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Heating-induced glass-glass and glass-liquid transformations in computer simulations of water

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Water exists in at least two families of glassy states, broadly categorized as the low-density (LDA) and high-density amorphous ice (HDA). Remarkably, LDA and HDA can be reversibly interconverted via appropriate thermodynamic paths, such as isothermal compression and isobaric heating, exhibiting first-order-like phase transitions. We perform out-of-equilibrium molecular dynamics simulations of glassy water using the ST2 model to study the evolution of LDA and HDA upon isobaric heating. Depending on pressure, glass-to-glass, glass-to-crystal, glass-to-vapor, as well as glass-to-liquid transformations are found. Specifically, heating LDA results in the following transformations, with increasing heating pressures: (i) LDA-to-vapor (sublimation), (ii) LDA-to-liquid (glass transition), (iii) LDA-to-HDA-to-liquid, (iv) LDA-to-HDA-to-liquid-to-crystal, and (v) LDAto-HDA-to-crystal. Similarly, heating HDA results in the following transformations, with *decreasing* heating pressures: (a) HDA-to-crystal, (b) HDA-to-liquid-to-crystal, (c) HDA-to-liquid (glass transition), (d) HDA-to-LDA-to-liquid, and (e) HDA-to-LDA-to-vapor. A more complex sequence may be possible using lower heating rates. For each of these transformations, we determine the corresponding transformation temperature as function of pressure, and provide a P-T "phase diagram" for glassy water based on isobaric heating. Our results for isobaric heating dovetail with the LDA-HDA transformations reported for ST2 glassy water based on isothermal compression/decompression processes [Chiu et al., J. Chem. Phys. 139, 184504 (2013)]. The resulting phase diagram is consistent with the liquid-liquid phase transition hypothesis. At the same time, the glass phase diagram is sensitive to sample preparation, such as heating or compression rates. Interestingly, at least for the rates explored, our results suggest that the LDA-to-liquid (HDA-to-liquid) and LDA-to-HDA (HDA-to-LDA) transformation lines on heating are related, both being associated with the limit of kinetic stability of LDA (HDA). © 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4868028]

I. INTRODUCTION

Water is a polyamorphic material. In the glass state, it can exist in at least two different forms: low-density amorphous (LDA) and high-density amorphous (HDA) ice (see, e.g., Refs. 1–4). These amorphous forms exhibit very different structural,^{5,6} dynamic,^{7,8} and thermodynamic properties.^{9,10} For example, at normal pressure, HDA is $\approx 25\%$ denser than LDA.¹¹⁻¹⁴

The nature of water glass polymorphism is rather puzzling.¹⁻⁴ LDA and HDA can be interconverted by isobaric heating^{11, 12, 15–17} or isothermal compression/decompression^{15, 18, 19} and, during these transformations, thermodynamic and structural properties change abruptly. Indeed, experiments using properly annealed samples indicate that the transformations between LDA and HDA are surprisingly similar to first-order phase transitions.^{12–15} Specifically, during the pressure-induced LDA-HDA transformations, (i) $(\partial P/\partial V)_T \approx 0,^{13, 15, 18, 20}$ (ii) hysteresis occurs between the LDA-to-HDA and HDA-to-LDA transformations, ^{15, 19, 20} and (iii) samples containing LDA and HDA coexisting with one another have been prepared.^{21–23}

An explanation for water glass polymorphism is provided by the liquid-liquid phase transition (LLPT) hypothesis.^{1,24} In this view, which was proposed in 1992 from results obtained from molecular dynamics (MD) simulations²⁴ using the ST2 model,²⁵ LDA and HDA are two "phases" separated by a first-order phase transition. In the P-T plane, the LDA-HDA coexistence line extends above the glass transition temperature into the liquid domain, ending in a liquid-liquid critical point (LLCP). Hence, in this scenario, water is believed to exist in two liquid phases. The liquids related to LDA and HDA are referred to as low-density (LDL) and high-density liquid (HDL). We note that alternative interpretations for the LDA-HDA transformations that do not consider an underlying LLPT are also available (see, e.g., Refs. 26–28).

There is an extensive literature on experimental work focused on the behavior of glassy water (see, e.g., Refs. 4 and 10); computer simulation studies of glassy water are comparatively more limited. To our knowledge, only a few fullatom water models have been employed in computational studies of glassy water: the TIP4P,^{29–31} SPC/E,^{32–36} and ST2 model.^{24,29,37,38} As is the case in the liquid state, these models have limitations in reproducing experimental data. For example, compared to experiments, the ST2 model reproduces better the qualitative behavior of the pressure dependence of density during the pressure-induced LDA-HDA transformations. However, the density values and structure of LDA and HDA are better predicted by the SPC/E model than by the ST2 model.³⁸ The main qualitative difference between these

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models is that equilibrium MD simulations indicate the existence of a LLPT in ST2 water^{24, 39–45} (see, however, Refs. 46– 49). Such a LLPT has not been observed in standard MD simulations using the SPC/E model, although Ref. 48 suggested a possible transition; extrapolation of MD results indicates that a CP in SPC/E water may exist at very low-temperatures, within the glass domain.^{50,51} Regarding the TIP4P model, a LLCP has been reported at low temperatures^{52,53} using modified versions of the original TIP4P model⁵⁴ (see, however, Ref. 55).

We emphasize that the search for a quantitative description of glass polymorphism is a fundamental problem in statistical mechanics and thermodynamics. It involves extending the concepts of "state" and "phase transitions" to the outof-equilibrium domain as well as including the effects of aging on this phenomenon, characteristic of glasses. Moreover, fundamental concepts in the field of glasses, such as *the* glass transition, have to be revisited since in polyamorphic materials, each glass has its own glass transition temperature, with distinct pressure dependence.^{37,56} It follows that a quantitative description of glass polyamorphism requires to go beyond the comfortable domain of equilibrium statistical mechanics/thermodynamics.

A logical first step towards improving the understanding of polymorphic glasses is to establish a "phase diagram" indicating all transformations between LDA and HDA. Such a phase diagram has been reported for glassy water based on experiments involving isothermal compression/decompression and isobaric heating processes; see Fig. 3(a) of Ref. 15. One of the goals of this work is to provide a similar phase diagram from computer simulations of glassy water using the ST2 model, where a LLPT has been reported. We note that glass polymorphism is not particular to water. Experiments indicate that other materials, such as silicon,^{57,58} germanium,^{59,60} silica,⁶¹ aluminium-oxide yitrium-oxide mixtures,⁶² n-butanol,^{63,64} triphenyl phosphite,^{65,66} and water-glycerol solutions,⁶⁷ also exhibit glass polymorphism, with low and high-density amorphous forms. Hence, characterizing water glass polymorphism may help to understand polyamorphism in other substances as well.^{3,68–70}

In this work, we study the transformations exhibited by LDA and HDA when they are heated isobarically in a wide range of pressures. This work complements previous computational studies where we explored the interplay between the LLPT and glass transition in glassy water³⁷ as well as the LDA-HDA transformations induced by pressure.³⁸ Here, we extend the heating studies from Ref. 37 to very high $(P \approx 2000 \text{ MPa})$ and very negative $(P \approx -1000 \text{ MPa})$ pressures. This allows us to explore the phenomena of glass sublimation (at negative pressures) and crystallization (at high pressures). In addition, we compare the present results, based on isobaric heating runs, to those reported in Ref. 38, based on compression-decompression runs. This enables us to construct a phase diagram that includes pressure, as well as heating-induced LDA-HDA transformations. We note that standard (out-of-equilibrium) MD computer simulations can only be performed with time scales that are much shorter than the corresponding experimental time scales.³⁸ Moreover, one expects that the (T, P) loci for the pressure-induced and heating-induced transformations between LDA and HDA will quantitatively depend on heating/cooling and compression/decompression rates. However, in most cases, the qualitative features of these loci will be only weakly dependent on rates.

This work is organized as follows. In Sec. II, we discuss the computer simulation details. The transformations observed upon heating LDA and HDA at different pressures are described in Secs. III A and III B, respectively. In Sec. IV, we summarize our results and present a phase diagram for real water, adapted from the results obtained with the ST2 model.

II. COMPUTER SIMULATION DETAILS

We perform extensive out-of-equilibrium MD simulations of water using the ST2 model.²⁵ The long-range (electrostatic) interactions are treated using the reaction field technique.⁷¹ The basic potential parameters, such as the cutoff distance used to calculate short-range interactions, are identical to those used in Refs. 37–39 and 72 where a discussion of many equilibrium thermodynamic, dynamic, and glass properties can be found.

Our computer simulations involve isobaric heating of amorphous ices obtained via different thermodynamic paths. During the heating simulations, the temperature and pressure are controlled using the Berendsen thermostat and barostat.⁷³ While the pressure is kept constant, the temperature is increased steadily at a heating rate $q_T = 30$ K/ns. Specifically, at every simulation time step dt = 1 fs, the thermostat temperature is increased by $\Delta T = q_T dt$. We note that this is a slightly different protocol from that used in Ref. 37, but with the same mean rate. The present results are in full agreement with those of Ref. 37. For each glass and pressure studied, we perform 10 independent runs to improve statistics. All simulations are performed using a cubic box with N = 1728 water molecules, with periodic boundary conditions.

We heated compressed LDA and decompressed HDA at pressures ranging from P = -500 MPa to P = 1700 MPa. LDA is obtained by cooling the equilibrated liquid from T = 350 K to T = 0 K at P = 0.1 MPa at our standard cooling rate $q_T = -30$ K/ns, identical in magnitude to the subsequent heating rate of the glass. The glass obtained by this process corresponds to the experimental variant "hyperquenched glassy water" (HGW), the low-density glass originally produced by spraying micrometer-sized droplets onto a solid cryoplate.⁷⁴ However, our cooling rate is 3–5 orders of magnitude larger than the experimental cooling rates. HDA is obtained by compression of LDA at T = 20 or 80 K using a compression rate of $q_P = 300$ MPa/ns. These glasses are the same amorphous ices obtained in Ref. 38 for the purposes of studying pressure induced glass-glass transitions; further preparation details can be found in that work.

A. Determination of transformation temperatures

As a consequence of the complex thermodynamic phase behavior of the ST2 model, we observe a diverse range of transformations during heating a particular glass. Depending on the starting glass and heating pressure considered, one or more of the following transformations may occur: (i) glassto-liquid (the canonical glass transition), (ii) glass-to-glass, (iii) glass-to-crystal, (iv) liquid-to-crystal, (v) glass-to-vapor, or (vi) liquid-to-vapor. In addition, for a given starting glass, independent simulations following the *same* thermodynamic path may exhibit different sets of transformations, due to the non-equilibrium nature of the glass state. For example, over the 10 simulation runs starting from LDA at P = 700 MPa, one run exhibits transformations (i) and (ii), five runs exhibit transformations (i), (ii), and (iv), and four runs exhibit transformations (ii) and (iii). In these cases, we separate the different runs into sets with a common sequence of transformations, and for each set, we average the thermodynamic properties, such as volume V(T).

In this work, we define all transformation temperatures from the temperature-dependence of volume. One of the reasons for focusing on V(T) instead of, e.g., the constant pressure specific heat $c_P(T)$, is that experimental calorimetric studies at high pressures are challenging, and more recent progress has been made at high pressure by volumetric (dilatometry) studies.⁸ Additionally, we also wish to compare the heating-induced transformation (T, P) values with those obtained from volume changes during compression/decompression reported both experimentally¹⁵ and in simulations of the present model.³⁸ We note that in a previous work,³⁷ we defined the transformation temperatures by identifying inflections of $c_P(T)$ during heating runs. However, we find that at very low and high pressures, it is in practice difficult to identify the transition features in $c_P(T)$ associated with glass-glass transformations. In any case, the transformation temperatures obtained from $c_P(T)$, when this is possible, are consistent with the corresponding temperatures defined from V(T) (see also Ref. 37).

For the glass-to-liquid and glass-to-glass transformation temperatures [cases (i) and (ii)], we follow the same procedure used in dilatometry experiments⁸ to define the glass transition temperature. Specifically, we fit V(T) with a straight line at low temperature, before the transformation occurs. The deviation of V(T) from such a fitting line defines the glassto-liquid or glass-to-glass transformation temperature. For the transformation temperatures to the crystal state [cases (iii) and (iv)], we take advantage of the fact that the change in V(T)is very abrupt (nearly discontinuous) at the transformation. In these cases, the transformation temperature is defined as the midpoint of the change in V(T). These temperatures are consistent with the temperatures at which $c_P(T)$ has a minimum, which is a characteristic of crystallization processes [see e.g., Fig. 5(c)]. For the transformation temperatures of glass or liquid-to-vapor [cases (v) and (vi)], the transformation temperature is defined as the temperature at which the volume first exhibits unbounded growth (vaporization).

III. HEATING INDUCED TRANSFORMATIONS

A. Heating LDA

In this section, we discuss the transformations of LDA that occur on heating at both positive and negative pressures.



FIG. 1. Transformation temperatures determined during isobaric heatings of LDA at different pressures (solid up-triangles). Green up-triangles indicate the LDA-to-liquid ($P \le 400$ MPa) and LDA-to-HDA (P > 400 MPa) transformations. This temperature locus follows closely the pressure-induced LDAto-HDA (or LDL-to-HDL, at high temperatures) transformation line reported in Ref. 38 (red right-triangles). Upon further heating at $480 \le P \le 700$ MPa, independent simulations exhibit HDA-to-HDL (blue up-triangles), HDA-toice VII (orange up-triangles), or HDA-to-HDL-to-ice VII transformations (blue and orange up-triangles); see Table I. For comparison, we include the compression-induced crystallization of HDL/HDA (black right-triangles) to ice VII from Ref. 38. Magenta up-triangles at negative pressures, indicate the LDA-to-vapor ($P \leq -200$ MPa) and LDL-to-vapor (P = -100 MPa) transformations. For comparison, included are the equilibrium liquid-vapor coexistence line (squares) from Ref. 39, decompression-induced LDA-tovapor transformation line (maroon left-triangles) from Ref. 38, as well as the liquid-liquid (LL) coexistence line, LL spinodal lines, and LLCP reported in Ref. 91. Dashed lines are guides to the eye.

The corresponding transformation temperatures as function of pressure are indicated in Fig. 1. We discuss these transformations in different pressure ranges, based on the phenomenology observed.

1. Heating LDA at $0 \le P \le 400$ MPa

At $0 \le P \le 400$ MPa, heating LDA results in the liquid phase (via a standard glass transition). The liquid at $P > P_c$ corresponds to HDL, where $P_c \approx 185$ MPa is the LLCP pressure.³⁹ At $P < P_c$, the distinction between LDL and HDL becomes less evident, in particular, as the LLCP is approached. The locus of this glass transition temperature, $T_g^{LDA}(P)$, is indicated by the green up-triangles located at $0 \le P \le 400$ MPa in Fig. 1. These temperatures are in agreement with those reported in Ref. 37 which were obtained using a slightly different heating protocol than that used in the present work. As discussed in Ref. 37, the pressure-dependence of $T_g^{LDA}(P)$ is anomalous since it decreases monotonically with increasing pressure, a consequence of water's diffusion anomaly.

The LDA-to-liquid (be it LDL or HDL) transformation is evident from the evolution of LDA's properties upon heating. As an example of isobaric heating, Fig. 2 shows the density $\rho(T)$, potential energy PE(T), and isobaric specific heat $c_P(T)$ as function of T during heating LDA at P = 0.1 MPa (ambient pressure). All these properties are approximately linear with T in the glass domain. However, at the glass



FIG. 2. (a) Density $\rho(T)$, (b) potential energy PE(T), and (c) constantpressure specific heat $c_P(T)$ upon heating LDA at P = 0.1 MPa. The glass transition occurs at $T_g^{LDA} = 270$ K. In the glass domain $(T < T_g^{LDA})$, all quantities increase approximately linearly with increasing temperature. At $T = T_g^{LDA}$, the density and potential energy deviate from this linear behavior and $c_P(T)$ develops a wide maximum, characteristic of the glass transition.

transition temperature, $T_g^{\text{LDA}}(P) \approx 270$ K, $\rho(T)$, and PE(T)start to increase more sharply with temperature, and $c_P(T)$ exhibits a pronounced peak. While the behavior of $c_P(T)$ and PE(T) is typical for most glasses (see, e.g., Refs. 75 and 76), $\rho(T)$ increases anomalously with increasing temperature (see, e.g., Refs. 77 and 78), i.e., the liquid (LDL) is denser than the glass. This anomalous behavior may be a consequence of the well-known density anomaly of (equilibrium) liquid water, which is less dense than ice at ambient pressure. Alternatively, it could be due to the nature of the resulting liquid which, at these temperatures, may contain HDL-like domains, leading to higher densities than pure LDL. Simulations using much slower heating rate, not accessible within our simulation time scales, will clarify this issue.

To confirm that the thermodynamically defined glassto-liquid transition of LDA corresponds with a change to liquid-like dynamics, we include in Fig. 3 the temperature dependence of the cumulative *translational* mean-square displacement (MSD) $\langle r^2(T) \rangle$ and *rotational* MSD $\langle \phi^2(T) \rangle$ (the MSDs are relative to the starting configuration of the heating



FIG. 3. (a) Mean-square displacement and (b) rotational mean-square displacement upon heating LDA at P = 0.1 MPa. While in the glass domain both quantities are practically zero, they increase sharply at $T > T_e^{LDA} = 270$ K.



FIG. 4. Oxygen-oxygen radial distribution function obtained upon heating LDA at P = 0.1 MPa, across the LDA-to-liquid transition. RDFs at $T < T_g^{\text{LDA}} = 270$ K correspond to LDA; the RDF at T = 300 K corresponds to the liquid. All distributions have same extrema positions but the RDF of LDA is sharper than for the liquid, as expected.

simulations). This is distinct from a Debye-Waller type measurement, which quantifies MSD over a fixed time interval. The rotational MSD is defined in Refs. 79 and 80, based on the rotation of water molecule's dipole moment vector. Both $\langle r^2(T) \rangle$ and $\langle \phi^2(T) \rangle$ are nearly zero in the glass domain, and increase sharply for $T \gtrsim T_e^{LDA}(P)$.

We note that the LDA-to-liquid transition is also evident from structural properties. For example, the oxygen-oxygen radial distribution function (OO RDF) is shown in Fig. 4 at different temperatures. While the RDF of LDA shows almost no *T* dependence at low temperatures (compare T = 100 and 200 K), it evolves suddenly to the liquid RDF at T = 300 K > $T_g^{LDA}(P)$. As expected, the maxima and minima in LDA and liquid RDF are located at the same positions. However, the value of the extrema of the corresponding RDFs are much more pronounced in the case of LDA than for the liquid. We also confirmed that these glass states are not crystalline, based on the structure factor.

2. Heating at $P \ge 480 MPa$

At $480 \le P \le 1700$ MPa, it is found that LDA transforms to a glass similar to HDA upon heating. The LDAto-HDA transition temperatures are indicated by the green up-triangles located at $P \ge 480$ MPa in Fig. 1. As discussed in Ref. 37, the LDA-to-liquid (either LDL or HDL, at $P \le 400$ MPa) and LDA-to-HDA transformation temperatures (at $P \ge 480$ MPa) constitute a single continuous locus in the P - T plane, indicated by *all* the green up-triangles in Fig. 1. This locus, $T^{\text{LDA}}(P)$, defines the limit of kinetic stability of LDA relative to other phases, LDL, HDL, or HDA (which is weakly dependent on heating rate). In particular, these results suggest that the heating-induced (i) glass transition of LDA and (ii) the LDA-to-HDA transformation are not independent phenomena, as usually considered, and that they share a common origin.

If $T^{\text{LDA}}(P)$ indeed indicates the limit of stability of LDA upon *heating* then one would expect that it should be related to the *pressure*-induced LDA-to-HDA transformation locus. In fact, in the LLPT hypothesis scenario, there is a limiting LDA-to-HDA transformation locus in the P-T plane (i.e., the extension of the LDL-to-HDL spinodal line into the glass domain) that indicates the conditions at which LDA transforms to HDA, whether it is heating- or pressure-induced (see Fig. 1 in Ref. 29). Thus, in this view, it is implicitly assumed that the heating- and pressure-induced LDA-to-HDA transformations occur at the same (T, P) conditions and compression/heating rates play a secondary role.

In order to explore the relationship between the LDAto-HDA transformations induced by heating and compression, we include in Fig. 1 the compression-induced LDA-to-HDA $(T < T_g^{\text{LDA}})$ and LDL-to-HDL $(T > T_g^{\text{LDA}})$ transformation pressure loci from Ref. 38. The combined pressure-induced LDA/LDL-to-HDL/HDA locus, $P^{\text{LDA}}(T)$, is indicated by the red right-triangles in the figure. Figure 1 shows that the $T^{\text{LDA}}(P)$ and $P^{\text{LDA}}(T)$ loci are indeed very similar to one another over the entire range, in agreement with the LLPT hypothesis scenario.²⁹ We note, however, that heating and compression rates are indeed quantitatively important, at least within the present computer simulation time scales. Specifically, it follows from Ref. 38 that the $P^{\text{LDA}}(T)$ locus shifts slightly when the rate q_P varies. Similarly, heating simulations of SPC/E water using similar time scales as those employed in this work indicate that $T_g^{\text{LDA}}(P)$ shifts when the rates q_T varies.⁸¹ We also note that since $T^{\text{LDA}}(P) \equiv T_g^{\text{LDA}}(P)$ at low pressures, it follows that $T_g^{\text{LDA}}(P)$ should approach $P^{\text{LDA}}(T)$ at high pressures and hence, the slope of the $T_{a}^{\text{LDA}}(P)$ locus must have the same sign as the slope of the $P^{\text{LDA}}(T)$ line.

The heating-induced LDA-to-HDA transformation occurs for all of the 10 independent runs performed at each $P \ge 480$ MPa studied. However, upon further heating, HDA transforms to different phases, depending on the pressure and/or particular run considered. For example, at a given pressure, a particular simulation may exhibit HDA-to-HDL-tocrystal transformations, while a different run may exhibit only the HDA-to-crystal transformation. The sequence of transformations found in individual runs are summarized in Table I.

To describe the multiple transformations observed during heating LDA at $P \ge 480$ MPa, we focus on an example case, P = 700 MPa. At this pressure, all possible scenarios occur; we find (i) one simulation showing LDA-to-HDA-to-HDL transformations, (ii) five runs showing LDA-to-HDA-to-HDL-to-crystal, and (iii) four runs showing LDA-to-HDA-to-crystal.

TABLE I. Number of independent simulations at $480 \le P \le 700$ MPa that exhibit LDA-to-HDA-to-liquid, LDA-to-HDA-to-liquid-to-crystal, and LDA-to-HDA-to-crystal transformations. At each pressure, 10 independent simulations are performed. At $700 < P \le 1700$ MPa, all simulations show LDA-to-HDA-to-crystal transformations. At $0.1 \le P \le 400$ MPa, all simulations show LDA-to-liquid transformations. At P = -100 MPa, all simulations show LDA-to-liquid-to-vapor transformations. See also the P-T phase diagram of Fig. 1.

Transformation sequence	<i>P</i> = 480 МРа	<i>P</i> = 500 МРа	P = 600 MPa	P = 700 MPa
LDA-to-HDA-to-liquid	9	9	4	1
LDA-to-HDA-to-liquid-to-crystal	1	1	6	5
LDA-to-HDA-to-crystal	0	0	0	4



FIG. 5. (a) Density, (b) potential energy, and (c) constant-pressure specific heat during heating LDA at P = 700 MPa. Three different scenarios occur among the independent runs, LDA-to-HDA-to-HDL (black lines), LDA-to-HDA-to-HDL-to-ice VII (blue lines), and LDA-to-HDA-to-HDL-to-ice VII (red lines) transformations. In the last case, the glass transition peak (at $T \approx 250$ K, black line) is suppressed by the crystallization minimum (at T = 270 K, blue line), resulting in a small peak at $T \approx 240$ K (red line).

The corresponding average $\rho(T)$, PE(T), and $c_P(T)$ for cases (i)-(iii) are shown in Figs. 5(a), 5(b), and 5(c), respectively. In all cases, in the LDA state (approximately T < 150 K), $\rho(T)$ and $c_P(T)$ vary weakly, while PE(T) increases linearly with increasing T (as expected for any harmonic solid). At $T \approx 150$ K, a sharp increase in $\rho(T)$ and PE(T) occurs which signals the LDA-to-HDA transformation. This transformation is dramatic, being accompanied by a $\approx 50\%$ change in density. In addition, the LDA-to-HDA results in an exothermic peak in $c_P(T)$, with minimum at $T \approx 170$ K.

Upon further heating, depending on the set of runs considered, HDA either transforms to HDL, crystallizes, or exhibits HDA-to-HDL-to-crystal transformations; see Figs. 5(a)–5(c). In the first case (black lines), we observe a glass transition of HDA (to HDL), with $T_g^{HDA} \approx 240$ K. We note that, as shown in Figs. 5(a)–5(c), the phenomenology associated with HDA glass transition is not different from that observed in normal liquids.^{76–78} Specifically, the density decreases and the potential energy increases across the HDA-to-HDL transformation, and the glass transition is accompanied by a maximum in $c_P(T)$. We note that the liquid (HDL) is less dense than the glass (HDA), as is the case in most liquids.

In the second scenario, i.e., where HDA crystallizes, the density exhibits a sharp increase upon heating; see blue line in Fig. 5(a). The crystallization temperature is ≈ 250 K, defined by the midpoint of the density change. Similarly, PE(T) decreases suddenly during the crystallization event [see blue line in Fig. 5(b)]. We note that PE(T) shows no particular feature previous to the crystallization, such as a pre-peak, which could indicate the formation of an intermediate phase. Crystallization is also evident from the behavior of $c_P(T)$. Specifically, $c_P(T)$ develops a large exothermic peak during crystallization; see blue curve in Fig. 5(c). We note that $c_P(T)$ remains practically constant in the HDA state, and a very weak pre-peak, barely noticeable, occurs at the beginning of the crystallization event.

Crystallization at high pressure was observed in Ref. 38 upon isothermal compression of HDL and HDA. The region



FIG. 6. Oxygen-oxygen (OO), oxygen-hydrogen (OH), and hydrogenhydrogen (HH) radial distribution functions of ice VII at T = 280 K and P = 900 - 1100 MPa. Ices are obtained by compression of HDL at T = 280 K (black lines), isobaric heating of compressed LDA (red dashedlines), and isobaric heating of decompressed HDA (blue dashed-lines).

where crystallization occurred on compression is shown in Fig. 1 (area enclosed by the black dashed-line). At these conditions, ST2 water crystallizes into ice VII on compression (in contrast, experimental compression of HDA leads to ice XII^{82–85}). Interestingly, we find that the ice formed upon heating compressed LDA is also ice VII. The RDFs of the ices formed during compression of HDL at T = 280 K and upon heating LDA at P = 1100 MPa, are shown in Fig. 6 at (T = 280 K, P = 900 - 1100 MPa). The RDFs of the ices formed by the alternate paths are nearly indistinguishable. We also calculate the structure factor, S(q), of both ices (not shown) and find that they are very similar to the S(q) of ice VII reported in Fig. 9 of Ref. 38. While the peaks of the S(q)for both ices have same location, they vary slightly in intensity. Thus, ice VII appears to be recovered, independent of the path. The specific polymorph formed is a feature of ST2 water, and likely not relevant for experiments. However, the general emergence of high pressure crystallization is relevant to experiments, and such a progression of states is plausible.

In the third scenario, corresponding to the HDA-to-HDLto-crystal (ice VII) transformation sequence, all properties studied exhibit a mixed behavior, with characteristics common to both the HDA-to-HDL and HDA-to-crystal transformations, making it challenging to distinguish separate events in a narrow *T* range. Figures 5(a) and 5(b) show that upon heating (red lines), $\rho(T)$ and PE(T) tend to follow the behavior observed during the HDA-HDL transition (black curves), instead of following the behavior observed during the HDAto-crystal (blue curves) transformation. This occurs only over a small range of temperatures, approximately 240–245 K. At higher *T*, both properties exhibit a sudden jump, and they follow the temperature evolution observed in the crystal phase (blue lines).

The behavior of $c_P(T)$ during the HDA-to-HDL-tocrystal transformation sequence is particularly interesting since it resembles the experimental specific heat measurements performed during the heating of LDA at P = 0.1 MPa, where LDA exhibits a glass transition followed by crystallization (see, e.g., Refs. 86–88), and more recently during heating eHDA (expanded HDA, an annealed version of HDA) at P = 0.1 MPa, where HDA transforms to HDL at P = 0.1 MPa.⁵⁶ The LDA experiments have been rather controversial, and questions were raised about the existence of an accessible glass transition for LDA at normal pressure (see, e.g., Ref. 3). At present, the consensus is that LDA indeed exhibits a glass transition at normal pressure, before crystallization occurs. Our simulations at P = 700 MPa during the HDA-to-HDL-to-crystal transformation show the same qualitative behavior of $c_P(T)$ observed in the heating experiments of LDA and eHDA at P = 0.1 MPa,^{56,86–88} supporting the idea that there can be a narrow window of accessible liquid states between the glass and crystal, as we next discuss.

For the HDA-to-HDL-to-crystal transformation sequence at P = 700 MPa, $c_P(T)$ is shown in Fig. 5(c) (red line). A pre-peak develops in $c_P(T)$ at $T \approx 240$ K indicating the HDA-to-HDL glass transition. This pre-peak is followed by a sharp minimum associated to the HDA-to-crystal transformation (blue line). A comparison of the red and black lines in Fig. 5(c) shows that the pre-peak in the HDA-to-HDL-tocrystal transformations is the result of $c_P(T)$ developing the glass transition peak (shown by the black line), but suppressed by the crystallization exothermic minimum (shown by the blue line). Accordingly, when HDL does not form (blue line), the pre-peak in $c_P(T)$ is barely noticeable. It follows that the heating simulations of HDA at high pressure supports the interpretation of multiple transformations reported in Ref. 56 and 86-88 upon heating LDA and eHDA at P = 0.1 MPa.

To establish the liquid nature of this narrow intermediate range, we also evaluate translational and rotational MSDs. The insets to Figs. 7(a) and 7(b) show $\langle r^2(T) \rangle$ and $\langle \phi^2(T) \rangle$ for the three scenarios encountered, LDA-to-HDA-to-HDL, LDA-to-HDA-to-HDL-to-crystal, and LDA-to-HDAto-crystal transformation sequences. To more clearly see the distinct states, the main panels of these figures show the differentials $d\langle r^2(T)\rangle/dT$ and $d\langle \phi^2(T)\rangle/dT$, which are more closely related to a traditional experimental measurement of Debye-Waller factor with a fixed time scale. When the system is in a solid (glass or crystal) state, there is no diffusion and hence $\langle r^2(T) \rangle$ and $\langle \phi^2(T) \rangle$ are very weakly dependent on T, so that their differentials are nearly zero. At the LDA-to-HDA and HDA-to-crystal transformations, a sudden change in $\langle r^2(T) \rangle$ and $\langle \phi^2(T) \rangle$ occurs, as molecules re-arrange from one structure to another, giving rise to a peak in $d\langle r^2(T)\rangle/dT$ and $d\langle \phi^2(T) \rangle/dT$. Accordingly, peaks in $d\langle r^2(T) \rangle/dT$ and $d\langle \phi^2(T) \rangle/dT$ correspond to transformations between solids (glass-glass or glass-crystal). For solid-to-liquid transformations (ordinary glass transition), diffusive liquid motion gives rise to unbounded increase of displacements and their differentials. For the case of the red curve in Figure 7, the transformation from HDA to crystal has a very narrow window of liquid-like states. Consequently $\langle r^2(T) \rangle$, $\langle \phi^2(T) \rangle$, and their differentials increase noticeably more than for cases where HDA converts directly to a crystal. This supports the possibility of a narrow region of liquid states. Additionally, the simultaneity in the changes of $d\langle r^2(T)\rangle/dT$ and $d\langle \phi^2(T)\rangle/dT$ demonstrates the strong coupling between rotational and translational motion of water due to hydrogen bonds.

Regardless of particular progression of states, the LDA, HDA, HDL, or ice VII found in all transformation sequences



FIG. 7. (a) Differential mean-square displacement $d\langle r^2(T)\rangle/dT$ and (b) rotational mean-square displacement $d\langle \phi^2(T)\rangle/dT$ upon heating LDA at P = 700 MPa. Solid-solid transitions (glass-glass or glass-crystal) are characterized by a peak, while a glass transition to the liquid state shows a marked increase of $d\langle r^2(T)\rangle/dT$ and $d\langle \phi^2(T)\rangle/dT$. Three scenarios are observed among the independent simulations, LDA-to-HDA-to-HDL (black), LDA-to-HDA-to-HDL-to-ice VII (red), and LDA-to-HDA-to-ice VII transformation (blue). Compare with Fig. 5. The insets of (a) and (b) show the data ($\langle r^2(T) \rangle$ and $\langle \phi^2(T) \rangle$) from which the derivatives are made.

are identical. Specifically, Fig. 8 shows the RDF at T = 100, 200, and 300 K, during the LDA-to-HDA-to-HDL (black lines), LDA-to-HDA-to-ice VII (blue lines), and LDA-to-HDA-to-HDL-to-ice VII (red lines) transformation sequences. The RDF at these temperatures correspond, respectively, to LDA, HDA, and HDL or ice VII. In all cases, the RDFs for a given state overlap among the three different transformation sequences.

3. Heating LDA under tension

To study the transformation upon heating LDA under tension (P < 0 MPa), we decompressed LDA at T = 80 K to the desired pressure, followed by isobaric heating. The starting LDA form for the decompression process is obtained by cooling the liquid at P = 0.1 MPa (i.e., HGW), as explained in Sec. II.

During heating at P = -100 MPa, LDA transforms to the liquid, and then the liquid transforms to the vapor phase. The LDA-to-liquid transition temperature is indicated in Fig. 1, green up-triangle at P = -100 MPa, and it coincides with an extension of $T^{\text{LDA}}(P)$ into the negative pressures domain. The liquid-to-vapor transformation occurs at



FIG. 8. Oxygen-oxygen radial distribution function obtained upon heating LDA at P = 700 MPa at T = 100 K (LDA), T = 200 K (HDA), and T = 300 K (HDL or ice VII). Distributions are obtained for an independent set of simulations that exhibit LDA-to-HDA-to-HDL (black lines), LDA-to-HDA-to-ice VII (blue lines), or LDA-to-HDA-to-HDL-to-ice VII (red lines) transformations; see Fig. 5.

 \approx 340 K (magenta up-triangles in Fig. 1). This transition temperature falls on the liquid-to-vapor spinodal line determined in Ref. 39 (see brown squares in Fig. 1). At larger tensions, $-500 \le P < -100$ MPa, heating LDA results in direct sublimation without a glass-to-liquid transition. The corresponding transformation temperatures (magenta up-triangles) are a smooth continuation of the metastable liquid-to-vapor spinodal and the decompression-induced LDA-to-vapor transition pressures reported in Ref. 38 (maroon left-triangles). Summarizing, we obtain a unique locus in the P-T plane that defines the liquid- and LDA-to-vapor transitions that is independent of whether the transition is induced by decompression or heating. Of course, large changes in the rates of decompression or heating may yield quantitative differences in the transition loci, but our findings suggest these differences should not be large.

We note that the liquid-to-vapor spinodal line is not re-entrant, i.e., it has a positive slope in the *T-P* plane. Our simulations clearly indicate that the liquid-to-vapor spinodal and LDA-to-vapor transformation line are not independent. It is not clear whether a positively sloped LDA-to-vapor transformation line, as is found here, is compatible with scenarios proposed for water where the liquid-to-vapor spinodal is re-entrant.^{89,90}

B. Heating decompressed HDA

In order to complete the "phase diagram" of glassy water, we also heat HDA over the pressure range $-500 \le P \le 900$ MPa. HDA is produced by compression of LDA at T = 20 and 80 K from 0.1 MPa to P > 1000 MPa, using a compression rate $q_P = 300$ MPa/ns, as explained in Ref. 38. The resulting HDA is then decompressed at rate $q_P = -300$ MPa/ns to the desired pressure, followed by isobaric heating. For each heating pressure, we perform 10 independent compression/decompression cycles, followed by heating runs and observe, as for the case of LDA, that different runs along the same thermodynamic path may exhibit different sequences of amorphous, crystal, and liquid transformations. The transformation temperatures found during isobaric heating of HDA



FIG. 9. Transformation temperatures determined during isobaric heatings of decompressed HDA at many pressures (empty up-triangles). Maroon up-triangles indicate the HDA-to-HDL (300 $\leq P \leq$ 700 MPa) and HDA-to-LDA (P < 300 MPa) transformations. At $300 \le P \le 700$ MPa, further heating of HDL results in crystallization to ice VII in some of the independent runs (orange up-triangles); at P > 700 MPa, all heating runs of HDA produce ice VII (orange up-triangles), see Table II. At approximately -200 < P < 200 MPa, LDA transforms to LDL (up-red triangles) while it sublimates at $P \leq -200$ MPa. Blue up-triangles indicate the LDA and LDL transformation temperatures to the vapor phase. Orange left-triangles are the decompression-induced HDA-to-LDA (and HDL-to-LDL, at high temperatures) transformation pressures; indigo left-triangles are the decompression-induced LDA-to-vapor (and LDL-to-vapor, at high temperatures) transformation pressures reported in Ref. 38. Orange, black, blue, magenta, and green dashed-lines are taken from Fig. 1. For comparison, included are the metastable equilibrium liquid-vapor coexistence line (squares) from Ref. 39, liquid-liquid (LL) coexistence line, LL spinodal lines, and LLCP reported in Ref. 91. Dotted-lines are guide to the eye.

are indicated in Fig. 9. Next, we discuss these transformations in detail, from high to low pressures.

1. Heating HDA at $P \ge 400$ MPa

At $P \ge 400$ MPa, decompressed HDA, and the HDA form obtained by *heating* compressed LDA at P > 480 MPa (see Sec. III A 2), are practically indistinguishable. The OO, OH, and HH RDFs of these HDA forms are shown in Fig. 10 at T = 160 K and P = 900 MPa. For comparison, we also include the RDFs of the HDA form prepared by isothermal compression of LDA at T = 160 K from Ref. 38. It follows from Fig. 10 that the three HDA forms share a common structure, which is remarkable given the very different preparation processes.

Decompressed HDA and the HDA form obtained by *heating* compressed LDA (at P > 480 MPa) exhibit the same kinds of transformations and show quantitatively similar thermodynamic properties upon heating, as we shall show. Moreover, for both HDA forms, independent runs show either (i) HDA-to-crystal, (ii) HDA-to-HDL, or (iii) HDA-to-HDL-to-crystal transformations, at nearly identical temperatures. For example, Fig. 9 shows that both HDA forms crystallize to ice VII at $T_x \approx 250$ K and that the HDA-to-ice VII transformation temperature is practically independent of pressure (see orange up-triangles and orange dashed-line). Similarly, both HDA forms exhibit comparable glass transition temper



FIG. 10. Oxygen-oxygen (OO), oxygen-hydrogen (OH), and hydrogenhydrogen (HH) radial distribution function of HDA at P = 900 MPa and T = 160 K. HDA is prepared by (i) decompression of HDA at T = 80 K to 900 MPa followed by isobaric heating, (ii) compression of LDA at T = 160 K (red dashed lines), or (iii) compression of LDA at T = 20 K to P = 900 MPa followed by isobaric heating (blue dotted-dashed); see Fig. 1. All HDA forms exhibit very similar OO, OH, and HH RDFs suggesting that they belong to a single "HDA" family of glasses.

atures, $T_g^{\text{HDA}} \approx 220\text{--}240$ K in the range $P \approx 500\text{--}800$ MPa (see maroon up-triangles and blue dashed-line at $500 \le P \le 700$ MPa).

If decompressed HDA is the same HDA form obtained upon heating LDA (Sec. III A 2) then both forms should exhibit the same quantitative behavior in thermodynamics (e.g., $\rho(T)$, PE(T), and $c_P(T)$) and dynamics (e.g., MSD and rotational MSD) upon heating. To show that this is the case, we discuss separately the three transformation scenarios (i)–(iii) found at $P \ge 400$ MPa.

(i) In order to describe the HDA-to-crystal transformation, we focus on the example case P = 900 MPa. At this pressure, all 10 runs indicate that decompressed HDA crystallizes upon heating. We note that the resulting high-pressure crystal is, once again, ice VII. The RDFs of this ice, obtained by heating decompressed HDA, as well as the ice VII forms resulting from compressing HDL and from heating LDA, are shown in Fig. 6. It follows that the structure of ice VII, obtained from three very different thermodynamic paths, are nearly indistinguishable.

The behavior of $\rho(T)$, PE(T), and $c_P(T)$ upon heating HDA at P = 900 MPa are shown in Figs. 11(a)–11(c), and compared with the properties of HDA obtained upon heating LDA at P = 700 MPa (taken from Fig. 5). It follows from these figures that for both HDA forms, $\rho(T)$, PE(T), and $c_P(T)$ exhibit the same qualitative behavior suggesting that these forms can be considered part of the same HDA "family." In both cases, the HDA-to-crystal transformation is accompanied by a sudden change in density and potential energy while $c_P(T)$ exhibits a large exothermic peak.

(ii) and (iii) The HDA-to-HDL and HDA-to-HDL-tocrystal transformations for decompressed HDA can be clearly observed at P = 500 MPa; at this pressure, independent simulations exhibit one of these two scenarios (see Table II). The behavior of $\rho(T)$, PE(T), and $c_P(T)$ upon heating are shown in Figs. 12(a)–12(c); the corresponding properties for the HDA forms obtained by heating LDA (at P = 700 MPa) are shown in Figs. 5(a)–5(c), black and red lines. As expected from the



FIG. 11. (a) Density $\rho(T)$, (b) potential energy PE(T), and (c) constantpressure specific heat $c_P(T)$ obtained upon heating decompressed HDA at P = 900 MPa (black lines). At this pressure, all independent runs show HDA-to-crystal (ice VII) transformations. For comparison, included are $\rho(T)$, PE(T), and $c_P(T)$ obtained during heating of LDA at P = 700 MPa (blue lines taken from Fig. 5). At this pressure, LDA transforms to HDA which transforms to ice VII upon further heating. Independently of the preparation process of HDA, both HDA transforms to ice VII at the same temperature (≈ 250 K) and $\rho(T)$, PE(T), and $c_P(T)$ exhibit similar T-dependence during the HDA-to-ice VII transformation.

previous comparison at 900 MPa, the HDA transformations for both preparations are very similar. In both cases, while the system is in the HDA state, $\rho(T)$, PE(T), and $c_P(T)$ show a weak temperature dependence and, at the HDA-to-HDL transformation, $\rho(T)$ and PE(T) change suddenly (black lines), at ≈ 225 K for P = 500 MPa [Figs. 12(a) and 12(b)], and at ≈ 240 K for P = 700 MPa [Figs. 5(a) and 5(b)]. In addition, at these temperatures, the corresponding $c_P(T)$ starts to develop a wide maximum [black lines in Figs. 12(a) and 5(c)].

When crystallization of HDL occurs (scenario (iii)), $\rho(T)$ and PE(T) show a sharp change (red lines) at $\approx 240-250$ K for P = 500 MPa [Figs. 12(a) and 12(b)] and [Figs. 5(a) and 5(b)]. In addition, $c_P(T)$ develops the expected characteristic large exothermic peak. As discussed in Sec. III A 2, the behavior of $\rho(T)$, PE(T), and $c_P(T)$ evolves from HDL-like at low temperatures [scenario (ii)] to crystal-like [scenario (i)], as shown by the red lines in Figs. 12(a)-12(c). We note that, in agreement with the discussion in Sec. III A 2, the liquid-to-glass transition is reflected in the appearance of a small peak in $c_P(T)$ that is rapidly suppressed by the crystallization exothermic peak; see red line in Fig. 12(c). Figures 12(a)-12(c) also suggest that the crystal starts to melt approaching 300 K. Specifically, at T > 300 K, $\rho(T)$ decreases, while PE(T) increases, upon heating. In addition, $c_P(T)$ exhibits oscillations at these temperatures. As is shown



FIG. 12. (a) Density, (b) potential energy, and (c) constant-pressure specific heat upon heating decompressed HDA at P = 500 MPa. Two different scenarios occur among the independent runs, HDA-to-HDL (black lines) or HDA-to-HDL-to-ice VII (red lines) transformations. In the last case, the glass transition peak in $c_P(T)$ (at $T \approx 240$ K, black line) is suppressed by the crystallization minimum that occurs at $T \approx 250$ K (red line) resulting in a small peak at $T \approx 230$ K (red line).

next, the differentials MSD and rotational MSD also exhibit a smooth increase with temperature for T > 300 K, indicative of molecular motion.

The differential MSD $d\langle r^2(T)\rangle/dT$ and rotational MSD $d\langle \phi^2(T) \rangle/dT$ during heating of decompressed HDA at P = 500 MPa are shown in Fig. 13. As for the case of HDA formed by heating LDA (Fig. 7, black and red lines), the HDA-to-crystal transition is evident by the peak in $d\langle r^2(T)\rangle/dT$ and $d\langle \phi^2(T)\rangle/dT$ at intermediate temperatures $(T \approx 250 \text{ K})$; such a feature is absent in the case of HDAto-HDL transformation. As is also the case in Fig. 7, Fig. 13 shows that the changes in $d\langle r^2(T)\rangle/dT$ and $d\langle \phi^2(T)\rangle/dT$ are coincident, demonstrating that translations and rotations become active simultaneously upon reaching the HDA glass transition in ST2 water. This is consistent with the recent experiments of Amann-Winkel et al.,56 who argue that the HDA transition is a proper glass-to-liquid transition, as opposed to an orientational glass transition where only orientations become free (a plastic solid).

2. Heating HDA at P ≤ 300 MPa

For P = 300 MPa, all independent simulations show that heating HDA results in HDL, with no intermediate states. The phenomenology associated with the HDA-to-HDL transformation is similar to the corresponding transformation

TABLE II. Number of independent simulations at $300 \le P \le 700$ MPa that exhibit HDA-to-liquid and HDA-to-liquid-to-crystal transformations. At each pressure, 10 independent simulations are performed. At $700 < P \le 900$ MPa, all simulations show HDA-to-Crystal transformations. At $-100 \le P \le 200$ MPa, all simulations exhibit HDA-to-LDA-t0-LDA-t0-LDA-t0-LDA-

Transformation sequence	P = 300 MPa	P = 400 MPa	P = 500 MPa	P = 600 MPa	P = 700 MPa
HDA-to-liquid	10	7	4	1	0
HDA-to-liquid-to-crystal	0	3	6	9	10

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FIG. 13. (a) Differential mean-square displacement and (b) rotational meansquare displacement upon heating decompressed HDA at P = 500 MPa. Black and red lines correspond to the average over the independent runs that exhibit HDA-to-HDL or HDA-to-HDL-to-ice VII transformations, respectively.

discussed in Sec. III B 1 for the case P = 500 MPa. At $-500 \le P < 300$ MPa, we find that HDA always transforms to LDA upon heating. In these cases, further heating of LDA results in either liquid ($-100 \le P < 200$ MPa) or vapor phase ($-500 \le P < -100$ MPa).

The HDA transformation temperature $T^{\text{HDA}}(P)$, whether the transformation is to LDA or to HDL, constitutes a single locus in the P-T plane (Fig. 9, maroon up-triangles). These results suggest that the glass transition of HDA and the HDAto-LDA (glass-glass) transformation are not independent phenomena, as is sometimes considered. Instead, this locus may be more properly understood as the (rate dependent) locus of dynamical stability of HDA, regardless of the phase to which HDA transforms. It follows that $T^{\text{HDA}}(P)$ plays the same role for HDA to the role played by $T^{\text{LDA}}(P)$ for the case of LDA.

In Sec. III A, we noted that the heating-induced $T^{\text{LDA}}(P)$ locus approximately merges with the compression-induced $P^{\text{LDA}}(T)$ at high pressure and low temperature, at least for the compression and heating rates considered. We test if an analogous correspondence holds for the case of heating-induced $T^{\text{HDA}}(P)$ and decompression induced $P^{\text{HDA}}(T)$. Accordingly, we show $P^{\text{HDA}}(T)$ in Fig. 9. $P^{\text{HDA}}(T)$ and $T^{\text{HDA}}(P)$ exhibit a similar slope for most temperatures (T = 20 - 180 K), but the $T^{\text{HDA}}(P)$ locus is shifted relative to the $P^{\text{HDA}}(T)$ line by ≈ 200 MPa. However, it was shown in Ref. 38 that the $P^{\text{HDA}}(T)$ locus shifts to higher pressures as the decompression rate decreases. Therefore, the present results suggest that the corresponding loci may overlap at high pressure and low



FIG. 14. (a) Density, (b) potential energy, and (c) constant-pressure specific heat upon heating HDA at P = 0.1 MPa. At this pressure, all runs exhibit HDA-to-LDA-to-liquid transformations.

temperature for much lower rates than those employed in this work.

At $-100 \le P \le 200$ MPa, further heating of LDA results in the liquid phase. The LDA-to-liquid transformation locus is indicated in Fig. 9 by red up-triangles. These temperatures fall on the $T^{\text{LDA}}(P)$ line (see Sec. III A) and hence, as expected, support the view that the LDA formed upon (i) isothermal decompression of HDA or (ii) isobaric heating of HDA belong to the same "family." In particular, these results further support the previous conclusion that $T^{\text{LDA}}(P)$ indeed represents the limit of dynamical stability of LDA relative to *all* other phases.

The HDA-to-LDA-to-liquid transformation sequence, at low pressures, is analogous to the LDA-to-HDA-to-liquid transformation sequence, at high pressures, discussed in Sec. III A 2. To show this, we include in Figs. 14(a)-14(c)the temperature dependence of $\rho(T)$, PE(T), and $c_P(T)$ upon heating HDA at P = 0.1 MPa. This figure can be compared with Figs. 5(a)-5(c), black lines, that shows the same properties during the LDA-to-HDA-to-HDL transformations. In both cases, the glass-glass and glass-liquid transformations are accompanied by sharp changes in $\rho(T)$ and PE(T). These transformations are particularly evident in the behavior of $c_P(T)$; while the LDA-to-HDA and HDA-to-LDA transformations are accompanied by an exothermic minimum in $c_P(T)$, the LDA-to-liquid and HDA-to-liquid (glass) transitions are signaled by the wide maximum in $c_P(T)$. Interestingly, in the intermediate glass phase [LDA in Fig. 14(c) and HDA in Fig. 5(c) (black line)], $c_P(T)$ remains practically constant. We note that the HDA-to-LDA transformation at P = 0.1 MPa is also evident from the peaks of $d\langle r^2(T)\rangle/dT$ and $d\langle \phi^2(T)\rangle/dT$ (Fig. 15(a)), occurring at $T \approx 185$ K. Both translational and rotational displacement are needed for the HDA-to-LDA transformation. Once the liquid forms, diffusion occurs and accordingly, $d\langle r^2(T)\rangle/dT$ and $d\langle \phi^2(T)\rangle/dT$ increase monotonically with increasing temperature. Figures 15(a) and 15(b)are qualitatively similar to Figs. 7(a) and 7(b) obtained during the LDA-to-HDA-to-HDL transformation at high pressure. This suggests that in all cases, transformations consist of both translational displacement and reorientation.



FIG. 15. (a) Differential mean-square displacement and (b) rotational meansquare displacement upon heating decompressed HDA at P = 0.1 MPa, during the HDA-to-LDA-to-liquid transformation.

At very negative pressures, LDA sublimes upon further heating. The LDA-to-vapor locus is shown in Fig. 9. Interestingly, these temperatures (blue up-triangles) are much lower than the temperatures at which decompression induced LDA sublimates (violet left-triangles). It follows that the LDA forms obtained by decompression of HDA are more stable, relative to the vapor, than the LDA forms obtained by heating decompressed HDA. So while these LDA forms may be part of the same family, there are certainly quantitative differences.

IV. SUMMARY AND DISCUSSION

We described the phase behavior of ST2 water in the glass state and related it to the equilibrium liquid phase diagram reported in Refs. 24, 29, 39, 40, 43, 72, and 91. The present results were based on isobaric heating simulations starting from LDA and HDA at pressures in the range -500 $\leq P \leq 1700$ MPa. It was found that, depending on pressure, individual runs may exhibit diverse transformations, including glass-glass (LDA-HDA), glass-liquid (HDA/LDAliquid), glass-crystal (HDA-crystal), and glass-vapor (LDAvapor) transformations. Combining the present results with those obtained in a previous work based on isothermal compression/decompression of LDA and HDA,38 we have constructed a relatively complete P-T phase diagram for ST2 glassy water (Figs. 1 and 9). The significance of this phase diagram depends upon the ability to treat the LDA and HDA families as reasonable representatives of metastable phases as is the case of ST2 water. It should be understood that such a phase diagram for the glass state may be sensitive to compression/decompression and heating/cooling rates. However, the relevance of such a phase diagram resides on the condition that its qualitative features do not change significantly with reasonable rates, and that nearly the same transition loci occur, whether transitions are driven by temperature or pressure.

Although it may be somewhat speculative, it is relevant to consider what the results obtained from glassy ST2 water simulations predict for the case of real water.



FIG. 16. Schematic phase diagram proposed for the case of real water based on the results for ST2 water (Figs. 1 and 9) and available data for uHDA. Symbols are experimental data: liquid-to-vapor spinodal (blue circles),94 pressure-induced LDA-HDA transformation pressures (orange and red triangles¹⁵), pressure-induced ice I_h -to-HDA transformation (green triangles¹⁵), equilibrium liquid-crystal coexistence line (thick grey line¹ 5). and glass-to-crystal transformation temperature, $T_x(P)$ (thick black line¹⁵). Dotted-dashed lines at $T < T_x(P)$ are linear extrapolation of experimental data to $T \rightarrow 0$. Dotted-dashed lines at $T > T_x(P)$ are the hypothesized LDL-HDL spinodal lines ending at the hypothesized LLCP. Dashed-lines are estimated transformation lines based on ST2 water simulations: heating induced LDA/LDL-to-vapor (blue line), heating-induced LDA-to-liquid or HDA $(T^{LDA}(P))$, green line), heating-induced HDA-to-liquid or LDA $(T^{HDA}(P), \text{ maroon line})$. The inset shows an expanded view of the region near the glass transitions and crystallization limit, where an ultra-viscous liquid is expected to be accessible.

A schematic *P*-*T* phase diagram for the case of real water is shown in Fig. 16, expected to hold in the limit of slow compression/decompression/heating rates. This phase diagram includes available experimental data for uHDA. In Fig. 16, the (i) compression-induced ice I_h -to-HDA and LDA-to-HDA transformation ($P_{LDA}(T)$) pressures are negatively sloped while (ii) the decompression-induced HDA-to-LDA transformation pressure ($P_{HDA}(T)$) is positively sloped. In addition, (iii) the pressure-induced LDA-to-HDA and HDA-to-LDA transformation lines merge smoothly with the *hypothesized* LDL-to-HDL and HDL-to-LDL spinodal lines, respectively, as predicted by the LLPT hypothesis.^{1,29}

One of the main characteristics of Fig. 16 (best seen in the inset) is the relationship between the heating-induced glass-glass transformation and glass transition lines. Specifically, (iv) the heating-induced LDA-to-HDA transformation line at high pressures is an extension of LDA's glass transition temperature locus, at low pressures. This locus, $T^{\text{LDA}}(P)$, constitutes the limit of stability of LDA relative to all other phases, i.e., HDA and the liquid, during heating processes. In Fig. 16, $T^{\text{LDA}}(P)$ intersects the *T*-axis at 136 K since this is the standard value of LDA glass transition temperature. As in the case of glassy ST2 water, (v) the $T^{\text{LDA}}(P)$ locus is negatively sloped in the *T-P* plane, and merges smoothly with the $P_{\text{LDA}}(T)$ locus at high pressures.

In a symmetric fashion, (vi) the heating induced HDAto-LDA transformation line at low pressures is a smooth extension of HDA's glass transition locus, at high pressures. This locus, $T^{\text{HDA}}(P)$, constitutes the limit of stability of HDA relative to all other phases, i.e., HDL and LDA, during the heating processes. In Fig. 16, $T^{\text{HDA}}(P)$ intersects the *T*-axis at 117 K since this is the standard value of the uHDA-to-LDA transformation temperature at normal pressure. (vii) The $T^{\text{HDA}}(P)$ locus is positively sloped in Fig. 16 and it is *assumed* to merge with the $P_{\text{HDA}}(T)$ locus at low pressures.

Our heating simulations of HDA at low pressure show only the HDA-to-LDA transformation followed by the LDAto-liquid transition. We point out that the form of HDA we use is unrelaxed (uHDA). Recently, using expanded HDA (eHDA), Loerting and co-authors found evidence for an intermediate liquid state between eHDA and LDA.^{8,56} It is not clear if such a scenario applies in ST2, e.g., if we could relax HDA to the expanded form and heat much more slowly.

As observed in our simulations, as well as in experiments,⁸ (viii) the $T^{\text{HDA}}(P)$ locus ends at the crystallization line, $T_x(P)$, at high pressures. At very negative pressures, (ix) the $T^{\text{LDA}}(P)$ locus is expected to either intersect the crystallization line, $T_x(P)$ or merge with the LDA sublimation line, as observed in ST2 water simulations.

Combining the above facts, the $T^{\text{LDA}}(P)$, $T^{\text{HDA}}(P)$, and $T_x(P)$ lines bound a small region (inset of Fig. 16) where we expect an ultra-viscous metastable liquid to be accessible; this is already partially confirmed by some experiments.^{8, 15, 23, 56} Experimentally mapping the LDA/HDA-to-liquid and LDA-HDA transformation lines would serve to test the hypothesis that the glass-glass transition is a continuous extension of the glass-liquid transition, as well as the existence of multiple liquid states.

We stress that the phase diagram of Fig. 16 should be valid in the limit of very slow rates (provided the crystal is avoided). Indeed, it was found that, within the range of rates explored in standard MD simulations, the LDA-HDA transformation, as well as the glass transition loci of LDA and HDA, depend on the rates employed (see, e.g., Refs. 38 and 81). Similar effects cannot be excluded a priori even for experimental time scales. For example, the glass transition of LDA at P = 0.1 MPa is 136 \pm 2 K at $q_T = 30 \text{ K/min}^{88,92}$ but it is 124 K for $q_T = 0.17 \text{ K/min.}^{87}$ Similarly, a mild sensitivity of the LDA-to-HDA transformation pressure is apparent from Fig. 3 of Ref. 20. The present simulations suggests what should be the effect of altering heating/compression/decompression rates on the different transformation lines in the P-T phase diagram of glassy water. Specifically, increasing the compression (decompression) rate is expected to increase (decrease) the LDA-to-HDA (HDA-to-LDA) transformation pressure $P_{LDA}(T)$ ($P_{HDA}(T)$). Decreasing the heating rate is expected to shift the $T_{LDA}(T)$ and $T_{HDA}(T)$ to lower temperatures.

Finally, we note that in Fig. 16 the LLCP has been located at P = 50 MPa and T = 205 K. The LLCP pressure of 50 MPa is based on the results of Ref. 93. The LLCP temperature of 205 K is obtained by extrapolating the LDA-to-HDA experimental data linearly to P = 50 MPa. This value is different from the LLCP temperature estimated in Ref. 93, \approx 223 K. Assuming a LLCP temperature of \approx 223 K and critical pressure of 50 MPa would imply that the slope of the LDL-to-HDL spinodal line should increase (i.e., become less negative) with increasing temperature.

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