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Liquid to quasicrystal transition in bilayer water

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The phase behavior of confined water is a topic of intense and current interest due to its relevance in biology, geology, and materials science. Nevertheless, little is known about the phases that water forms even when confined in the simplest geometries, such as water confined between parallel surfaces. Here we use molecular dynamics simulations to compute the phase diagram of two layers of water confined between parallel non hydrogen bonding walls. This study shows that the water bilayer forms a dodecagonal quasicrystal, as well as two previously unreported bilayer crystals, one tiled exclusively by pentagonal rings. Quasicrystals, structures with long-range order but without periodicity, have never before been reported for water. The dodecagonal quasicrystal is obtained from the bilayer liquid through a reversible first-order phase transition and has diffusivity intermediate between that of the bilayer liquid and ice phases. The water quasicrystal and the ice polymorphs based on pentagons are stabilized by compression of the bilayer and are not templated by the confining surfaces, which are smooth. This demonstrates that these novel phases are intrinsically favored in bilayer water and suggests that these structures could be relevant not only for confined water but also for the wetting and properties of water at interfaces. © *2010 American Institute of Physics*. [doi:10.1063/1.3499323]

I. INTRODUCTION

Water has a rich phase diagram with at least 15 ice crystals and two glasses, which suggest the existence of two distinct liquids.[1,2] Confinement introduces new thermodynamic variables, resulting in even more complex phase behavior that involves a wealth of new ice polymorphs.[3–8] Water confined between two parallel plates can form *n*-layered ice polymorphs in which each of the layers is fully tiled with hexagons. Of the *n*-layered forms of hexagonal ice, only the bilayer ($n=2$) satisfies the ice rules for all the water molecules.[6] This hexagonal bilayer ice (H) has been shown to be the stable crystal of a water bilayer in hydrophobic and mildly hydrophilic confinement at lateral pressures up to 0.2 GPa.[4,6,9,10]

In H, water forms two layers of planar hexagons in registry and the angles between water molecules depart strongly from the preferred 109.5°: each water molecule forms 120° in-plane angles and 90° out-of-plane angles with its neighbors. These distorted angles allow each molecule to form hydrogen bonds with four neighbors. Despite its nontetrahedral angles, H has the highest melting temperature (T_m) of the hexagonal *n*-layered ices.[6] The T_m of H is even higher than the T_m of bulk hexagonal ice, Ih.[6] Interestingly, the structure of H resembles a two-dimensional, flat, projection of Ih.

Similar to bulk Ih, H melts to a disordered liquid (L) of higher density.[4,6] A H crystal with defects has been observed on cooling of L at room pressure and ascribed to a distinct amorphous phase, a bilayer analog of low-density amorphous ice (LDA).[11] Nevertheless, it was later determined that this defective H, in which five- and seven-membered water rings replace pairs of six-membered rings found in H, has the same T_m as crystalline H.[12] This strongly suggests that the phase classified as an amorphous solid may actually be a defective form of H that results from the difficulty in annealing water crystals with atomistic simulations, and not a distinct phase of bilayer water. It is, therefore, an unresolved issue whether a water bilayer presents polyamorphism, as bulk water does, what phases a water bilayer forms under pressure, and whether the analogy between bilayer H and Ih extends to other phases of bilayer and bulk water. These are the questions addressed by this study.

We use molecular dynamics simulations to investigate the phase behavior of water confined between two parallel, smooth Lennard-Jones (LJ) 9-3 walls at an interplate distance that accommodates two layers of water molecules. We employ a smooth, atomless surface instead of an atomistic one to ensure that the structures obtained are inherent to water and not templated by the structure of the interface. We consider two force fields for water: (i) the atomistic model that best reproduces the phase diagram of bulk water, TIP4P/ice,[13] and (ii) the monatomic water model mW that represents each water molecule as a single particle that interacts through short-ranged potentials that mimic the effect of hydrogen bonds.[14] mW reproduces the structure and phase relations of liquid water, low-density amorphous ice, and ice in both bulk and confined geometries.[6,15,16] The main advantage of the mW model is its computational efficiency; simulations with mW take less than 1% of the computing time of the atomistic simulations, making it possible to determine a large number of points in the phase diagram. A second ad-

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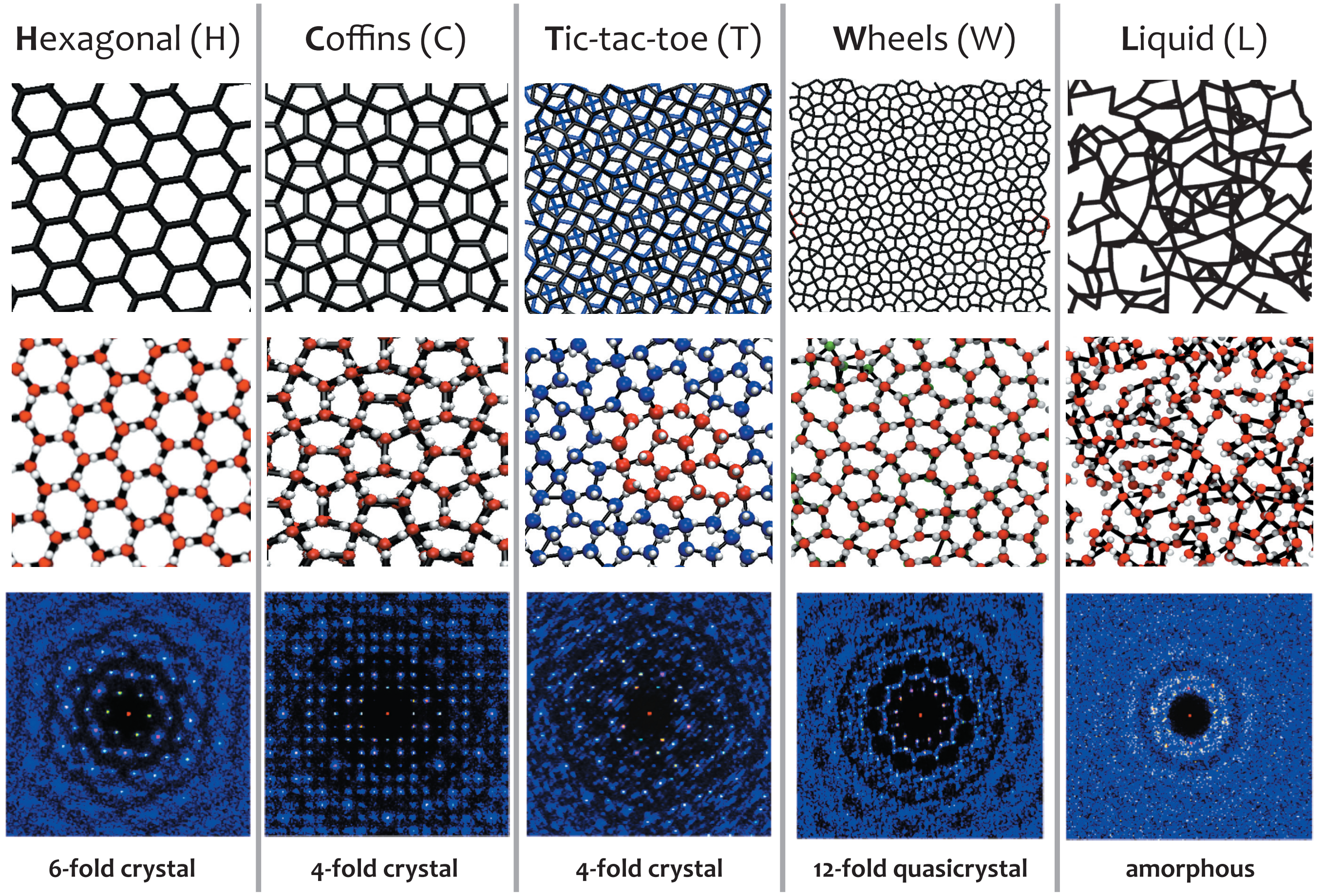

FIG. 1. Top view of the phases of bilayer water. Upper row: coarse-grained mW structures; lines connect molecules within the first neighbor shell. The lower layer is displayed in blue for the tic-tac-toe (T) crystal and in red for the hexagonal (H), coffins (C), and energy-minimized wheels (W) where it is barely seen because the two layers are in registry. The liquid L presented in the picture is at $p_L = 0.1$ MPa and $T = 320$ K; the change in structure of L at 0.51 GPa on cooling can be appreciated in the movie (Ref. 19). Middle row: the same phases of bilayer water, as obtained with the TIP4P/ice atomistic model (O as red balls and H as smaller white balls). The oxygen atoms of the lower layer of the atomistic H, C, and W are shown in green, but are only noticeable in the defects caused by misaligned water molecules in W. Only the lower layer is shown for the (defective) atomistic T, to emphasize the repeating motif (red oxygen atoms) within one of the layers (other oxygen atoms shown in blue). Lower row: diffraction patterns of each of the phases (enlarged in the SM) (Ref. 19) that show that H, C, and T are crystals, W is a dodecagonal quasicrystal and L is a liquid.

vantage is that by comparing the phase diagram and structures predicted by mW and TIP4P/ice we can elucidate whether the explicit introduction of hydrogen atoms is necessary to describe the phase behavior of confined water.

II. METHODS

Model. The system consisted of two layers of water molecules confined between two parallel walls at a fixed interplate distance of 8.5 Å, interacting with water through a Lennard-Jones 9-3 (LJ 9-3) potential with $\sigma = 3$ Å and $\varepsilon = 0.5$ kcal mol^{-1}.[6] Simulations were performed in the isothermal-isostress Np_LT ensemble, where p_L is the lateral pressure. Temperature and pressure were controlled with a Nose–Hoover thermostat and barostat, with relaxation times of 2.5 and 12.5 ps, respectively. For systems with mW water,[14] the number of confined molecules ranged from 1377 to 1711 (corresponding to linear cell dimensions of about 85 Å). The atomistic systems contained 216–432 water molecules modeled with the TIP4P/ice force field.[13]

Quenching simulations. All quenching simulations from the high-temperature liquid L were performed at constant lateral pressure p_L. L was continuously cooled at a rate of 1 K ns^{-1} for mW, and at least five independent cooling simulations were performed for each pressure. For TIP4P/ice the ramp consisted of temperature jumps of 10 or 5 K followed by equilibration for 8–40 ns.

Phase diagrams. Melting temperatures between the liquid L and low temperature structures were determined using the phase coexistence method[17] following the protocols of Ref. 6. For atomistic structures of the two phases we name *wheels* and *tic-tac-toe*, the melting temperature was instead estimated as the lowest temperature at which the one-phase system decomposes to L after 15 ns waiting time.

Ring statistics. We defined two water molecules to be connected if they are at a distance within the first peak of the oxygen-oxygen radial distribution function. The rings formed by connected water molecules were found using the code by Matsumoto *et al.* in Ref. 18. The statistics represent averages over simulation trajectories of the number of rings in each layer.

Alignment between the two layers. The fraction of molecules in registry between the two layers was computed considering molecules in different layers to be aligned if their projections in the $x-y$ plane are within a distance of 0.8 Å, to account for thermal fluctuations. The values of alignment reported resulted from averaging over an ensemble of configurations of the corresponding phase at a given T and p_L.

Diffraction patterns. The diffraction patterns of the bilayer phases were computed from the intensity of the static structure factors for each phase,

$$S(\vec{q}) = \frac{1}{N}\left\langle \left| \sum_{j=1}^{N} \exp(-i\vec{q}\vec{r}_j) \right|^2 \right\rangle .$$

Diffusion. Diffusion coefficients of bilayer water were computed from the mean square displacement parallel to the confining planes in up to 150 ns equilibrium Np_LT simulations, $\langle x(t)^2\rangle + \langle y(t)^2\rangle = 4Dt$, at the temperatures indicated in Fig. 4.

III. COMPRESSION FAVORS WATER PHASES BUILT FROM PENTAGONS

The structures reported here were spontaneously produced through quenching bilayer liquid water at lateral pressures p_L of up to 0.5 GPa. Cooling of bilayer liquid (L) water exclusively yields hexagonal bilayer ice (H) up to $p_L = 0.3$ GPa for mW and 0.2 GPa for TIP4P/ice. Three novel phases that we name coffins (C), wheels (W), and tic-tac-toe (T) are obtained from quenching L at pressures exceeding those listed directly above. Figure 1 displays the five phases of bilayer water and their diffraction patterns: L is amorphous, H, C, and T are crystals, and W is a quasicrystal, the first ever reported for water.

Five-membered rings of water molecules predominate in the high-pressure phases T, C, and W. Pentagons are not unexpected at high-pressure as, first, they are denser than hexagons and, second, regular pentagons have internal angles of 108°, close to the tetrahedral 109.5° favored by water. Regular pentagons, however, cannot tile two-dimensional (2D) space. *Coffins*, obtained from quenching simulations at 0.5 GPa with the mW model, is a bilayer ice crystal composed of two layers of water molecules in registry, with each layer tiled exclusively by five-membered hydrogen-bonded rings. In geometry this 2D structure is referred to as the (3^2.4.3.4) Archimedean tiling or Cairo pentagonal tiling. The coffins has fourfold rotational symmetry. Similar to hexagonal bilayer ice, all molecules in C are four-coordinated and follow the ice rules; however, unlike H, coordination is maintained through a slight nonplanarity. Two coordination environments are present in C: a water molecule may have three in-plane hydrogen bonds and a fourth out-of-plane hydrogen bond or it may have four in-plane bonds. The front and side views of the coffins are shown in Fig. 1 and supplementary material (SM),[19] respectively. Coffins is the first example of a quasi-2D ice polymorph exclusively tiled by (irregular) pentagons. A recent report indicates that 1D chains of water pentagons form on a Cu surface, with the pentagons templated by the position of the Cu atoms.[20] In the present work, the C crystal is favored at high-pressure by its higher density, not by the structure of the confining surfaces, which are smooth.

The enthalpy difference between C and H at 0.1 MPa and 100 K is just 0.88 kJ/mol for TIP4P/ice and 0.83 kJ/mol for mW. This enthalpy difference between H and C is comparable to the thermal energy at 100 K and about one-fourth of the difference between the enthalpy of H and L at the same pressure (Table I). As the water-water distances and number of hydrogen bonds are the same for C and H, the small gap in energies reflects the minor differences in water-water-water angles between the two crystals and suggests that C could be made more stable than H at room pressure through modest changes in the interactions with the confining interfaces. This cannot be achieved by changing the interaction strength ε of the smooth LJ walls for which the wall-water energy depends only on the distance perpendicular to the wall plane; to reverse the relative stabilities of C and H the walls must have structure. In a separate communication,[21] we show that the coffins also form between atomically structured surfaces, even when these sur-

TABLE I. Phase change volume, enthalpy, and entropy from the low temperature phases to liquid (L).

Water model	p_L, T_m (GPa, K)	Phase transition	ΔV (cm^3 mol^{-1})	ΔH (kJ mol^{-1})	ΔS (J K^{-1} mol^{-1})
mW	0, 297.5	H→L	−0.331	3.38	11.4
mW	0.46, 237.5	H→L	−1.39	1.73	7.1
mW	0.41, 242.5	T→L	0.555	1.48	6.1
mW	0.51, 250	T→L	0.455	1.66	6.6
mW	0.41, 240	C→L	0.151	1.25	5.2
mW	0.51, 242.5	C→L	0.085	1.13	4.7
mW	0.41, 235	W→L	−0.063	0.79	3.4
mW	0.51, 230	W→L	−0.120	0.49	2.1
TIP4P/ice	0.0, 317.5	H→L	−1.303	4.02	12.7
TIP4P/ice	0.2, 267.5	H→L	−3.265	2.22	8.3
TIP4P/ice	0.51, 300[a]	[d]T→L[b]	~0	2.1	7.0
TIP4P/ice	0.51, 282.5[a]	C→L	0.5	3.0	10.8
TIP4P/ice	0.3, 265[a]	C→L	1.2	2.7	10.1
TIP4P/ice	0.3, 270[a]	W→L	~0	1.7	6.2
TIP4P/ice	0.5, 270[a]	W→L	−0.2	1.6	5.3

[a] One phase decomposition temperature.

[bd] T indicates defective T crystal.

faces do not have the symmetry of the C phase, and that tuning of the strength of the water-surface interactions can result in a higher stability of the coffins with respect to the hexagonal bilayer without application of an external lateral pressure (i.e., at $p_L = 0$).

Tic-tac-toe (T), a bilayer ice that contains pentagons and hexagons, is the highest density bilayer ice found by cooling liquid bilayer water at p_L up to 0.5 GPa. The motif that repeats in each layer of T is highlighted in the lower panel of Fig. 1. The two layers in T are identical and, unlike H and C, not in registry with each other. The layers in the T crystal are unbuckled[19] (nonplanar) with the same coordination environments as the C crystal. This buckling leads to an increase in the pressure in the direction perpendicular to the plates, p_{zz} (p_{zz} for all phases at interplate distance D=8.5 Å are summarized in the SM).[19] As with C and H, all water molecules in T are four-coordinated. We have not been able to obtain a defect-free T crystal. Nevertheless, its diffraction pattern (Fig. 1 and SM) (Ref. 19) confirms the crystallinity of T and shows that it has fourfold rotational symmetry.

IV. BILAYER WATER FORMS A DODECAGONAL QUASICRYSTAL

Cooling the liquid L at $p_L > 0.3$ GPa for mW water or at $p_L > 0.25$ GPa for TIP4P water produces the phase that we call wheels (W) (Fig. 1). Five-membered rings dominate the structure of W, accounting for 86% of the counted rings. The two layers of the wheels are more than 90% in registry at 230 K, and their inherent (i.e., energy-minimized) structures are 100% in registry. In the plane of confinement, W has well-defined medium-ranged order (the wheel motif, similar to the one present in each layer of the T crystal). A similar ring structure is apparent in both W and C: the edge-sharing pentagonal prism (ESPP) water 20mer formed by a bilayer of three edge-sharing pentagons. This structure has been predicted by high-level *ab initio* calculations to be most stable for the $(H_2O)_{20}$ cluster.[22] The ESPP comprises three-fourths of an individual coffin. Full coffins also appear, sparsely, in the wheels. The water molecules in the quasicrystal have an average coordination of 4.4.

The diffraction pattern of wheels displays 12-fold rotational symmetry: W is a dodecagonal quasicrystal. Quasicrystals are phases with long-range orientational order but no translational periodicity.[23,24] They present rotational symmetries forbidden to crystals, such as five-, eight-, ten- or twelve-fold symmetries. One-component quasicrystals have never been found in nature or synthesized in the laboratory. In simulations, single component three-dimensional quasicrystals have been reported for the isotropic nonmonotonic Dzugutov potential,[25] a two-dimensional quasicrystal with fivefold symmetry has been reported for the square well potential,[26] and a decagonal and two dodecagonal quasicrystals have been obtained for another isotropic nonmonotonic potential, the 2D Lennard-Jones-Gaussian (LJG) model.[27] Wheels is the first quasicrystal ever reported for water or for a single component system modeled with a potential parametrized to reproduce the properties of a specific substance.

Interestingly, each layer of the wheels seems to have the same structure as the dodecagonal quasicrystal produced by the 2D LJG system with parameters $r_G = 1.42$, $\varepsilon = 1.8$, and $\sigma^2 = 0.041$.[27] While the LJG model produces a truly 2D quasicrystal (with a single layer of particles and no interfaces), the water quasicrystal found in this study is a confined bilayer. It is noteworthy that this LJG potential presents a double-well (or rather a well with a shoulder at short distances) that is also characteristic of isotropic models of water.[28]

Dodecagonal quasicrystals in 3D are always periodic in one of the dimensions. In the wheels, the crystalline order occurs in the direction perpendicular to the confining plane, through the alignment of the two layers of water. Could water form a 3D dodecagonal quasicrystal by stacking layers of wheels? In previous work,[6] we demonstrated that a water bilayer optimizes water-water interactions by maximizing the number of four-coordinated molecules when compared with other *n*-layered structures, thus we do not expect a stacking of wheels to be a stable (or even metastable) phase of water.

V. BILAYER AND BULK WATER HAVE ANALOGOUS PHASE DIAGRAMS

In this section we discuss the relative stability of the phases of bilayer water as a function of temperature and lateral pressure and draw analogies between the phase behavior of bilayer and bulk water. The phase equilibria between the high-temperature liquid L and the low temperature phases, H, T, C, and W, for the mW and TIP4P/ice models were computed through the phase coexistence method.[17] Figure 2 presents the resulting $T - p_L$ phase diagrams and Table I summarizes the volumes, enthalpies, and entropies associated with the phase changes.

The shape of the phase diagrams and the relative stabilities of the bilayer phases are the same for the coarse-grained and atomistic water models: H is the stable low-pressure ice polymorph and the denser crystal T becomes the stable bilayer ice upon compression. The C crystal and W quasicrystal are metastable, although both models show that around the H-T-L triple point pressure the stability of wheels is close to that of the bilayer crystals. We find that cooling of bilayer water around 0.35 GPa for mW and 0.3 GPa for TIP4P/ice exclusively yields the metastable *wheels* quasicrystal. The direct transformation of the liquid to the metastable quasicrystal indicates that the kinetic barrier for the nucleation of W from L is relatively small (nucleation temperatures for H, C, T, and W are signaled as stars in Fig. 2). The liquid to *wheels* transition is analyzed in Sec. VI.

There are several interesting analogies between the phase diagram of bilayer water shown in Fig. 2 and that of bulk water. As we noted earlier, bilayer hexagonal ice H looks like a 2D projection of bulk hexagonal ice Ih. H, like Ih, has a negative melting slope $dT/dp = \Delta V/\Delta S$ due to the negative ΔV upon melting. mW underestimates the ΔV leading to a higher H-L-T triple point pressure, around 0.45 GPa with the mW model, compared to the 0.2 GPa predicted by TIP4P/ice (mW similarly underestimates ΔV for bulk Ih/liquid[14]). As we have previously shown for mW water in Ref. 6, we find that T_m of H is considerably larger than T_m of hexagonal ice Ih, the stable phase of bulk ice. For the atom-

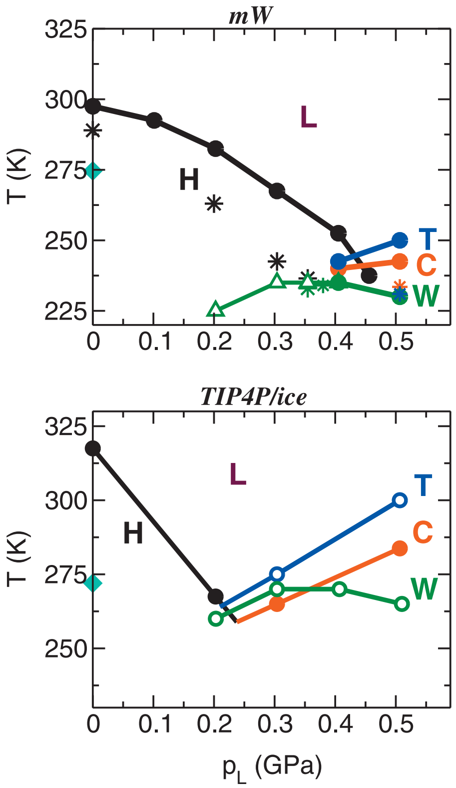

FIG. 2. Phase diagrams of bilayer water computed with the mW model (top) and TIP4P/ice model (bottom). Filled circles indicate equilibrium coexistence between the liquid L and hexagonal bilayer ice (black), coffins bilayer ice (red), tic-tac-toe bilayer ice (blue), and wheels quasicrystal (green). Empty circles indicate one phase transformation temperatures to L and green triangles signal the limit for the W to H transformation. Stars show the freezing temperatures (color same as for the equilibrium symbols). Lines are added to assist the visualization of the phase diagrams and may not represent the actual slopes $dT/dp=\Delta V/\Delta S$ of Table I. Filled cyan diamonds indicate the melting temperature of bulk hexagonal ice at 0.1 MPa in each model, considerably lower than that of hexagonal bilayer ice.

istic bilayer, the T_m of the H bilayer ice is 45 K higher than for bulk Ih, thus predicting that hexagonal bilayer ice is stable under ambient conditions. The origin of this unusually high melting temperature is discussed in Ref. 6.

Tic-tac-toe, the stable high-pressure ice polymorph, may be related to bulk ice III, which is the stable phase of bulk ice from 0.2 to 0.35 GPa. The pentagons in T are twisted out of the plane, a rare characteristic shared with ice III. Coincidentally, the H-L-T triple point for TIP4P/ice water, around 265 K and 0.2 GPa, is very close to the triple point for bulk Ih-liquid-III, 231.8 K and 0.2955 GPa of that model.[13] In experiments, Ih-liquid-III coexistence occurs at 251.16 K and 0.2090 GPa. We note here that the entropy difference between L and T with the TIP4P/ice model may be underestimated in Table I, as we were unable to anneal a defect-free atomistic T crystal.

It is interesting to note that the in-plane view of the coffins looks like a 2D projection of ice XII, a metastable ice polymorph of bulk water.[29] Nevertheless, there are no five-membered rings in ice XII (its smallest ring contains seven molecules),[30] while each plane of C is exclusively tiled by five-membered rings of hydrogen-bonded water molecules. The similarity between ice XII and C extends to the conditions at which they are obtained from the liquid: we crystallized C by cooling L at 0.51 GPa; ice XII was first crystallized from liquid water at 0.55 GPa and 260 K,[29] 25 K below the L-C melting line for TIP4P/ice water. Additionally, Koza *et al.*[31] report that ice XII is metastable when decompressed to 0.1 MPa at 77 K and that on warming up at 0.1 MPa ice XII transforms to ice I at 135 K. Similarly, we find that C remains metastable if decompressed to 0.1 MPa at 100 K and decomposes to H around 200 K in warming up simulations at ambient pressure.

Experiments suggest that there may be a relationship between ice XII and high-density amorphous ice (HDA): Koza *et al.*[31] and Kohl *et al.*[32] reported formation of HDA in the pathway to ice XII crystallization. Only ice XII is formed at 100 K, but ice III also forms at 140 and 160 K.[31] Similarly, compression of *wheels* (W) at 100 K yields *coffins* (C), while it produces *tic-tac-toe* (T) at 120, 140, or 180 K. Given the relation between ice XII and HDA and between C and W, we conjecture that W could be a quasi-2D analog of HDA (although, we note, at $p_L>0.3$ GPa W is actually less dense than L). This suggests that, as W is structurally related to C in that they both contain the ESPP 20-mer motif, HDA could be a structurally similar amorphous relative of ice XII without its long-range order, as previously suggested by Koza *et al.*[33] By drawing an analogy between W and HDA we do not imply that the latter is a quasicrystal, although a status between glass and quasicrystal has been suggested for the bulk water glasses[34] as both LDA and HDA have extremely low excess entropies with respect to ice Ih, 1.1 and 2.1 J/kmol, respectively.[35,36]

We did not find two-phase coexistence of W and C for the confinement conditions of this study with either water model. This is expected, as their coexistence temperature at 0.4 GPa, $T_m=\Delta H/\Delta S\approx 0.46\ \text{kJ mol}^{-1}/1.8\ \text{J K}^{-1}\ \text{mol}^{-1}\approx 250$ K for mW, is above the limit of superheating at which W transforms to L. This is also the case for W-C coexistence with the TIP4P/ice model. Although the quasicrystals is always metastable with respect to the coffins under the conditions of this study, the transformation from W to C does not occur readily. We have observed spontaneous transformation of W to C at 0.51 GPa at temperatures 140 K and lower. Under those conditions, very far from the equilibrium temperature, the transformation appears to be continuous. The small gap in thermodynamics and structure between C and W leaves the question of whether a first-order transition would be possible between these two phases under other conditions of confinement. A continuous transition has been previously reported for the transformation of liquid water in narrow carbon nanotubes into a crystal formed by a stacking of pentagonal rings.[8] A scenario involving a continuous transition between the coffins crystal and the wheels quasicrystal is provocative and invites further study.

VI. LIQUID TO QUASICRYSTAL TRANSITION IN BILAYER WATER

We now discuss the thermodynamics of the L-W transition and the temperature dependence of the diffusion coefficients of these phases. The liquid to quasicrystal transformation between L and W is first-order. Figure 3 shows the evolution of the potential energy as bilayer water is cooled at

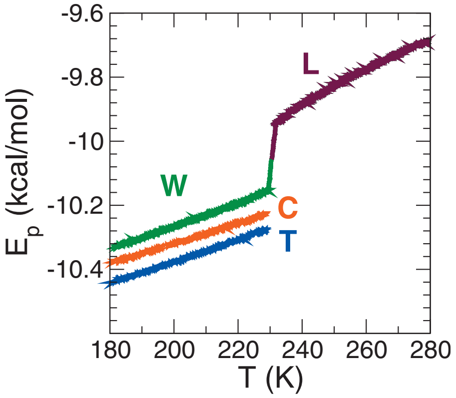

FIG. 3. Potential energy of liquid bilayer water as it is cooled at 0.51 GPa. The liquid (L) transforms to the wheels (W) quasicrystal through a first-order transition. At 0.51 GPa, the energy of the wheels is higher than the energy of the coffins (C) and tic-tac-toe (T) bilayer ices. The transformation of L to W along the cooling trajectory is presented in a movie as supplementary material (Ref. 19).

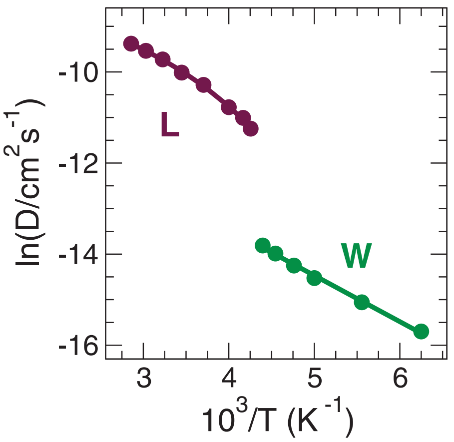

FIG. 4. Temperature evolution of the diffusion coefficient D of water in the plane of the confinement. The liquid to wheels quasicrystal transition is accompanied by a drop of diffusivity and a change in the character of the mobility from super-Arrhenius (fragile) in the liquid to Arrhenius in the quasicrystal.

0.51 GPa. A movie showing the structure of the bilayer (the upper layer in blue and the lower layer in red) along the cooling ramp is presented as supplementary material.[19] A sharp drop in energy accompanies the transition from L to W that occurs with negligible supercooling. Warming up the quasicrystal results in an equally sharp transformation to the liquid. There is very little hysteresis (less than 5 K in 1 K/ns cooling and heating ramps) in the $W\rightarrow L$ and $L\rightarrow W$ transformation temperatures. The phase transformation close to the coexistence point signals a low kinetic barrier for the transition, consistent with the relatively small changes in enthalpy and entropy associated with the phase transition (Table I) and the appearance of wheel-like motifs in L as it approaches the W-L coexistence line (see movie).[19] Figure 3 also shows the energy of the C and T crystals, which are slightly lower in energy than the wheels. The $L\rightarrow C$ and $L\rightarrow T$ transformations, however, occur only after significant supercooling (indicated by the stars in Fig. 2).

Both the mW and TIP4P/ice models predict a maximum in the temperature of W-L coexistence around 0.3 GPa. The maximum corresponds to $\Delta V_{\text{W-L}}=0$. The inversion in the sign of $\Delta V_{\text{W-L}}$ is due to the larger compressibility of the L phase. The volume and coordination number of the wheels quasicrystal is rather insensitive to pressure: the average coordination is 4.4 from 0.2 to 0.51 GPa, while that of L increases from 4.2 to 4.4 from 0 to 0.51 GPa. The existence of an extremum in the coexistence line of the bilayer liquid-quasicrystal transition has no analog in the bulk LDA to HDA line and its proposed liquid-liquid extension.[2]

Is there a liquid-quasicrystal critical point in the phase diagram of bilayer water? The entropy $\Delta S_{\text{W-L}}$ and enthalpy $\Delta H_{\text{W-L}}$ difference between liquid and wheels decrease when the pressure is increased from 0.4 to 0.51 GPa, suggesting that the gap could close at higher pressures. The volume difference, on the other hand, increases in that pressure interval. These results do not suggest the existence of a continuous transformation of L into W. Nevertheless, more studies are necessary to determine the high-pressure behavior of the bilayer. On the lower pressure side, we find that for $p_L < 0.3$ GPa the equilibrium W-L temperature is lower than the temperature of homogeneous nucleation of H from L, resulting in L to H transformation on cooling and W to H on warming up. The latter seems to be mediated by the transient formation of L, but W-L coexistence cannot be attained at low pressures using atomless LJ 9-3 surfaces.

The first-order transition between L and W is accompanied by a discontinuity in the diffusion coefficient D (Fig. 4). The quasicrystal presents long-range mobility intermediate between the diffusivity of the liquid and the crystals: at 0.51 GPa and 235 K, $D_L=1.3\times10^{-5}$ cm^2 s^{-1}, one order of magnitude greater than for the ordered liquid W, $D_{\text{W}}=1.2\times10^{-6}$ cm^2 s^{-1} at 230 K, which is, in turn, about one order of magnitude more diffusive than the bilayer crystals. For reference, the diffusion of bulk water evaluated with the mW model is 4.6×10^{-5} cm^2 s^{-1} under similar conditions (the coarse-grained model is more mobile than the fully atomistic model because the hydrogen atoms, effectively, add friction to the motion of the water's center of mass).[14] The diffusion constant of the TIP4P bilayer L at 275 K and H at 270 K, both at 0.1 MPa, are 1.3×10^{-5} and 3.0×10^{-9} cm^2 s^{-1}, respectively.[11] Our TIP4P/ice simulations were not long enough to determine the diffusivity of atomistic L and W at high pressures. The lower diffusivity and high computational cost of the atomistic models make their equilibration extremely difficult in simulations. D of the bilayer corresponds to the diffusion in the plane parallel to the surfaces. The water molecules also exchange between the two layers faster in L than in W.

The L and W phases present different temperature dependences of D (Fig. 4). The liquid L is fragile (super-Arrhenius) and its diffusion coefficient with the mW model is well represented by $D=D_0\exp[-T_0/(F(T-T_0))]$, with $T_0=143$ K and fragility $F=0.47$. This behavior is analogous to diffusion in a system with activation barriers that increase on cooling. We attribute the increase in activation barriers to the ordering of L on cooling; the fraction of water molecules in registry increases from 45% to 65% when L is cooled from 280 to 232 K at 0.51 GPa (and jumps to 92% when L transforms to W). The diffusion coefficient of the *wheels* is very well represented by an Arrhenius law, i.e., the activation energy seems to be independent of temperature. This dynamical behavior is consistent with the invariant structure that W displays when the temperature is changed. It has been recently reported by Engel *et al.*[37] that a two-dimensional dodecagonal quasicrystal with the same structure as each layer of W produced by the LJG potential follows an Arrhenius law. The mechanism of mobility of the wheels is dominated by phason flips,[38] involving single molecule jumps and ring-like motion of the water molecules (see movie)[19] that inspired the wheels name for the quasicrystal. The mechanism seems to be the same as recently described for the equivalent 2D LJG dodecagonal quasicrystal,[37] although a detailed investigation of the effect of the second layer in the mechanisms of diffusion of the wheels and its comparison with the monolayer crystal in 2D is merited.

VII. CONCLUSIONS

Using atomistic and coarse-grained simulations we computed the phase diagram of bilayer water confined between smooth (non templating) interfaces. The relative stabilities of the phases, and their structures, are the same for the TIP4P/ice and mW models, suggesting that the configurations of water in the bilayer are well described by the very efficient mW model which has no explicit hydrogen atoms or electrostatic interactions but favors tetrahedral "hydrogen-bonded" configurations between water molecules.

Our work indicates that compression of the water bilayer leads to the formation of crystals and a quasicrystal based on pentagonal rings of hydrogen-bonded water molecules. The crystals we name tic-tac-toe (T) and coffins (C), and the quasicrystal we name wheels (W), are novel ordered phases of water. Of particular notice are the structures of the wheels, the first quasicrystal reported for water, and the coffins, a quasi-two-dimensional ice polymorph tiled exclusively by irregular pentagonal rings.

Wheels is a dodecagonal quasicrystal, and its structure seems to be the same than one of the 2D dodecagonal quasicrystals (Dod II) (Ref. 27) previously found for the isotropic LJG potential, a force field that has common features with isotropic coarse-grained models of water. This suggests that the quasicrystal wheels may also form in bilayers of simpler, isotropic, waterlike models.

Although the structures of the bilayer phases of water are unique, this work reveals interesting analogies between the phase behavior of bilayer and bulk water. First, like for bulk water, an increase in pressure does not increase the coordination of the bilayer water crystals: the stable bilayer ices, H and T, and the metastable C are all four-coordinated and satisfy the ice rules. Second, there are structural analogies between the bilayer and bulk phases: H looks like a 2D projection of ice Ih and the metastable crystal C looks like a 2D projection of the metastable ice XII. Our work suggests that W could be a quasi-2D form of HDA, supporting a scenario in which HDA is a highly ordered amorphous phase with local ordering similar to ice XII.

We have previously demonstrated n-layered forms of hexagonal ice satisfy the ice rules for all molecules only if $n=2$.[6] This suggests that the analogy between bilayer and bulk water does not extend to other values of n. Recent work on monolayer water supports our conjecture.[39] The analogies in the phase behavior of bilayer and bulk water suggests that the water bilayer could assist in the understanding of the complex behavior of bulk supercooled water and the structural relation between ice XII and high-density amorphous ice.

We did not find true polyamorphism in bilayer water: defective hexagonal ice formed under certain cooling conditions in the atomistic system, as reported in Ref. 11, but, consistent with the results of Ref. 12, it annealed to a more perfect H before melting. We speculate that highly defective forms of the crystals can persist as metastable amorphous phases in 3D (e.g., the random tetrahedral network structure of LDA, compared to the perfect tetrahedral structure of ice I) but the equivalent defective 2D amorphous structures (if they ever form) rapidly convert into the corresponding crystal. Even in bulk water the low-density amorphous phase can persist for long times only as a glass, while its liquid form quickly crystallizes and cannot be equilibrated.[15]

The conditions under which the water quasicrystal was produced in this study are not easily attainable in experimental studies; the pentagonal structures become more stable than hexagonal bilayer ice only after considerable lateral compression, on the order of 0.3 GPa, and the wheels and coffins sustain a pressure perpendicular to the plates of about 0.15 GPa when confined between the LJ-9-3 surfaces at $D=8.5$ Å.[19] A key question is whether the novel phases found in this work, particularly the quasicrystal and the ice polymorph made of pentagonal rings, can be stabilized at room pressure. We address this question in a separate communication, where we show that the relative stability of C and H at 1 atm can be reversed through the tuning of the water-surface interactions with atomically detailed walls, and the wheels quasicrystal can be formed without the application of pressure.[21] It is an open question whether the wheels, coffins, and tic-tac-toe can be obtained by water deposition on an open surface, as it has been recently demonstrated for H.[40] If that was possible, the dodecagonal water quasicrystal and the pentagon-based bilayer ices would not only be relevant for confined water but could play an important role in the wetting and solvent properties of interfacial water.

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