Diffusive dynamics during the high-to-low density transition in amorphous ice


Abstract

Water exists in high- and low-density amorphous ice forms (HDA and LDA), which could correspond to the glassy states of high- (HDL) and low-density liquid (LDL) in the metastable part of the phase diagram. However, the nature of both the glass transition and the high-to-low-density transition are debated and new experimental evidence is needed. Here we combine wide-angle X-ray scattering (WAXS) and X-ray photon-correlation spectroscopy (XPCS) in the small-angle X-ray scattering (SAXS) geometry to probe both the structural and dynamical properties during the high-to-low-density transition in amorphous ice at 1 bar. By analyzing the structure factor and the radial distribution function, the coexistence of two structurally distinct domains is observed at $T = 125$ K. XPCS probes the dynamics in momentum space, which in the SAXS geometry reflects structural relaxation on the nanometer length scale. The dynamics of HDA are characterized by a slow component with a large time constant, arising from viscoelastic relaxation and stress release from nanometer-sized heterogeneities. Above 110 K a faster, strongly temperature-dependent component appears, with momentum transfer dependence pointing toward nanoscale diffusion. This dynamical component slows down after transition into the low-density form at 130 K, but remains diffusive. The diffusive character of both the high- and low-density forms is discussed among different interpretations and the results are most consistent with the hypothesis of a liquid–liquid transition in the ultraviscous regime.

Significance

The importance of a molecular-level understanding of the properties, structure, and dynamics of liquid water is recognized in many scientific fields. It has been debated whether the observed high- and low-density amorphous ice forms are related to two distinct liquid forms. Here, we study experimentally the structure and dynamics of high-density amorphous ice as it relaxes into the low-density form. The unique aspect of this work is the combination of two X-ray methods, where wide-angle X-ray scattering provides the evidence for the structure at the atomic level and X-ray photon-correlation spectroscopy provides insight about the motion at the nanoscale, respectively. The observed motion appears diffusive, indicating liquid-like dynamics during the relaxation from the high-to-low-density form.


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It has been postulated that water’s hydrogen-bonding network can exist in two liquid forms of different density, namely high- and low-density liquid water (HDL and LDL, respectively) (1). These forms were recently simulated as metastable free-energy basins and a liquid–liquid transition was observed in the ST2 molecular model of water (2), but direct experimental evidence is still missing. Furthermore, it is hypothesized that the observed high- and low-density amorphous ice forms (HDA and LDA, respectively) are the glassy counterparts of the two liquid forms found deeply in the metastable supercooled regime (3). The HDA-to-LDA transition has been proposed to be a first-order phase transition (4–8) and could occur in the ultraviscous liquid state at temperatures above the glass transition (9). Similar observations have been reported by studying water confined in protein crystals and aqueous solutions (10, 11), which indicate the occurrence of the transition between two viscous liquid states of water. However, there is contradicting evidence that the transition from HDA to LDA involves several intermediate forms (12, 13) and it is questioned whether the amorphous ices are thermodynamically linked with supercooled water (14, 15). Based on experimental studies using calorimetry (9, 16–18), dielectric spectroscopy (9, 19), isotope exchange (20), and diffusion in amorphous solid water (ASW) (21, 22), it was suggested that there is a glass–liquid transition in LDA around $T_{g, LDA} \sim 136$ K (heating rate 30 K/min) (16). In addition, there have been indications of a glass–liquid transition in HDA at elevated pressures (23, 24), as well as at ambient pressure at $T_{g, HDA} \sim 116$ K (heating rate 10 K/min) (9). Several alternative interpretations have been proposed involving an orientational glass transition (25) or crystal-like behavior (14, 26, 27), which would rule out the appearance of translational diffusion at the previously proposed glass transition.

To address the open questions concerning the nature of the glass transition and hypothesized polymorphism of water, we use experimental X-ray techniques that probe the structure and dynamics of amorphous ice, as HDA transitions to the low-density form at ambient pressure. The experimental setup is shown in Fig. 1A, where the diffraction pattern was recorded both in wide- and small-angle X-ray scattering (WAXS and SAXS, respectively) geometry. Using X-ray diffraction at WAXS geometry, one can distinguish between the high- and low-density forms (Fig. 1B) due to changes in the static structure factor $S(Q)$, with...
Q being the momentum transfer. In the SAXS geometry, we use X-ray photon-correlation spectroscopy (XPCS) (28–30), which is based on the observation of X-ray speckle patterns that arise due to the interference of X-rays scattered off density heterogeneities within the illuminated volume (31) (Fig. 1C). In the low-Q range, changes in the speckle pattern reflect the dynamics at the nanometer length scale. For longer exposure time the speckle contrast is gradually lost due to dynamics in the sample, giving rise to a more uniform scattering pattern (Fig. 1C). The corresponding diffusion constants can be evaluated on the nanoscale through the Q dependence of the characteristic time constant (29).

**Structural Information from WAXS**

The WAXS data were recorded using high-photon energies of 100 keV (Materials and Methods). The first S(Q) diffraction peak of HDA is observed at Q = 2.1 Å⁻¹ (Fig. 2A) and with increasing temperature, a second peak appears at Q = 1.7 Å⁻¹. Using unannealed HDA (6) (uHDA) the first diffraction peak shifts toward the LDL position upon warming, involving several intermediate states (32) (Fig. 2A and SI Appendix). This is consistent with previous X-ray scattering studies where no isosbestic point was observed (12, 13, 32), referring to points where S(Q) is constant with temperature. Instead, using an annealed form of HDA (6, 7) (equilibrated HDA, eHDA) we observe two distinct peaks, without any intermediate peak positions (see also SI Appendix), which exhibit an isosbestic point at Q = 1.9 Å⁻¹ followed by several crossings at higher Qs (Fig. 2B). The total X-ray scattering radial distribution function g(r), obtained by Fourier-transforming S(Q) (Materials and Methods), is shown in Fig. 2C, with r being the interatomic distance. Upon heating, g(r) decreases between the first and second coordination shell (r ≈ 3.5 Å), indicating loss of interstitial molecules and increased tetrahedral contribution in the low-density form (33) with an isosbestic point at 4.15 Å.

The complex shift observed in uHDA is attributed to strain release and large interface scattering of interpenetrating structures, and the transition to the low-density form involves several intermediate states (32). In eHDA the observed double peak in S(Q) indicates coexistence of high- and low-density domains, as suggested by earlier experimental (5, 7) and theoretical investigations (15). In this case, the decomposition of both the static structure factor and the radial distribution function into the sum of two components can be justified by assuming that the contribution of interfaces to the scattering is negligible due to the large domain sizes. The temperature dependence of S(Q) (Fig. 2) signifies the transition of HDA to a low-density form. The question is whether this transition occurs between amorphous ice forms, i.e., an HDA-LDL transition, or whether the transition occurs between two liquid states, inferring instead an LDL-LDA transition in the ultraviscous regime. Another possibility would be that the transition involves both the liquid and glassy forms (such as HDL→LDL→LDA or HDL→LDA→LDA). Such cases cannot be distinguished purely from the static structure factor and therefore dynamical information like the intermediate scattering function accessible by XPCS is needed.

**Dynamical Information from XPCS**

The XPCS data at SAXS geometry were measured at a photon energy of 8.4 keV (Materials and Methods). The pronounced signal at small scattering angles of Q ∼ 0.01 Å⁻¹ reflects nanometer length-scale heterogeneities presumably due to the grainy nanostructure of the sample. Previous neutron-scattering studies discuss structural heterogeneities as a result of scattering in the Porod-limit region (13) (Q ∼ 0.1 Å⁻¹), which is beyond the scope
of the present study. The present XPCS measurement is performed in the \( Q \) range of 0.003–0.01 Å\(^{-1}\), a wave-vector range inaccessible to visible light (34), which is connected to structural rearrangements on the ~100-nm length scale (35, 36). The dynamics are recorded by measuring the temporal autocorrelation function \( g_2(Q, \delta t) \) where \( \delta t \) is the correlation time, which can be related to the intermediate scattering function \( F(Q, \delta t) \) through

\[
g_2(Q, \delta t) = \beta |F(Q, \delta t)|^2 + 1,
\]

where \( \beta \) is the speckle contrast that depends on the experimental parameters.

Fig. 3 A and B shows the WAXS scattering patterns that were recorded giving the static structural information and the \( |F(Q, \delta t)|^2 \) dynamics measured in SAXS geometry. Here, the displayed \( I(Q) \) and \( |F(Q, \delta t)|^2 \) shown were recorded at the same sample position, using two detectors at different scattering angles. The \( |F(Q, \delta t)|^2 \) data are fitted with a double-exponential function (Materials and Methods), which at \( T = 89 \) K yields a single time constant, whereas at temperatures \( T > 110 \) K it captures an additional faster component. The WAXS scattering pattern at 130 K changed during the XPCS measurement (Fig. 3A), as indicated by the pattern recorded before (solid line) and after (dashed line) the XPCS measurement. In Fig. 3B, at 130 K the solid and dashed lines depict the fits at early and late times, respectively, during the high-to-low-density transition (the first 0–400 s and last 700–1,000 s of the total 1,000 s recorded), which is accompanied by a heat release during the transformation (SI Appendix).

Two-time temporal correlation maps \( C(Q, \delta t, t) \) (28, 37–40) (Fig. 3C; Materials and Methods) provide a very sensitive measure of the underlying dynamics and allow resolving whether the system exhibits dynamical heterogeneities, or if the recorded dynamics are homogeneous. In the former case the linewidth of \( C(Q, \delta t, t) \) would fluctuate during the measurement time \( t \); in the latter, the width would remain constant. For \( T = 89 \) K the \( C(Q, \delta t, t) \) exhibits fluctuations with a multiplicity of relaxation times, whereas at \( T = 125 \) K, the dynamics speed up during the measurement. At 130 K dynamics are initially fast and more homogeneous (region 1) but after ~400 s a transition to slower and more heterogeneous dynamics is observed (regions 2 and 3).

The time constants \( \tau \) obtained by the double-exponential fit are shown in Fig. 4A. The slower component appears nearly temperature-independent, whereas the faster component manifested at \( T = 115 \) K accelerates ~100-fold upon heating to \( T = 130 \) K. The relative amplitudes of the two components change with increasing temperature \( T > 110 \) K, with the slow component gradually decaying and the fast component gaining in amplitude, shown in SI Appendix, Fig. S7. At \( T = 130 \) K the time constants obtained for the initial 0–400 s (1) and the final 700–1,000 s (3) are shown, connected by arrows to indicate the time ordering.

The solid and dashed lines in Fig. 4A are obtained from Arrhenius fits (Materials and Methods). A similar trend is seen by the normalized variance \( \chi_t \) extracted from the \( C(Q, \delta t, t) \) (38), which is an experimental estimator of the four-point dynamical susceptibility (41). The amplitude of \( \chi_t \) of \( C(Q, \delta t, t) \) (Fig. 4B) is proportional to the relative width \( \Delta \tau / \tau \) of the characteristic relaxation time; the maximum peak value \( \chi_0 \) is thus a measure of the dynamical heterogeneities in the system. Fig. 4B (Inset) shows an abrupt decay in \( \chi_0 \) for \( T > 115 \) K, indicating a transition to a more dynamically homogeneous regime.

With XPCS in the low-\( Q \) regime one can derive the diffusion constant on nanometer length scales by the \( Q \) dependence of the characteristic time constant (29). For hyperdiffusion or ballistic
motion \( \tau \) exhibits \( 1/\tau \sim Q^2 \) dependence, whereas \( 1/\tau \sim Q^2 \) dependence is typical for diffusion, with the diffusion constant \( D_0 \) as the proportionality constant. Fig. 4C shows the \( 1/\tau \) versus \( Q^2 \) for temperatures of 115 K and above. At temperatures below 115 K and for the slow component no \( Q^2 \) dependence is observed. This observation indicates that the slow component is not diffusive and can be associated with viscoelastic relaxation due to release of inner stresses and convective flow (29, 42). From the fits in Fig. 4C \( D_0 \) is determined for the fast component to vary from 0.8 to 47.5 nm²/s at 115–130 K. No corresponding faster fluctuation or diffusive dynamics are observed in crystalline ice as discussed in SI Appendix, Fig. S8).

Discussion

It is essential to discuss whether the experimental evidence provides further insight about the glass transition and whether the observed high-low-density transition occurs between amorphous or liquid states. The glass-transition temperature \( T_g \) depends on the heating rate (SI Appendix). Previous investigations using calorimetry proposed \( T_g \) for HDA \( \sim 116 \) K (9) using a heating rate of 10 K/min. In dielectric spectroscopy measurements, where a much slower heating rate was used, the glass-transition temperature for HDA was determined at \( T_g \) for HDA \( = 110 \) K; the present heating rate is comparable to that used for the dielectric spectroscopy measurements. Therefore, we propose that the observed faster component at temperatures above 110 K (Fig. 4A), accompanied by the decrease of \( \chi_0 \), indicate a glass-to-liquid transition from HDA to HDL. Because the observed glass transition is kinetically in nature, the diffusivity exhibits continuous behavior during the transition. Therefore, we conclude that the reason for not observing the diffusive component below 110 K is that it occurs on a timescale longer than the experimental observation time, where the dynamics are dominated by the viscoelastic component. The acceleration of the dynamics at 125 K (Fig. 3C) is due to the ongoing HDA–HDL transition within the 1,000-s duration of the XPCS measurement. Because XPCS is measured in the SAXS geometry, it is sensitive to diffusion occurring due to structural rearrangements of the nanoscale heterogeneities. The diffusion involves translational motion at the nanometer length scale and therefore we can determine that the fast component does not reflect purely molecular reorientation, responsible for an orientational glass transition (25). However, there can be reorientation occurring, coupled to translational motion (43). We also conclude that the observed diffusive behavior near the glass transition would not manifest itself in a crystal-like amorphous ice (14, 26), but instead indicates that the amorphous matrix exhibits HDL-like dynamics.

In Fig. 4D, the dynamical properties are analyzed in three different time domains during the high-to-low-density transition. This transition is kinetically driven and accelerated due to the heat release, which is associated with a temperature change to the order of 10 K (SI Appendix) and will therefore lead to a step-like change between regions 1 and 2. Directly after the jump between regions 1 and 2 (Fig. 4D), both \( \tau \) and \( \chi_0 \) increase and \( D_0 \) decreases, followed by a more significant change in region 3, whereas a similar behavior is seen from the angularly integrated SAXS signal (SI Appendix, Fig. S6). The data indicate that the transformation to the low-density form is completed upon entering region 2. The corresponding dynamics in region 2 still show diffusive characteristics and we therefore conclude that HDL transforms into LDL rather than LDA. The slowing down in region 3 can be explained by cooling after the heat release in combination with the difference in \( T_g \) between the high- and low-density forms, respectively, 110 and 126 K. This observation is consistent with the dielectric relaxation measurements, where a deceleration by a factor of \( \sim 100 \) was observed upon transforming HDA to the low-density state (9). However, it cannot be excluded that the observed deceleration is also due to the transformation of small cubic ice nuclei with a size much below 10 nm, thus preventing detection in WAXS (44). The alternative of revitrification into LDA form is not consistent with the observed diffusive dynamics (Fig. 4C) at the low-density form and therefore we derive that the final stage corresponds to the LDL state. The diffusivity obtained here is the strongest indication of liquid-like motion between 115 and 130 K and evidence for HDL and LDL. During the HDA-to-LDL transition at 130 K, the diffusion coefficients slow down by nearly an order of magnitude, from 48 nm²/s (~5 × 10⁻¹⁰ m²/s) for HDL to 5 nm²/s for LDL (~5 × 10⁻¹⁰ m²/s). The latter is in fair agreement with previous experiments on ASW using \( T_g \) (~8 × 10⁻¹⁰ m²/s at 130 K) and molecular dynamics simulations (~1.5 × 10⁻¹⁰ m²/s at 135 K) (45). The diffusion of ASW at the liquid/ice interface was measured using nanoscale films (~10⁻¹⁰ m²/s at 135 K) (21), which is considerably slower as the diffusivity in this case is presumably related to the mobility of molecules at the liquid/solid interface. Despite the difference in magnitude, the observed diffusivities exhibit a similar continuous trend across the ASW glass transition (21, 22). This interpretation was validated by measuring the LDA-to-LDL transition, where a diffusive component was observed at \( T = 130 \) K with nearly identical diffusion constants as those obtained in region 3 for LDL (SI Appendix, Fig. S9).

Summarizing our observations: (i) At temperatures \( T < 110 \) K a slow dynamical component is observed due to viscoelastic relaxation of HDA. (ii) Above 110 K a fast component appears exhibiting
diffusive character, which is attributed to the HDL. (iii) With increasing temperature HDA domains transform to HDL that further transform to the low-density form. (iv) During the high-to-low-density transition the dynamics slow down but remain diffusive, suggesting that the HDL is converting to LDL at 130 K. The question remains whether there exists also a stringent first-order phase transition at constant Gibbs free energy (8). Previous studies, varying pressure at temperatures above the glass transition, showed the presence of sharp boundaries between regions of HDA and LDA character (7, 46, 47). In accordance with these observations, our results point to the existence of a first-order phase transition at the transition between two 50-μm-thick Kapton windows [WAXS at Advanced Photon Source (APS)] and 50-μm-thick diamond windows (XPCS at Deutsches Elektronen-Synchrotron (DESY)), respectively, resulting in a sample thickness of 2 mm (APS) or 1 mm (XPCS). The windows were held in place by a copper sample holder connected to the cold finger of the cryostat. The samples were measured in vacuum, i.e., without He-exchange gas. For the diffraction measurements at APS the cryostat was equipped with two Kapton windows and the pressure was \( p < 1 \times 10^{-2} \) mbar. For the XPCS measurements the cryostat was connected directly to the beamline under vacuum without using additional windows.

### WAXS Measurements and Data Analysis

X-ray diffraction measurements were performed at APS at beamline 6-ID-D using a 2D amorphous silicon area detector (Perkin-Elmer XRD1621) at \( E = 100 \) keV photon energy. CeO\(_2\) powder was used for sample–detector distance calibration \((L = 348 \text{ mm})\) and Q calibration. The 2D diffraction image, showing the typical water ring, was angularly integrated by using the software Fit2D (V.17.006) after applying polarization and geometrical corrections. The scattering intensity \( I(Q) \) was corrected for background signal mainly from the Kapton windows and air measuring an empty sample holder and applied corrections for multiple scattering, detector efficiency, oblique incidence, and self-absorption (48). The static structure factor and the radial distribution function were calculated as described elsewhere (49). The \( I(Q) \) data were normalized to the molecular form factor and the Compton scattering was subtracted. The total structure factor \( S(Q) \) is given by

\[
S(Q) = 1 - \frac{I(Q) - FF(Q)}{WF(Q)},
\]

where \( FF(Q) \) corresponds to the molecular form factor and \( WF(Q) \) to the weighting factor. The radial distribution function \( g(r) \) is calculated by a Fourier transformation of the static structure factor \( S(Q) \):

\[
g(r) = \frac{1}{2\pi^2r^2} \int_0^{Q_{\text{max}}} M(Q, \Delta r)/Q \sin(Qr)dQ = \frac{1}{1 - \Delta r/\rho},
\]

where \( \rho \) is the density per \( \AA^3 \) and \( M(Q, \Delta r) \) is a Lorch-like function

\[
M(Q, \Delta r) = \frac{\sin(Q\Delta r)}{Q\Delta r}
\]

where \( \Delta r \) is in the form

\[
\Delta r = a \left[ 1 - \exp \left( -2.77 \left( \frac{r_{\text{c}}}{\omega_1} \right)^2 \right) \right] + \frac{1}{2} \left[ 1 + \arctan \left( \frac{r_{\text{c}} - \omega_2}{2\omega_2} \right) \right] r_{\text{c}}^2,
\]

with parameters \( a = \pi/4Q_{\text{max}}, \quad r_{\text{c}} = 2.8 \AA, \quad \omega_1 = 0.5 \AA, \quad \omega_2 = 12.0 \AA, \quad Q_{\text{max}} = 24.5 \AA^{-1}. \)

### XPCS Measurements and Data Analysis

XPCS measurements were performed at DESY, at the core coherence beamline P10 at the PETRA III synchrotron source, using a photon energy of 8.4 keV set by a channel-cut Si(333) monochromator. The WAXS patterns were recorded with a PILATUS 300k detector and the XPCS was performed with a Lambda detector. The following parameters were used: 5-m sample–distance (for SAXS), 3.4-μm horizontal and 2.8-μm vertical beam focus, exposure time 1 s, and 1,000 frames per measurement point. The corresponding photon counts for the lowest flux that was used can be assessed from SI Appendix, Fig. 5S, with an average of \(-0.5 \) photons per second. The reproducibility of the observed dynamics was verified by two independent beam times, where, during the first one, multiple sample positions were recorded for each temperature (10 sample positions per temperature separated by 100 μm) and thereby averaging in space, and during the second experiment the dynamics were recorded for longer times (up to 1,000 s) for each temperature.

The dynamics are calculated using the temporal intensity autocorrelation function:

\[
g_2(Q, t\delta t) = \frac{1}{N} \left\langle I(Q, t) I(Q, t + \delta t) \right\rangle,
\]

where \( \delta t \) denotes the correlation time delay, \( I(Q, t) \) is the intensity at momentum transfer \( Q \), \( N \) the normalization factor \( N = \langle I(Q, t) \rangle^2 \), and the (…) indicates the average over all frames at different times \( t \). The 2D correlation maps were calculated by

\[
C(Q, t_1, t_2) = \frac{1}{N} \langle I(Q, t_1) I(Q, t_2) \rangle,
\]

where the normalization factor is given by \( N = \langle I(Q, t_1) \rangle \langle I(Q, t_2) \rangle \). To estimate \( C \) in the frame \((\delta t, t)\) we apply a 45° rotation to the \((t_1, t_2) \) system forming it to the \((\delta t, t) \) reference frame and the corresponding maps are plotted logarithmically along \( \delta t \) shown in Fig. 3C.

The functional form of the double-exponential function that was used to model the temporal autocorrelation is

\[
g_2(t) = A_e e^{-t/2\tau_e} + (B - A_e) e^{-t/2\tau_i} + C,
\]

where \( A_e \) is the amplitude bound to the interval \([0, \beta_e, \beta_i] \) is the contrast parameter which for the given conditions is \( \beta = 0.4 \pm 0.02 \), and \( C \) is the offset ranging between \([0.0, 0.02] \) which is attributed to residual scattering from streaks (SI Appendix). In addition, the flux dependence was investigated to ensure that the beam-induced heating is minimized (SI Appendix).

The Arrhenius analysis was performed by fitting the functional form \( \tau(T) = A e^{-E/RT} \), where \( R \) is the natural gas constant and \( E \) is the apparent activation energy; the fit results in activation barriers of 1.4 and 37.9 kJ/mol for the slow and fast component, respectively, where the component was fitted only for \( T ≥ 110 \) K. The difference in activation barrier height reflects the different nature of the two processes as discussed here in the main text, with the latter being in fair agreement with the activation energy 34 kJ/mol obtained by dielectric measurements (9).

The normalized variance \( \chi^2 \) of the temporal autocorrelation function \( C(Q, t\delta t) \) is a quantitative measure of the dynamical heterogeneities (38–40), which is an experimentally accessible estimator of the four-point dynamical susceptibility \( \chi^4 \) (41). The variance is calculated along axis \( t \) by using the relation

\[
\chi^2(Q, t\delta t) = \frac{1}{N} \left[ C^2(Q, t, t\delta t) - \langle C(Q, t, t\delta t) \rangle^2 \right],
\]

where \( N \) is the normalization parameter \( N = \langle C(Q, t, t\delta t) \rangle^2 \). The normalized

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variance is shown in Fig. 4B, where the peak position follows the trend exhibited by the result of the exponential fit (the position should be $\chi$ for a simple exponential) and the relative amplitude quantifies the heterogeneities. At $T = 89$ K, we observed a double peak, which can be related to the underlying multiple dynamical components, assigned as fast and slow dynamics in the main text. Interestingly those are not evident in the $g_2$ but can be seen as separate peaks in the normalized variance $\chi^2$.

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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 $\leq 0.5 \text{ K/min}$.

![Fig. S1. Comparison between eHDA and uHDA.](image)

(A) The angularly integrated intensity $I(Q)$ of eHDA (blue curve, $T = 92 \text{ K}$) while warming to the low-density state (black curve, $T = 128 \text{ K}$). 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. The structure factor with faster heating rate. (A) The structure factor for the high- to low-density transition starting with eHDA at 90 K (blue), with a fast overall heating rate of 3-4 K/min. (B) shows the corresponding values for $S(Q)$ at the maximum position of the first diffraction peak for the high- and low-density form, respectively.

Temperature calibration

The sample temperature was measured by two Si-diodes at the upper and lower end of the copper sample holder. The two Si-diodes did not show any difference in temperature but the temperature of the sample between the two windows could not be directly measured in situ. Due to the position of the Si-diode and the lack of He-exchange gas a systematic offset for the sample temperature is expected. Therefore, the temperature was calibrated afterwards using the well-known transition temperatures between the amorphous ices and additional measurements with a thermocouple (Fig S3). For the wide-angle x-ray scattering (WAXS) measurements at APS we used different heating rates, by varying the accumulation time at a certain temperature as well as the step size, as shown in sections 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 ≈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 ±2 K.

This offset of ≈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 ≈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 ±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 ≈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 ≈ 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 ~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>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></td>
<td>slow heating</td>
<td>fast heating</td>
</tr>
<tr>
<td>eHDA</td>
<td>110 ± 2 (6)</td>
<td>116 ± 2 (6)</td>
</tr>
<tr>
<td>LDA</td>
<td>126 ± 2 (6)</td>
<td>136 ± 2 (6)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></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 (2-10$^7$ 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.

![Streaks](image)

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 $4\times10^8$ 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 $Q^2$ dependence, 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 $|F(Q, \delta t)|^2$ 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 $I(F(Q, \delta t))$ 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