Interplay of the Glass Transition and the Liquid-Liquid Phase Transition in Water (Supplementary Information)

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I. GLASS TRANSITION FROM DILATOMETRY

Recent experiments have started to explore the pressure dependence of $T_g(P)$ for amorphous ices at high pressure [1, 2]. Particularly relevant to our findings is Ref. [1], where the T_g of recovered HDA as function of pressure is reported from dilatometry experiments (*i.e.*, from $\rho(T)$) over the pressure-range $100 \leq P \leq 300$ MPa. It is not obvious how the $T_g(P)$ loci determined from DSC experiments (*i.e.*, from $c_P(T)$) compare with the $T_g(P)$ loci measured from dilatometry experiments. Consequently, we examine the $T_g(P)$ loci estimated from $\rho(T)$ for the ST2 model, so that we can compare with the calorimetric determination and ultimately with the experimental findings of Loerting and co-workers.

To determine T_g from $\rho(T)$, we follow the same procedure used in the dilatometry experiments [1]. In these experiments, $\rho(T)$ is measured upon heating amorphous ices at constant pressure. It is found that in the glass state, $\rho(T) \propto T$. Assignment of $T_g(P)$ is given by the temperature where $\rho(T)$ deviates from this linear behavior. In some of our cases, we have a glass-glass transition before the ultimate glass-liquid transition. The glass-glass transition is identified in the same manner as the glass-liquid transition.

The resulting $T_g(P)$ loci obtained from $\rho(T)$ for the ST2 model case are shown in Fig. S1 and contrasted with our previous results from $c_P(T)$ (Fig. 3 of manuscript).It is remarkable how similar the $T_g(P)$ loci are for the two methods – particularly evident in Fig. S1b and S1c. Indeed, $T_g^{\rm HGW}(P)$, $T_g^{\rm LDA}(P)$, and $T_g^{\rm HDA}(P)$ from the two different methods are nearly identical. We note that a different definition of T_g, based on $c_P(T)$, $\rho(T)$, or other macroscopic property, might not necessarily show such a quantitative similarity. However, the qualitative similarity in the shape of the $T_g(P)$ locus should be robust. The similarity in the $T_g(P)$ loci provides confidence that the $T_g(P)$ measurements obtained experimentally through density should correlate well with $T_g(P)$ measured by more traditional means, such as DSC techniques. This provides justification to compare our T_g findings for the ST2 model with data obtained from dilatometry experiments of Ref. [1], as discussed in the main text.

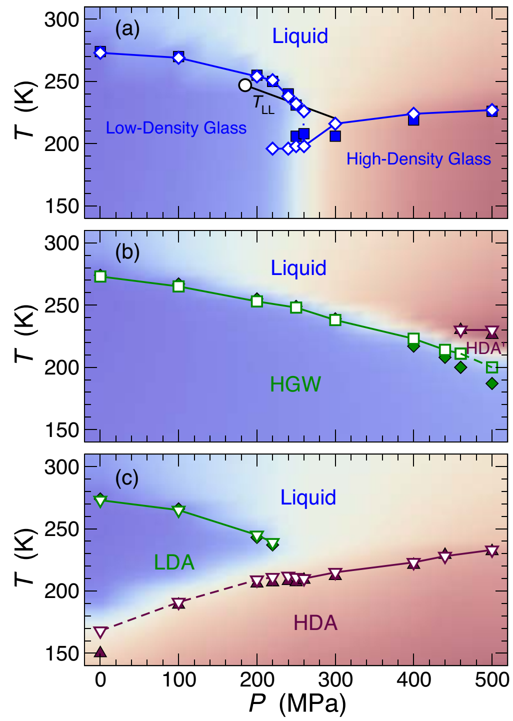

FIG. S1: Comparison of the $T_g(P)$ loci calculated from $\rho(T)$ with those obtained from $c_P(T)$ for ST2 water. The panels and color gradients follow the same sequence as Fig. 3 of the manuscript; in each panel, the open symbols are from $\rho(T)$ data, and filled symbols are from $c_P(T)$ data (Fig. 3 of manuscript).In many cases the results from the two methods are so close that the open symbols obscure the filled symbols. (a) $T_g^{\rm HQG}(P)$ determined by hyper-quenching the equilibrium liquid at the desired pressure P, and reheating at that same pressure. At $P \approx 250$ MPa, $T_g^{\rm HQG}(P)$ and the equilibrium liquid-liquid coexistence line $[T_{\rm LL}(P)]$ intersect one another. At $210 \leq P \leq 260$ MPa, two features are observed in the density (see Fig. 5a of manuscript for the case $P = 250$ MPa) suggesting an HDA-to-LDA transformation at low-T and an LDA-to-liquid transformation at higher-T; hence there are multiple symbols in this pressure range. (b) The glass transition temperature of compressed HGW, $T_g^{\rm HGW}(P)$. A small deviation between the $T_g^{\rm HGW}(P)$ locus obtained from $\rho(T)$ and $c_P(T)$ appears at approximately $P \geq 460$ MPa where compressed HGW converts to a high-density glass, HDA' (dashed-line). The solid violet line at $P \geq 460$ MPa represents the glass transition of HDA' to HDL. (c) The glass transition temperature of decompressed HDA, $T_g^{\rm HDA}(P)$. A small deviation between the $T_g^{\rm HDA}(P)$ locus obtained from $\rho(T)$ and $c_P(T)$ appears at low P where decompressed HDA converts to LDA (dashed line) before a glass transition to the liquid occurs.

[1] Seidl, M. *et al.* Volumetric study consistent with a glass-to-liquid transition in amorphous ices under pressure. *Phys. Rev. B* **83**, 100201 (2011).

[2] Andersson, O. Glass-liquid transition of water at high pressure. *P Natl Acad Sci Usa* **108**, 11013–11016 (2011).