Supporting Information

Comparison of eHDA and uHDA

Fig. S1 shows the wide-angle x-ray scattering (WAXS) pattern recorded at the high-energy beamline 6-ID-D at the Advanced Photon Source (APS), where panels (a) and (b) show the scattered Intensity $I(Q)$ for the eHDA and uHDA samples respectively. It is well known in the literature that eHDA and uHDA have comparable density and structure (1) but show a distinct difference in thermal stability (1, 2). The structures of eHDA and uHDA can be compared by looking at the two blue curves (lowest temperature) in panels (a) and (b). In the case of uHDA (b) a shift of the first diffraction maximum from $Q = 2.1 \ \text{Å}^{-1}$ towards the low-density state with $Q = 1.7 \ \text{Å}^{-1}$ indicates that the complex transition involves many intermediate states, which is consistent with previous studies (3–5). Most interestingly, eHDA instead shows a distinctly different behavior. As seen in panel (a) the peak of eHDA splits into a double maximum when the sample is heated. As eHDA relaxes from the freeze-quenched state to the low-density state at 1 bar it passes through a situation where both states coexist. This is discussed in detail in Fig. 2 of the main manuscript. The significant difference in thermal stability between the two HDA samples is clearly seen in the temperature evolution of the first diffraction maximum Fig. S1c, $i.e.$ the $Q$-value with highest scattering intensity. eHDA (red squares) transforms rather abruptly to the low-density state at 124 K whereas uHDA (black triangles) shows a continuous annealing process before it finally transforms to LDA at around 114 K. Each temperature point was measured with an accumulation rate of $120 \times 1\text{s}$ in steps of 2 or 3 K, $i.e.$ including waiting time this results in an overall heating rate of $\leq 0.5$ K/min.

![Fig. S1.](image)

**Fig. S1.** Comparison between eHDA and uHDA. (A) The angularly integrated intensity $I(Q)$ of eHDA (blue curve, $T = 92$ K) while warming to the low-density state (black curve, $T = 128$ K). Intermediate temperatures are plotted in green (122 K), red (124 K) and yellow (126 K). (B) $I(Q)$ for the uHDA measured in the same temperature range as eHDA, but in that case the intermediate temperatures correspond to green (112 K), red (114 K) and yellow (116 K). (C) The $Q$-values of the first diffraction maximum as a function of temperature for both eHDA (red squares) and uHDA (black triangles).
Heating rate dependence

Fig. S2 shows another eHDA sample that was heated from 90 K to 170 K using a much faster heating rate compared to the sample in Fig. S1, where the latter is the eHDA sample discussed in the main text as well. Each temperature point was measured with an accumulation rate of $10 \times 0.7$ s in steps of 2 K, i.e. including waiting time this results in an overall heating rate of 3-4 K/min. Panel (a) shows $S(Q)$ for three selected temperatures, the initial eHDA state at 90 K (blue), the final low-density state at 129 K (red) and the intermediate state at 127 K (yellow). An isosbestic point is visible at $Q = 1.9 \, \text{Å}^{-1}$. Panel (b) shows the evolution of $S(Q)$ at the position of the two first diffraction peaks, namely $Q = 1.7 \, \text{Å}^{-1}$ and $2.1 \, \text{Å}^{-1}$. The transition between the high- and low-density form appears to be even sharper compared to the slow heating rate in Fig. 2 and at slightly higher temperature, namely 127 K.

![Fig. S2.](image)

Section A.2 and A.3. This results in overall heating rates of $\leq 0.5$ K/min for the “slow” case and 3-4 K/min for the “fast” case. The estimated heating rate for the XPCS measurements is $< 0.1$ K/min and comparable to the “slow” heating rates in the independent WAXS measurements. Fig. S1 shows both eHDA and uHDA heated at a slow rate on the already calibrated
temperature scale, the corresponding temperature values that have been measured with the Si-diode are tabulated in Table S1 (first column).

The literature values for the high-to-low density phase transitions are summarized in the second column of Table S1. The slow heating rates are derived from dielectric spectroscopy measurements (6) and heat-flow calorimetry by Handa et al. (7, 8). The difference between the measured temperatures and the literature values in the sharp high-to-low density transition at slow heating rates is $\approx$10 K. All temperatures given in the paper including all figures are thus calibrated by adding 10 K to the measured values. The given temperatures have an estimated error of $\pm$2 K.

This offset of $\approx$10 K is verified by an additional measurement using a thermocouple inside the sample holder in close contact with the ice. Fig. 3 shows heating of an eHDA sample with a rate of 5 K/min, the temperature increase is measured by a Si-diode (blue) and a thermocouple Type E (red). When inserting the HDA powdered sample into the sample holder, the packing fraction is less than 100 %, therefore the lacking thermal contact leads to an offset of $\approx$10 K. We did three independent measurements that are consistent with each other; however, due to the handling of the thermocouple inside the sample holder we estimate the error to be $\pm$3 K. The exothermic transition between the high- and the low-density state is detected by the thermocouple (red) at 130 K. After the transformation, the thermal contact increases due to the volume expansion within the sample, therefore the temperature offset decreases. The crystallization takes place at $\approx$160 K.

The thermocouple measurement (Fig. S3) also allows estimating the heat of transformation for the exothermic transition between the high- and the low-density state. Using a heating rate of 5 K/min the temperature in the ice increases by $\approx$ 8 K. Although the overall heating rate in the XPCS is much slower and the heat release is expected to be less, the temperature is not increased continuously but stepwise using a rate of 3 K/min. For the small temperature intervals at the XPCS measurements the heating rate is comparable to the thermocouple measurement. Due to the partial thermal conduction, we estimate a temperature increase of $\sim$ 8 K during the transition at 130 K.

**Fig. S3.** Temperature calibration and determination of temperature increase during the high- to low-density transition in amorphous ice samples. A silicon diode (blue) is mounted on the copper sample holder, this is also how the temperature was measured during the x-ray measurements. To obtain further information about the sample temperature a thermocouple (type E) (red) was mounted inside the sample holder in close contact with the ice. eHDA was heated with a rate of 5 K/min.
Glass transition temperatures in the literature

The glass transition temperature $T_g$ of LDA and HDA at ambient pressure is tabulated for different heating rates in table S2. $T_g$ for the fast heating rate is measured as the characteristic onset of the heat capacity increase determined by DSC (6) using heating rates of 10 or 30 K/min (2). $T_g$ for the slow heating rate represents the temperature with a relaxation time $\tau = 100$ s, derived from dielectric measurements (6). For the slow heating rate in the case of LDA, $T_g$ was also determined using heat-flow calorimetry by Handa et al. (7, 8).

<table>
<thead>
<tr>
<th>High-to-low density transition temperature</th>
<th>$T_{\text{measured}}$ (K)</th>
<th>$T_{\text{lit}}$ (K)</th>
<th>$\Delta T$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>slow heating</td>
<td>slow heating</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\leq 0.5$ K/min</td>
<td>$\leq 0.2$ K/min</td>
<td></td>
</tr>
<tr>
<td>eHDA</td>
<td>114 ± 1</td>
<td>124 ± 2 (6)</td>
<td>10</td>
</tr>
<tr>
<td>uHDA</td>
<td>104 ± 3</td>
<td>113 (7)</td>
<td>9</td>
</tr>
</tbody>
</table>

Table S1. Measured and literature temperatures of the transition between the high-density amorphous ices eHDA and uHDA and the corresponding low-density state at 1bar.

<table>
<thead>
<tr>
<th>Glass transition at ambient pressure</th>
<th>$T_{\text{lit}}$ (K)</th>
<th>$T_{\text{lit}}$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>fast heating</td>
<td>$\approx 0.01$ K/min (6)</td>
<td>10-30 K/min</td>
</tr>
<tr>
<td>LDA</td>
<td>110 ± 2 (6)</td>
<td>116 ± 2 (6)</td>
</tr>
<tr>
<td>uHDA</td>
<td>126 ± 2 (6)</td>
<td>136 ± 2 (6)</td>
</tr>
</tbody>
</table>

Table S2. Literature values of the glass transition for LDA and HDA at ambient pressure.

Flux dependence

The x-ray beam was attenuated in order to prevent beam-induced effects. Multiple silicon foils of 25 µm thickness were placed along the beam to reduce the photon flux and both WAXS as well as the dynamics with XPCS at SAXS geometry were measured at the coldest temperature. For very high flux we observed that the beam induced a large temperature offset that led to crystallization. At the lowest flux, even though the WAXS pattern was identical before and after measuring the XPCS time series, the temperature offset led to a decrease of the time constant as shown in Fig. S4. In Fig. S4a is shown the calculated $F(Q,dt)$, where the contrast was fixed for comparison and in Fig. S4b are shown the extracted time constants. To ensure that the beam-induced heating is minimized, we measured the dynamics always at the lowest photon flux shown here ($2\times10^7$ photons/sec for a 10 µm$^2$ focus area corresponding to 16 silicon foils). An additional confirmation was performed for all temperatures, where the WAXS scattering pattern was recorded and compared before and after each XPCS measurement.
**Fig. S4.** Flux dependence of the temporal autocorrelation function. (A) The temporal autocorrelation function $F(Q, dt)$ of HDA at $T = 88$ K measured with different number of Silicon absorbers (thickness 25 µm per foil), indicated in the legend. The colored lines indicate results of a single exponential fit. (B) The extracted time constants as a function of photon flux.

**Streak masking**

Streaks were often observed (Fig. S5) due to scattering from the edges and interfaces between grain boundaries and the potential presence of nanocrystalline impurities (9), and were masked in order to estimate the dynamics. The streaks were identified by examining the intensity as a function of the azimuthal angle (Fig. S5c), where the comparison is made before (green line) and after (blue line) the masking. The dashed lines are different thresholds, including the value $I_{thr} = 2.0$ that was used.

**Fig. S5.** (A,B) The recorded scattering pattern in SAXS geometry before and after masking the streaks. (C) The radially integrated intensity as a function of the azimuthal angle $\phi$, before (green line) and after masking (blue line).

**SAXS angularly integrated signal**

In addition to dynamical information we also can recover the structural content in the SAXS geometry, by performing angular integration. This is shown in Fig.S6 during the high-to-low density transition for different acquisition times. The average signal increases during the first 300 seconds and then levels off, in the same timescale with the observed dynamical heterogeneities.
Fig. S6. (A) The angularly integrated scattering pattern in SAXS geometry at 130 K, for different times $t$. (B) The integrated SAXS intensity up to $Q = 0.01 \text{Å}^{-1}$ as function of time peaks at ~300 s and then levels off.

**Time constants relative amplitudes**

The amplitudes that were obtained from the exponential fits (see methods) are presented in Fig.S7. In this case, they have been normalized to the reported contrast ($\beta=0.4\pm0.02$) to indicate the relative contribution of the two dynamical components. For temperatures below 115 K, a single component is obtained, whereas at higher temperatures a faster component manifests with gradually increasing amplitude.

Fig. S7. The relative amplitudes of the fast (blue circles) and slow (red squares) components presented in Fig.4a, which are obtained from the double exponential fit.

**Crystalline ice dynamics**

In order to confirm that no faster fluctuations or diffusive dynamics appear in crystalline ice above 115 K, we have performed measurements after fully crystalizing the low-density amorphous samples. In Fig.S8a the results for crystalline ice at 170 K are shown. For the data presented the following settings were used are: detector-sample distance was 5 m, 3.4 µm horizontal and 2.8 µm vertical beam focus and photon flux $4 \times 10^8$ photons/sec. The angularly integrated scattering intensity (Fig.S8A) exhibits distinct Bragg peaks, characteristic of crystalline ice. The corresponding intermediate scattering function (Fig.S8B) shows a single dynamical component, with
a time constant $\tau = 110$ s. The time constant does not exhibit pronounced $Q^2$ dependency, but instead remains largely independent of $Q$, as can be seen in Fig. S8 C.

![Fig. S8](A) The angularly integrated intensity in WAXS geometry of crystalline ice at 170K after crystallization has occurred from the low-density form. (B) The corresponding intermediate scattering function $|I(Q, \delta t)|^2$ recorded in SAXS geometry at $Q = 0.01 \, \text{Å}^{-1}$. A single slow component is observed with a time constant $\tau = 110$ s. (C) The time constant obtained from the exponential fit plotted as $1/\tau$ over $Q^2$.

**The LDA-to-LDL transition**

The LDA-to-LDL transition was measured as an additional confirmation of the proposed interpretation of the SAXS results for liquid-like dynamics (Fig. S9). The dataset presented here is a continuation of the temperature series presented in the main manuscript. The samples were prepared by cooling LDL after the HDL-to-LDL transition to 80K and then gradually heating up to the estimated glass transition for LDL, which for the slow heating rate used here is 126K (See Table S.2). As expected, an additional fast component manifests in this temperature range, which exhibits diffusive dynamics at 130K (Fig.S9 D), where the residual offset is attributed to contributions from the slower component. The diffusion coefficient obtained is $(6.2 \pm 1.0) \, \text{nm}^2/\text{s}$ which is in agreement with the diffusion $(4.9 \pm 1.0) \, \text{nm}^2/\text{s}$ obtained after the HDL-LDL transition at 130K (region 3).
Fig. S9 (A) The angularly integrated intensity in WAXS geometry at different temperatures of LDA. In this case, the LDA was produced by cooling after the HDL-to-LDL transition to 80K and then heating to observe the LDA-to-LDL transition. (B) The intermediate scattering function $F(Q, \delta t)$ at different temperatures recorded in SAXS geometry at $Q=0.01\,\text{Å}^{-1}$. (C) A fast component is observed near the glass transition temperature at 126 K, as can be seen by the temperature dependence of the time constants, despite the limited number of temperature points. (D) The fast time constant obtained from the double exponential fit at 130 K plotted as $1/\tau$ over $Q^2$. The solid lines depict the result of a fit $1/\tau \propto D_0 \cdot Q^2$, where $D_0$ is the diffusion constant at 130 K.

References