions of water in (4,13) SWCNT into continuous and discontinuous ones. The liquid–solid continuous transition is mainly driven by temperature and the solid–solid discontinuous transition is driven by electric field.

By varying E and T over a wide range, we can map out the phase diagram of water confined in a (4,13) SWCNT in the E – T plane (Fig. 6). The phase diagram is obtained by performing ~ 1000 independent 5-ns MD runs starting from disordered liquid state. Red and dark green lines in Fig. 6 are the estimation of the melting curve and the ice–ice boundary, respectively. It is found that in the presence of electric field, the melting point of ice NT is slightly higher than that in the absence of electric field. As shown in Figs. 2(a)–2(c) and Fig. 3(b), the transition between disordered liquid and ordered solid phases [(5,0), (5,1), and (5,2) ice NTs] is continuous, consistent with the continuous liquid–solid transition of nanotube-confined water and of nanoplate-confined water reported in previous MD studies.^{23,32} The continuous transition boundary line (red curve) in our E – T phase diagram of SWCNT-confined water (Fig. 6) is similar to the re-

ported continuous liquid–solid transition line at high density in the temperature–density (T – ρ) phase diagram of nanoplate-confined water (the dashed line in Fig. 5 of Ref. 32). As shown in Figs. 3(d) and 4(a), the first-order phase transitions are very sharp and discontinuously changes. On one hand, the two first-order phase boundary lines (dark green) that separate the pentagonal (5,0) phase from the helical (5,1) phase and the helical (5,1) from the (5,2) phase in the low- T range meet with the continuous liquid–solid phase transition line at ~ 295 K, similar to the rhombic–hexagonal ice boundary line in the T – ρ phase diagram of nanoplate-confined water.³² On the other hand, our first-order solid–solid phase transition line terminate at a critical point [$T = 295$ K, $E = 1.25$ V/nm for (5,0) $\leftrightarrow$ (5,1) and $T = 295$ K, $E = 2.25$ V/nm for (5,1) $\leftrightarrow$ (5,2)], similar to the first-order solid–solid (square–pentagonal ice nanotubes) phase transition line in the temperature–pressure (T – P) phase diagram.²³ Taken together, the feature of the phase diagram reported here is an intermediate between the T – P phase diagram of nanotube-confined water and the T – ρ phase diagram of nanoplate-confined water.^{23,32} Figure 6 also demonstrates that water inside (4,13) SWCNT can adopt three different ice NTs under different strengths of electric field. Thus, distinct ice NTs would be attained by cooling the high temperature liquid states and simultaneously applying electric field with appropriate strengths along the SWCNT axis.

We have also investigated the influences of chiralities of SWCNTs ($d \approx 1.2$ nm, length = 3.1 nm) on the structures of ice NTs by performing multiple independent MD runs (50 ns each) on water inside armchair (9,9) ($d = 1.22$ nm) and zigzag (16,0) ($d = 1.25$ nm) SWCNTs at various strengths of electric field ($E = 0, 2, 3$ V/nm). We found that (5,0), (5,1), and (5,2) ice NTs can also be formed in these two SWCNTs implying that the chiralities of SWCNTs with similar diameters do not affect the phase behaviors of ice NTs both in the absence and presence of electric field.

IV. CONCLUSIONS

We have computationally investigated the effects of electric field on the structures and the phase transition of water inside a (4,13) SWCNT ($d = 1.2$ nm). The results show that liquid water can freeze continuously into either pentagonal (5,0) or helical (5,1) and (5,2) ice NTs at low temperature, depending on the strengths of electric field. Remarkably, the helical ones are new ice phases that were not observed previously in (4,13) SWCNT by merely freezing the water.²⁰ Ice–ice phase transition occurs discontinuously as the strengths of electric field change. This solid–solid phase transition may result from the interplay between strong intermolecular hydrogen bonding and collective water dipole orientation along electric field. The phase transitions observed in this study can be classified into two types: liquid–solid transition mainly driven by temperature and solid–solid transition driven by electric field. These results are obtained from the MD simulations of water confined in carbon nanotubes, but similar results should be gotten for other nanopores of comparable geometry and low polarity, such as BN and SiC nanotubes. Our findings that three different ice NTs are obtained at different strengths of electric field suggest that distinct ice NTs would be attained

FIG. 6. Calculated phase diagram of water in (4,13) SWCNT in the E – T plane. Red and green lines are, respectively, the estimation of the melting curve and the ice–ice boundary. The error bars for E and T are respectively 0.1 V/nm and 5 K. The phase diagram is obtained by performing ~ 1000 independent 5-ns MD runs in the E – T ensemble, starting from (E , T) at (0 V/nm, 230 K) and ending up at (4 V/nm, 350 K), with an interval of (0.5 V/nm, 10 K) between two neighboring (E , T). All MD runs start from random arrangement of water molecules. The data in the last 1 ns of each MD run is used for the calculation of the diagram.

by cooling the liquid water and simultaneously applying electric field with appropriate strengths along the SWCNT axis.

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