Evidence of low-density and high-density liquid phases and isochore end point for water confined to carbon nanotube

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Contributed by Joseph S. Francisco, March 7, 2017 (sent for review January 31, 2017; reviewed by Yuko Okamoto and Limei Xu)

Possible transition between two phases of supercooled liquid water, namely the low- and high-density liquid water, has been only predicted to occur below 230 K from molecular dynamics (MD) simulation. However, such a phase transition cannot be detected in the laboratory because of the so-called “no-man’s land” under deeply supercooled condition, where only crystalline ices have been observed. Here, we show MD simulation evidence that, inside an isolated carbon nanotube (CNT) with a diameter of 1.25 nm, both low- and high-density liquid water states can be detected near ambient temperature and above ambient pressure. In the temperature–pressure phase diagram, the low- and high-density liquid water phases are separated by the hexagonal ice nanotube (hINT) phase, and the melting line terminates at the isochore end point near 292 K because of the retracting melting line from 292 to 278 K. Beyond the isochore end point (292 K), low- and high-density liquid becomes indistinguishable. When the pressure is increased from 10 to 600 MPa along the 280-K isotherm, we observe that water inside the 1.25-nm-diameter CNT can undergo low-density liquid to hINT to high-density liquid reentrant first-order transitions.

low-density liquid | high-density liquid | confined water | free energy surface | molecular dynamics simulation

Phase transition is a ubiquitous phenomenon that permeates many disciplines—from science to engineering and nanotechnology. A well-known example of phase transition is the freezing of water, which depending on the external temperature and pressure, can give rise to at least 18 crystalline phases (ice I to ice XVII) (1–4) and 3 amorphous phases (low-density amorphous, high-density amorphous, and very high-density amorphous) (5–12). Molecular dynamics (MD) simulations have revealed unusual phase behavior of supercooled water, including coexistence of two forms of metastable liquid water (i.e., low- and high-density liquid water) (13–17), although this phase behavior is still under debate (18). MD simulations have also predicted that, when water is confined inside isolated zigzag carbon nanotubes (CNTs) with diameters of 1.10, 1.17, 1.25, and 1.33 nm, square, pentagonal, hexagonal, and heptagonal ice nanotubes (INTs), respectively, can be formed (19–22). Other unusual phase behavior predicted from MD simulation includes continuous phase transition between a solid and a liquid in CNTs (19) and existence of multiple solid–liquid critical points (CPs) (22). Indeed, various INT phases, such as pentagonal, hexagonal, heptagonal, and octagonal INTs as well as an octagonal INT filled by a water wire, have been observed experimentally in CNT bundles with different tube diameters (23–25).

Not only can CNTs dramatically change phase behavior of water, but also, they can serve as indispensable tools or media in nanotechnology, such as nanofluidic sensors (26), ferroelectric nanodevices (27), gas nanovalves (28), and coherence resonance in CNT ion channels (29). Recently, a major experimental breakthrough has been reported by Strano and coworkers (30), who observed extreme phase transition temperatures of water confined inside isolated

single-walled carbon nanotubes (SWCNTs) with precisely measured diameters (ranging from 1.05 to 1.52 nm). They found reversible melting of solid water bracketed to 378–424 K for 1.05-nm-diameter SWCNTs and 360–390 K for 1.06-nm-diameter SWCNTs. Not only is it remarkable to see that a 1/100th-nm change in the diameter of SWCNT can incur such a large effect on the melting behavior of water inside, but also, this state of the art experiment represents a testimony of today’s advanced nanotechnology in synthesis of isolated SWCNTs with diameter precision up to two decimal points in nanometers.

In this article, we show that the 1.25-nm-diameter CNT can elevate the phase region of low- and high-density liquid water to near ambient temperature and thereby, may serve as a nanotest tube for future experimental verification of the existence of the two types of liquid water near ambient temperature.

Results and Discussion

Replica Exchange MD Simulation and Computation of Free Energy Surfaces. Computational determination of the temperature–pressure (T – P) phase diagram of water and ice requires simulation approaches that can account for all possible ice and liquid water phases over the range of temperatures and pressures of interest. To this end, an efficient algorithm to compute the free energies of ice and water at any given T and P is required. Herein, we focus exclusively on the simple system—specifically, water confined

Significance

Bulk water is known for its rich phase behavior, including 18 crystalline phases and 3 amorphous phases. Although computer simulations have uncovered coexistence of metastable low- and high-density liquid water below the freezing point, experimental evidence is still lacking because of the predicted coexistence below 230 K. Here, we show simulation evidence that, inside an isolated carbon nanotube with a diameter of 1.25 nm, both low- and high-density liquid water states can be detected near ambient temperature (278–292 K) and above ambient pressure. In the temperature–pressure phase diagram, the low- and high-density liquid phases are separated by hexagonal ice nanotube phase. The latter has already been observed in the laboratory.

Author contributions: K.N., T.K., J.B., J.S.F., K.Y., and X.C.Z. designed research; K.N., T.K., K.Y., and X.C.Z. performed research; J.S.F., K.Y., and X.C.Z. contributed new reagents/analytic tools; K.N., T.K., J.B., K.Y., and X.C.Z. analyzed data; and K.N., J.S.F., and X.C.Z. wrote the paper.

Reviewers: Y.O., Nagoya University; and L.X., Peking University.

The authors declare no conflict of interest.

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This article contains supporting information online at www.pnas.org/lookup/suppl/doi:10.1073/pnas.1701609114/-DCSupplemental.

within a 1.25-nm-diameter CNT. In previous simulation studies, both hexagonal and heptagonal INTs have been observed to form spontaneously within the 1.25-nm-diameter CNT at a relatively high hydrostatic pressure and near ambient temperature (23–26). Even for this 1.25-nm-diameter CNT system, the computation of free energies over a wide range of temperatures and axial pressures is still a highly demanding task. To increase computation speed, we have devised an in-house simulation code that takes advantage of the massive parallelization scheme of graphics processing units (GPUs), such that the free energy computation can be executed with considerably shorter wall time (*Methods*).

Specifically, at any given temperature T and axial pressure P within the region of interest in the T - P phase diagram, the free energy surface $g(E, V; T, P)$ that scans the 2D space of potential energy E and volume V of the system supercell can be computed by combining the GPU-accelerated replica exchange molecular dynamics (REMD) method (31) with the weighted histogram analysis method (WHAM) (*Methods*). We performed three independent series of REMD simulations with different numbers of water molecules ($n = 210, 420$, and 630) (*Methods*). For each REMD simulation in the three series, 96 replicas are used and evenly distributed over two or three GPU boards (each board has more than 1,000 GPU cores), where 96 independent isothermal–isobaric (NPT) MD simulations are carried out concurrently. As

shown in Fig. S1, 96 replicas cover a temperature interval $[T_1, T_M]$ and axial pressure interval $[P_1, P_M]$, with the detailed $[T_1, T_M]$ and $[P_1, P_M]$ datasets in each REMD series given in Table S1. The combination of the $[T_1, T_M]$ and $[P_1, P_M]$ datasets allows us to construct the T - P phase diagram over a wide range of temperatures ($240 \text{ K} \leq T \leq 420 \text{ K}$) and axial pressures ($100 \text{ MPa} \leq P \leq 4,200 \text{ MPa}$) in which rich phase transition behaviors are observed (see below).

The landscapes of the free energy surface along 181 independent isobars are derived, with selected evolving free energy surfaces shown in Movies S1–S14 for 14 isobars and Movies S15–S22 for 8 isotherms. These evolving free energy landscapes provide the crucial free energy minimum information for determining the phase behavior of the confined water. In most cases, the free energy surface exhibits a single minimum (or “mono well”), indicating a single phase (either a liquid or solid phase) at the considered T and P . In some cases, however, the free energy surface exhibits double minima (or “double wells”) corresponding to the coexistence of two phases. Indeed, Fig. 1A (a snapshot in Movie S1 for $T = 280 \text{ K}$) and B (a snapshot in Movie S18 for $T = 280 \text{ K}$) illustrates two examples of the scaled free energy surface at the two-phase coexistence and their projection onto the 2D E - V plane. In the case of Fig. 1A, close examination of the structures of the confined water after equilibration (Fig. 1C and D), the lateral density profile $\rho(r)$, and the oxygen–oxygen pair correlation function in the axial direction

Fig. 1. (A and B) Scaled free energy surface (Left) corresponding to the x point on the relevant T - P phase diagram (Right). (C–E) Snapshots of the confined water or INT inside the 1.25-nm-diameter CNT after the system reaches equilibrium (Left); computed density profiles in the lateral direction (Upper Right) and oxygen–oxygen pair correlation functions in the axial direction (Lower Right). LDL, low-density liquid. Blue and red spheres (in the center of CNT) refer to oxygen atoms; white spheres refer to hydrogen atoms; and yellow lines refer to hydrogen bonds.

Fig. 3. Quantitatively constructed T - P phase diagram including two liquid phases (low- and high-density liquid) and three solid phases [INT(6,0), INT(6,0)pf, and INT(7,0)f] for water inside the isolated 1.25-nm-diameter CNT. Other notable features in the T - P phase diagram include two solid-solid-liquid TPs (TP1 and TP2), one solid-liquid CP, and one IEP. The INT(6,0) intrusion region looks like a peninsula surrounded by different liquid regions, where the high-density liquid region is located above the peninsula (upper bay region) and the low-density liquid region is located below the peninsula (lower bay region). HDL, high-density liquid; LDL, low-density liquid.

the INT(6,0) phase and the evidence for two liquid phases for the model water inside the isolated 1.25-nm-diameter CNT (i.e., low- and high-density liquid). To our knowledge, the existence of a solid–liquid IEP has not been observed in bulk matter. According to the Clausius–Clapeyron relation, because the local slope $dP/dT|_{\text{IEP}}$ is infinite, the volume change from INT(6,0) to liquid water inside the 1.25-nm-diameter CNT should be zero at the IEP. Because the volume change near the IEP is very small, the phase transition from INT(6,0) to the liquid water inside the 1.25-nm-diameter CNT could be either weakly first order or continuous. To determine the order of the phase transition near the IEP, we use the finite size scaling method to compute two Challa–Landau–Binder (CLB) parameters: the volume parameter Π_V and the entropy parameter Π_S (*Methods*). Fig. S3 shows the pressure dependence and the gradual convergence of $\Pi_V^{\min}$ and $\Pi_S^{\min}$ in the limit of $N \rightarrow \infty$ within the pressure range

100 MPa $< P < 500$ MPa. Indeed, $\Pi_V^{\min}$ converges to the value of two/three for P ranging from 180 to 400 MPa. This result is consistent with the continuous transition region predicted previously (25). However, $\Pi_S^{\min}$ does not converge to the value two/three for $P < 0.5$ GPa, indicating that the phase transition from INT(6,0) to a liquid water near the IEP is very weakly first order. Below the IEP, a retracing melting line arises (Movies S1–S3); as a result, the INT(6,0) protrusion region in the T – P phase diagram juts out as a “peninsula” surrounded by two different liquid regions, where the high-density liquid region is located above the peninsula (“upper bay”) and the low-density liquid region is located below the peninsula (“lower bay”). The two liquids are separated by the solid INT(6,0) and INT(6,0)pf phase regions. Therefore, the confined water will undergo liquid to solid to liquid reentrant first-order transitions along the 280-K isotherm line (Movie S18) as P increases from 10 to 600 MPa. Beyond the IEP, the low- and high-density liquids merge into a single-liquid water phase in CNT (Movie S20). By contrast, for bulk supercooled water, the low- and high-density liquids are predicted to arise below 230 K for model water (16–21), and the two metastable liquids are separated by the first-order liquid–liquid phase transition line and terminated at the liquid–liquid CP. Between the two TPs TP1 and TP2, the melting curve between the high-density liquid and the INT(6,0)pf exhibits a negative slope (Movies S4–S6), a feature akin to the melting curve of bulk hexagonal ice I_h . This feature is also consistent with the Clausius–Clapeyron relation, because the high-density liquid phase in CNT has an average density greater than that of the INT(6,0)pf. That is, when the high-density liquid freezes into the INT(6,0)pf phase in CNT at 500 MPa, its volume would expand, such as in the case of the freezing of bulk liquid water into the hexagonal ice phase I_h .

Last, we confirm the existence of the solid-liquid CP (CP in Fig. 3) that terminates the melting line of INT(7,0)f as predicted by Mochizuki and Koga (22). [Movies S8–S12](#) and [S21](#) depict the scaled free energy surface when crossing the melting line from 700 MPa to 3.0 GPa. At $P = 700$ MPa (Fig. 2B and [Movie S8](#)), the free energy surface exhibits a clear double-minimum feature, with the two minima separated by a free energy barrier. With the increase of P along the melting line, the free energy barrier gradually decreases and eventually disappears at and beyond $P = 3.0$ GPa ([Movie S14](#)), where the two minima merge into a single minimum (Fig. 4A). Hence, beyond the CP (383.3 K and 2.95 GPa), the free energy surface indicates a continuous phase transition from the liquid to the INT(7,0)f phase in CNT ([Movies S13, S14, and S22](#)). In Fig. 4B, we plot the computed CLB parameters, $\Pi_{\nu}^{\min}$ and

Fig. 4. (A) Scaled free energy surface (*Left*) corresponding to the x point on the relevant T - P phase diagram (*Right*). (B) Computed CLB parameters along the melting line between the INT(7,0)f and liquid phases for water confined inside the 1.25-nm-diameter CNT in the hydrostatic pressure range from 1.0 to 2.6 GPa.

$\Pi_S^{\min}$, in the pressure range 1 GPa < P < 4.2 GPa (Methods). The $\Pi_V^{\min}$ and $\Pi_S^{\min}$ parameters gradually converge to the value of two/three at $P \sim 2.0$ and 2.95 GPa, respectively. This result indicates that the solid-liquid CP exists near 2.95 GPa.

Conclusions

On the basis of the entire landscape of free energy surfaces over the T - P phase diagram, we show that, using an isolated 1.25-nm-diameter CNT as a nanoscale medium to confine water, rich and even unique phase behaviors of the confined water can be promoted near ambient temperature—notably, the existence of an IEP, a retracing melting line, and low-density and high-density liquids. None of these phase behaviors have been experimentally observed in bulk materials. As pointed above, in bulk supercooled water, the low- and high-density liquids are predicted to coexist below 230 K, making the experimental verification nearly impossible because of the well-known “no man’s land” problem (8, 12). By contrast, for the confined water in CNTs, the hexagonal INT(6,0), the heptagonal INT(7,0), and the octagonal INT containing a single-file water chain have already been observed in the laboratory (24–26). Thus, confirmation of the IEP, the retracing melting line, and the low- and high-density liquid water in the 1.25-nm-diameter SWCNT near ambient temperature is readily tested, especially in light of the recent breakthrough in detection of extreme phase transition temperatures of water confined inside isolated SWCNTs with precisely measured diameter up to two decimal points in nanometers (30).

Methods

GPU Implementation. We implemented an REMD (see below) simulation to run on multiple GPUs (31). Ninety-six replicas involved in the REMD simulation are distributed on multiprocessors of GPUs manufactured by NVIDIA Corporation, each having 192 or 128 cores in Kepler and Maxwell architecture. Each core in the multiprocessors executes time integrations and force calculations for the molecules. We used either two or three GPUs to perform the REMD simulation. GPUs and the host central processing unit (CPU) iterate two processes. (i) GPUs execute 1-ps MD simulations of replicas and send the obtained data (physical properties) of replicas to the host CPU. (ii) The host CPU executes a trial of exchange of the temperature-pressure conditions between two replicas by calculating the probability on the basis of obtained data (enthalpy) associated with the two replicas.

Simulation Models and Systems. The simulation system consists of the number of water molecules (N) confined inside an SWCNT, where the 1D periodic boundary condition is applied in the axial direction (z). Here, $N = 210, 420$, and 630 in three independent series of simulations. The plots shown in Figs. 1–3 are based on the simulation results for $N = 420$. The diameter of the SWCNT is fixed to be 12.5 Å. The potential of TIP4P (here TIP4P refers to transferable intermolecular potentials 4-point charge) model water (32) multiplied by the switching function that smoothly becomes zero at the distance of 8.655 Å is used to describe the water–water interaction. Interaction between oxygen and carbon atoms is described by the 12–6 Lennard-Jones potential function integrated over the cylindrical 1.25-nm-diameter CNT (under the assumption that carbon atoms are distributed uniformly). The temperature and axial pressure ($P = P_{zz}$) are controlled by the extended Nosé–Poincaré thermostat and Andersen barostat, respectively (33).

REMD Simulations. The REMD simulation consisting of $M = 96$ independent constant P and constant T MD simulations (each in a replica) with different T - P conditions is performed (34) for the previously described system of confined water. A schematic of the exchange of T - P conditions among neighboring replicas with either the same pressure condition or the same temperature condition is shown in Fig. S1. More specifically, each REMD simulation entails $M = M_T \times M_P = 96$ simulations under M_P pressure conditions, whereas each pressure condition entails M_T temperature conditions. The T - P conditions in all M replicas are within $[P_1, P_M]$ and $[T_1, T_M]$ intervals. Detailed $[P_1, P_M]$ and $[T_1, T_M]$ intervals for each series of REMD simulations are shown in Table S1. The exchange is enforced, alternately, for all neighboring replicas with M_T temperature conditions but the same pressure condition and then, all neighboring replicas with M_P pressure conditions but the same temperature condition. In our simulations, the exchange of T - P conditions between the two neighboring replicas is implemented every 1 ps in

accordance with detailed balance: the probability for the exchange, $P_{\text{exc}}(i, j)$, between the i th and j th replicas is given by

$$P_{\text{exc}}(i, j) = \min(1.0, e^{-\Delta}), \Delta = (\beta_j - \beta_i)(E_i - E_j) + (P_j\beta_j - P_i\beta_i)(V_i - V_j), \quad [1]$$

where $\beta = 1/k_B T$ (k_B is the Boltzmann constant), E is the potential energy of the replica, and V is the volume of the replica supercell. The exchange of T - P conditions between neighboring replicas enables the entire system (M replicas) to sample the 2D E - V space without becoming trapped in a metastable state (typically solid state) at low temperatures.

WHAM. The probability distribution in E - V space in constant P and constant T ensemble $P(E, V; T, P)$ is given by

$$P(E, V) = \frac{1}{Z(T, P)} n(E, V) e^{-\beta(E+PV)}, \quad [2]$$

where $n(E, V)$ is the density of states in E - V space, and $\beta = 1/k_B T$. The distribution function $Z(T, P)$ is given by

$$Z(T, P) = \iint n(E, V) e^{-\beta(E+PV)} dE dV. \quad [3]$$

The ensemble average of any mechanical or thermodynamic property X is obtained as

$$\langle X \rangle_{T, P} = \frac{1}{Z(T, P)} \iint X(E, V) n(E, V) e^{-\beta(E+PV)} dE dV. \quad [4]$$

To compute $n(E, V)$, the WHAM is used (35). Specifically, from the REMD simulation, accurate histograms $H(E, V; T, P)$ in 2D E - V space under given T - P conditions can be recorded, where an E - V pair corresponds to one of the states that the confined water can assume and is thus counted once in the histogram $H(E, V; T, P)$. Using the obtained histogram data $H(E, V; T, P)$ and the sum of the histograms over 2D E - V space, $h(T, P) = \sum_{E, V} H(E, V; T, P)$, at given T - P conditions, $n(E, V)$ can be computed via iterating the following two equations:

$$n(E, V) = \frac{\sum_{T, P} H(E, V; T, P)}{\sum_{T, P} h(T, P) e^{-\beta(E+PV)+G(T, P)}}, \quad [5]$$

$$e^{-G(T, P)} = \sum_{E, V} n(E, V) e^{-\beta(E+PV)}, \quad [6]$$

where $G(T, P)$ is the Gibbs free energy of the confined water system. The isobaric heat capacity $C_P(T)$ of the system and the scaled free energy surface $g(E, V; T, P)/k_B T$ at the given T - P conditions are computed via the following equations:

$$C_P(T) = \frac{\langle (E+PV)^2 \rangle_{T, P} - \langle E+PV \rangle_{T, P}^2}{k_B T^2} + 3Nk_B, \quad [7]$$

$$\frac{g(E, V; T, P)}{k_B T} = -\ln n(E, V) e^{-\beta(E+PV)}. \quad [8]$$

Structural Analysis. To compute the oxygen–oxygen radial distribution function along the CNT direction $g_{O-O}(z)$ and the lateral density distribution $\rho(r)$ at given T - P conditions, we used snapshots obtained from REMD simulations. Parameter $g_{O-O}(z)$ is computed on the basis of the equation

$$g_{O-O}(z) = \frac{\langle n_{\text{axial}}(z) \rangle}{2Adz}, \quad [9]$$

where $\langle n_{\text{axial}}(z) \rangle$ is the average number of oxygen atoms within the cylindrical layer from z to $z + dz$ and from $-z$ to $-(z + dz)$, and A is the local area of the base of the cylindrical layer within the CNT. Parameter $\rho(r)$ is computed according to the equation

$$\rho(r) = \frac{m \langle n_{\text{radial}}(r) \rangle}{2\pi r dr L_z}, \quad [10]$$

where $r = \sqrt{x^2 + y^2}$, m is the water molecule mass, $\langle n_{\text{radial}}(r) \rangle$ is the average number of oxygen atoms within the circular ring from r to $r + dr$ in the lateral direction, and L_z is the length of the supercell of the system in the axial direction.

Finite Size Scaling Analysis of Volume and Entropy to Determine Order of Transition. We performed finite size scaling of the volume and entropy over a wide P range to examine the order of the transitions near the IEP and the CP. To this end, we used two CLB parameters: $\Pi_V = 1 - \langle V^4 \rangle / 3 \langle V^2 \rangle^2$ of the volume and $\Pi_S = 1 - \langle S^4 \rangle / 3 \langle S^2 \rangle^2$ of the entropy of the system [$S(E, V) = \ln n(E, V) e^{-(E+PV)/k_B T}$] (36). The CLB parameters verify the bimodality of the distribution function $Q(\alpha)$, where $\alpha = V$ or S . The minimum of the CLB parameter $\Pi^{\min}$ along an isobar approaches the value of two/three linearly with $1/N$ as $N \rightarrow \infty$ if $Q(\alpha)$ is unimodal, whereas $\Pi^{\min}$ approaches another limiting value less than two/three if $Q(\alpha)$ is bimodal. We compute $\Pi^{\min}$ for the system in the pressure range from 100 to 2,600 MPa and $N = 210, 420$, and 630. At the continuous phase transition, the distribution of both the volume and entropy should be unimodal in the limit of $N \rightarrow \infty$.

REMD Simulation with Another Two Water Models to Test Model Dependence. To examine whether the existence of two types of liquid water in the CNT is dependent on specific water model, we performed two independent series of REMD simulations with the TIP3P and TIP5P models. For the TIP5P model, the REMD simulation consists of 128 independent replicas with different T - P conditions within the range of 260 K $< T < 310$ K and 100 MPa $< P < 500$ MPa. Again, the solid-liquid phase transitions between hexagonal INT and liquid phases were observed. [Movie S23](#) shows the evolution of the free energy

surface along an isotherm of $T = 303.1$ K (comparable with the room temperature) for $P = 100$ –500 MPa. The low-density liquid to hexagonal INT to high-density liquid phase transitions were observed. The separation of two liquid water phases by the hexagonal INT is clearly seen as for the case of using the TIP4P model. For the TIP3P model, the number of independent replicas is 32, and the T - P conditions are 260 K $< T < 310$ K and 60 MPa $< P < 140$ MPa. [Movie S24](#) shows the evolution of the free energy surface along an isobar of $P = 100$ MPa for $T = 260$ –310 K. Solid-liquid phase transition between hexagonal INT and low-density liquid in the 1.25-nm-diameter CNT was observed. We, therefore, conclude that the unique phase behavior of existence of two types of liquid water inside the 1.25-nm-diameter CNT is quite generic, regardless of the choice of water model in the simulation.

ACKNOWLEDGMENTS. This work was supported by Ministry of Education, Culture, Sports, Science, and Technology (MEXT) in Japan Grant-in-Aid for Research Activity Start-Up 25889054. K.N. is supported, in part, by an MEXT in Japan Grant-in-Aid for the Program for Leading Graduate Schools. X.C.Z. is supported by National Science Foundation Grants CHE-1500217 and CBET-1512164, a fund from the Beijing Advanced Innovation Center for Soft Matter Science & Engineering for the summer visiting scholar, and the University of Nebraska Holland Computing Center.

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