

The glass-to-liquid transition of high-density amorphous ice, revealed from $\tau(T)$, $V(T)$ and $C_p(T)$

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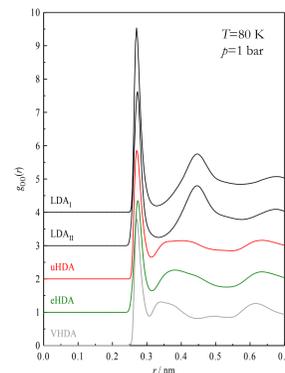
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Introduction

Amorphous ices may be distinguished by their density ρ at 1 bar and structurally characterized by, e. g., their pair distribution function $g_{OO}(r)$ [1]:

- Low-density amorphous ices (LDA_I and LDA_{II}), $\rho = 0.94 \text{ g/cm}^3$
- High-density amorphous ices (uHDA and eHDA), $\rho = 1.13\text{--}1.15 \text{ g/cm}^3$
- Very high-density amorphous ice (VHDA), $\rho = 1.26 \text{ g/cm}^3$

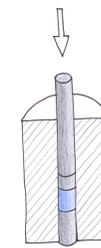
Pressure-induced amorphization of hexagonal ice (I_h) represents one method to form HDA [2]. Two competing mechanisms describing this transformation are debated: “thermodynamic melting” followed by vitrification of the liquid to a glass and “mechanical melting” leading to a nanocrystalline material, respectively [3]. There are studies supporting as well as contradicting the view of HDA being a glass. For example, HDA



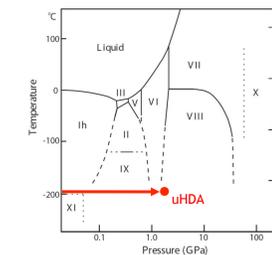
shows the textbook behavior of glasses [4], but it has also been regarded to be structurally heterogeneous, e. g., in ref. [5].

Here we investigate the **glass-to-liquid** transition of HDA between ambient pressure and 0.3 GPa *via* multiple experimental approaches, showing results that strongly support the view of HDA being a glass. We determine the glass transition temperature $T_g(p)$ from the temperature-dependence of the relaxation time τ , the volume change ΔV and the heat capacity C_p .

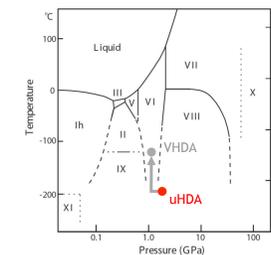
Preparation of (metastable) amorphous samples



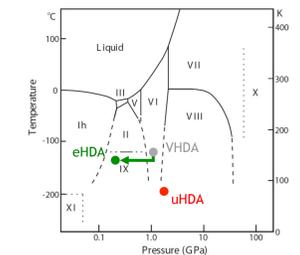
Setup: steel cylinder and pistons, ice



Step 1: amorphization of ice I_h produces unannealed HDA, uHDA [2]



Step 2: annealing of uHDA under pressure leads to VHDA [6]



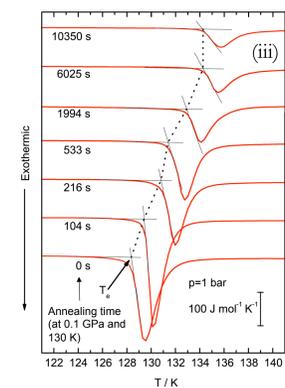
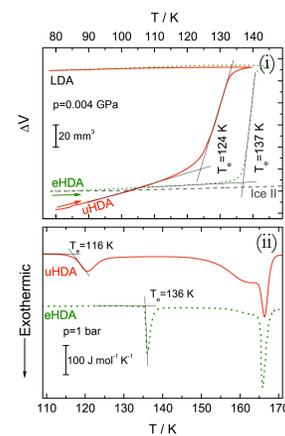
Step 3: decompression of VHDA leads to a form of expanded HDA, eHDA [7]

Characterization of the relaxation state of HDA and determination of its relaxation time $\tau(T)$

Even though the structural characteristics of uHDA and eHDA are similar, they differ in terms of relaxation. uHDA is a strained material that is able to relax upon warming, whereas eHDA is well relaxed from the start. This difference is reflected by the fact that uHDA expands much

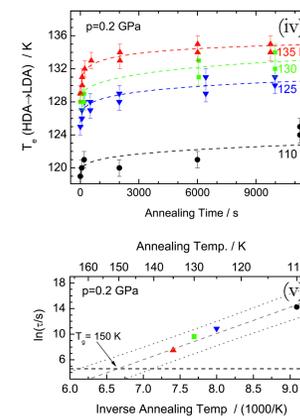
more with increasing temperature than eHDA does [8], and it governs the thermal stability of HDA at low pressure: eHDA can be heated to higher temperature than uHDA before the transition to LDA takes place [9], which shows up (i) as a step following ΔV and (ii) as a peak in differential scanning calorimetry (DSC) curves.

Therefore, (iii) starting with uHDA, the relaxation state of samples annealed for certain times can be probed by **following the transition to LDA** using DSC.



Based on the HDA-to-LDA transition temperature $T_e(t) = T_{e,\infty} + (T_{e,0} - T_{e,\infty}) \cdot e^{-(t/\tau)^n}$ we determine the relaxation time τ (and n) from the best fit [8], see (iv).

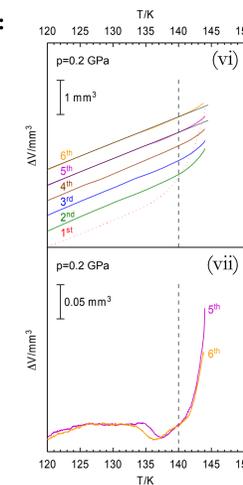
The values gained for different temperatures are then collected in an Arrhenius-type plot (v), from which $T_g = T(\tau = 100 \text{ s})$ can be calculated by extrapolation [8].



The glass transition temperature, revealed from $\Delta V(T)$ and $C_p(T)$

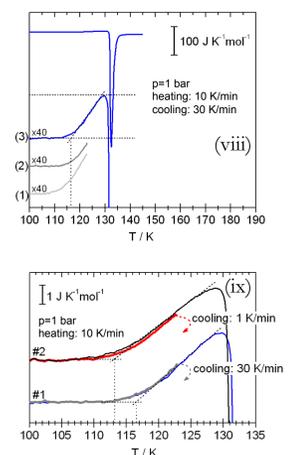
Volumetry (eHDA):

(vi) At T_g (marked by vertical lines), the isobaric thermal expansion coefficient changes, and, as a result, the volume change ΔV vs. temperature curve starts to deviate from linearity [4]. A magnified view of the non-linear part of the original data (vi) is shown in (vii).



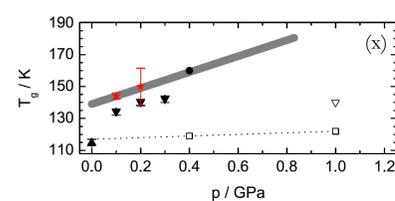
Differential Scanning Calorimetry (eHDA):

Characteristic for a glass transition upon heating is also a reversible increase of C_p at T_g (viii), where T_g depends on the previously applied cooling rate (ix). For HDA it is only possible to observe the onset of T_g (marked by vertical lines), because of the exothermic transformation to LDA at ambient pressure (viii and ix).



Summary and Discussion: Pressure-dependence of amorphous ices' T_g values

(x) Our results for **HDA's** T_g extracted from the temperature dependence of the relaxation time [8] (\star), from volumetry (\blacktriangledown) and calorimetry [4] (\blacktriangle) coincide well and show good agreement with the values obtained by Mishima from the temperature change in emulsified water [10] (\bullet and gray area, extrapolation). T_g values reported by Andersson and Inaba using dielectric relaxation spectroscopy [11] (\square and dotted line, extrapolation), high-pressure calorimetry and thermal conductivity measurements [12] (∇) are somewhat lower than the data by Mishima [10] and our own data [4,8]. We attribute this to the fact that Andersson and Inaba probably studied VHDA rather than HDA.



Knowledge of the pressure-dependence of both HDA's and LDA's T_g offers a **key-test** of theoretical scenarios: If their T_g values at same pressures differ, then the polyamorphism would extend above T_g , i. e., two distinct liquid states with a thermodynamic phase transition would indeed exist, ruling out scenarios without such a transition [13].

While T_g at 1 bar is known for both HDA and LDA [4] –showing values differing by 21 K–, data for LDA's T_g at higher pressures don't exist yet.

References

- [1] T. Loerting *et al.*, Phys. Chem. Chem. Phys. **13** (2011) 8783–8794. [2] O. Mishima *et al.*, Nature **310** (1984) 393–395. [3] T. Loerting *et al.*, Adv. Chem. Phys. **143** (2009) 29–82. [4] M. Seidl *et al.*, Phys. Rev. B **83** (2011) 100201. [5] G. P. Johari, Phys. Chem. Chem. Phys. **2** (2000) 1567–1577. [6] T. Loerting *et al.*, Phys. Chem. Chem. Phys. **3** (2001) 5355–5357. [7] K. Winkel *et al.*, J. Chem. Phys. **128** (2008) 044510. [8] P. H. Handle *et al.*, Phys. Rev. Lett. **108** (2012) 225901. [9] R. J. Nelmes *et al.*, Nature Phys. **2** (2006) 414–418; O. Mishima, Nature **384** (1996) 546–549; K. Winkel *et al.*, J. Phys. Chem. B **115** (2011) 14141–14148. [10] O. Mishima, J. Chem. Phys. **121** (2004) 3161–3164. [11] O. Andersson *et al.*, Phys. Rev. B **74** (2006) 184201; O. Andersson, Phys. Rev. Lett. **95** (2005) 205503. [12] O. Andersson, Proc. Natl. Acad. Sci. U.S.A. **108** (2011) 11013–11016. [13] L. Xu *et al.*, J. Chem. Phys. **130** (2009) 054505; N. Giovambattista *et al.*, Sci. Rep. **2** (2012) 390.