

Pressure-induced transformations in computer simulations of glassy water

Janet Chiu, Francis W. Starr, and Nicolas Giovambattista

Citation: The Journal of Chemical Physics **139**, 184504 (2013); doi: 10.1063/1.4829276 View online: http://dx.doi.org/10.1063/1.4829276 View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/139/18?ver=pdfcov Published by the AIP Publishing



This article is copyrighted as indicated in the abstract. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP: 129.133.93.79 On: Wed, 13 Nov 2013 16:27:13



Pressure-induced transformations in computer simulations of glassy water

Janet Chiu,¹ Francis W. Starr,² and Nicolas Giovambattista¹

¹Department of Physics, Brooklyn College of the City University of New York, Brooklyn, New York 11210, USA ²Department of Physics, Wesleyan University, Middletown, Connecticut 06459, USA

(Received 23 May 2013; accepted 24 October 2013; published online 13 November 2013)

Glassy water occurs in at least two broad categories: low-density amorphous (LDA) and highdensity amorphous (HDA) solid water. We perform out-of-equilibrium molecular dynamics simulations to study the transformations of *glassy* water using the ST2 model. Specifically, we study the known (i) compression-induced LDA-to-HDA, (ii) decompression-induced HDA-to-LDA, and (iii) compression-induced hexagonal ice-to-HDA transformations. We study each transformation for a broad range of compression/decompression temperatures, enabling us to construct a "P-T phase diagram" for glassy water. The resulting phase diagram shows the same qualitative features reported from experiments. While many simulations have probed the liquid-state phase behavior, comparatively little work has examined the transitions of glassy water. We examine how the glass transformations relate to the (first-order) liquid-liquid phase transition previously reported for this model. Specifically, our results support the hypothesis that the liquid-liquid spinodal lines, between a lowdensity and high-density liquid, are extensions of the LDA-HDA transformation lines in the limit of slow compression. Extending decompression runs to negative pressures, we locate the sublimation lines for both LDA and hyperquenched glassy water (HGW), and find that HGW is relatively more stable to the vapor. Additionally, we observe spontaneous crystallization of HDA at high pressure to ice VII. Experiments have also seen crystallization of HDA, but to ice XII. Finally, we contrast the structure of LDA and HDA for the ST2 model with experiments. We find that while the radial distribution functions (RDFs) of LDA are similar to those observed in experiments, considerable differences exist between the HDA RDFs of ST2 water and experiment. The differences in HDA structure, as well as the formation of ice VII (a tetrahedral crystal), are a consequence of ST2 overemphasizing the tetrahedral character of water. © 2013 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4829276]

I. INTRODUCTION

Given the vast list of anomalous properties,¹ water is perhaps one of the most complex liquids in Earth. Among *liquid* water's anomalous properties are the well-known increase of density upon isobaric cooling,² the increase of the response functions, such as specific heat and compressibility, upon isobaric cooling,^{3,4} and the increase of diffusivity upon isothermal compression⁵ (see, e.g., Refs. 6–8). Perhaps less well known are water's anomalous properties in the *glass* state. Like the well-known polymorphism of crystal states, water exhibits glass polymorphism, that is, it can be prepared in at least two different amorphous glass states, which are broadly categorized as low-density (LDA) and high-density amorphous ice (HDA) (see, e.g., Refs. 6 and 9–11). Both HDA and LDA can have further, more minor, variations, depending on the preparation of the glass.

HDA is most commonly prepared by compressing hexagonal or cubic ice at constant temperature.^{12–15} Experiments show that the pressure at which the low-pressure ice transforms to HDA, $P_{ice \rightarrow HDA}(T)$, increases with decreasing temperature.¹⁶ $P_{ice \rightarrow HDA}(T)$ is indicated in Fig. 1(a), which shows the experimental "phase diagram" for water in the glass domain. We use this term loosely, since the glass is an inherently non-equilibrium, but extremely long-lived state, and the quantitative details of this diagram will be dependent on the rates pressure and temperature changes during preparation. Interestingly, the ice-to-HDA transformation at low temperatures (e.g., T = 77 K) is not reversible, so that HDA can be "recovered" at atmospheric pressure upon decompression. The thick line in Fig. 1(a) represents $T_x(P)$, the temperature above which glassy water readily crystallizes.

LDA can be formed from a variety of routes, including rapid quenching at atmospheric pressure—referred to as the variant hyper-quenched glassy water (HGW). Moreover, LDA can be formed from HDA by either (a) isothermal decompression of HDA at $T \approx 130-140$ K,¹⁶⁻¹⁸ or (b) isobaric heating of recovered HDA at low pressure, approximately P < 50 MPa.^{12,16,19–21} The experimental HDA-to-LDA transformation line is shown in Fig. 1(a). Contrary to the behavior of $P_{ice \rightarrow HDA}(T)$, the pressure at which HDA transforms to LDA, $P_{HDA \rightarrow LDA}(T)$, decreases with decreasing temperature.

What makes the polyamorphism of glassy water so interesting is the relationship between LDA and HDA. Specifically, LDA and HDA can be reversibly interconverted under appropriate conditions, suggesting that these substances may be related to underlying proper thermodynamic phases. In analogy to the decompression-induced HDA-to-LDA transformation, isothermal compression of LDA produces HDA.^{14, 16, 19, 22} The experimental pressure at which LDA transforms to HDA, $P_{\text{LDA} \rightarrow \text{HDA}}(T)$, is shown in



FIG. 1. (a) Experimental phase diagram of glassy water. On compression, LDA transforms to HDA at the red line, while on decompression HDA transforms to LDA at the orange line. Compression of ice I_h results in amorphization to HDA at the green line. Heating above the crystallization temperature $T_x(P)$ (thick black line), the glassy phases crystallize to various ice forms. Adapted from Ref. 16. Triangles-right and triangles-left indicate transformations obtained upon compression and decompression, respectively. (b) Phase diagram obtained from MD simulations of glassy ST2 water using our faster compression rate, $q_P = \pm 300$ MPa/ns. The colors of the HDA/LDA and ice I_h transformation lines are the same as part (a). Compression of HDA results in crystallization to ice VII at the magenta line. LDA sublimes on decompression at the violet line; for comparison, we include the sublimation line of HGW (brown line). The metastable liquid-to-vapor spinodal is also included (from Ref. 29). The LLCP (circle), LL spinodal (blue lines), and LL coexistence (black line) lines are reproduced from Ref. 70. The HDL-to-LDL and LDL-to-HDL spinodal lines extend to T = 205 K and T = 235 K, respectively; these are the lowest metastable equilibrium temperatures currently reported for ST2 water.¹⁰ (c) Comparison of the phase diagram obtained from MD simulations of glassy ST2 water for the "fast" ($q_P = \pm 300$ MPa/ns, filled symbols) and "slow" ($q_P = \pm 30$ MPa/ns, open symbols) rates. Additionally, we include the LDA-to-HDA transformation studied at rate $q_P = 3$ MPa/ns, at T = 240 K (green triangle). The out-of-equilibrium LDA-HDA transitions converge toward the LL spinodals as the compression rate decreases.

Fig. 1(a). As for the case of $P_{\text{ice} \rightarrow \text{HDA}}(T)$, $P_{\text{LDA} \rightarrow \text{HDA}}(T)$ increases with decreasing temperature.¹⁶ Additionally, the pressure-induced LDA-HDA transformation resembles a first-order phase transition.¹⁹ Specifically, during the pressure-induced LDA-HDA transformations, (i) the volume changes nearly discontinuously,^{14,16,17,22} (ii) hysteresis occurs between the LDA-to-HDA and HDA-to-LDA transformations,^{14,16,18} and (iii) samples containing LDA and HDA coexisting with one another have been prepared²³⁻²⁵ (it is possible that in some of these experiments, surface effects play a relevant role). If the LDA-HDA transformation is indicative of an underlying first-order phase transition, the continuation of this transition to higher T would imply a first-order phase transition between two metastable liquid states of water. Such a transition is either terminated by a critical point at some low T, or extends to negative pressures, since no such a transition occurs in the stable region of the liquid state. This liquid-liquid phase transition hypothesis was proposed originally by Poole et al.²⁶ in 1992, based on the apparent liquid-liquid phase transition in the ST2 model of water. This hypothesis can account for many of the anomalous liquid properties. We note that alternative interpretations for glass-glass transformations that do not consider an underlying first-order LLPT are also available (see, e.g., Refs. 18 and 27). It is precisely the possibility of different views to explain water glass polymorphism that motivates this work.

The main focus of this work is to characterize the phase diagram of glassy water as observed from computer simulations using the ST2 water model,²⁸ and to relate the behavior of the glass phases to (metastable) equilibrium phases of water. We show that, even when the time scales available in MD simulations are several orders of magnitude shorter than those probed experimentally, MD simulations qualitatively reproduce the pressure-induced transformations between LDA and HDA discussed above, as well as the pressure-induced amorphization of hexagonal ice (I_h) , which results in HDA. We also compare the glass "phase diagram" of ST2 glassy water with the previously reported phase diagram of lowtemperature liquid ST2 water.²⁹ In this liquid phase diagram, ST2 water exhibits two liquids, a low-density (LDL) and high density liquid (HDL).²⁶ Moreover, LDL and HDL are separated by a first-order phase transition line, and the liquidliquid phase transition (LLPT) line ends at a liquid-liquid

critical point (LLCP). Although some recent works question the existence of a LLPT in ST2 water,^{30,31} most recent computational works robustly demonstrate that ST2 water exhibits a metastable LLPT at low temperature.^{32–36} In addition, the possibility of a LLPT has been seen in computer simulations of many other pure fluids.^{37–44} More importantly, technical questions regarding equilibration raised in Refs. 30 and 31, have no bearing on the qualitative transformations of the glassy states we examine, which are inherently nonequilibrium.

We note that computer simulations of *glassy* water are not abundant—curious, since experiments focus primarily on the glass state. Thus, simulations have an opportunity to shed some new light on the nature of glass polyamorphism in water. Scattered results have been reported using different water models, such as the SPC/E^{9,45–50} and TIP4P^{9,51,52} models. Even for the case of the ST2 model, which is the first model found to exhibit liquid polymorphism, the corresponding glass behavior is relatively unexplored.^{26,53} In this work we use the ST2 model — not because it may or may not quantitatively reproduce the properties of water — but rather because it has been demonstrated to qualitatively reproduce the behavior of the glass transition temperature of water as function of pressure,⁵⁰ which appears to be associated with a LLPT.

As alluded to above, LDA and HDA are not unique glass states, but instead represent families of two glass forms.^{9,13,46,54} This view is based on the potential energy landscape approach (PEL),^{55–57} in which a glass is mapped into a PEL minimum (for a detailed discussion on this interpretation, where LDA and HDA are considered to be two families of glasses, we refer the reader to Refs. 9 and 54). Different members within each (LDA or HDA) family exhibit similar structure and thermodynamic behavior. Members of a given glass family may differ slightly depending on their preparation methods, which may lead to different degrees of relaxation. The different degree of relaxation may result, in some cases, to slightly different thermodynamic behavior (see, e.g., Refs. 13 and 20, 21, 54, and 58-60). In the case of HDA, two different forms are commonly discussed, unrelaxed HDA (uHDA) and expanded HDA (eHDA).54,59 Similarly, a few sub-families of LDA have been introduced, such as LDA₁ and LDA₁₁.⁵⁸ Other well-known low-density amorphous ices, such as hyperquenched glassy water (HGW)⁶¹ and amorphous solid water (ASW),⁶² are usually considered to belong to the LDA family.⁶ For simplicity, in this work, we will classify the amorphous ices obtained in our computer simulations as LDA or HDA. We will only distinguish between LDA and HGW as required.

This work is organized as follows. In Sec. II, we discuss the details of simulations and glass preparation. The phase diagram of ST2 water in the glass domain is described in Sec. III. In Sec. IV we study the pressure-induced glass-glass transformation, as well as the structure of LDA and HDA. The crystallization of HDA at high pressures and the sublimation of LDA at low pressures are discussed in Secs. V and VI, respectively. The pressure-induced amorphization of hexagonal ice is discussed in Sec. VIII. A summary is presented in Sec. VIII. Finally, Appendices A and B are included where we discuss briefly size effects and the reversibility of the LDA-to-HDA transformation.

II. METHODS

A. ST2 molecular dynamics simulations

Our findings are based on extensive out-of-equilibrium molecular dynamics (MD) simulations of water using the ST2 model,²⁸ with long-ranged (electrostatic) interactions treated using the reaction field technique.⁶³ We follow precisely the potential parameters, such as the cutoff distance used to calculate short-range interactions, etc., as used in Refs. 29 and 64; those references serve as benchmarks for the equilibrium thermodynamic and dynamic properties.

Most of our computer simulations involve isothermal compression and decompression runs starting from an ensemble of independent configurations. In these simulations, the temperature is controlled using the Berendsen thermostat and barostat.⁶⁵ The thermostat temperature is held constant during these runs at the desired compression/decompression temperature while the pressure is increased continuously with time. Specifically, at every simulation time step, the barostat pressure is increased by $\Delta P = q_P \,\delta t$, where $\delta t = 1$ fs is the simulation time step and q_P is the compression/decompression rate. In this work, we use two rates, a "fast" rate of $q_P = \pm 300$ MPa/ns and a "slow" rate of $q_P = \pm 30$ MPa/ns, one order of magnitude slower. We note, however, that these rates are 8-12 orders of magnitude larger than experimental compression/decompression rates, $\approx \pm 0.1$ –100 MPa/s (see, e.g., Ref. 14). For each compression/decompression temperature, we use 10 independent starting configurations to improve statistics. For simulations originating from liquid configurations, we use a cubic box with N = 1728 water molecules; in the case of simulations originating from ice I_h configurations, we use an orthorhombic box with N = 1024water molecules.

B. Preparation of glassy states

Previous studies have shown that the glassy states LDA and HDA can be clearly identified in computer simulations using the ST2 model.^{26,50,53} As in previous works, we prepare these glassy states by following analogous procedures used in experiments in the preparation of LDA and HDA. However, due to the comparatively short time scales accessible to simulation, cooling and compression/decompression rates used are significantly faster than those used in experiments. The protocols followed are very similar to those described in Ref. 50.

To obtain a low-density glass, we quench the equilibrated liquid from T = 350 K to T = 0 K with a cooling rate of $q_T = -30$ K/ns, while keeping the pressure constant at P = 0.1 MPa. While other computational methods are available, that may produce more stable glasses (see, e.g., Refs. 66–68), our approach mimics experiments and thus simplifies comparison to experimental data, which is the main motivation of this work. We note that the glass obtained by this cooling process corresponds to HGW, the low-density glass form originally produced by spraying micrometer-sized droplets onto a solid cryoplate.⁶⁹ However, the experimental cooling rates are $\approx 10^5 - 10^7$ K/s, i.e., 3–5 orders of magnitude smaller than our cooling rate. We note that in experiments and simulations, the differences between HGW and LDA (obtained from decompressed HDA), are minor; in the experimental case, such differences disappear after proper annealing.⁶

We obtain HDA by two different process: (i) isothermal compression of HGW starting from P = 0.1 MPa, or (ii) isothermal compression of ice I_h starting from P = 0.1 MPa. As it will be shown, the forms of HDA that result from processes (i) or (ii) are practically indistinguishable both from the structural and thermodynamic point of view. By decompressing HDA at constant temperature, we produce LDA. In order to compare the LDA-HDA transformation lines and the LL spinodal lines (see Sec. III). we also perform compression runs of LDL, followed by decompression runs of HDL. HDA and HDL are decompressed from P = 1700 MPa at T = 210 K and from P = 700 MPa at T > 210 K. It is not simple to provide a precise temperature above which compression/decompression runs involve LDL-HDL transformations, and below which they involve LDA-HDA transformations. We estimate that at approximately T < 200 K, the simulations can be considered to be in the glass state, at least within the time scale of our simulations (\approx 10–100 ns), since annealing is negligible or not observed. For example, aging runs of LDA at T = 80 K and P = 0.1 MPa indicate that the density remains constant for at least 100 ns. Similarly, aging HDA at T = 80 K and P = 1700 MPa for 100 ns results in a minor density change $(<0.05 \text{ g/cm}^3)$ during the first 10 ns with no density change occurring in the remaining 90 ns. These are glasses in the sense that they are amorphous structures with dynamical arrest. Consistent with this, metastable equilibrium studies have shown that diffusion is becoming vanishing small on simulation scales at these temperatures.⁶⁴

III. P-T PHASE DIAGRAM OF GLASSY ST2 WATER

We begin by summarizing the glass transformations for the ST2 water model [Fig. 1(b)] obtained from compression and decompression runs for a wide range of temperature. The data from which these transformations are derived will be subsequently presented. For each *T* studied, we start by compressing HGW, which converts to HDA at a transformation pressure $P_{\text{LDA} \rightarrow \text{HDA}}(T)$. In some cases, further compression of HDA results in the formation of high pressure ice VII at pressure $P_{\text{HDA} \rightarrow \text{VII}}(T)$. We then decompress HDA, and eventually recover LDA at a pressure $P_{\text{HDA} \rightarrow \text{LDA}}(T)$. Hysteresis effects — either of kinetic or thermodynamic origin — mean that $P_{\text{LDA} \rightarrow \text{HDA}}(T) > P_{\text{HDA} \rightarrow \text{LDA}}(T)$. Further decompression of LDA (or HGW) results in sublimation to the gas at negative pressures.

The *low-temperature* domain of this phase diagram (conservatively, T < 160 K) is analogous to the experimental phase diagram of Fig. 1(a) for $T < T_x(P)$. The main qualitative difference between the experiments [Fig. 1(a)] and simulations [Fig. 1(b)] is that crystallization *at low pressures* does not spontaneously occur in ST2 water within our simulation time scales. Accordingly, simulation results show the behavior of liquid ST2 water in the low-temperature regime, where ST2 water exhibits liquid polymorphism. The corresponding liquid-liquid (LL) coexistence line, LL spinodal lines, and LLCP reported in Refs. 36 and 70 are also included in Fig. 1(b). The HDL-to-LDL and LDL-to-HDL spinodal lines extend to T = 205 K and T = 235 K, respectively; these are the lowest metastable equilibrium temperatures currently reported for ST2 water with reaction field (the version studied here).^{70,71} Due to the relatively large rate of cooling and compression in our work, there is a small overlap between prior studies of equilibrium dynamics with our out-of-equilibrium results.

One of the most important results from Fig. 1(b) is the possible relationship between the LL spinodal lines and glassglass transition lines. In the simplest scenario, when extended into the glass domain, the LDL-to-HDL spinodal line becomes the compression-induced LDA-to-HDA transformation; similarly, the HDL-to-LDL spinodal line becomes the decompression-induced HDA-to-LDA transformation line. This scenario appears valid for the case of a monatomic polymorphic liquid⁷² with Fermi-Jagla pair interactions.⁴³

In the case of the ST2 model, the relation between the spinodals and glass transformation lines is slightly less evident. Fig. 1(b) shows that indeed the LDA-to-HDA and HDA-to-LDA glass transformation lines approach, respectively, the LDL-to-HDL and HDL-to-LDL spinodal lines as temperature approaches the critical point, where metastable equilibrium becomes accessible to simulation. However, the glass-glass transformation lines do not overlap with the previously reported liquid-liquid spinodals when extended into the liquid regime. Instead, kinetic effects, due to the compression/decompression rate, alter the shape of glass-glass transition lines of the ST2 model.

To test the idea of the correspondence between the LL spinodals and the glass-glass transformation lines, we examine how the glass-glass transformation lines change when the compression/decompression rate is reduced by a factor of 10 (reducing $|q_P| = 300$ MPa/ns down to 30 MPa/ns). The results are summarized in Fig. 1(c). The main result from Fig. 1(c)is that, by reducing q_P , the LDA-to-HDA and HDA-to-LDA transformation lines approach the previously reported LDLto-HDL and HDL-to-LDL spinodal lines, respectively.⁷⁰ Further testing this idea, we performed one compression at an additional factor of 10 slower ($|q_P| = 3$ MPa/ns) for T = 240 K, and see the continued approach to the spinodal limit. The approach of the glass-glass lines to the spinodals supports the LLPT hypothesis scenario, so that the glass-glass transformation lines are an extension into the glass domain of the liquid-liquid spinodal lines.⁵³ Note that, not surprisingly, the location of the HDA-to-ice VII transformation (discussed in Sec. V) shows a similar shift as the LDA-HDA transformation lines when the compression rate is reduced by a factor 10.

IV. PRESSURE-INDUCED LDA-HDA TRANSFORMATIONS

We now describe in detail the LDA-HDA transformations as function of temperature, as well as the structure

of the amorphous states. As shown in Figs. 1(a) and 1(b), the LDA-to-HDA and HDA-to-LDA transformation lines exhibit a qualitatively similar behavior in ST2 water simulations and experiments. In both cases, $P_{\text{LDA}} \rightarrow \text{HDA}(T)$ increases and $P_{\text{HDA}} \rightarrow \text{LDA}(T)$ decreases as the temperature decreases. Moreover, the slopes of these loci are quantitatively similar between experiment and simulation. Specifically, the slope of the $P_{\text{LDA} \rightarrow \text{HDA}}(T)$ locus is approximately -0.15 K/MPa for ST2 glassy water [Fig. 1(b)] and -0.25 K/MPa for experiments [Fig. 1(a)]. Similarly, the slope of the $P_{\text{HDA} \rightarrow \text{LDA}}(T)$ locus is approximately 0.2 K/MPa for ST2 glassy water and 0.1 K/MPa for experiments. However, we note that the values of $P_{\text{LDA} \rightarrow \text{HDA}}(T)$ obtained in simulations are much larger than those reported in experiments, which is expected given the large compression rates used in simulations. As we discussed previously, a slower compression will reduce the HDA-to-LDA transition pressure toward the LDL-to-HDL spinodal. Similarly, simulations predict much smaller values of $P_{\text{HDA} \rightarrow \text{LDA}}(T)$ than the pressures obtained from experiments. In particular, it is found that for our rapid decompressions rates, HDA transforms to LDA at negative pressures (tension) for approximately T < 200 K. Similar to the LDAto-HDA transformation, a slower rate increases the pressure of the HDA-to-LDA transformation toward the HDL-to-LDL spinodal. Experiments [at a much slower decompression rate (Fig. 1(a))] also find that HDA may transform to LDA at negative pressures for approximately T < 115 K but transforms at positive pressures for approximately T > 115 K.

A. Density during the LDA-HDA transformations

Figure 2(a) shows the density as function of pressure during the compression-induced LDA-to-HDA transformation, followed by the corresponding decompression-induced HDAto-LDA transformation at three representative temperatures, T = 20, 80, and 140 K. As observed in experiments, ^{14, 19, 22} at low pressure, the density of LDA increases approximately linearly with increasing pressure. This behavior is followed by a sharp change in density upon further compression, which signals the LDA-to-HDA transformation. Figure 2(a) shows that further compression of HDA results in a weak change in density. Experiments indicate that, at slow compression rates (≤ 20 MPa/s¹⁴), HDA transforms to a very-high density amorphous (VHDA)⁷³ ice, and that this transformation is accompanied by a small, continuous density change.¹⁴ We explore this possibility by extending our compression runs up to 6000 MPa. However, for all temperatures explored, we find no change in density that could be identified with the HDA-to-VHDA transformation. Instead, it is found that at these high pressures, some samples crystallize to ice VII, as we discuss later.

In order to study the HDA-to-LDA transformation, we decompress HDA at different temperatures. As observed in experiments,^{16,18} Fig. 2(a) shows that the density of HDA decreases smoothly upon decompression until HDA transforms to LDA. At the transition, the density exhibits a sharp change, as observed in Fig. 2(a). For $T \leq 200$ K, we can recover LDA only at negative pressures for our decompression rates [see also Fig. 1(b)]. Continued decompression results



FIG. 2. (a) Pressure-dependence of density $\rho(P)$ during the compressioninduced LDA-to-HDA transformation, and subsequent decompressioninduced HDA-to-LDA transformation, at the "fast" compression rate ± 300 MPa/ns. Temperatures are T = 20, 80, and 140 K. The sharp density changes correspond to the LDA-to-HDA and HDA-to-LDA transformations; the midpoints of the density change define the corresponding transformation lines in Fig. 1(b). $\rho(P)$ is obtained by averaging over the 10 independent runs. (b) The average $\rho(P)$ at T = 80 K [black line, from (a)], and the density obtained from the corresponding individual simulations (red lines). Compared to the averaged density, the density change of the individual runs is noticeably sharper at the glass-glass transformations. The apparent divergences in density at negative pressures corresponds to the sublimation of LDA [violet line in Fig. 1(b)].

in the sublimation of LDA. The sublimation of LDA is signaled by the rapid drop in density [Fig. 2(a)] when stretched to $P \leq -500$ MPa. We stress that the LDA samples recovered at negative pressures are *mechanically* stable relative to the vapor phase. Specifically, we perform one simulation of LDA at P = -450 MPa and T = 80 K for 100 ns and confirm that the system remains in the LDA phase, with no signs of sublimation.

The density of LDA obtained upon decompression of HDA (P < -400 MPa) is lower than observed experimentally, in the range 0.76–0.83 g/cm³ at T = 20, 80, and 140 K; experimentally, the density of LDA at P = 0.1 MPa and T = 77 K is 0.94 g/cm³.¹⁹ The same observation holds when considering the density of the starting LDA forms (i.e., HGW) at P = 0.1 MPa; in this case, the density of LDA is approximately 0.87 g/cm³ [Fig. 2(a)]. Such low density values are consistent with the fact that ST2 more strongly emphasizes low density, tetrahedral structures than water does. For example, ice I_h has an experimental density of about 0.92 g/cm³ at ambient melting conditions, while in the ST2 model ice I_h has a lower density, about 0.86 g/cm³. Regarding the density of HDA, it is found that the values from ST2 water simulations are also

off from the corresponding experimental value. For example, the experimental density of HDA, recovered at T = 77 K and P = 0.1 MPa, is approximately 1.19 g/cm³. At similar conditions, the HDA density is 1.34–1.42 g/cm³ in ST2 water, depending on the starting pressure of HDA [see, e.g., Fig. 2(a), and Fig. 7(b) of Ref. 50].

As shown in Fig. 2(a) the density changes accompanying the LDA-HDA transformations in ST2 water are very sharp and surprisingly similar to the corresponding experimental density changes (e.g., see Fig. 2 in Ref. 16). The data shown in Fig. 2(a) is the average density over the 10 independent runs. Examining this more carefully [Fig. 2(b)], we see that the density changes at the LDA-HDA transformation are *even sharper* for individual simulation runs. Additionally, the pressure of the transition varies from run-to-run. Consequently, the density jump for the system average is less pronounced, obscuring the phase-transition like behavior of individual runs.

For comparison, other water models where a LLPT is not accessible on available simulation time scales, such as the SPC/E and TIP4P models,9,50,53 exhibit smooth density changes accompanying the LDA-HDA transformations at similar compression/decompression rates. Additionally, examining ensembles of independent compression runs in SPC/E shows that the LDA-HDA transformation occurs always at nearly the same pressure,⁵⁰ rather than the run-torun variation we see in ST2. This supports the notion that the transformation in ST2 has an underlying phase transition as its origin, while in SPC/E the transformation is rapid, but continuous. Of course, it is possible that for much slower cooling and compression rates than are presently feasible, phase-transition like behavior might also emerge in the SPC/E model. Moreover, the purpose of the distinction is not to say that other models lack value-only that they do not readily reproduce a phase-transition like behavior of LDA-HDA transformation at the studied compression/decompression rates. As a counter point, the densities of LDA and HDA-like glasses in SPC/E and TIP4P more closely match the experimental densities (see, e.g., Ref. 9).

B. Structure of LDA and HDA

In order to characterize the structure of LDA and HDA, we focus on compression/decompression cycles at temperature T = 80 K, very near to the liquid nitrogen boiling point 77 K, where many experiments are performed. At this temperature, radial distribution functions (RDFs) g(r) of LDA and HDA from experiments are available.^{74,75} Figure 3 shows the oxygen-oxygen (OO) g(r) at five selected points during the compression/decompression cycle at T = 80 K. All RDFs reach a constant value of 1 for approximately r > 1 nm, consistent with the fact that the system is amorphous, with no long-range order. The amorphous character of these states is further evident from the snapshots shown in Fig. 4, which show molecules colored based on their coordination number (CN), at different pressures. The CN of a given molecule is the number of nearest-neighbors with oxygenoxygen distance $r_{OO} \le 0.35$ nm, and hence it is proportional to the local density at the molecules location. It follows from



FIG. 3. The structure of LDA and HDA in ST2 water during a compression/decompression cycle at 80 K, as measured by the radial distribution function g(r) for the oxygen atoms. Each data set is offset vertically by 0.5 for clarity of the figure. As indicated by the inset, state points A and B are LDA (HGW) during compression; points C and D are HDA; finally, point E is LDA recovered from HDA at very low pressure P = -500 MPa, prior to sublimation.

Fig. 4(b) that during the LDA-to-HDA transformation, the glass exhibits large spatial correlations of LDA- and HDAlike molecules. Interestingly, these images do not show a distinguishable nucleus, as one would expect in equilibrium firstorder phase transitions. Instead they show structure similar to a bi-continuous state that would be expected near the spinodal limit [see also Appendix B]. Indeed, for the highly nonequilibrium path that we follow, it is not evident how the LDA-to-HDA transformation should proceed, i.e., whether it should exhibit spontaneous nucleation, as in equilibrium liquid-to-crystal first-order phase transitions, or if it should exhibit spinodal decomposition, with no distinct phase separation. Experiments performed by Tanaka and collaborators with triphenylphosphite (TPP)⁷⁶ and n-butanol,⁷⁷ as well as mixtures of glycerol and water⁷⁸ (where LDL and HDL have same composition), indicate the existence of a LLPT. In all these works, it was observed that, in some cases, the LLPT exhibited spontaneous nucleation, while in others, it showed spinodal decomposition.



FIG. 4. Snapshots of LDA (red), HDA (blue), and during transformation at T = 80 K. (a) LDA (HGW) at P = 0.1 MPa. (b) During the transformation from LDA to HDA at P = 1060 MPa; note that the pressure of the transformation varies from run-to-run. (c) HDA at P = 1600 MPa. Oxygen atoms are shown as either red or blue spheres, and the white bonds approximate the hydrogen bond network. Following the convention of Ref. 70, oxygens are drawn red if there are no more than 4 neighbors within a distance 0.35 nm (i.e., CN \leq 4), and blue if there are 5 or more neighbors within this distance (i.e., CN \geq 5). The three configurations differ significantly in density (and thus, in volume), but are drawn at different scales to facilitate the visualization.

The RDF for states A and B (indicated in the inset of Fig. 3) correspond to LDA. These distributions practically overlap, even when the corresponding pressures differ by 800 MPa. Similarly, the RDFs for states C and D correspond to HDA, and are practically indistinguishable, although the corresponding pressures differ by \approx 2000 MPa. We also include the RDF for state E, which corresponds to the LDA form produced by decompression of HDA. As expected, the RDF of state E is comparable to the RDF of the LDA forms corresponding to states A and B.

In the RDFs of both LDA and HDA, the first peak is located at r = 0.28 nm, dictated by the formation of a hydrogen bonds to the nearest neighbors. The main differences between these RDFs occur at intermediate separations, beyond the first hydration shell. Figure 3 shows that the transformation of LDA to HDA in ST2 water is accompanied by a shift of the second peak, from r = 0.45 nm to r = 0.50 nm. In addition the third and fourth peak of LDA RDF, located at r = 0.68 nm and r = 0.86 nm, respectively, are barely distinguishable in HDA. Interestingly, Fig. 3(b) shows that the first minimum of LDA OO-RDF is nearly zero, indicating an empty first interstitial hydration shell (located at $r \approx 0.33$ nm). Instead, in the case of HDA, the first minimum is non-zero, i.e., the interstitial hydration shell is populated. Experiments also show that LDA is characterized by an empty interstitial hydration shell.⁷⁴ This first interstitial shell is populated by one molecule, in average, in the case of HDA.74

While the RDFs of the ST2 model have features that are qualitatively similar to experiments, it is natural to consider to what degree the structure can be quantitively compared to experiments. In general, rigid water models, such as the ST2 and SPC/E models, are limited in reproducing the experimental RDFs, even at ambient conditions. Figures 5(a) and 5(b) show the OO, oxygen-hydrogen (OH), and hydrogen-hydrogen (HH) RDFs of LDA and HDA for both the ST2 and SPC/E water models, as well as experiments.⁷⁴ All distributions are obtained at similar conditions, $T \approx 80$ K and $P \approx 0.1$ MPa. In the case of LDA, all RDFs obtained with the SPC/E and ST2 model are remarkable similar to one another and are consistent with the experimental data. While the location of the RDFs maxima and minima are well reproduced by simulations, the first peak of the OO, OH, and HH RDFs is overestimated by both SPC/E and ST2 models.

In contrast, the RDFs of HDA are better reproduced by the SPC/E model than by the ST2 model [Fig. 5(b)], as noted previously.⁴⁵ Deviations of g(r) for the ST2 model from experiment are most noticeable in the OO RDF. Specifically, the OO RDF of HDA obtained from experiments (and SPC/E simulations) exhibits a wide second peak that extends from roughly 0.35 nm to 0.55 nm; instead, in the ST2 model, the second peak of the OO RDF is narrower and is centered at 0.52 nm. The deviations in the ST2 model are understood from its over-emphasis of tetrahedral order, which limits the tendency for molecules to occupy interstitial locations around 0.33 to 0.35 nm. Similarly, the ST2 model also exhibits deeper minima in the HH and OH RDFs, and has additional maxima and minima that are not observed in the corresponding experimental (and SPC/E model-based) RDFs. Consequently, the



FIG. 5. Oxygen-oxygen (OO), oxygen-hydrogen (OH), and hydrogenhydrogen (HH) RDFs obtained from MD simulations using the ST2 (this work) and SPC/E⁴⁷ models as well as from experiments.⁷⁴ (a) LDA and (b) HDA. Experimental RDFs are for P = 0.1 MPa and T = 80 K. SPC/E RDFs are calculated at T = 77 K and P = 20 MPa ($\rho_{LDA} \approx 0.95$ g/cm³ and $\rho_{HDA} \approx 1.15 - 1.24$ g/cm³).⁴⁷ ST2 RDFs are calculated at T = 80 K and P = -9.9 MPa ($\rho_{LDA} = 0.85$ g/cm³ and $\rho_{HDA} = 1.35$ g/cm³).

ST2 model is not well suited to study glass structure at highpressures, and therefore not helpful to understand the relationship between the various HDA sub-groups uHDA, eHDA and VHDA.

In short, compared to the SPC/E model,⁵⁰ the ST2 model is better at reproducing the qualitative behavior of $\rho(P)$ during the pressure-induced LDA-HDA transformations, but at the expense of poorly predicting HDA structure. We stress that our conclusions are limited to the glass state and have no implications on the performance of these models (i.e., whether ST2 or SPC/E is better at reproducing experimental data) at different conditions, such as in the liquid phase at room temperatures or in the ice domain.

An alternate way to quantify the structural differences between LDA and HDA is through a tetrahedral order parameter, since the hydrogen-bond network is significantly altered across the LDA-HDA transformation. For example, Fig. 6 shows the *average* tetrahedral order parameter q(P)(introduced in Ref. 79; see also Ref. 80 for a similar definition of tetrahedral order parameter) during the compressiondecompression cycle shown in Fig. 3. q(P) can take values in the range -3 to 1, where q = 1 implies a perfect tetrahedral local arrangement; the average value of q is ≈ 0 for a random distribution of particles. Figure 6 shows that molecules in LDA have a highly tetrahedral local arrangements, with $q \approx 0.9$ [state point labeled A, see Fig. 3]. The tetrahedral



FIG. 6. Tetrahedral order parameter q(P) of glassy ST2 water during the compression of LDA (black line), followed by the decompression of HDA (red line) at T = 80 K. The value of q(P) for the state points labeled A, B, C, D, and E in Fig. 3 are indicated.

order parameter drops to q = 0.47 in the case of HDA [state point labeled *C*, see Fig. 3]. For comparison, we note that in the SPC/E model, the tetrahedral order for LDA (or, more precisely, HGW) and HDA at T = 77 K are, respectively, 0.82-0.84 (at $-500 \le P \le 400$ MPa and $0.9 \le \rho$ ≤ 1.0 g/cm³) and 0.67 - 0.70 (at $1400 \le P \le 2200$ MPa and $1.3 \le \rho \le 1.4$ g/cm³).⁴⁹

The distribution of tetrahedral order parameter for the individual molecules, P(q), during the LDA-HDA compression cycle at T = 80 K is shown in Fig. 7 for selected pressures. For comparison, we also include the P(q) distribution for ice I_h at low pressure. The P(q) distribution of ice I_h is reminiscent of a delta distribution at $q \approx 1$, as expected for a perfect tetrahedral structure. Interestingly, the P(q) distributions for both the starting LDA form (i.e., HGW) and the LDA form obtained by decompression of HDA are practically identical. These LDA forms are characterized by a wide P(q) distribution, expanding from $q \approx 0.5$ to $q \approx 1$. We note that while there is some overlap between the P(q) distributions of LDA/HGW and ice I_h , the corresponding distributions are very different. The P(q)distribution of HDA is very wide, expanding from $q \approx 0$ to $q \approx 1$ and indicating the presence of a rich variety of local structure.



FIG. 7. Distribution of tetrahedral order parameter for the *individual* molecules, P(q), during the LDA-HDA compression cycle at T = 80 K, for selected pressures. For comparison, we also include the P(q) distribution for ice I_h at low pressure. The P(q) distribution of ice I_h is very sharp and it is centered at $q \approx 1$. Instead, the distributions for the amorphous ices are much wider, as expected.



FIG. 8. Snapshot of ice VII, formed upon compression of HDA at T = 200 K. Note that, just left of center, there is small region of the crystal that formed in a different orientation. Oxygens are shown in red, hydrogens are not drawn; links approximate the hydrogen bond structure.

V. CRYSTALLIZATION OF HDA TO ICE VII

We next discuss the compression-induced transformation of HDA (or HDL, for $T > T_g$) to a crystal that closely resembles ice VII at high pressures [see Fig. 1(b)]. For reference, we show a simulation snapshot of the crystal in Fig. 8. We note that bulk crystallization of all-atom water models is rather unusual in MD simulations,^{35,81,82} but high-pressure crystallization to an ice VII-like structure has been previously reported for the ST2 model.^{35,83} We confirm that the crystal formed is ice VII by evaluating the structure factor S(q). Fig. 9 shows that the primary peaks of S(q) line up remarkably well with the expected locations of primary crystal planes of ice VII.⁸⁴ Given the strong tendency for ST2 to favor tetrahedral structures, it is not surprising that ice VII might be a favored crystal state, since ice VII has the structure of two interpenetrating (but non-bonded) tetrahedral lattices. Experiments also show crystallization of HDA on compression,^{85–88} however the crystal formed is ice XII. The discrepancy in the high



FIG. 9. Structure factor S(q) of ice VII, obtained in computer simulations of glassy ST2 water during the compression of HDA at T = 200 K. The arrows indicate the expected locations of the first 4 crystal planes for ice VII.⁸⁴

TABLE I. Number of independent simulations, *n* (out of 10), that exhibit the HDA-to-ice VII transformation. Crystallization of HDA is observed at $T \ge 160$ K for $P \le 6000$ MPa. $P_{\text{HDA} \rightarrow \text{VII}}$ is the lowest pressure at which HDA crystallizes [see magenta line in Fig. 1(b)].

Compression T (K)	n	$P_{\rm HDA \rightarrow VII} (\rm MPa)$
140	0	
160	3	4780
180	3	3652
200	8	2188
210	9	1828
220	6	1456
230	10	869
240	10	812
250	10	765
260	10	819
270	10	968
280	10	1041

pressure phase is a consequence of the ST2 model's strong preference for tetrahedral arrangements. This is again evidence that the ST2 model is not ideal for studying water structure at high pressure. We note, however, that slower compression rates than those explored in this work may allow the system to relax to other crystalline structures, including possibly ice XII.

In the ST2 model, we observe crystallization to ice VII only at $T \ge 160$ K for $P \le 6000$ MPa; at lower T, crystallization is likely possible for slower compression rates. Furthermore, we note that not all individual compression runs exhibit crystallization and, like the LDA-to-HDA transformation, the crystallization pressures vary considerably among the independent runs. Thus, there must be a significant kinetic barrier to crystallization, exacerbated by the stochastic nature of crystal nucleation in the out-of-equilibrium process. We list the number of runs that result in a high-pressure crystal in Table I, along with the minimum pressure at which HDA crystallizes upon compression. The corresponding HDL/HDA-to-ice transformation line is shown in Fig. 1(b).

We define the crystallization locus $P_{\text{HDA} \rightarrow \text{VII}}(T)$ given in Fig. 1(b) by the lowest (rather than mean) pressure at which HDA crystallizes upon compression over the independent runs. The $P_{\text{HDA}} \rightarrow \text{VII}(T)$ locus has a nose-like shape. This behavior can be understood by considering the T-dependence of water's crystallization time, $\tau_x(T)$. Both simulations and theory predict that $\tau_x(T)$ exhibits a minimum as function of temperature,^{30,42,82,89} and such a minimum is common for most liquids,⁹⁰ referred to as a "time-temperature transformation." Qualitatively, this minimum is a consequence of the balance between the growing free energy gap between liquid and crystal states that enhances crystallization rates, and the slowing of liquid dynamics that inhibits crystal nucleation. Since all our compression runs are performed at the same rate, a nose-like shape of $\tau_x(T)$ will yield a similar shape for $P_{\text{HDA} \rightarrow \text{VII}}(T)$. We note that the HDL/HDA-to-ice transformation line shown in Fig. 1(b) is only indicative of the kinetic tendency of HDA to crystallize at a given compression temperature, and should not be taken as a thermodynamic transition line.



FIG. 10. (a) Density as function of pressure during the compression of HDA at T = 200 K for two independent runs, one where crystallization occurs (black line) and another where it does not (red line). The LDA-to-HDA transformation occurs at low pressures (not shown). (b) Tetrahedral order parameter, q(P), for the same simulations.

Examining the density and structure, crystallization is easily detected in the case of the ST2 model. Figure 10(a) shows the evolution of $\rho(P)$ at high pressure for two individual runs performed at T = 200 K, one which crystallizes, and one that does not. Crystallization to ice VII is accompanied by a small density change in $\rho(P)$, following the large density change accompanying the LDA-to-HDA transformation. We also evaluate the tetrahedral order parameter, and see that, on crystallization, q increases relative to HDA to ≈ 0.43 [Fig. 10(b)]. The tetrahedral order parameter for HDA is $q \approx 0.39$. For comparison, we note that for ice I_h at P = 0.1 MPa and T = 80 K, $q_{I_h} = 0.99$. Since ice VII is tetrahedral, such a small value for q might seem surprising. However, since the evaluation of q examines the 4 nearest neighbors, as opposed to 4 bonded neighbors, interpenetration results in some non-bonded (and thus non-tetrahedral) neighbors to be counted.

While the structure factor provides the best indicator of crystal periodicity, the real space structure measured by the RDF is often more intuitively valuable. Figure 11 shows the OO RDF for ice VII, and compares it with that for ice I_h , LDA, and HDA, for reference. As expected, the primary peak is located at the ideal hydrogen bond distance for all states.



FIG. 11. Oxygen-oxygen RDF of ice VII (top curve) obtained in computer simulations of ST2 water at T = 200 K. For comparison, we also show g(r) for ice I_h , LDA, and HDA. The most notable feature of the ice VII RDF is the shoulder of the first peak, due the interpenetrating structure of ice VII.

The interpenetrating nature of ice VII gives rise to a pronounced "shoulder" in the first peak of the RDF. Since ice VII consists of interpenetrating diamond lattices, the locations of the ice I_h peaks are preserved—except those that correspond to the differences between hexagonal and cubic tetrahedral lattices (i.e., the difference between ice I_h and ice I_c).

We have also examined the change in the crystallization locus $P_{\text{HDA} \rightarrow \text{VII}}(T)$ using the slower compression rate. Not surprisingly, reducing q_P shifts $P_{\text{HDA} \rightarrow \text{VII}}(T)$ to lower pressures [Fig. 1(c)]. This results suggest that HDL will be inaccessible at $P \gtrsim 400$ MPa and low temperatures for simulations performed at much slower compression/decompression rates. At slow enough rates, potentially accessible to simulations in a few years, lower pressure ices may also spontaneously crystallize, giving rise to a crystallization zone analogous to the "no-man's land" in experiments where the LLCP would be hidden.⁵³ Hence, the slow compression rate phase diagram would become much more similar to that observed experimentally, where such rapid cooling rates under pressure are not presently feasible.

VI. SUBLIMATION OF LDA

We also study the stability of LDA relative to the vapor phase by extending the decompression runs to rather large negative pressure (tension). Figure 1(b) shows the sublimation pressures, $P_{\text{LDA} \rightarrow \text{vapor}}(T)$, at which the decompressed form of LDA obtained from HDA sublimes upon further decompression, using the fast rate (violet triangles-left). For comparison, included in Fig. 1(b) is the liquid-to-gas spinodal line for ST2 water (squares) reported in Ref. 29. As expected, the $P_{\text{LDA} \rightarrow \text{vapor}}(T)$ locus merges smoothly with the liquid spinodal line for high enough $T \gtrsim T_g$. For comparison, when HGW (obtained upon rapid cooling the liquid) is decompressed at the same rate ($q_P = -300$ MPa/ns), we obtain a different sublimation pressure, $P_{\text{HGW} \rightarrow \text{vapor}}(T)$, (brown triangles-left). Figure 1(b) shows that at all temperatures $P_{\text{HGW} \rightarrow \text{vapor}}(T) < P_{\text{LDA} \rightarrow \text{vapor}}(T)$, indicating that the LDA form obtained from HDA is less stable, relative to the vapor, than the LDA form obtained upon cooling the liquid (HGW). It follows that these forms of LDA have some structural and thermodynamic differences. As shown in Appendix A, these differences are rather minor and depend on the q_P considered.

VII. PRESSURE-INDUCED AMORPHIZATION OF HEXAGONAL ICE

In addition to the LDA-HDA transformations, water exhibits another unusual transition at low temperatures. Specifically, it has been long known that isothermal compression of ice I_h , the stable ice at normal pressure and low temperature, produces HDA.¹² The experimental pressures at which this transformation occurs, as function of temperature, are shown in Fig. 1(a) (green line). In this section, we examine the pressure-induced amorphization (PIA) of ice I_h at different temperatures using computer simulations. At low temperatures, ice I_h transforms to HDA; at high, temperatures, ice I_h transforms to HDA; at high, temperatures, ice I_h



FIG. 12. Phase diagram of glassy ST2 water showing the pressures at which ice I_h transforms to HDA upon compression at different temperatures (green triangles-right). Upon further compression, HDA and HDL transform to ice VII (maroon triangles-right). For comparison, we include the transformation lines shown in Fig. 1(b). The resulting phase diagram at low temperature (e.g., T < 220 K) is qualitatively similar to Fig. 1(a).

Figure 12 shows the ice I_h -to-HDA/HDL transition pressures $[P_{I_h \to HDA}(T)]$ for ST2 water. At our faster compression rate, the values of the transition pressure are much higher than those reported in experiments [see Fig. 1(a)]. Nonetheless, the qualitative experimental behavior of $P_{I_h \to HDA}(T)$ at low temperatures is reproduced by simulations. Specifically, simulations predict correctly that $P_{I_h \to HDA}(T)$ should increase as the compression temperature decreases. The corresponding slopes at low temperatures are -0.20 K/MPa [Fig. 1(a)] and -0.08 K/MPa [Fig. 12] for the experimental and simulation case, respectively.

Experiments using emulsified ice indicate that the $P_{\text{I}_{\text{h}} \rightarrow \text{HDA}}(T)$ locus exhibits a kink at $T \approx 160$ K. The experiments of Ref. 12 indicate that above this temperature, PIA of ice I_h results in (emulsified) liquid water and the transformation corresponds to the metastable extension of the equilibrium melting of ice I_h . Accordingly, experiments show that the $P_{I_b \to HDA}(T)$ locus at low temperatures is an extrapolation of the metastable melting temperature of ice I_h , $T_M(P)$, at high temperatures, similar to the relationship we see between the liquid-liquid spinodals and the glass-glass transitions. Instead, below T = 160 K, PIA of ice I_h results in HDA via a pressure-induced mechanical collapse of ice I_h . Hence, the pressure-induced I_h -to-HDA and I_h -to-HDL transformations have a different origin.¹³ Accordingly, at very low temperatures, the $P_{I_{h} \to HDA}(T)$ locus deviates from the corresponding extrapolation of $T_M(P)$ (see, e.g., Fig. 2(a) of Ref. 13).

Contrary to experiments, in the ST2 model, the $P_{I_h \rightarrow HDA}(T)$ locus exhibits no kink [Fig. 12]. This may be not surprising, giving the fast rate used in our simulations. A similar result was obtained in MD simulations using the Fermi-Jagla model.⁷² Interestingly, the smooth behavior of the $P_{I_h \rightarrow HDA}(T)$ locus suggests an alternative interpretation for the pressure-induced I_h -to-HDA transformation. Specifically, the ice I_h -to-HDA, could be interpreted as the *out-of-equilibrium*, fast compression-induced melting of ice I_h at high temperature, extended to low temperatures, into the glass domain. This interpretation for the origin of the ice I_h -to-HDA transformation is consistent with simulations using the Fermi-Jagla model.⁷²



FIG. 13. OO-, OH-, and HH-RDFs of HDA obtained in computer simulations of glassy ST2 water during compression of LDA (black lines) and compression of ice I_h (red dashed lines). T = 160 K and P = 3000 MPa. The similarities in the RDFs indicate that both compression processes lead to the same HDA forms.

A natural question that follows from Fig. 12 is whether the same form of HDA is obtained by (i) PIA of ice I_h and (ii) compression of LDA. To answer this question we compare the RDFs of HDA obtained from LDA and ice I_h at P = 3000 MPa and T = 160 K. The OO, OH, and HH RDFs are shown in Fig. 13. The RDFs are nearly quantitatively identical, indicating that both glass preparations lead to the same HDA form.

We note that if the same HDA form results from compression of either ice I_h or LDA, then the ice I_h -to-HDA transformation should be followed by a HDA-to-ice VII transformation at high pressures. This is indeed confirmed by our simulations. Figure 12 shows the pressures at which HDA (and HDL, at high temperatures), obtained by PIA of ice I_h , crystallizes into a high-pressure crystal (brown trianglesright). At T > 300 K, one finds the ice I_h -liquid transformation, followed by the liquid-to-ice VII transformation. As we expect, the liquid-to-ice VII crystallization line (brown line in Fig. 12) at $T \approx 300$ K is continuous with the HDA-to-VII locus obtained by starting from LDA at low pressures (magenta line in Fig. 12). In addition, the HDA-to-ice VII transformation pressure at T = 200 K when starting from ice I_h (brown triangle-right) is consistent with the corresponding pressure when starting from LDA (magenta right-triangle).

The crystallization of ice VII from HDA results in a small, but noticeable density change during the compression of ice I_h [Fig. 14(a)], just as observed in the compression of LDA. For example, the large density change at $P \approx 1890$ MPa corresponds to the I_h -to-HDA transformation; the small density change at $P \approx 2813$ MPa, indicates the crystallization of HDA. The states labeled A, B, and C in the figure correspond to ice I_h , HDA, and high-pressure ice, respectively, and the corresponding OO RDFs are shown in Fig. 14(b). The density change at either the I_h -to-HDL and I_h -to-HDA transformations is very sharp, reminiscent of a first-order transition.

VIII. SUMMARY AND DISCUSSION

In this work, we described the phase behavior of the ST2 water model in the glass state and related it to the metastable equilibrium liquid phase diagram reported in



FIG. 14. (a) Density as function of pressure during the compression of ice I_h at T = 160 K, from computer simulations of glassy ST2 water. The sharp large change in density signals the ice I_h -to-HDA transformation; the small density change at $P \approx 2830$ MPa indicates the crystallization of HDA to ice VII. (b) OO RDFs at state points labeled A (ice I_h), B (HDA), and C (ice VII) in (a).

Refs. 29 and 70. The ST2 model is the most studied water model that exhibits a LLPT. Indeed, the LLPT hypothesis proposed to explain the thermodynamic anomalies in the liquid and glass domains was originally proposed based on MD simulations using the ST2 model.²⁶ While the behavior of this model in the liquid domain is well-documented (see, e.g., Refs. 26, 29, 32–34, and 64, its behavior in the glass domain has not been well explored.^{26,50,53} Paradoxically, most experimental work has been performed in the glass domain, since experiments around the expected LLPT temperatures have not been possible due to rapid crystallization. Hence, the present work fills a gap between ST2 model simulations and experiments, and provides a logical test for the LLPT hypothesis.

We showed that the ST2 model reproduces qualitatively the (i) compression-induced LDA-to-HDA, (ii) decompression-induced HDA-to-LDA, and (iii) compression-induced ice I_h -to-HDA transformations that have been reported in experiments. Compared to experiments, the transformation pressures are overestimated, i.e., compression- (decompression-) induced transformation pressures are higher (lower) than those reported in experiments. This is not surprising given the simplicity of the ST2 water model (which assumes a rigid structure molecule with five interacting sites), and the extremely fast compressions rates required by simulations.

In addition to transformations (i)-(iii), we found that HDA (or the liquid, at high T) in the ST2 model rapidly

crystallizes at high-pressures to ice VII, which consists of two interpenetrating tetrahedral lattices. Crystallization of HDA in experiments results in ice XII. We attributed this difference to the fact that ST2 overemphasizes the tetrahedral character of water. We note that crystallization in MD simulations using water models is rather unusual. The (out-of-equilibrium) crystallization pressure as function of temperature has a minimum at intermediate temperatures, as expected from time-temperature transformation curves of many more simple liquids. By extending the simulations to negative pressures, it was found that LDA sublimes. Interestingly, the minimum pressure accessible to LDA is sensitive to its preparation process.

By constructing a *P-T* "phase diagram" with the pressures corresponding to transformations (i)-(iii), we compared the glass phase diagram of ST2 water with its (metastable) equilibrium liquid phase diagram, which includes the LLCP and LL spinodals lines. Our results support the proposal that the LDA-to-HDA and HDA-to-LDA transformation lines at slow compression rates are the continuation into the glass domain of the LDL-to-HDL and HDL-to-LDL spinodal lines, respectively. At the two compression/decompression rates studied, we observed some deviations between the spinodal and glass-glass transformation lines. However, these differences become less pronounced as the compression/decompression rate decreases. These results are in agreement with the predictions of the LLPT hypothesis.

One may wonder, is there any statistical mechanics basis underlying the relationship between the reported liquid and glass polymorphism in ST2 water? A potential explanation is provided by the potential energy landscape (PEL) approach,55,56 a helpful formalism based on statistical mechanics/thermodynamics that can be used to study supercooled liquids and glasses. In the PEL formalism, it can be shown that the pressure of a glass can be formally separated in $P = P_{IS} + P_{vib}$,⁹¹ where P_{IS} is the pressure of the system at the corresponding IS of the glass and P_{vib} is the pressure of the system due to vibrational motion within the basin associate to the corresponding IS. If the IS of the glass are not structurally different from the low-temperature configurations of the subcritical $(T < T_{LLCP})$ liquid (even when the corresponding IS may differ), then one would expect that the P_{IS} of the glass and subcritical liquid will be similar. Hence, if during the compression/decompression cycle of the glass, P_{vib} plays a secondary role, e.g., due to the low temperature, then $(\partial P/\partial rho)_{glass} \approx (\partial P/\partial rho)_{sub-critical liquid} + (less relevant)$ terms). Therefore, any structural change of the subcritical liquid leading to a discontinuity in $\rho(P)$ at the LDL-HDL transformation (which is accompanied by changes of IS) would also be reflected in the glass state, resulting in a sharp density change at the LDA-HDA transformations. Support of this view can be found in Ref. 46, where the PEL of SPC/E glassy water was studied during the pressure-induced LDA-HDA transformations. It was found that, during these pressure cycles, $P_{IS}(\rho)$ indeed changes suddenly (but smoothly, since there is no accessible LLCP in SPC/E water) with density at the LDA-HDA transformations. In particular, the rate at which $P_{IS}(\rho)$ changes during the LDA-HDA transformations are also observed in $P(\rho)$ itself,⁴⁷ supporting that the main contribution to $P(\rho)$ is $P_{IS}(\rho)$. By the same token, one can conclude that it is possible that other water models that do not exhibit a LLPT, such as the SPC/E and mW water models, may still exhibit glass polymorphism.⁹² In these cases, however, the change in pressure with density at the LDA-HDA transformation would be rather smooth, as observed for the SPC/E model.

While the ST2 model is a good model to reproduce qualitatively the transformation loci and density behavior during the LDA-HDA transformations, it is not optimal to quantitatively reproduce experimental densities or the detailed properties of water at high pressure. As noted above, spontaneous crystallization at high pressure favors an incorrect ice polymorph, and high pressure structure (measured by RDFs) of HDA does not compare well to experimental data. This implies that one should be careful if the ST2 model is employed to study the detailed properties of HDA or other high pressure water glasses. However, we note that these conclusions are based on the results obtained at our relatively fast compression rates, and it is unclear if slower rates may improve the performance of ST2 model. For comparison, we showed that the SPC/E model better reproduces the RDF of HDA. However, at accessible quench and compression rates, the SPC/E model fails to reproduce the qualitative glass diagram found in experiments and the ST2 model, as discussed in Ref. 50.

We also studied the compression-induced amorphization of the low-pressure crystal, ice I_h . At both compression rates considered, it was found that the crystal transforms to HDA (HDL) at low (high) temperatures. HDA formed upon compression of the crystal was, from the thermodynamic and structural point of view, nearly indistinguishable from the HDA form obtained from compression of LDA. Interestingly, we found that the ice I_h -to-HDA locus in the PT plane was a smooth extension of the *metastable* ice I_h -to-HDL locus, obtained at high temperature. It follows that the ice I_h -to-HDA transformation locus can be thought of as the extension into the glass state of the *metastable* ice I_h -to-HDL line found at high temperatures. Therefore, apparently both phenomena have a common origin, i.e., the crystal reaches its metastable limit relative to the high-density amorphous state, transforming to HDA or HDL.

The present work is meant to present basic information on the phase diagram of ST2 *glassy* water that may be useful for future studies of glassy water polymorphism. The present simulations are based on compression and decompression runs, and further work is needed to show how these glass-glass transformations relate to heating-induced glassglass transformations.⁵⁰ A comparative study of heatingand pressure-induced LDA-HDA transformations will be presented in a subsequent work.

ACKNOWLEDGMENTS

Support for this project was provided by a PSC-CUNY Award, jointly funded by The Professional Staff Congress and The City University of New York. This research was supported, in part, under National Science Foundation, Grant Nos. CNS-0959856, CNS-0958379, and CNS-0855217 and the City University of New York High Performance Computing Center at the College of Staten Island.

APPENDIX A: REVERSIBILITY OF THE LDA-HDA TRANSFORMATION

In this appendix, we discuss briefly the properties of the LDA forms obtained (i) upon cooling the liquid at P = 0.1 MPa, i.e., HGW, and (ii) upon decompression of HDA. We already mentioned that these two forms of LDA are very similar, but not identical, since the corresponding decompression-induced sublimation pressures are different [Fig. 1(b)].

To compare these LDA forms, we decompress HGW to negative pressures, in order to have both forms of LDA at same pressure at temperature. As an example, we show in Fig. 15(a) the density of HGW during its decompression at T = 80 K from P = 0.1 MPa. Included in the figure is $\rho(P)$ during the LDA-HDA cycle at the same temperature. It is evident from Fig. 15(a) that the two LDA forms have different thermodynamic behavior. Specifically, although both decompression lines intersect at P = -450 MPa, these glasses have different densities at P < -450 MPa. Moreover, their compressibilities, which are defined from the slope of $\rho(P)$, are very different. These differences become less pronounced at higher temperatures, as one approaches the



FIG. 15. (a) Density of LDA obtained from computer simulations of glassy ST2 water, upon decompressing HGW at T = 80 K from P = 0.1 MPa at T = 80 K (red line). Included in the figure is the density during the pressure induced LDA-HDA transformations at the same temperature (black line). At state point *A*, the LDA forms obtained upon decompression of HGW and HDA have the same density. $\rho(P)$ for both LDA forms behave differently upon further decompression. (b) OO RDF for the two LDA forms considered in (a), at P = -450 MPa (point labeled *A*).



FIG. 16. Pressure-dependence of density $\rho(P)$ during the compressioninduced LDA-to-HDA transformation at T = 80 K. Black line is obtained from a *single* computer simulation of a very large system composed of N = 13824 molecules. Red line is taken from Fig. 2(a) and is an *average* over 10 independent runs of a smaller system composed of N = 1728 molecules. $\rho(P)$ is practically independent of the system size considered.

liquid phase. Not surprising, these differences also diminish when the slower compression rate $q_P = \pm 30$ MPa/ns is used.

We note that structurally, both LDA forms are strikingly similar. For example, Fig. 15(b) shows that the OO RDF of both LDA forms differ only in the magnitude of the first two peaks and depth of the RDF first minimum. However, both LDA forms exhibit the same general RDF, indicating that they can be considered as members of a unique LDA family. We stress that our simulations do not indicate that the same LDA configuration (or sub-state within the LDA family) is recovered after the LDA-HDA pressure cycle; reversibility of the LDA-HDA transformations is meaningful only in the context



FIG. 17. Snapshots during the LDA-to-HDA transition from a computer simulation of a very large system, composed of $N = 13\,824$ molecules, at T = 80 K and P = 1070, 1080, 1090, and 1100 MPa (see Fig. 16). Snapshots are very similar to those shown in Fig. 4, showing no signature of a HDA nucleus developing within the LDA matrix.

of LDA and HDA being families of amorphous structures (see the Introduction); see, e.g., Refs. 9 and 54.

APPENDIX B: SIZE EFFECTS ON THE LDA-HDA TRANSFORMATION

In this appendix, we study whether our results are sensitive to the system size. We focus on the LDA-to-HDA transformation performed at T = 80 K and using the fast rate 300 MPa/ns. Figure 16 shows the evolution of density with pressure for *one* system composed of N = 13824 molecules (8 times larger than the system previously studied). For comparison, we include the results shown in Fig. 2(a) obtained with the 1728-molecule systems, after averaging over the 10 independent runs. For both system sizes, we obtain practically the same transformation pressure and the corresponding curves of $\rho(P)$ practically overlap. Interesting, $\rho(P)$ is sharper at the transition for the larger system. These results constitute strong evidence that the results obtained for the N = 1728molecules system are not affected by the system size.

Snapshots during the LDA-to-HDA transition for the N = 13824 molecules system are included in Fig. 17. These snapshots are very similar to those shown in Fig. 4. In particular, we note that, even for this large system, there is no signature of a HDA nucleus developing within the LDA matrix.

- ¹M. Chaplin, see http://www.lsbu.ac.uk/water/models.html for a list of water anomalous properties.
- ²O. Mishima, J. Chem. Phys. 133, 144503 (2010).
- ³R. J. Speedy and C. A. Angell, J. Chem. Phys. 65, 851 (1976).
- ⁴C. A. Angell, J. Shuppert, and J. C. Tucker, J. Phys. Chem. **77**, 3092 (1973).
 ⁵F. X. Prielmeier, E. W. Lang, R. J. Speedy, and H.-D. Lüdemann, Ber. Bunsenges. Phys. Chem. **92**, 1111 (1988); available at http://epub.uni-regensburg.de/16772/.
- ⁶P. G. Debenedetti, J. Phys.: Condens. Matter 15, R1669 (2003).
- ⁷H. E. Stanley, S. V. Buldyrev, M. Canpolat, O. Mishima, M. R. Sadr-Lahijany, A. Scala, and F. W. Starr, Phys. Chem. Chem. Phys. **2**, 1551 (2000).
- ⁸C. A. Angell, Ann. Rev. Phys. Chem. **34**, 593 (1983).
- ⁹T. Loerting and N. Giovambattista, J. Phys.: Condens. Matter 18, R919 (2006).
- ¹⁰C. A. Angell, Annu. Rev. Phys. Chem. **55**, 559 (2004).
- ¹¹O. Mishima and H. E. Stanley, Nature (London) **396**, 329 (1998).
- ¹²O. Mishima, L. D. Calvert, and E. Whalley, Nature (London) **310**, 393 (1984).
- ¹³O. Mishima, Nature (London) **384**, 546 (1996).
- ¹⁴T. Loerting, W. Schustereder, K. Winkel, C. G. Salzmann, I. Kohl, and E. Mayer, Phys. Rev. Lett. 96, 025702 (2006).
- ¹⁵O. Andersson, Proc. Natl. Acad. Sci. U.S.A. **108**, 11013 (2011).
- ¹⁶O. Mishima, J. Chem. Phys. **100**, 5910 (1994).
- ¹⁷K. Winkel, M. Bauer, E. Mayer, M. Seidl, M. S. Elsaesser, and T. Loerting, J. Phys.: Condens. Matter **20**, 494212 (2008).
- ¹⁸K. Winkel, E. S. Elsaesser, E. Mayer, and T. Loerting, J. Chem. Phys. **128**, 044510 (2008).
- ¹⁹O. Mishima, L. D. Calvert, and E. Whalley, Nature (London) **314**, 76 (1985).
- ²⁰M. M. Koza, H. Schober, H. E. Fischer, T. Hansen, and F. Fujara, J. Phys.: Condens. Matter 15, 321 (2003).
- ²¹C. A. Tulk, C. J. Benmore, J. Urquidi, D. D. Klug, J. Neuefeind, B. Tomberli, and P. A. Egelstaff, Science 297, 1320 (2002).
- ²²S. Klotz, Th. Strässle, R. J. Nelmes, J. S. Loveday, G. Hamel, G. Rousse, B. Canny, J. C. Chervin, and A. M. Saitta, Phys. Rev. Lett. **94**, 025506 (2005).
- ²³K. Winkel, E. Mayer, and T. Loerting, J. Phys. Chem. B **115**, 14141 (2011).
- ²⁴O. Mishima, K. Takemura, and K. Aoki, Science **254**, 406 (1991).
- ²⁵O. Mishima and Y. Suzuki, Nature (London) **419**, 599 (2002).

- ²⁶P. H. Poole, F. Sciortino, U. Essmann, and H. E. Stanley, Nature (London) 360, 324 (1992).
- ²⁷P. G. Debenedetti and H. E. Stanley, Phys. Today **56**(6), 40 (2003).
- ²⁸F. H. Stillinger and A. Rahman, J. Chem. Phys. **60**, 1545 (1974).
- ²⁹P. H. Poole, I. Saika-Voivod, and F. Sciortino, J. Phys.: Condens. Matter 17, L431 (2005).
- ³⁰D. T. Limmer and D. Chandler, J. Chem. Phys. **135**, 134503 (2011).
- ³¹D. T. Limmer and D. Chandler, J. Chem. Phys. **138**, 214504 (2013).
- ³²Y. Liu, A. Z. Panagiotopoulos, and P. G. Debenedetti, J. Chem. Phys. **131**, 104508 (2009).
- ³³F. Sciortino, I. Saika-Voivod, and P. H. Poole, Phys. Chem. Chem. Phys. **13**, 19759 (2011).
- ³⁴T. A. Kesselring, G. Franzese, S. V. Buldyrev, H. J. Herrmann, and H. E. Stanley, Sci. Rep. 2, 474 (2012).
- ³⁵Y. Liu, J. C. Palmer, A. Z. Panagiotopoulos, and P. G. Debenedetti, J. Chem. Phys. **137**, 214505 (2012).
- ³⁶P. H. Poole, R. K. Bowles, I. Saika-Voivod, and F. Sciortino, J. Chem. Phys. 138, 034505 (2013).
- ³⁷E. A. Jagla, J. Chem. Phys. **111**, 8980 (1999).
- ³⁸E. A. Jagla, Phys. Rev. E **63**, 061501 (2001).
- ³⁹S. Sastry and C. A. Angell, Nature Mater. 2, 739 (2003).
- ⁴⁰G. Franzese, J. Mol. Liq. **136**, 267 (2007).
- ⁴¹C. W. Hsu, J. Largo, F. Sciortino, and F. W. Starr, Proc. Natl. Acad. Sci. U.S.A. **105**, 13711 (2008).
- ⁴²W. Dai, C. W. Hsu, F. Sciortino, and F. W. Starr, Langmuir **26**, 3601 (2010).
- ⁴³J. Y. Abraham, S. V. Buldyrev, and N. Giovambattista, J. Phys. Chem. B 115, 14229 (2011).
- ⁴⁴P. Gallo and F. Sciortino, Phys. Rev. Lett. 109, 177801 (2012).
- ⁴⁵F. W. Starr, M.-C. Bellissent-Funel, and H. E. Stanley, Phys. Rev. E 60, 1084 (1999).
- ⁴⁶N. Giovambattista, H. E. Stanley, and F. Sciortino, Phys. Rev. Lett. **91**, 115504 (2003).
- ⁴⁷N. Giovambattista, H. E. Stanley, and F. Sciortino, Phys. Rev. E 72, 031510 (2005).
- ⁴⁸N. Giovambattista, H. E. Stanley, and F. Sciortino, Phys. Rev. Lett. 94, 107803 (2005).
- ⁴⁹N. Giovambattista, P. G. Debenedetti, F. Sciortino, and H. E. Stanley, Phys. Rev. E 71, 061505 (2005).
- ⁵⁰N. Giovambattista, T. Loerting, B. R. Lukanov, and F. W. Starr, Sci. Rep. 2, 390 (2012).
- ⁵¹R. Martonâk, D. Donadio, and M. Parrinello, Phys. Rev. Lett. **92**, 225702 (2004).
- ⁵²J. S. Tse and M. L. Klein, Phys. Rev. Lett. **58**, 1672 (1987).
- ⁵³P. H. Poole, U. Essmann, F. Sciortino, and H. E. Stanley, Phys. Rev. E 48, 4605 (1993).
- ⁵⁴T. Loerting, K. Winkel, M. Seidl, M. Bauer, C. Mitterdorfer, P. H. Handle, C. G. Salzmann, E. Mayer, J. L. Finney, and D. T. Bowron, Phys. Chem. Chem. Phys. **13**, 8783 (2011).
- ⁵⁵F. H. Stillinger, Science **267**, 1935 (1995).
- ⁵⁶P. G. Debenedetti and F. H. Stillinger, Nature (London) **410**, 259 (2001).
- ⁵⁷C. A. Angell, Science **267**, 1924 (1995).
- ⁵⁸K. Winkel, D. T. Bowron, T. Loerting, E. Mayer, and J. L. Finney, J. Chem. Phys. **130**, 204502 (2009).
- ⁵⁹R. J. Nelmes, J. S. Loveday, T. Strässle, C. L. Bull, M. Guthrie, G. Hamel, and S. Klotz, Nat. Phys. 2, 414 (2006).
- ⁶⁰P. H. Handle, M. Seidl, and T. Loerting, Phys. Rev. Lett. **108**, 225901 (2012).
- ⁶¹P. Brüggeller and E. Mayer, Nature (London) **288**, 569 (1980).
- ⁶²C. G. Venkatesh, S. A. Rice, and A. H. Narten, Science 186, 927 (1974).
- ⁶³M. P. Allen and D. J. Tildesley, *Computer Simulation of Liquids* (Oxford University Press, UK, 2002).
- ⁶⁴P. H. Poole, S. R. Becker, F. Sciortino, and F. W. Starr, J. Phys. Chem. B 115, 14176 (2011).
- ⁶⁵H. J. C. Berendsen, J. P. M. Postma, W. F. van Gunsteren, A. DiNola, and J. R. Haak, J. Phys. Chem. **81**, 3684 (1984).
- ⁶⁶S. Karmakar and G. Parisi, Proc. Natl. Acad. Sci. U.S.A. 110, 2752 (2013).
- ⁶⁷W. Kob and L. Berthier, Phys. Rev. Lett. **110**, 245702 (2013).
- ⁶⁸R. L. Jack, L. O. Hedges, J. P. Garrahan, and D. Chandler, Phys. Rev. Lett. 107, 275702 (2011).
- ⁶⁹E. Mayer, J. Appl. Phys. 58, 663 (1985).
- ⁷⁰M. J. Cuthbertson and P. H. Poole, Phys. Rev. Lett. **106**, 115706 (2011).
- ⁷¹Computer simulation studies of ST2 water using the Ewald sum technique have been performed; see, e.g., J. Chem. Phys. **123**, 044515 (2005) and

Ref. 32. We note that while in J. Chem. Phys. **123**, 044515 (2005) it is found multiple LLCPs in ST2 water, such a finding is in disagreement with Ref. 32 and works based on ST2 water using the reaction field technique.

- ⁷²S. Reisman and N. Giovambattista, J. Chem. Phys. **138**, 064509 (2013).
- ⁷³T. Loerting, C. Salzmann, I. Kohl, E. Mayer, and A. Hallbrucker, Phys. Chem. Chem. Phys. 3, 5355 (2001).
- ⁷⁴J. L. Finney, A. Hallbrucker, I. Kohl, A. K. Soper, and D. T. Bowron, Phys. Rev. Lett. 88, 225503 (2002).
- ⁷⁵M.-C. Bellissent-Funel and L. Bosio, J. Chem. Phys. **102**, 3727 (1995).
 ⁷⁶H. Tanaka, R. Kurita, and H. Mataki, Phys. Rev. Lett. **92**, 025701 (2004).
- ⁷⁷R. Kurita and H. Tanaka, Science **306**, 845 (2004).
- ⁷⁸K.-I. Murata and H. Tanaka, Nature Mater. **11**, 436 (2012).
- ⁷⁹J. R. Errington and P. G. Debenedetti, Nature (London) 409, 318 (2001).
- ⁸⁰P.-L. Chau and A. J. Hardwick, Mol. Phys. 93, 511 (1998).
- ⁸¹M. Matsumoto, S. Saito, and I. Ohmine, Nature (London) **416**, 409 (2002).

- ⁸²M. Yamada, S. Mossa, H. E. Stanley, and F. Sciortino, Phys. Rev. Lett. 88, 195701 (2002).
- ⁸³P. H. Poole, private communication (2013).
- ⁸⁴B. Kamb and B. L. Davis, Proc. Natl. Acad. Sci. U.S.A. **52**, 1433 (1964).
- ⁸⁵I. Kohl, E. Mayer, and A. Hallbrucker, Phys. Chem. Chem. Phys. **3**, 602 (2001).
- ⁸⁶S. Klotz, G. Hamel, J. S. Loveday, R. J. Nelmes, and M. Guthrie, Z. Kristallogr. **218**, 117 (2003).
- ⁸⁷C. G. Salzmann, I. Kohl, T. Loerting, E. Mayer, and A. Hallbrucker, Phys. Chem. Chem. Phys. 5, 3507 (2003).
- ⁸⁸C. G. Salzmann, I. Kohl, T. Loerting, E. Mayer, and A. Hallbrucker, Can. J. Phys. 81, 25 (2003).
- ⁸⁹E. B. Moore and V. Molinero, Nature (London) **479**, 506 (2011).
- ⁹⁰P. G. Debenedetti, *Metastable Liquids* (Princeton University Press, Princeton, 1996).
- ⁹¹F. Sciortino, J. Stat. Mech. 05 (2005) P05015.
- ⁹²D. Limmer and D. Chandler, e-print arXiv:1306.4728.