

Water polyamorphism: Reversibility and (dis)continuity

Katrin Winkel,¹ Michael S. Elsaesser,² Erwin Mayer,¹ and Thomas Loerting^{2,a)}

¹*Institute of General, Inorganic and Theoretical Chemistry, University of Innsbruck, Innrain 52a, A-6020 Innsbruck, Austria*

²*Institute of Physical Chemistry, University of Innsbruck, Innrain 52a, A-6020 Innsbruck, Austria*

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An understanding of water's anomalies is closely linked to an understanding of the phase diagram of water's metastable noncrystalline states. Despite the considerable effort, such an understanding has remained elusive and many puzzles regarding phase transitions in supercooled liquid water and their possible amorphous proxies at low temperatures remain. Here, decompression of very high density amorphous ice (VHDA) from 1.1 to 0.02 GPa at 140 K is studied by means of dilatometry and powder x-ray diffraction of quench-recovered states. It is shown that the three amorphous states of ice are reversibly connected to each other, i.e., $LDA \leftrightarrow e\text{-HDA} \leftrightarrow \text{VHDA}$. However, while the downstroke $\text{VHDA} \rightarrow e\text{-HDA}$ transition takes place in the pressure range of $0.06 \text{ GPa} < p < 0.40 \text{ GPa}$, the $e\text{-HDA} \rightarrow LDA$ transition takes place quasi-discontinuously at $p \sim 0.06 \text{ GPa}$. That is, two amorphous-amorphous transitions of a distinct nature are observed for the first time in a one-component system—a first-order-like transition ($e\text{-HDA} \rightarrow LDA$) and a transition which is not first-order like but possibly of higher order ($\text{VHDA} \rightarrow e\text{-HDA}$). VHDA and e-HDA are established as the most stable and limiting states in the course of the transition. We interpret this as evidence disfavoring the hypothesis of multiple first-order liquid-liquid transitions (and the option of a third critical point), but favoring a single first-order liquid-liquid transition (and the option of a second critical point). © 2008 American Institute of Physics.

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INTRODUCTION

The search for an explanation regarding the anomalous properties of water lasts for more than a century. A number of theories have been put forward over time, but still no single theory is generally accepted.^{1–3} A particularly appealing hypothesis was offered by Poole *et al.*,⁴ who suggested a first-order liquid-liquid phase transition between a low-density liquid (LDL) and a high-density liquid (HDL). They furthermore, conjectured that the line of co-existence between LDL-HDL may end in a liquid-liquid critical point (T_{C2}, p_{C2}), which would be the second critical point in water's phase diagram following the first (gas-liquid) critical point at $T_{C1} = 647 \text{ K}$ and $p_{C1} = 22 \text{ MPa}$. It seems to be agreed upon from computer simulations that this postulated second critical point could be somewhere below the homogeneous nucleation line T_H , while it is not clear if this second critical point could be located close to ambient pressure, at slightly negative pressures⁵ or rather at elevated pressures such as 100 MPa.⁶ Experimental studies on the decompression induced melting of high-pressure crystalline ice in emulsified water point toward a second critical point at positive pressures.^{7,8} Studies on water confined in nanopores up to 18 Å are consistent with $p_{C2} > 0$, but not with $p_{C2} < 0$.^{9–11} These studies infer a fragile-to-strong crossover from a high-density liquid to a low-density liquid upon cooling to T

$< 220 \text{ K}$ (at 1 bar). From the pressure dependence of the transition, the location of the second critical point for nanoscopically confined water is estimated to be $p_{C2} = 160 \pm 40 \text{ MPa}$ and $T_{C2} = 200 \pm 10 \text{ K}$.¹⁰ It is a matter of current debate whether the observed transition is expected to occur also in bulk water or rather due to the confinement-induced vanishing of the α relaxation^{12,13} or due to the onset of finite-size effects at $T < 225 \text{ K}$.¹⁴ Similarly, a transition from HDL to LDL is inferred for interfacial hydration water (two dimensional). However, while studies on hydration water in biopolymers^{15–17} point to a fragile-to-strong transition incurred upon crossing the Widom line¹⁸ at 1 bar (extension of the liquid-liquid coexistence line beyond the second critical point), studies on hydration water of Vycor glass¹⁹ point to a first-order liquid-liquid transition at 1 bar. Water confined in a fully hydrated Na vermiculite clay shows a fragile-to-strong transition in the temperature range of 215–254 K.²⁰ It seems, therefore, that the nature of the transition and the locus of the possible second critical point are influenced by the surrounding medium in confined water. In Fig. 1, the possible second critical point for *bulk* water is plotted at 100 MPa and 220 K.⁴ Even though no direct experimental probes of bulk liquid behavior can be conducted because of rapid crystallization in the so-called “no-man's land” at temperatures below the homogeneous nucleation temperature T_H , the presence of such a second critical point could cause, e.g., the “power law singularity,” i.e., an anomalous power law *increase* in isobaric heat capacity and isothermal compressibility observable *upon cooling* supercooled water to 228 K.²¹ Fluctuations between low- and

^{a)} Author to whom correspondence should be addressed. Electronic mail: thomas.loerting@uibk.ac.at. Tel.: +43-512-507-5072. Fax: +43-512-507-2925.

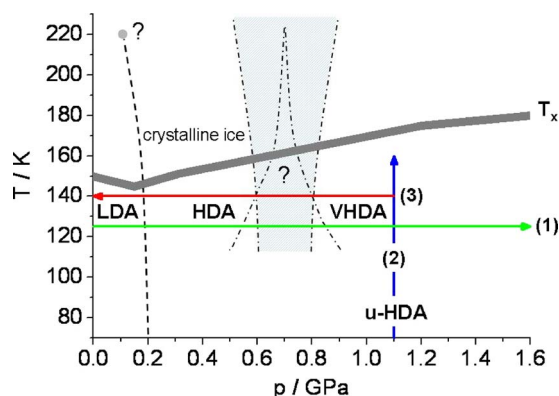


FIG. 1. (Color online) Schematic phase diagram of water's metastable states. Line 1 indicates the upstroke transition LDA \rightarrow HDA \rightarrow VHDA, which we reported recently (Ref. 42). Line 2 indicates the preparation procedure of VHDA used for the present study. Line 3 indicates the decompression path at 140 K, which shows the reverse VHDA \rightarrow HDA \rightarrow LDA transition sequence. The thick gray line marked T_x represents the crystallization temperature above which rapid crystallization is observed [adapted from Mishima (Ref. 25)]. The metastability fields for LDA and HDA are delineated by a sharp dashed line, which is the possible extension of a first-order liquid-liquid transition ending in a hypothesized second critical point. The metastability fields for HDA and VHDA are delineated by a broad area, which may either become broader (according to the singularity free scenario Refs. 52 and 53) or alternatively become more narrow (in case the transition is limited by kinetics) as the temperature is increased. The question marks indicate that the extrapolation of the abrupt LDA \leftrightarrow HDA and the smeared HDA \leftrightarrow VHDA transitions at 140 K to higher temperatures are speculative. For simplicity, we average out the hysteresis effect observed upon upstroke and downstroke transitions as previously done by Mishima (Ref. 25), which results in a HDA \leftrightarrow VHDA transition at $T=140$ K and $p\sim 0.70$ GPa, which is ~ 0.25 GPa broad and a LDA \leftrightarrow HDA transition at $T=140$ K and $p\sim 0.20$ GPa, which is at most 0.01 GPa broad, i.e., discontinuous within the experimental resolution.

high-density clusters above the critical point are speculated to be at the origin of these anomalies in this view.

Some experimental support for the theory was provided from studies of noncrystalline bulk water conducted below the crystallization temperature T_x by Mishima *et al.*²² They first succeeded in pressure amorphizing hexagonal ice at $T=77$ K,²³ which results in an x-ray amorphous state nowadays called *unrelaxed* high-density amorphous ice (u-HDA).²⁴ Upon first bringing u-HDA to $T\sim 130$ K and then releasing pressure a sharp transition characterized by a significant density decrease is found to occur.^{22,25} The state recovered after release of pressure is again x-ray amorphous and called low-density amorphous ice (LDA). Thus, water was the first liquid found to show “amorphous polymorphism” (“polyamorphism”). The number of liquids found to show this kind of anomaly is steadily increasing²⁶ and comprises atomic and molecular liquids; organic, inorganic and metallic liquids; and open polyhedral and densely packed networks. A thorough knowledge of polyamorphism and the phase diagram of metastable states²⁷ are likely the key to an understanding of anomalous liquid properties.

Nelmes *et al.* have demonstrated that u-HDA first relaxes to form what is called *expanded* HDA (e-HDA). The e-HDA substate (and not u-HDA) in the HDA megabasin then experiences a first-order-like transition to LDA.²⁴ Using *in situ* neutron diffraction and Raman spectroscopy coexistence between e-HDA and LDA was inferred.^{28,29} Upon pres-

surizing LDA a sharp transition to e-HDA demonstrates with some hysteresis the reversibility.^{25,30} All these experimental findings are consistent with a first-order-like transition. In order to view these experimental findings as a support for the liquid-liquid transition hypothesis, it is assumed that the first-order-like LDA \leftrightarrow e-HDA transition maps into a first-order liquid-liquid phase transition when extended to higher temperatures. This also implies the occurrence of a glass \rightarrow liquid transition upon heating the nonequilibrium amorphous states LDA and e-HDA and a structural resemblance between LDA and LDL and e-HDA and HDL. There is much controversy about the glass \rightarrow liquid transition,^{31,32} and it is debated whether LDA and HDA behave like glasses or rather like microcrystals.^{33–35} However, most experiments are consistent with a glass \rightarrow liquid transition temperature $T_g\sim 136$ K for LDA at 1 bar,¹ and also recent experiments have suggested liquidlike properties for HDA close to the crystallization line.^{36,37}

Our discovery of a third distinct structural state of amorphous ice called very-high-density amorphous ice (VHDA) (Refs. 38–40) poses a threat to the liquid-liquid transition hypothesis. Since it is $\sim 10\%$ more dense than HDA the possibility of a first-order-like HDA \leftrightarrow VHDA transition, which maps into HDL \leftrightarrow VHDL arises. This raises the question if water has possibly even a multiple liquid nature, which has been suggested from simulations.⁴¹ Our recent results show that there is an upstroke transition HDA \rightarrow VHDA in the pressure range of ~ 0.80 – 0.95 GPa,^{30,42–44} which appears to be quite similar to the LDA \rightarrow e-HDA transition at lower pressures, albeit somewhat broader. Similar multiple amorphous-amorphous transitions are discussed for the cases of Si (Ref. 45) and SiO₂.⁴⁶ However, our upstroke results are ambiguous whether the nature of the transition is first-order-like, second-order-like, or continuous.⁴³ Whereas the presence of a quasiphase boundary between HDA and VHDA would point toward a multiple liquid nature of water and a possible third (liquid-liquid) critical point, its absence would restore the validity of the single liquid-liquid transition hypothesis.^{47,48} This issue has been called “a key unanswered question” in understanding metastable water by Debenedetti.¹

EXPERIMENTAL AND RESULTS

In order to tackle this question whether there are an infinite number of structures on the way from e-HDA to VHDA (“continuous transition”) or if there is a discontinuity somewhere along the path, here we analyze the downstroke transition of VHDA at 140 K. Since the polyamorphic transitions are discussed as the extensions of true phase boundaries between liquids to low temperatures, it is necessary to directly probe the extensions of the phase boundaries under *in situ* conditions (rather than to probe relaxation effects observable by heating amorphous samples at 1 bar). We note that Mishima²⁵ has already demonstrated the “reversible first-order transition between two H₂O amorphs,” namely, LDA and HDA, with hysteresis on the up- and downstroke transitions at ~ 135 K. However, at his rate of (de)compression of 600 MPa/min the stepwise increase in density of the

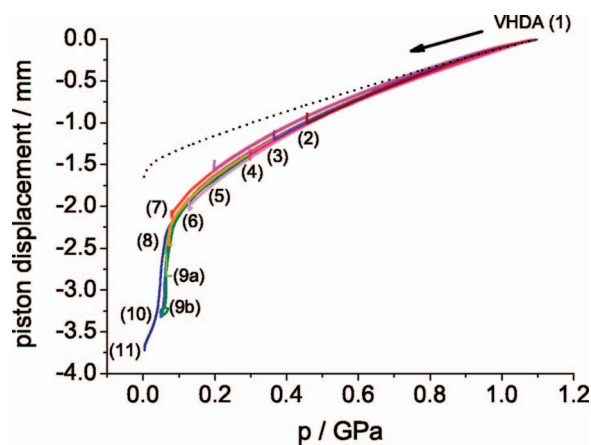


FIG. 2. (Color) Piston displacement curves for isothermal decompression of VHDA at 140 K with a rate of 20 MPa/min. Eleven runs stopped at different pressures are shown, marked with bracketed numbers. The hooks near the end of decompression are indicative of the onset of the quench-recovery procedure bringing the samples to 77 K and 1 bar. All measurements were done with a computerized “universal material testing machine” (Zwick, model BZ100/TL3S), with a positional reproducibility of $0.5\ \mu\text{m}$ and a spatial resolution of $0.01\ \mu\text{m}$, in a piston-cylinder apparatus of 8 mm bore diameter. The sample volume is $300\ \mu\text{l}$ of de-ionized water (H_2O). To avoid sudden pressure drops during the measurements, all samples were kept in a container of 300 mg indium. Decompression of an empty indium container is shown as the black dotted line.

HDA \rightarrow VHDA transition flattens out and does not become observable anymore.^{30,42,43} At our rate of 20 MPa/min, we can study two amorphous-amorphous transitions in a single experiment. Further experimental details are given in the figure captions.

Using piston-cylinder studies we show that LDA is produced from VHDA via a series of HDA-states including e-HDA. If the reverse transition VHDA \rightarrow HDA were discontinuous, one would expect to observe a steplike change in density, probably with hysteresis, i.e., at pressures $p < 0.95$ GPa. However, we do observe a continuous decrease in density, which accelerates in the pressure range of $0.06 < p < 0.40$ GPa. The structural states along the decompression path were probed on quench-recovered samples by x-ray diffraction. While the structural state of VHDA is barely affected upon decompressing from 1.1 to 0.40 GPa, a continuous shift from the approximately six-coordinated VHDA structural state³⁹ to the approximately five-coordinated HDA structural state⁴⁹ is observed in the pressure range $0.06 < p < 0.40$ GPa.

VHDA was produced by isobaric annealing of u-HDA at 1.1 GPa to 160 K as indicated in Fig. 1.³⁸ After annealing to 160 K the sample was cooled at 1.1 GPa to 140 ± 0.5 K, which serves as the starting point (Ref. 1) in Fig. 2. Subsequently, the VHDA sample was decompressed along the path indicated in Fig. 1 with a rate of 20 MPa/min under isothermal conditions, which finally results in the formation of LDA at $p < 0.06$ GPa. In order to investigate the intermediate states along the isothermal decompression path, we stopped decompression at several pressures by quenching to 77 K first (bracketed numbers in Fig. 2) and then released the pressure with a rate of 20 MPa/min. The recovered samples were characterized by powder x-ray diffraction as shown in Fig. 3(a). The highest possible temperature, which does not result in crystallization upon decompression is

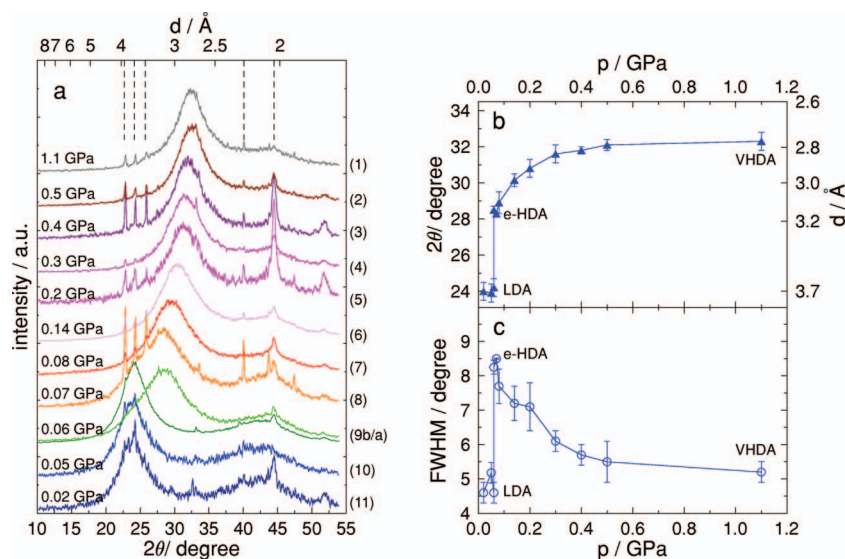


FIG. 3. (Color) (a) Powder x-ray diffractograms for eleven different samples (2–11), obtained by isothermal decompression of VHDA at 140 K to several selected pressures (as labeled), subsequent quenching to 77 K and recovery to ambient pressure. The diffractograms ($\text{Cu K}\alpha$) were recorded at ~ 83 K on a diffractometer in Θ - Θ geometry (Siemens, model D 5000), equipped with a low-temperature camera of Anton Paar. Sample 1 is VHDA produced by isobaric annealing of u-HDA at 1.1 GPa to 160 K. Curves are shown on the same scale and smoothed with a 21-point Savitzky-Golay polynomial of fifth order. Data are offset for clarity. We want to emphasize that the diffractograms of the samples 10 and 11 have been recorded with an aging x-ray tube, this is why the signal to noise ratio is worse compared to the other diffractograms. All other measurements have been done with a new x-ray tube. Also the sample amount differs from measurement to measurement and therefore the data are scaled. The right panel shows (b) the peak position and (c) the full width at half maximum (FWHM) of the first broad diffraction peak as function of the selected decompression pressure. The first broad diffraction peak and the FWHM were determined by fitting two Lorentz-functions to the diffraction pattern. We have done two x-ray measurements for every sample and, therefore, the plotted values are a median of the two. The experimental error of a single measurement is $\pm 0.5^\circ$. In some powder diffractograms sharp features marked by the dashed lines can be seen. They arise from traces of I_h , which had formed by condensation of water vapor during transfer of the sample onto the precooled sample holder (Ref. 56), the x-ray sample holder itself (chrome-plated Cu: $2\Theta = 44.5^\circ$) or remnants of indium. The samples themselves are fully amorphous.

140 K. Independent experiments at 141 (143) K have resulted in crystallization at 0.10 (0.13) GPa since the crystallization temperature (T_X) minimum was crossed (cf. Fig. 1). This is evidenced by a sudden, discontinuous change in pressure and piston displacement and sharp Bragg peaks in the powder diffractogram. At lower temperatures such as 125 K, the transformation to LDA does not take place for kinetic reasons, decompression of VHDA at 125 K leads to the formation of a HDA-like state at 1 bar. That is, at 140 K the amorphous ices produced represent the best experimentally attainable proxies for the supercooled liquids to which they may be connected. A direct structural relation between amorphous ice and supercooled water was recently inferred from *in situ* Raman spectroscopy.²⁹ From dielectric relaxation spectroscopy HDA at 0.4 GPa and VHDA at 1.0 GPa are even suggested to show liquidlike behavior at $T < 140$ K,³⁷ whereas thermal studies suggest that emulsified HDA remains glassy up to 160 K at 0.4 GPa.³⁶

Figure 2 shows the piston displacement of VHDA (sample 1), decompressed at 140 K to ten selected pressures (samples 2–11). Decompression of an empty indium container (and no ice sample) is shown as the black dotted line as a “blind experiment.” Full decompression of VHDA at 140 K to 0.02 GPa leads to the formation of LDA (sample 11). An abrupt volume change of $\sim 20\%$ at ~ 0.06 GPa is observed, which we attribute to the e-HDA \rightarrow LDA transition. In contrast to our isothermal compression-measurements on LDA at 125 K (Ref. 42), we cannot find a two step process upon decompressing VHDA. The piston displacement continuously changes down to ~ 0.06 GPa, where a sharp, steplike density decrease of $\sim 20\%$ takes place. The corresponding x-ray diffraction patterns of the intermediate states, with VHDA (sample 1) as starting material, are shown in Fig. 3(a). In accordance with the literature data, the diffraction pattern of VHDA (sample 1) has its first broad maximum at $d = 2.77$ Å ($2\Theta = 32.3^\circ$). The state recovered after decompression at 140 K to 0.5 GPa shows a diffraction pattern with a first broad maximum at $d = 2.79$ Å ($2\Theta = 32.1^\circ$). Both of these patterns can be called VHDA according to the definition of Salzmann *et al.*⁴⁴ That is, only minor structural changes take place upon decompressing VHDA from 1.1 to 0.40 GPa at 140 K. Further decompression is continuously shifting the position of the first diffraction peak to higher d spacing, i.e., a series of HDA-states differing in structure is produced. Figure 3(b) shows the position of the maximum of the first diffraction peak, plotted versus the pressure at which the sample was decompressed and recovered. The “full width at half maximum (FWHM)” as shown in Fig. 3(c), indicates a continuously increasing FWHM. e-HDA as the “final” state in the HDA-megabasin²⁴ shows the highest FWHM and the highest d spacing. All amorphous ice powder patterns measured are indicative of homogeneous amorphous structures on the length scale probed with our setup ($2\Theta > 10^\circ$, Cu $K\alpha$). It remains to be studied whether the reversible *in situ* transformation from VHDA to LDA is fully homogeneous also in small angle scattering experiments or possibly involves a state of strongest heterogeneity, which was recently reported for the irreversible transformation of VHDA to LDA via HDA-like

states at 1 bar.^{50,51} In summary, the sixfold coordination in VHDA is unaffected on decompressing from 1.1 to 0.40 GPa, whereas it slowly changes from sixfold VHDA coordination to fivefold HDA coordination in the interval from 0.40 to 0.06 GPa. In this pressure range, we find several “HDA”-states with 2Θ ranging from 31.6° to 28.3° , i.e., an apparently continuous shift to lower d spacings (and higher FWHM). This implies that there is either no discontinuity between HDA and VHDA, or that both the volume change ΔV and the shift of the first broad diffraction peak Δd at a possible discontinuity are below the detection limit and/or experimental reproducibility.

At $p \sim 0.06$ GPa, we find a sudden shift in the first maximum from $d = 3.15$ Å ($2\Theta = 28.3^\circ$), which corresponds to e-HDA, to $d = 3.71$ Å ($2\Theta = 24.0^\circ$), which corresponds to LDA, accompanied by a sudden narrowing of the FWHM from 8.5° to 4.6° . In other words, the fivefold coordination in HDA abruptly changes to the fourfold coordination in LDA.⁴⁹ Upon repeating the decompression experiment to 0.06 GPa several times, we noted formation of e-HDA for some experiments and formation of LDA for the other experiments. The traces marked (9a) and (9b) are indicative of this finding. The experimental uncertainty is ± 0.0002 GPa and ± 0.5 K, and we attribute these reproducibility issues at ~ 0.06 GPa to the proximity of the downstroke e-HDA \rightarrow LDA transition. We emphasize, that we never produced a diffractogram with a first broad peak lying in-between LDA ($2\Theta = 24.0^\circ$) and e-HDA ($2\Theta = 28.3^\circ$), e.g., at $2\Theta = 26.0^\circ$, which is a necessary condition for a first-order-like transition. We did not observe a double-peaked powder pattern since we investigated small one “phase” chips from a large sample, which is very likely a two “phase” system.

DISCUSSION AND CONCLUSIONS

We conclude that upon decompression at 140 K VHDA transforms to LDA via a series of HDA states, i.e., the recently observed LDA \rightarrow HDA \rightarrow VHDA transition⁴² is reversible. VHDA continuously evolves toward e-HDA in the pressure range of $0.06 < p < 0.40$ GPa, whereas e-HDA quasidiscontinuously transforms to LDA on the downstroke transition at 140 K and ~ 0.06 GPa, i.e., two amorphous-amorphous transitions of a different nature were observed. The VHDA \rightarrow e-HDA transition is clearly not first-order-like, which rules out the possibility of phase coexistence and a quasiphase boundary between HDA and VHDA at high pressure (> 0.5 GPa). This view is consistent with simulation results showing a slowly evolving structural change from HDA to VHDA and an absence of a quasiphase boundary.^{47,48}

Does this imply then that VHDA is a substate in the HDA megabasin? Put in other words, the question is whether the “transition” from HDA to VHDA is similar to the “transition” from liquid water kept at 300 K and 0.5 GPa upon pressurizing it to 1.0 GPa or not? While the latter takes place continuously over the whole pressure range, the HDA \rightarrow VHDA transition can be observed close to T_X as an inflection in density at 0.80 GPa (see Fig. 2 in Ref. 44) and at 125 K as a broad step in density in the range of

0.80–0.95 GPa.⁴² Similarly, the structural changes accompanying the VHDA → e-HDA transition upon decompression shown here in Fig. 3 are confined to the pressure range of 0.40–0.06 GPa. That is, we interpret VHDA not to be a substate in the HDA megabasin since the transition is confined to definable pressure ranges. The transition between the two, while clearly not first-order-like, may be second—or higher-order-like.

In contrast, the e-HDA → LDA transition is consistent with a quasi-phase boundary and a possible first-order liquid-liquid transition scenario. That is, two distinct scenarios may be needed to appropriately describe bulk water at low temperatures over the whole pressure range up to 2 GPa. Whereas for the LDL ↔ HDL transition a true first-order scenario may apply as judging from the LDA ↔ e-HDA transition, the HDL ↔ VHDL transition may be smeared over a range of pressures and may involve an infinite number of intermediate states as judging from the HDA ↔ VHDA transition. In Fig. 1, we plot the transition to take place in the interval of 0.70 ± 0.10 GPa at 140 K, which is an average value combining the results for the upstroke transition reported earlier⁴² and the results for the downstroke transition reported here. We do not know whether the transition width increases or decreases as the temperature is increased above T_X and, therefore, draw two funnels in Fig. 1 in order to indicate the two possibilities. The metastability fields for HDA and VHDA are delineated by a broad area, which may either become broader (according to the singularity free scenario^{52,53}) or alternatively become more narrow (in case the transition is limited by kinetics) as the temperature is increased. The latter possibility of a phase transition, which becomes narrower as the temperature is increased, was demonstrated on the example of crystal-crystal transitions in ice.^{25,54} We do believe, though, that the VHDA → HDA transition observed here is too broad to allow for the option that it narrows down for kinetic reasons to a first-order transition at $T > T_X$. We, therefore, view our results as evidence against a third critical point. It is also conceivable, as predicted by the singularity free scenario,^{52,53} that the range over which the transition is smeared becomes wider as the temperature is increased, which would again be evidence disfavoring a third critical point. Note, however that the smeared “discontinuity” in density does only show up in the upstroke transition reported earlier, whereas it disappears and looks like a continuous transition on the downstroke VHDA → e-HDA transition, which accelerates somewhat in the pressure range of $0.06 < p < 0.40$ GPa. In this sense, e-HDA represents the limiting structure at the low-pressure end, and VHDA represents the limiting structure at the high-pressure end for the VHDA ↔ HDA transition.

This is, to the best of our knowledge, the first report of two fundamentally different amorphous-amorphous transitions in one substance involving three distinct amorphous states. Other studies, e.g., on the polyamorphic transition of triphenylphosphite found a change in character from a nucleation and growth type mechanism to a spinodal decomposition mechanism upon change in temperature (rather than upon change in pressure).⁵⁵ We view our results as evidence against a third critical point in water’s phase diagram restor-

ing the liquid-liquid transition hypothesis between LDL and HDL and a possible second critical point. As a final word of caution, we emphasize that the conclusions are valid within the experimental resolution; in other words, a slight chance of a discontinuous e-HDA ↔ VHDA transition remains, which can not be resolved within the experimental uncertainty using piston displacement (i.e., density) and first broad diffraction peak as observables. Likewise, the LDA ↔ e-HDA transition may be continuous since it is experimentally very hard to distinguish a sharp but continuous from a discontinuous transition.⁵³ Additional *in situ* studies using thermal properties, relaxation times, conductivity, sound velocity, etc., as observables are required to eliminate the remaining small uncertainty. Such studies have previously shown that the LDA ↔ HDA transition has a “complicated nonergodic nature combining the features typical for both the first-order transition and singularity free scenario.”⁵⁴

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