



Experimental evidence for two distinct deeply supercooled liquid states of water – Response to “Comment on ‘Water’s second glass transition’”, by G.P. Johari, Thermochim. Acta (2015)



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ABSTRACT

Recently, our earlier data which led us to conclude that deeply supercooled water displays a second glass transition (Amann-Winkel et al., 2013) was reinterpreted (Johari, 2015). In particular, the increase in heat capacity observed for high-density amorphous ice (HDA) samples at 116 K was reinterpreted to indicate sub- T_g features of low-density amorphous ice's (LDA's) glass transition. We reply to the criticism in detail and report an experiment triggered by the comment on our work. This experiment unequivocally confirms our original interpretation of the observations and reinforces the case for water's second glass transition, its polyamorphism, and the observation of two distinct ultraviscous states of water differing by about 25% in density.

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1. Brief introduction

Recently, we reported on a series of calorimetric and dielectric experiments carried out for high-density amorphous ice (HDA) and low-density amorphous ice (LDA) which led us to conclude that water displays two distinct glass transitions [1] linking the two amorphous ices to two distinct ultraviscous liquid states. In a subsequent contribution G.P. Johari [2] suggests a reinterpretation of our findings [1]. In particular, he suggests to reinterpret the increase in heat capacity $\Delta C_{p,2} = 4.8 \text{ J K}^{-1} \text{ mol}^{-1}$ observed at 116 K upon heating a sample of expanded high-density amorphous ice (eHDA) at ambient pressure. We note that recent theoretical work advances yet another interpretation of our results, involving two amorphous ices and facile crystallization of a single liquid [3].

In the comment [2], on which we respond in the present article, it is proposed that our observations, instead of being viewed as

the signature of eHDA's glass transition, need to be interpreted as a sub- T_g endotherm of LDA, whose $T_{g,1}$ is 136 K [4,5]. Ideas of a sub- T_g nature of LDA's heat capacity increase at $T_{g,1} = 136 \text{ K}$ were proposed in the past, with the implication that the real T_g of the low-density liquid (LDL) related to LDA would be above the crystallization temperature and thus experimentally unobservable [6,7]. These ideas were then scrutinized, vindicating the original interpretation that for LDA a glass transition occurs below its crystallization temperature [8,9]. Whether this glass transition is a glass-to-liquid transition or an orientational glass transition, is a separate matter on which consensus has not been reached so far [10,11]. Nevertheless, for LDA a glass-to-liquid transition is not questioned in Ref. [2] as exemplified by the quote: “water at $T > 136 \text{ K}$ is an ultraviscous liquid that crystallizes, and not a glass”.

Here we focus our attention on the question raised by Johari whether our recent experiments can be reconciled with a single glass transition scenario or whether they indicate two distinct glass transitions. First, we review several important aspects regarding the transitions among water's high- and low-density forms and then move on to report a novel experiment inspired by the discourse. This experiment is designed to be capable of deciding between the two scenarios. Ultimately, the observations we make exclude the interpretation given in Ref. [2].

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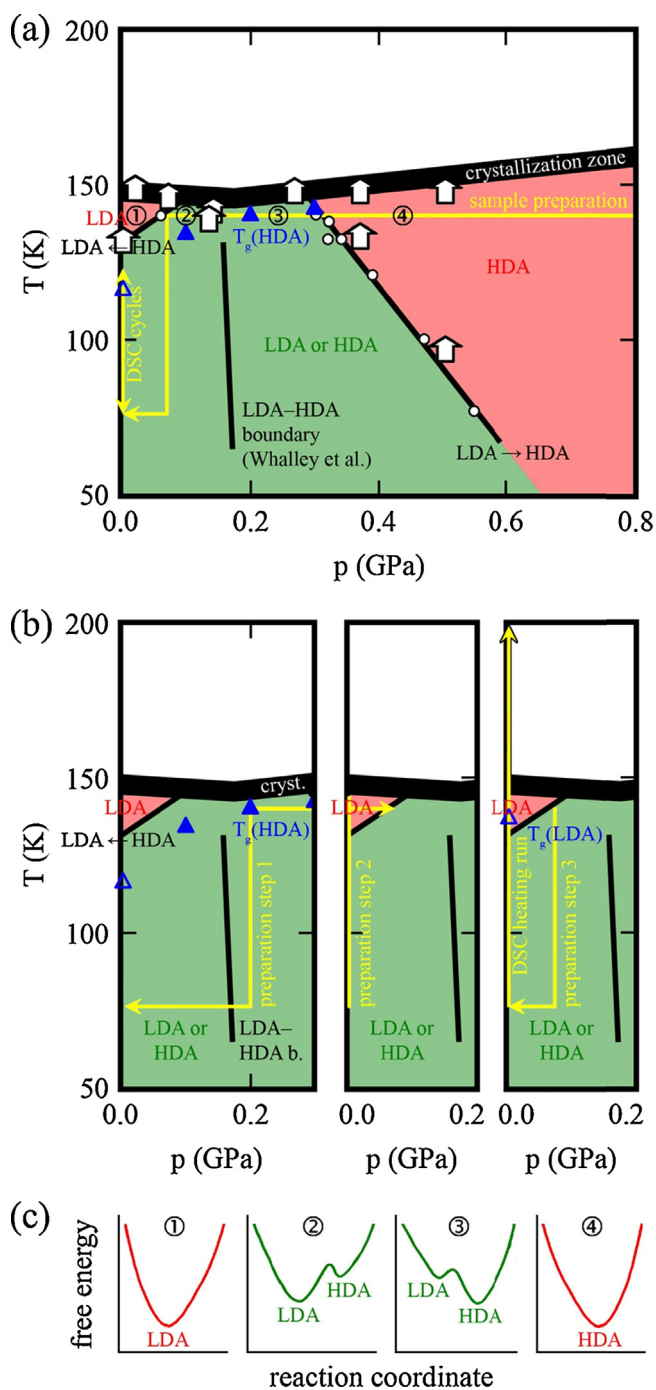


Fig. 1. (a) “Phase diagram” of the amorphous ices LDA and HDA. The word “phase diagram” is put in quotes here because, as explained in the text, not all states appearing in this diagram are necessarily phases in the thermodynamic sense. The area in green (labeled 2 and 3) shows p - T conditions, in which either LDA or HDA can be kept and studied for long times. Whether LDA or HDA is observed in experiments depends on the path of preparation. The two areas in red show p - T conditions, in which HDA transforms rapidly to LDA (red area labeled 1) and in which LDA transforms rapidly to HDA (red area labeled 4). The LDA-HDA boundary labeled “(Whalley et al.)” divides the green area and shows the location of equal free energy for HDA and LDA [22,23]. White circles and white arrows indicate the location of the sharp polymorphic transition observed in isothermal and isobaric experiments, respectively. HDA \rightarrow LDA transformation temperatures were taken from Refs. [19] and [1]. LDA \rightarrow HDA transition and crystallization temperatures were taken from Ref. [12]. The open blue triangle indicates the calorimetric glass transition for HDA at 116 K [1], and filled blue triangles indicate volumetric glass transition temperatures for HDA [25]. In the white area above the thick black line labeled “crystallization zone” only crystalline ices can be observed at long time scales. The yellow arrow labeled “sample preparation” indicates the path taken in Ref. [1] for preparing those HDA sample that were

2. Pressure-induced transitions between HDA and LDA

Not only based on the experiments to be reported below but also based on the following arguments our initial interpretation is reconfirmed. Fig. 1(a) shows the transformation behavior of amorphous ices established by Mishima in 1994 [12]. The key feature of this diagram is the large hysteresis between the HDA \rightarrow LDA and LDA \rightarrow HDA transitions. As a result, there is a region in the diagram, in which amorphous ice appears exclusively as LDA (red area labeled ① in Fig. 1(a)), a region, in which amorphous ice appears exclusively as HDA (red area labeled ④ in Fig. 1(a)) and a region, in which either LDA or HDA may persist (green area labeled ② and ③ in Fig. 1(a)). Whether the thermodynamically more stable form or the metastable form exists within the green area in Fig. 1(a) depends on the pressure-temperature path taken in the course of the experiment. The polymorphic transitions are very sharp and rapid both for the LDA \rightarrow HDA and for the HDA \rightarrow LDA [12] transitions and both for isothermal (circles in Fig. 1(a)) and for isobaric experiments (vertical arrows in Fig. 1(a)) at the locus of the transformation (black lines separating red and green areas in Fig. 1(a)). At pressures and temperatures away from the transformation boundaries, well inside the colored areas, transformations between LDA and HDA cannot be observed on the laboratory time scale of many hours [12–14].

Instead of the polymorphic transition, the HDA-matrix relaxes upon keeping the sample at high temperatures close to the crystallization temperature for a while. Unannealed HDA (uHDA) [15] slowly relaxes, e.g., at 0.2 GPa and converges to an expanded HDA (eHDA) state [16], which we regard to be an equilibrated form of HDA, if prepared properly [14]. Furthermore, eHDA is highly stable and resistant against crystallization [17,18]. The eHDA sample studied in our earlier work [1] was prepared by decompression of a VHDA sample at 140 K, i.e., by entering the green area ② in Fig. 1(a) coming from the high-pressure, HDA side (area ④). The yellow arrow labeled “sample preparation” in Fig. 1(a) indicates the p - T path taken to prepare the sample used in Ref. [1]. We have taken care to avoid the HDA \rightarrow LDA transition by quenching the sample just prior to entering the red LDA area ① in Fig. 1(a), i.e., by quenching the sample at 0.07 GPa from 140 K to 77 K, and then by releasing the pressure at 77 K [14,19]. The volume of the sample was monitored in situ by recording the piston displacement and did not show the jump-like change typical of the HDA \rightarrow LDA transition. Thus, this procedure results in a sample of eHDA. The sample

subsequently studied by DSC and dielectric experiments at ambient pressure. The double-headed arrow labeled “DSC cycles” indicates that HDA samples were cycled in the DSC experiments between 77 and 123 K without observing a transformation to LDA. (b) Schematic route of preparation of LDA-II. The first part illustrates the compression of VHDA from 1.10 to 0.20 GPa yielding eHDA, which is then quenched and subsequently decompressed to 0.002 GPa. In the second part eHDA is heated at 0.002 GPa–145 K and then compressed to 0.07 GPa where it is equilibrated for 60 s. Subsequently, the sample is quenched to 77 K and then decompressed to ambient pressure for ex situ DSC measurements as shown in part 3. (c) Sketch of Gibbs free energies of amorphous ices as a function of pressure. In the red area labeled ① LDA is the most stable amorphous form, and in the red area labeled ④ HDA is the most stable amorphous form. HDA is instable in area ① and LDA is instable in area ④, and so single-well Gibbs free energies result. In the green area labeled ② LDA is the most stable amorphous ice, and in the green area labeled ③ HDA is the most stable amorphous ice. At about 0.20 GPa LDA and HDA are of equal Gibbs free energy, which is the basis of the line labeled “(Whalley et al.)” in (a). To the left of this line (green area ②) HDA is metastable (rather than instable) with respect to LDA, whereas to the right of this line (green area ③) LDA is metastable with respect to HDA. That is, in the green area the Gibbs free energies show a double-well nature and an energy barrier, which cannot be surmounted on the basis of the available thermal energy. These two “megabasins” are at the origin of water polymorphism, water’s two glass transitions and the two deeply supercooled liquid forms LDL and HDL. Part (a) and (b) are adapted from [12]. (For interpretation of the references to color in figure legend, the reader is referred to the web version of the article.)

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