Volumetric study consistent with a glass-to-liquid transition in amorphous ices under pressure

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Dilatometry experiments on low- and high-density amorphous ices up to 0.30 GPa are presented together with powder x-ray diffraction data. Repeated isobaric heating and cooling cycles reveal three competing processes: irreversible (micro)structural relaxation, reversible relaxation, and (irreversible) crystallization. The third and subsequent heating runs produce identical curves, i.e., irreversible relaxation is absent. We interpret the deviation from linear expansivity in these curves as the onset temperature of the volumetric glass-to-liquid transition ($T_{g,\,\text{onset}}$) and report its dependence on pressure.

The glass-to-liquid transition in the polyamorphic forms of ice is at the heart of some theories aiming at explaining water's manifold anomalies, which become increasingly pronounced in the supercooled liquid state.[1–3] While experimental information regarding the glass-to-liquid transition is available for the low-density amorphous (LDA) form,[4–8] there is barely any information on the high-density amorphous (HDA)[9–11] and very-high-density amorphous (VHDA) forms of ice. HDA and the postulated glass-to-liquid transition to a deeply supercooled ultraviscous high-density liquid (HDL) play key roles in two scenarios providing a coherent picture of water's anomalies. In both scenarios, the amorphous states are smoothly connected to the liquid states: LDA to the low-density liquid (LDL) and HDA to HDL.[1–3] However, it is not yet clear whether LDA and HDA are glassy solids, transforming on heating under pressure into ultraviscous liquids, or whether they have to be considered nanocrystalline materials.[12] The dispute whether amorphous ices are glasses or not has recently been reviewed (see Chap. III.E in Ref. 13).

The LDA form can be prepared in different ways, namely, by depositing water vapor on cold substrates,[14] by hyperquenching small liquid droplets,[15] or by solid-state transformations from high-pressure forms.[16] In all of these forms the glass-to-liquid transition to LDL was observed calorimetrically at ambient pressure as an endothermic event at $T_g = 136 \pm 2$ K at a heating rate of 30 K/min.[4,6–8,17] At a heating rate of 0.17 K/min, T_g is at ~124 K.[5] There has been some debate as to whether this endothermic event corresponds to a shadow glass transition or a true glass transition.[18] Recent work supports the latter interpretation[19] and requires LDL not to be a fragile liquid above 136 K.[20] The liquid nature of the sample is consistent with a structural relaxation time of 42 ± 14 s at 136 ± 1 K,[21] with the penetration of a blunted indentor into a sample of LDA at $T \sim 136$ K (Ref. 22) and with significant isotope exchange in films kept at $T > 136$ K.[23]

By contrast, almost no information is available on a possible glass-to-liquid transition from HDA to HDL, except for an isothermal differential thermal analysis (DTA) study in emulsified water[9] and a dielectric study.[10] Mishima[9] observes a reproducible small temperature change at $p \sim 0.4$ GPa prior to crystallization, and attributes this event to the transition from HDA to HDL. Andersson[10] performs a set of dielectric relaxation measurements and concludes that the relaxation time of amorphous ice in the pressure range 0.4–1.0 GPa

amounts to $\tau = 1$ s at 140 K and $\tau = 30$ ms at 150 K, which indicates that the amorphous ice is, in fact, an ultraviscous liquid at $T > 140$ K, and that the glass transition temperature T_g is less than 140 K. Although this value is lower than the $T_g \sim 160$ K obtained by Mishima, both experiments indicate that, at high pressures, liquefaction of amorphous samples takes place prior to crystallization upon heating ($T_g < T_x$). It is the aim of the present study to test whether or not it is possible to observe the glass-to-liquid transition by volumetric measurements in amorphous ices by using isobaric heating experiments in a pressure range of up to 0.30 GPa.

We have shown previously by using glycerol as a benchmark case[24] that our experimental setup is capable of measuring reliably small volume changes at low temperatures and high pressures. The experiments were conducted with a piston cylinder apparatus with a bore of 8 or 10 mm. The bore was lined with indium foil[25] to avoid pressure drops during compression.[26] Sample preparation and measurements were done using a computerized "universal testing machine" (Zwick, Model BZ100/TL3S). The temperature was measured with a temperature sensor (Pt-100) inserted firmly in the piston cylinder apparatus. The volume changes during isobaric heating were calculated by multiplying the piston displacement with the area of the cross section of the bore (for further experimental details, see Ref. 27). LDA is prepared by isothermal decompression of VHDA at 140 K to 0.006 GPa, and HDA is prepared by isothermal decompression of VHDA at 140 K to 0.20 GPa.[28,29] While the Pt-100 temperature readings agree fairly well with the sample temperature for isothermal experiments, they start to be higher than the true sample temperature on performing a heating run. Calibration using the well-studied glass transition in glycerol indicates that the Pt-100 temperatures deviate by no more than 4–5 K when heating at ~3 K/min from 77 to 180 K. All temperatures reported in the present study, therefore, represent upper limits, where the absolute value may be lower by, at most, 5 K.

In Fig. 1 we show isobaric heating curves for LDA [Fig. 1(a)] and HDA [Fig. 1(b)] recorded at a heating rate of 2 K/min. The trace obtained for LDA at 0.006 GPa consists of a first linear part in the temperature range 100–135 K, a curved part at 135–150 K, a second linear part at 150–160 K, a bump at 160–165 K, and a third linear part at $T > 165$ K. In order to assess what happens to the LDA sample upon isobaric heating at 0.006 GPa, we have quench-recovered samples to
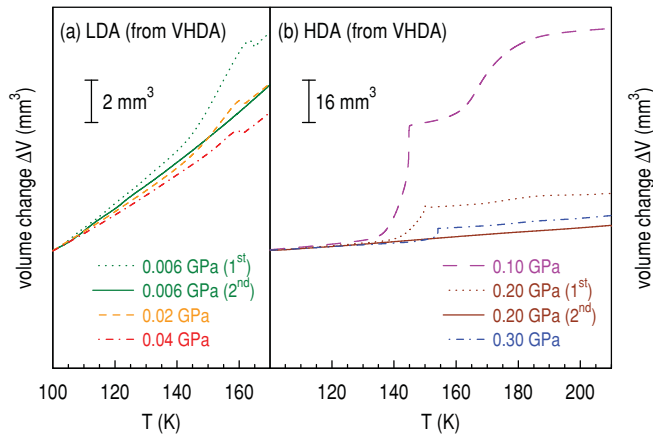
FIG. 1. (Color online) Dilatometry curves obtained upon isobari-
cally heating 300 mg of (a) LDA and (b) HDA. Both were prepared by
isothermal decompression of VHDA (Refs. 28 and 29). All samples
were heated to $T \geqslant 170$ K at heating rates of 2 K/min in order to
obtain fully crystalline samples. Traces labeled "2nd" were obtained
after cooling the crystallized samples and reheating at 2 K/min.

FIG. 2. (Color online) Powder XRDs for samples recovered to
77 K and ambient pressure. Data were recorded on a diffractometer
in θ-θ geometry (Siemens, model D 5000, Cu$K\alpha$), equipped with
a low-temperature camera from Paar at ~80 K. Curves are offset
for clarity. Temperature labels indicate the maximum temperature
experienced in isobaric heating runs for (a) LDA at 0.006 GPa and
(b) HDA at 0.20 GPa; the labels "1st," "2nd," "3rd," and "6th" indicate
that the samples have been heated one, two, three, and six times to
the labeled temperature, respectively.

77 K and 1 bar from different temperatures along this highly
reproducible curve. The powder x-ray diffractograms (XRDs)
recorded from samples heated to $\leqslant 155$ K at 0.006 GPa show
the broad halo peak with a maximum at $2\theta \sim 24°$ (Cu$K\alpha$),
typical of LDA [bottom four XRDs in Fig. 2(a)]. There are no
signs of Bragg peaks arising from crystalline material except
for the four sample holder peaks, indicated by tick marks. Also,
heating six consecutive times to 150 K does not produce any
detectable crystallinity. By contrast, after heating to 160 K,
sharp peaks at $2\theta \sim 24°$ (with a shoulder at 22°), 40°, and
47° indicate the presence of crystalline cubic ice (containing
some hexagonal stacking faults). After heating to 180 K, cubic
ice is still present. The shoulder at 22° is better separated
from the peak at 24°, and the intensity ratio has changed
from 1 : 3 (160 K) to 1 : 6 (180 K). This indicates a change
in cubicity (and hexagonal stacking faults) in the temperature
range 160–180 K at 0.006 GPa, which was also found to take
place at ~165 K at 1 bar in a recent neutron diffraction study.[30]
Thus, the volumetric trace obtained at 0.006 GPa [Fig. 1(a)] can
be interpreted as follows: The first linear part corresponds to
isobaric expansion of LDA. The curved part shows volumetric
changes owing to a combination of irreversible, reversible
structural relaxation processes, and possibly nucleation and/or
an onset of crystal-growth events. The irreversible processes
may be the release of strain or healing of (micro)structural
defects. The onset of crystal growth may result in nuclei below
the XRD detection limit (nanometer sized or smaller). When
heating crystalline material such as cubic ice in the same
manner, a highly linear dilatometry trace is obtained over
the whole temperature range (Fig. 1, curves labeled "2nd").
Similarly, the heating curves of HDA samples [Fig. 1(b)] can
be interpreted in terms of a linear expansion of HDA (up to
~130 K), a curved part containing irreversible and reversible
relaxation processes, and crystallization, which ends abruptly
at a kink (near 150 K). The XRDs for samples prepared at
0.20 GPa [Fig. 2(b)] show an amorphous pattern for heating to
148 K once, and also for heating six times to 144 K, but they
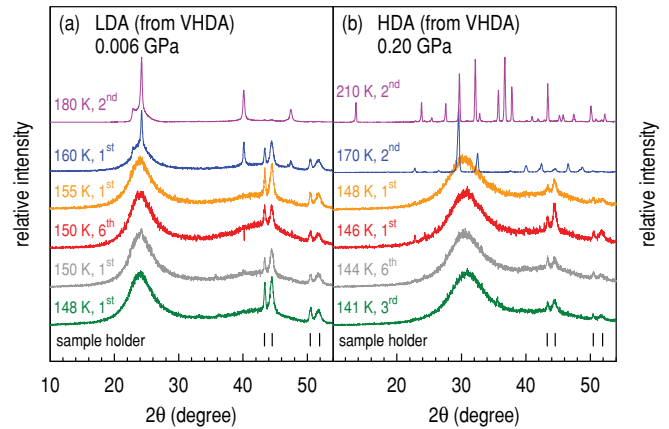show ice IX at 170 K and ice II at 210 K. That is, the curved part

in the range between 130 and ~145 K is owing to relaxation
of the amorphous phase, whereas the curved part at higher
temperatures (~180 K) is owing to a polymorphic transition.
In the absence of a polymorphic transition, a crystalline phase
such as ice II shows a linear expansion behavior [Fig. 1(b),
curve labeled "0.20 GPa, 2nd"].

In order to distinguish reversible from irreversible re-
laxation, we have performed repeated temperature cycles
(Fig. 3). If irreversible relaxation were at the origin of the
deviation from linearity, a shift of the curved part to different
temperatures is expected for subsequent heating runs. A
significant shift to higher temperatures is indeed observed from
the first to the second heating run, both in LDA and in HDA.
We attribute this shift to the release of strain in the amorphous
phase, e.g., by healing of (micro)structural defects such as
micropores or microcracks. The release of strain often takes
place in the vicinity of the glass-transition onset temperature
($T_{g, onset}$), as observed in many glasses such as glycerol.[24]
The presence of the defects in the sample during the first
heating run results in an increase of the expansivity change so
that a very feeble dilatometric glass-to-liquid transition (with
a small change in the expansion coefficient) becomes more
easily detectable. A similar enhancement of the glass-to-liquid
transition by defects was recently noted for the calorimetric
glass-to-liquid transition of doped amorphous ice films.[31]
An isotope-substitution neutron-diffraction study has recently
revealed subtle structural differences on the intermediate
range order in LDA,[32] which might be attributable to such
microstructural defects.

The third and subsequent heating runs, however, repro-
ducibly show coincident curves, and the onset of deviation
from linearity is located at the same temperature (Fig. 3,
top panels). Even in a highly magnified view, the fifth and
sixth heating runs produce practically coincident volumetric
curves (Fig. 3, bottom panels). The signal (deviation from
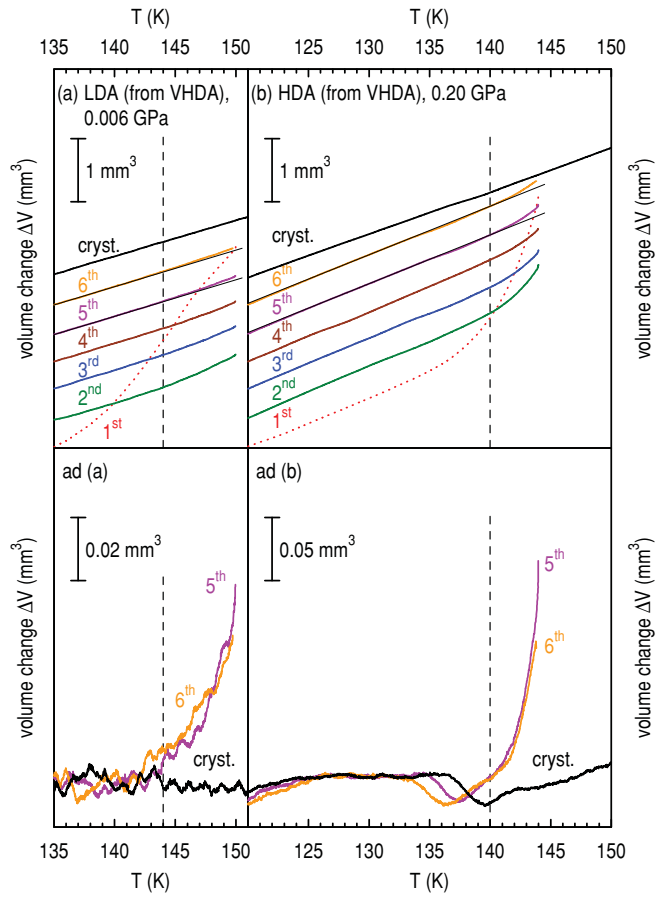linearity) clearly exceeds the noise level of the method, which

FIG. 3. (Color online) Test for repeatability of dilatometry curves. (a) LDA was heated six times at 2 K/min and 0.006 GPa to ~150 K and (b) HDA was heated six times at 2 K/min and 0.20 GPa to 144 K in order to avoid crystallization. Cooling rates were also 2 K/min. Vertical lines mark where the curves start to deviate from linearity, which we interpret to be the volumetric $T_{g,\,onset}$. For comparison, the dilatometry curves of crystalline ices are shown (labeled "cryst."). Top panel: Original data, offset for clarity. Bottom panel: Magnified view of the fifth and sixth heating runs of (a) LDA and (b) HDA are shown together with the data obtained on crystalline ices. The linear functions (black line) shown in the top panel have been subtracted from the original data, i.e., no volume change corresponds to perfectly linear expansion.

is determined by the erratic fluctuations on the order of ± 0.005 mm^3. These fluctuations are also seen when heating crystalline samples (curves labeled "cryst." in Fig. 3), which are expected to follow linear expansion behavior in the whole temperature range. Coincident curves would not be observed if the onset of crystallization or other irreversible processes were at the origin of the deviation from linearity. For example, sintering of grain boundaries or the growth of nanocrystallites in nonglassy amorphous solids would result in a shift of the onset upon repeated heating. This implies that irreversible relaxation processes are absent and that the curve shape is defined by reversible processes. The only reversible process in amorphous material we are aware of, which results in a deviation from linear expansivity, is the glass-to-liquid transition. We are not aware of any reversible process in nonglassy material, which would show these coincident heating curves.

Of course, this does not represent a rigorous proof for the existence of the glass-to-liquid transition in amorphous ices. However, it shows that the volumetric behavior of amorphous ices at ~130–150 K follows exactly the textbook behavior of glasses in the temperature region of their transition to a supercooled liquid. We therefore interpret the deviation from linearity as the onset of the glass-to-liquid transition, and mark $T_{g,\,onset}$ by dashed vertical lines in Fig. 3.

The deviation from linearity amounts to 0.05 ± 0.01 mm^3 in LDA at 0.006 GPa in a 6 K interval above $T_{g,\,onset}$. At 0.02 and 0.04 GPa a reliable detection of $T_{g,\,onset}$ is not possible for LDA, presumably because the size of the effect is comparable to the detection limit. In case of HDA, the size of the effect decreases with increasing pressure. It amounts to (0.43 ± 0.05 mm^3) (0.15 ± 0.03 mm^3) (0.09 ± 0.02 mm^3) in HDA at (0.10) (0.20) (0.30) GPa in a (5) (4) (4) K interval above $T_{g,\,onset}$. The volumetric $T_{g,\,onset}$ values are summarized in Fig. 4 using open symbols. In case of LDA, $T_{g,\,onset}$ at 0.006 GPa is a few Kelvin higher than the calorimetric T_g at 1 bar (filled circle).[8] We note that this difference is owing to a combination of pressure effect, different methodology, and a thermal lag of up to 5 K, inherent to our dilatometry experiments. In case of HDA, the increase of the volumetric $T_{g,\,onset}$ with pressure by 8 ± 2 K in the pressure interval 0.10–0.30 GPa suggests that the calorimetric T_g at 1 bar is expected to be $\leqslant 130$ K if a linear extrapolation is used, and even lower if an Avramov-type extrapolation is used.[33] That is, the data suggests the calorimetric T_g might be detectable prior to the HDA $\rightarrow$ LDA conversion at 1 bar.[34] Prompted by this finding and an anonymous reviewer's suggestion, we also performed calorimetric studies on HDA at 1 bar and indeed detected the calorimetric T_g in HDA at 115 ± 2 K (filled triangle in Fig. 4). Details about the calorimetric study will be reported elsewhere.[11]

Thus, the glass-to-liquid transition in HDA precedes crystallization and the HDA $\rightarrow$ LDA transition up to 0.30 GPa, i.e., $T_{g,\,onset} < T_x$. We emphasize that the window, in which one can study HDA above its $T_{g,\,onset}$, is most narrow at the high-pressure end. At 0.30 GPa, traces of ice IX are evident in the powder XRD after heating six times to 146 K, and fully
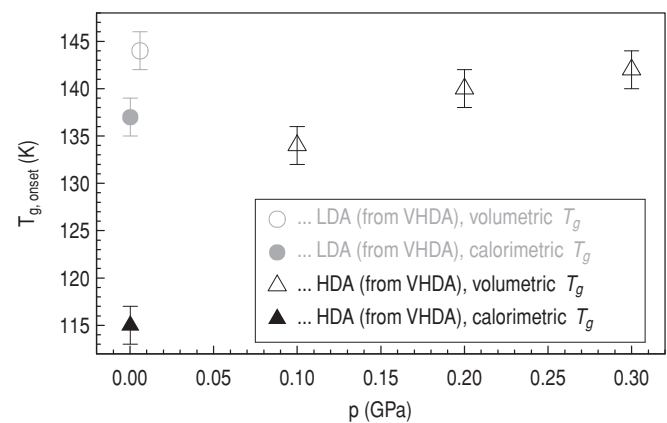

FIG. 4. Volumetric $T_{g,\,onset}$ for LDA (open circle) and HDA (open triangles) at heating rates of 2 K/min (not corrected for thermal lag). $T_{g,\,onset}$ is determined by the method shown in Fig. 3. Error bars of ± 2 K reflect the ambiguity in placing the vertical dashed line in Fig. 3. For comparison, the calorimetric T_g of LDA (Ref. 8) (filled circle) and HDA (Ref. 11) (filled triangle) at 1 bar are also shown.

crystalline samples are obtained after heating four times to 148 K (not shown). That is, at 0.30 GPa, $T_{g, onset}$ and T_x are very close. We expect that at higher pressures, e.g., 0.40 GPa, the glass transition is not detectable by using dilatometry at heating rates of 2 K/min because crystallization precedes it. This result can be rationalized when comparing the pressure dependence of T_x and $T_{g, onset}$. While $T_{g, onset}$ increases by $\sim 40 \pm 10$ K/GPa (from data in Fig. 4), T_x only increases by ~ 20 K/GPa.[27,35,36] Thus, $T_{g, onset} < T_x$ for low pressures, whereas $T_x < T_{g, onset}$ for high pressures, where the intersection occurs slightly above 0.30 GPa. Andersson[10] and Mishima[9] interpret their data to indicate a glass-to-liquid transition in bulk HDA also at 0.40 GPa, which we attribute to the facts that different experimental methods have been employed and T_x may shift by a few Kelvin when studying emulsions, other heating rates, or D_2O. The assignment to a glass-to-liquid transition is consistent with Mishima's interpretation that emulsified water can be quenched to HDA (via HDL) under pressure.[37]

In summary, we report a volumetric study of amorphous ices LDA and HDA in the pressure range up to 0.30 GPa. A deviation from linear expansion behavior in isobaric heating curves clearly indicates the temperature at which significant structural relaxation sets in. Recording of heating curves up to six consecutive times allows a clear distinction between irreversible and reversible volumetric relaxation processes.

Analysis of powder XRDs from samples recovered to 77 K and ambient pressure (Fig. 2) allows an additional distinction between irreversible processes related to crystallization and irreversible processes related to release of strain. We succeeded to obtain coincident curves in the third, fourth, fifth, and sixth heating runs (Fig. 3), which indicates the presence of exclusively reversible relaxation and the absence of any irreversible relaxation. The occurrence of a deviation from linearity in coincident curves is consistent with an underlying glass-to-liquid transition, and so we interpret it as $T_{g, onset}$ (Fig. 4). Other processes such as sintering processes in nonglassy material, disappearance of grain boundaries, or growth of nanocrystalline domains are not consistent with this phenomenology, and so we exclude these possibilities. Such processes would not result in coincident curves, but in a shift of onset temperatures and/or a volume contraction rather than an expansion. Therefore, a glass-to-liquid transition is the best explanation for the phenomenology, even though definite proof for this scenario requires direct measurement of viscosity, structural relaxation times, or diffusivity.

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