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Isocompositional liquid-liquid transition in dilute aqueous LiCl solutions

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We here demonstrate that small amounts of LiCl dissolved in water extend the existence window of deeply supercooled liquid water. This shift allows us to observe the isocompositional, sharp liquid-liquid transition (LLT), while this is not possible in pure water. Upon heating at ambient pressure, the hyperquenched and densified glass first turns into the high-density liquid (HDL) and then experiences the LLT to the low-density liquid (LDL) at 137–141 K and ambient pressure. At the LLT the viscosity suddenly jumps up by an order of magnitude, from $\sim 4.3 \times 10^9$ Pa s in HDL to $\sim 3.7 \times 10^{10}$ Pa s in LDL for the 3.1 mol % solution based on our calorimetric analysis. That is, the LLT takes place clearly in the ultraviscous liquid domain at ambient pressure. By contrast, the viscosity of the emerging LDL at the LLT is still in the domain of the soft glass for pure water and for solutions exceeding 5 mol % LiCl that were studied in the past. This is owing to our observation that, first, the LDL's glass transition is lowered by about 8 K to 126 K in the presence of small amounts LiCl, whereas the HDL's glass transition remains at 118 K. Second, the stability of HDL at ambient pressure is increased by high-pressure annealing, shifting the LLT to higher temperatures.

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I. INTRODUCTION

Water has many anomalies that are far from being well understood [1]. In particular, the behavior of amorphous ices is not only puzzling but also highly relevant to many fields. For example, they are found naturally in space [2] or used for applications like cryoelectron microscopy [3]. To the present day, three amorphous forms of ice are known, namely low-density amorphous ice (LDA) [4], high-density amorphous ice (HDA) [5], and very high-density amorphous ice (VHDA) [6]. Remarkably, a first-order-like transition between LDA and HDA has been observed [7], although amorphous materials are metastable with respect to crystalline phases. That said, they are prone to crystallization upon heating, limiting the temperature range in which they can be studied [8]. This circumstance leads to the so-called no man's land of water, which represents an experimentally barely accessible area in water's p-T diagram of noncrystalline states [9].

Several scenarios have been proposed to explain water's anomalous nature, with one of the most promising ones being the two-liquid scenario [10,11]. It suggests the possibility of a discontinuous transition between high- and low-density liquid water in the supercooled liquid regime. More precisely, this scenario implies the existence of a coexistence line between two liquid states differing in density, high-density liquid (HDL) and low-density liquid (LDL) water [11]. The liquid-liquid transition (LLT) coexistence line is located at elevated pressures (e.g., ~ 100 MPa and ~ 200 K) [12]. Under pressure (i.e., at the coexistence line), the chemical potentials of both liquid phases are equal, rendering it a genuine first-order transition. At ambient pressure (i.e., away from the coexistence line), the kinetically arrested high-density amorphous state might also experience an LLT [13,14]. In contrast to the previous case, the chemical potential of HDL water is way larger than the one of LDL water because HDL water is metastable with respect to LDL water at 1 bar. A huge advantage of studying an LLT at ambient pressure is that essentially every *ex situ* method can be used for characterization. In contrast, experimental techniques for studying an LLT under pressure are limited.

The problem with realizing an LLT at ambient pressure by heating HDA is that the glass transition of LDA ($T_{g,1}$) is quite high (136 K at 30 K min^{-1}) [15]. The sharp transition from high to low density, i.e., the polyamorphic transition, usually takes place between 105 K (for unannealed HDA, or uHDA [16]) and 135 K (for the most relaxed HDA samples, also called expanded HDA, or eHDA [13,17]). In other words, the transition to low density takes place in the glassy domain, just before the viscosity drops below 10^{12} Pa s, which by definition separates solids from liquids [18]. Our idea to tackle this issue is depicted in Fig. 1. The left column shows an illustration of the thermal behavior of HDA based on existing literature on pure water. Upon heating HDA at ambient pressure, one observes its glass transition temperature $T_{g,2}$ at 116 K (heating rate 30 K min^{-1}) [13]. Above this temperature, the ultraviscous HDL water is present. We emphasize that there is a scientific discourse about the nature of water's glass transition and the question whether or not HDA and LDA turn into liquids above their glass transition temperatures, showing translational diffusion, as discussed in detail in our recent review [19]. Based on the collected experimental

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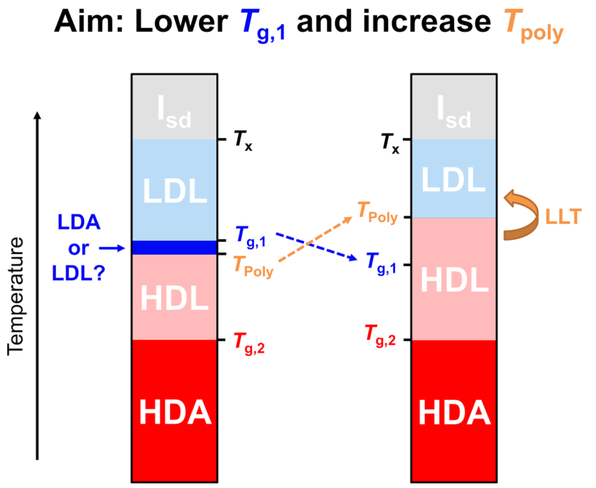

FIG. 1. Left: Schematic thermal behavior of pressure-annealed HDA (eHDA) upon heating at ambient pressure based on literature [13,15,19]. At $T_{g,2}$, HDA transforms to the corresponding liquid, HDL. Heating further leads to the polyamorphic transition to a low-density state, the glass transition temperature of which is $T_{g,1}$. In the pure water case, LDA is formed first as a soft glass since $T_{g,1}$ and T_{Poly} are quite close. Thus, to realize an LLT one needs to push T_{Poly} up and/or $T_{g,1}$ down, so that T_{Poly} is far above both $T_{g,1}$ and $T_{g,2}$. This scenario is shown in the column on the right-hand side. Further heating causes cold crystallization to stacking-disordered ice I (ice I_{sd}).

evidence we take the stand that HDA and LDA indeed turn into ultraviscous liquids; i.e., the glass transition is associated with a viscosity-lowering α process [18].

Heating HDL water even further initiates the polyamorphic transition to the low-density state at the temperature T_{poly} (see left column in Fig. 1) [13]. The crucial question is the nature of the low-density state right after it has formed from HDL in a process that involves nucleation and growth [20]. In case it is an ultraviscous liquid rather than an amorphous solid, the polyamorphic transition is also an LLT. In other words, it is necessary to know what the glass transition temperature $T_{g,1}$ for LDL water is, and whether it is above or below T_{Poly} [15,19]. This means if T_{Poly} is located at significantly higher temperatures than $T_{g,1}$, HDL water would transform to LDL water instead of LDA (see right column in Fig. 1). Now in the case of pure water HDL, even for the thermally most stable samples to date, $T_{g,1}$ and T_{Poly} are quite close to each other [21]. That is, it is hard to make the case for an LLT in pure water, as HDL water transforms to LDA in its soft glassy state, but not to LDL water in its ultraviscous liquid state. The definition criterion separating an amorphous solid in its soft glassy state from a deeply supercooled liquid is viscosity, where 10^{12} Pa s represents the boundary. Thus, to realize an LLT one would have to lower $T_{g,1}$ and increase T_{Poly} as depicted in the column on the right-hand side in Fig. 1.

In this work we demonstrate that both of these aims are reached by introducing a small amount of salt, where exactly 3.1 mol % of LiCl produces the largest shift, thereby allowing to observe the liquid-liquid transition at viscosities below 10^{10} Pa s, two orders of magnitude lower than the definition criterion for a liquid. For molar fractions >5.8 mol % that were studied in the past, polyamorphism disappears, and for lower fractions the shifts are smaller and the viscosities at the LLT are higher than for 3.1 mol %. The key problem in this context is that such dilute solutions are regarded as "non-glass-forming" so that elaborate techniques need to be employed to actually realize this situation, where we specifically use first hyperquenching of liquid droplets for complete vitrification and second densification in a piston-cylinder setup to make the highly dense glass. A complex high-pressure annealing protocol allows us to reach the highest possible polyamorphic transition temperatures (see Methods for more details). The calorimetric data used for this study are the same as the data in the companion publication [22], in which the focus is on the influence of LiCl on water's glass polymorphism. In the companion publication we focus on volumetric data, x-ray diffraction data, and calorimetry to learn more about the processes taking place, leaving the question aside whether the transition takes place in the glassy or supercooled liquid domain. In the present study we investigate the calorimetric data in more detail and quantify the viscosity of both liquids. This is crucial to discuss our results in the light of an LLT and the process of nucleation of one liquid in a second liquid.

II. RESULTS

A selection of the thermograms recorded for such samples at a heating rate of 20 K min^{-1} is shown in Fig. 2. For pure water HDA (bottom red curve in Fig. 2), a broad heat capacity increase with an onset temperature of 118 ± 1 K is observed in the first heating scan. Upon comparison with the data presented in Refs. [13] and [21], it is identified as $T_{g,2}$. The same feature is also found when heating the high-density LiCl-H_2O glasses (red curves in Fig. 2), albeit at slightly shifted temperatures and less pronounced at higher concentrations. In other words, dilute LiCl solutions also have a $T_{g,2}$, at which the high-density solid transforms into a high-density liquid. After each $T_{g,2}$, a sharp endothermic feature is observed between 132 and 136 K (T_{Spike} in Fig. 2), which becomes more pronounced with added LiCl. This endothermic feature, referred to as *spike*, has also been found in other studies dealing with pure water (eHDA) [13,21,23]. According to our recent work [21], it arises from a nucleation event that precedes the polyamorphic transition.

At temperatures above 137 K a strongly exothermic event is observed in all first heating traces (truncated in Fig. 1, where the vertical part of the red curve represents its onset; see the Supplemental Material (SM) [24] for full-range data). In the case of pure HDA water (bottom trace in Fig. 2), a similar exotherm is observed upon heating and known to be the polyamorphic transition to LDA [16]. This transition occurs right after T_{Spike}, but about 20 K above $T_{g,2}$, indicating that a high-density liquid experiences the polyamorphic transition to a low-density state. Since these exotherms are also observed for the LiCl solutions, we conclude that also the high-density LiCl solutions experience a similar polyamorphic transition to a low-density state (onset temperature T_{Poly}).

After quenching the low-density solutions to 93 K, we observe $T_{g,1}$ and the cold crystallization to ice, I_{sd} (also called devitrification). This is shown in the second heating scan

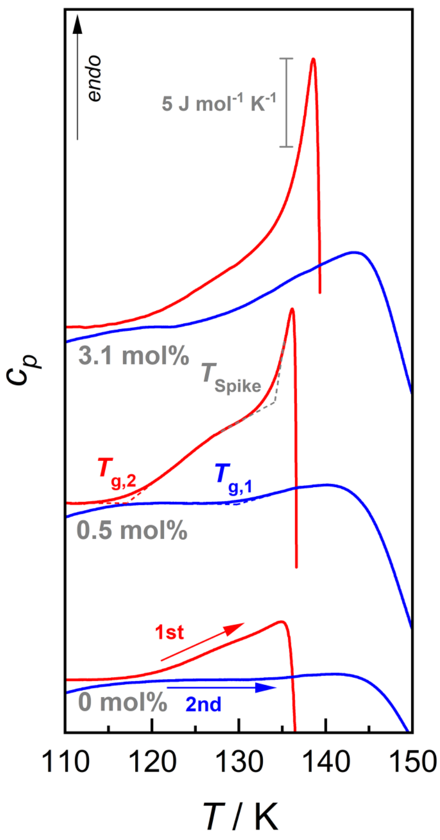

FIG. 2. Calorimetric heating scans of compressed glassy LiCl solutions at ambient pressure, focusing on water's two glass transitions. Compositions between 0 and 5.8 mol % were considered (for the remaining mole fractions please see the SM [24]). A heating rate of 20 K min^{-1} was employed, but the experiments were repeated for 40 K min^{-1} as well (see the SM [24]). Red curves indicate the first heating scan up to 143 K corresponding to HDA (or high-density solution) and blue curves correspond to LDA (or low-density solution), i.e., the second one after recooling. Sample mass was determined from the melting endotherm of ice (not shown) and the heat of fusion from the data by Monnin *et al.* [25].

(blue curves in Fig. 2) and strongly resembles the behavior of pure water LDA [16,26,27] and hyperquenched LiCl solutions [28]. $T_{g,1}$ involves a miniscule heat capacity increase at 134 ± 1 K in the case of pure water, in agreement with literature data recorded at 30 K min^{-1} [29–31]. $T_{g,1}$ shifts to lower temperatures upon adding LiCl, where our data exactly match the results by Hofer *et al.* [28]. That is, hyperquenched solutions by Hofer *et al.*, without experiencing the polyamorphic transition, and the low-density glasses studied here after the polyamorphic transition show the exact same behavior. This suggests that we deal with homogeneous glasses in both cases. The pronounced exothermic feature at temperatures above 150 K corresponds to the devitrification (onset temperature T_x), as reported in the literature [27,31,32].

Figure 3(a) shows our results on the thermal behavior of the high-density state ($T_{g,2}$ and T_{Poly}) while Fig. 3(b) maps the behavior of the low-density state ($T_{g,1}$ and T_x). The data are shown as a function of the molar fraction x_{LiCl} as extracted from the calorimetry scans in Fig. 2 and the SM [24]. To clearly distinguish between high- and low-density states of the solution and the polyamorphs of pure water, they are labeled as follows: HD or LD indicates whether the state is of high (>1.1 g cm^{-3}) or low density (<0.95 g cm^{-3}), and the subscript S or L indicates the state of matter (solid or liquid). When we consider each sample to be liquid right above the glass transition temperature, regions in which HD_L and LD_L are observed can be identified, as shown using red or blue shading in Fig. 3. Starting at $x_{\text{LiCl}} = 0$ in Fig. 3(c), T_{Poly} is very close to $T_{g,1}$, but significantly above $T_{g,2}$. That is, the HD state can safely be considered to be liquid at T_{Poly}, which occurs 17.5 K above $T_{g,2}$. It is, however, not obvious whether the same holds for the LD state when the difference between $T_{g,1}$ and T_{Poly} is only ~3 K. To clarify this, we estimate the viscosity at T_{Poly}, assuming that its temperature dependency can be described using an Arrhenius law. Given a temperature-independent activation energy E_A one obtains

$$\eta(T) = \eta_g e^{\frac{E_A}{R}\left(\frac{1}{T}-\frac{1}{T_g}\right)}, \tag{1}$$

where $\eta(T)$ is the viscosity at the temperature T, η_g is the viscosity at T_g, and R is the gas constant. Taking E_A of 34 kJ mol^{-1} from our previous work [13,14] and an η_g of 10^{12} Pa s [33], we obtain ~4.8 × 10^{11} Pa s for the viscosity of the LD state and ~1.2 × 10^{10} Pa s for the HD state at T_{Poly} in the pure case. Thus, the viscosity of the HD state is two orders of magnitude lower than η_g, which means that it can be considered a rather viscous HDL at T_{Poly}. The viscosity of the LD state, however, is very close to η_g, which represents the definition criterion to distinguish liquids from solids.

This changes significantly once LiCl is added: A large temperature gap between $T_{g,1}$ and T_{Poly} arises [pink shading in Fig. 3(c)]. At 3.1 mol %, the difference between $T_{g,1}$ and T_{Poly} reaches a maximum of ~14 K. In other words, the polyamorphic transition occurs at a temperature that is much higher than the glass transition temperature of the low-density state. This is our experimental evidence or smoking gun for the LDL phase being attained after the polyamorphic transition. Since also the high-density state is a liquid at this temperature (T_{Poly} being 22 K above $T_{g,2}$), the polyamorphic transition occurs between a high- and a low-density liquid, rendering it a sharp liquid-liquid transition. This assertion is supported by the estimated viscosities for HD_L and LD_L: At T_{Poly} we estimate ~3.7 × 10^{10} Pa s for LD_L and ~4.3 × 10^{9} Pa s for HD_L of 3.1 mol % using the same procedure as discussed above. We refrain from calling it a first-order liquid-liquid transition because at ambient pressure HDL and LDL do not show the same chemical potential, as indicated in the Introduction.

The temperature window for the observation of the LLT at ambient pressure closes near 5 mol %, where the $T_{g,1}$ line crosses the T_{Poly} line in Fig. 3(c). This means there is an upper concentration limit for the LLT in LiCl-water solutions. This also means the use of highly efficient hyperquenching techniques is mandatory to observe the LLT. Other cooling methods employed in earlier studies lead to crystallization or phase separation rather than homogeneous vitrification in this concentration range [34–36]. Another point we want to stress is that our data suggest the LLT to be isocompositional; i.e., the concentration of LiCl in the high- and low-density matrix

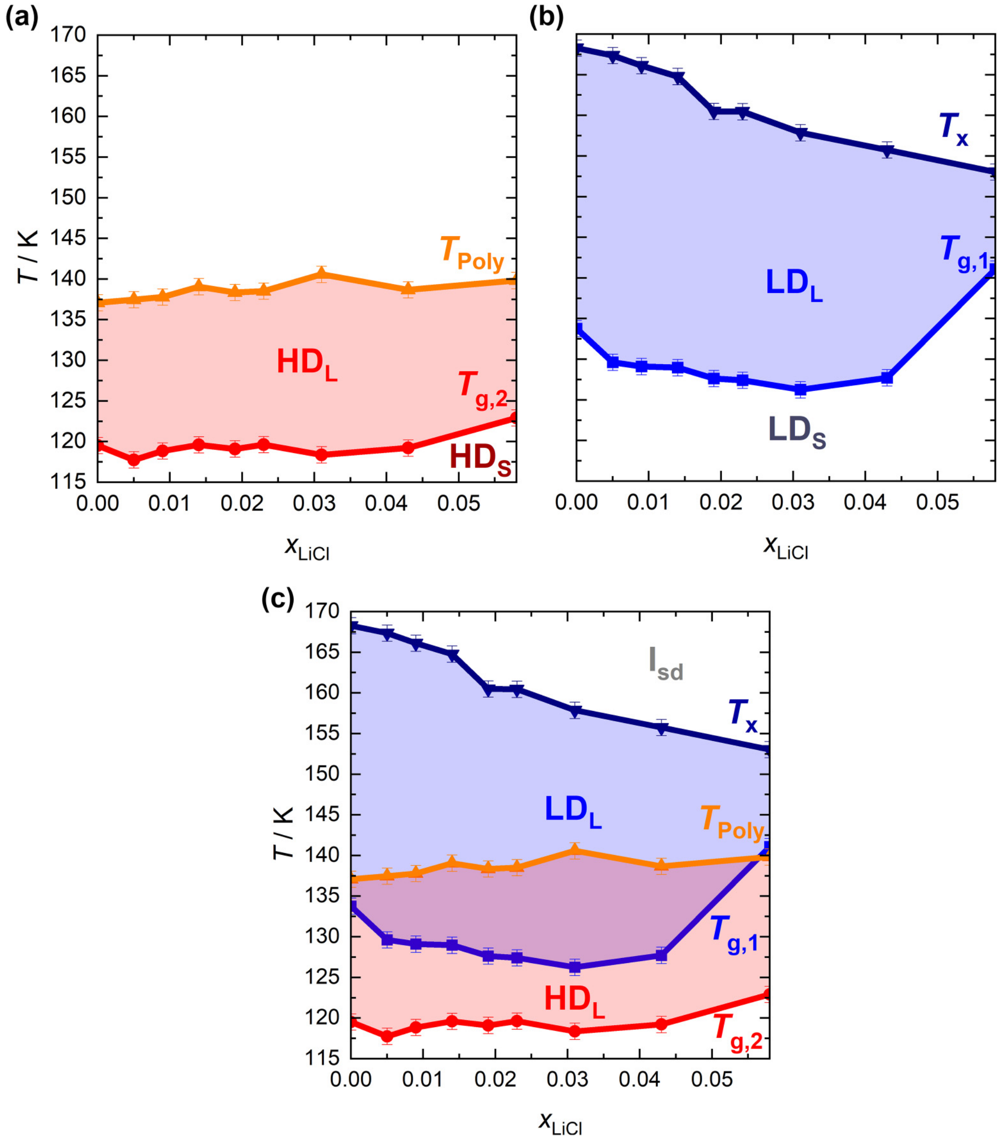

FIG. 3. (a) Thermal behavior of the high-density solid (HD$_S$): $T_{g,2}$ is the glass transition temperature of HD$_S$ and T_{Poly} the onset temperature of the polyamorphic transition at various molar fractions of LiCl, as calorimetrically determined at a heating rate of 20 K min^{-1}. (b): Thermal behavior of the low-density solid (LD$_S$): Glass transition temperature of LD$_S$ ($T_{g,1}$) and onset temperature of the cold crystallization T_x. (c) Combined results of (a) and (b). Note the gap opening up between $T_{g,1}$ and T_{Poly}. The temperature and concentration regimes where the corresponding liquids (HD$_L$ and LD$_L$) are found are colored accordingly. Error bars represent the experimental error of ~1 K which is estimated based on the reproducibility of onset temperatures between different batches.

is identical. That is, no signs of a phase separation, such as additional glass transitions stemming from concentrated aqueous LiCl like in Ref. [37] are observed. Instead, the exact same features as in pure water are present, just shifted in temperature.

III. DISCUSSION

We here study the thermal behavior of homogeneously vitrified and densified aqueous solid solutions of LiCl (HD$_S$) upon heating at ambient pressure. The key finding in this work is the observation of the polyamorphic transition occurring significantly above both glass transition temperatures ($T_{g,1}$ and $T_{g,2}$) between 0.5 and 4.3 mol % LiCl. At 3.1 mol %, the polyamorphic transition takes place 22 K above $T_{g,2}$ and 14 K above $T_{g,1}$. This implies that both the high- and low-density states are ultraviscous liquids when the transition commences and indicates an LLT from HD$_L$ to LD$_L$ at T_{Poly}. By contrast, the existence window of HD$_L$ and LD$_L$ and hence the LLT disappear for solutions above 5 mol % LiCl. Yet, such solutions were mainly studied in the context of supercooled water in earlier literature [34]. In the case of pure water $T_{g,1}$ and T_{Poly} are so close to each other that the low-density liquid is not accessed, but rather a soft glass at the verge of turning into an ultraviscous liquid. The addition of small amounts of LiCl plasticizes the water network, lowering $T_{g,1}$ by about 8 K and reducing the viscosity by about two orders of magnitude. This pushes the polyamorphic transition into the domain of ultraviscous liquids and allows us to study an LLT at ambient pressure.

Let us now discuss these findings in the context of literature on pure, supercooled liquid water. Authors of several studies [13,20,21,38–40] aimed at maximizing the thermal stability of HDA in order to access the corresponding HDL. Handle *et al.* [38] isobarically heated two types of amorphous ice differing in terms of density and found that both of them convert to the same metastable equilibrium phase that, they point out, is HDL. Further evidence is provided by Stern *et al.* [40] who conducted similar experiments but at higher pressures. They infer that there is a narrow pressure window (0.1–0.3 GPa) in which, regardless of preparation history, a metastable equilibrium state is assumed prior to the polyamorphic transition and the subsequent crystallization. They consider HDL as this equilibrated liquid phase. These results imply that HDL can be equilibrated; i.e., the structural relaxation time is shorter than the timescale of the polyamorphic transition. The study by Lemke *et al.* [39] employing dielectric spectroscopy at ambient pressure shows that both timescales are separated by roughly two to three orders of magnitude. Amann-Winkel *et al.* [41] identified the timescale of the LDL-to-HDL transition upon ultrafast heating of LDA to be less than 100 ns while the ice formation is observed at >1 μs. In other words, the structural relaxation is considerably faster than the transformation to the low-density state (for HDL) and the crystallization (for LDL). From all these results, one can conclude that HDL actually reaches a metastable equilibrium between $T_{g,2}$ and T_{Poly}. We infer that this is also the case when LiCl is added: $T_{g,2}$ is barely influenced and T_{Poly} is only shifted slightly by the addition of LiCl—by contrast to $T_{g,1}$. This causes the large temperature gap between $T_{g,2}$ and T_{Poly}, where the high-density liquid is found, to stay intact. Thus, we infer that LiCl-HD_L also reaches a metastable equilibrium prior to the LLT.

Perakis *et al.* [14] used x-ray photon correlation spectroscopy (XPCS) to study the polyamorphic transition in pure eHDA at ambient pressure. They state that at $T_{g,2}$, which was observed at 110 K in their slow-heating experiments, nanoscale diffusion is observed. These diffusive dynamics slow down after the transition to the low-density state at 130 K but stay diffusive. Their results are consistent with an LLT in pure water. We infer a similar behavior for the LiCl solutions, at least at 3.1 mol % based on our estimates of the viscosity at the LLT. However, for our samples, the temperature window in which the liquids are present is much wider than for pure water, which implies that diffusive dynamics is accelerated by the addition of LiCl. Thus, we suggest that XPCS measurements conducted on heating 3.1 mol % LiCl-HD_S will allow to measure much faster diffusive dynamics at the LLT than in the case of pure water. Apart from these studies, further evidence for the existence of an LLT is provided by ultrafast x-ray laser experiments [42] and a study of a pressurized trehalose solution [43].

Most literature studies discussed above rely on increasing T_{Poly} to temperatures above $T_{g,1}$ and $T_{g,2}$ to observe the LLT. Our approach here is different, namely, to lower $T_{g,1}$ in order to broaden the temperature window in which the LLT can be observed. Advantages of this strategy are that (i) *ex situ* experiments at ambient pressure are possible, which makes characterization via standard experimental techniques feasible; (ii) a large variety of solutes can be introduced via hyperquenching, so that $T_{g,1}$, and the width of the temperature window, can be tuned through choice and concentration of solute [28]; and (iii) the low-density glass is prepared directly from the liquid, which means that no crystalline ices are involved in the synthesis, avoiding criticism about a possible crystalline nature of the sample.

Our observation of T_{Spike} in Fig. 2 can also be related to previous work in pure water. It was reported by Tonauer *et al.* that nanosized LDA domains form in an HDA matrix at 140 K and 0.1 GPa [20]. These domains then serve as nuclei for the growth of LDA at the polyamorphic transition [21]. It was also inferred that said transition might be an LLT and hypothesized that nucleation of one liquid in the other occurs, but clear evidence for the liquid nature of the growing low-density domains was missing. In our case, only liquid-liquid nucleation is consistent with the calorimetric observations, whereas nucleation of amorphous domains can be ruled out. The spikelike feature that commences shortly after $T_{g,2}$ is reported in the literature, where it is assigned as nucleation of LDA [21]. The fact that we observe this spike in connection with the LLT gives strong support that LD_L indeed nucleates in the HD_L matrix. In other words, we interpret the spike as the nucleation of one liquid in another liquid. That is, the unique spike in the calorigrams represents new physics: the nucleation of one liquid in a second, isocompositional liquid.

The striking similarity between the LLT observed here and the polyamorphic transition of pure water indicates that both phenomena are connected. An important piece of evidence for this connection is that the thermal behavior of LiCl-HD_S for $x_{LiCl} < 5$ mol % is nearly identical to the one of pure water HDA. This includes the polyamorphic transition, both glass transitions and cold crystallization, which are observed for both pure water and LiCl solutions ($x_{LiCl} < 5$ mol %). The only differences are shifts in the onset temperatures of these features caused by LiCl. Thus, we conclude that the LLT observed in dilute LiCl solutions is caused by water's polyamorphism. Our observations are consistent with thermodynamic models [44] implying a shift of the LLT locus upon increasing the molar fraction. As shown in molecular dynamics (MD) simulations of NaCl solutions [45], the LLT might even become inaccessible as it shifts to negative pressures. While we here do not find direct proof of such a shift, these studies clearly show that a connection to the LLT of pure water is thermodynamically consistent.

This is in stark contrast to recent reports of an LLT in a hydrazinium trifluoroacetate (N_2H_5TFA) solution with a molar fraction of 15.6 mol % [46]. The authors of this study claim that the local water structure in this solution is similar to that of pure water under elevated pressure based on MD simulations. Furthermore, they observe a reversible first-order transition near 190 K using infrared spectroscopy and calorimetry. However, in the light of our results, the molar fraction of N_2H_5TFA used there seems unreasonably large given that we here observe waterlike behavior only at very small molar fractions. This raises the question whether this first-order transition is connected to water's LLT or if it is only a feature of the concentrated solution. This question was recently investigated by analyzing the polyamorphic behavior of pressure-amorphized N_2H_5TFA solutions of 0–40 mol % using an array of different techniques by Bachler *et al.* [47].

The authors find that waterlike polyamorphism is only present in solutions with less than 13 mol %, ruling out the possibility of an LLT connected to water as initially reported. Exploring the thermal behavior of a range of different cations and anions at 17.5 mol % led Bachler *et al.* to the conclusion that there is no LLT for fluorinated anions, such as N_2H_5TFA. Instead micellization and demicellization take place at the purported LLT upon cooling and heating through the transition temperature. That is, the first-order transition is a phase separation similar to the one when falling below the Krafft temperature [48]. Thus, we infer that the LLT can only be observed in very dilute solutions.

To conclude, our results provide strong arguments in favor of a sharp liquid-liquid transition at ambient pressure. The procedures outlined here pave the way for more detailed studies of the complex behavior of supercooled aqueous solutions and allow for novel experiments on the physics of the liquid-liquid transition that were not possible before.

IV. METHODS

As stated in the Introduction, the data used for this study are the same as the data used in the companion publication [22]. This section gives a brief overview on the methods while a more detailed description is given in Ref. [22]. The method for quantifying viscosities that is central for the present work is described on the fly in Sec. II, Results. Also the method for identification of the spike as a nucleation event of a liquid in a liquid matrix is described on the fly.

A. Lowering LDL's glass transition temperature $T_{g,1}$ using hyperquenching

It is well known that a decrease of $T_{g,1}$ is observed in dilute aqueous solutions that still show waterlike behavior, such as hyperquenched LiCl solutions [28,49]. A very interesting effect of LiCl on water was discovered by Hofer *et al.* [28], who showed that LiCl at less than 4 mol % lowers viscosity and decreases $T_{g,1}$ compared to pure water, thereby extending the window of the existence of the ultraviscous solution to lower temperatures. $T_{g,1}$ was found to be lowered to 130 K at 3.3 mol % of LiCl at ambient pressure. Such a substantial decrease of $T_{g,1}$ can be exploited to widen the temperature range where the low-density state is liquid, allowing access to the LLT. For this reason, we here focus our attention on dilute solutions of LiCl, the behavior of which is still dominated by water [50].

Vitrification of such dilute solutions is quite difficult, where they are often called non-glass-forming in the literature, e.g., by Angell and Sare [34]. They have revealed that at cooling rates of 15–17 $\mathrm{K\,s^{-1}}$ only solutions of more than 9 mol % LiCl vitrify completely, whereas more dilute solutions crystallize. To turn also dilute solutions into glasses, we use the hyperquenching technique developed by Mayer [51] and improved by Kohl *et al.* [26] here in Innsbruck in the present work. Using this technique the liquid is cooled at extremely high rates of $\sim 10^7\ \mathrm{K\,s^{-1}}$ and produces homogeneous glasses both for pure water and dilute solutions, called hyperquenched glassy water (HGW) or hyperquenched glassy solution (HGS) [28]. HGW is considered to be a form of LDA [52], which upon heating transforms into low-density liquid water (LDL) at its glass-transition temperature $T_{g,1} \approx 136$ K [15,29,31]. Just above $T_{g,1}$ also the onset of the cold crystallization $T_x \approx 150$ K is observed, resulting in stacking disordered ice I (I_{sd}) [53]. A similar behavior is found not only for pure HGW but also for dilute hyperquenched LiCl solutions [28], reflecting their low-density nature. For rates just a tiny bit lower than $\sim 10^7\ \mathrm{K\,s^{-1}}$ pure water still crystallizes upon cooling [26], and dilute solutions do not crystallize but experience phase separation into a water-rich and a salt-rich glassy state as pointed out by Suzuki [35].

The solutions for this study were made by dissolving water-free LiCl in Milli-Q water. The hyperquenching of all samples was carried out using the setup described by Kohl *et al.* [26]. Since our procedure is identical to theirs, we will only explain it briefly: The solutions were nebulized using an ultrasonic nebulizer operating at 3 MHz (LKB Instruments model 108) and producing droplets with a mean diameter of ∼3 µm. Using dry gaseous nitrogen as a carrier gas, the aerosol was transferred to a high-vacuum chamber via a 300-µm orifice. The aerosol develops supersonic speeds and impacts on a cooled copper substrate held at about 80 K. After 30 min of deposition time, the deposition was stopped and the substrate along with the sample was removed from the apparatus. Immediately after that, it was submerged in liquid nitrogen. To make sure that the approximately 1–2-mm-thick samples were amorphous, they were checked using calorimetry [31].

B. Increasing water's polyamorphic temperature T_{poly} by high-pressure annealing

To observe an LLT according to Fig. 1, we also have to increase T_{Poly} as much as possible. For pure water HDA, this is usually achieved by high-pressure annealing, i.e., heating at elevated pressures. This procedure shifts the polyamorphic transition to higher temperatures [54], where we showed in our recent study [21] that $T_{\text{Poly}} \sim 141$ K can be reached when employing an optimized annealing protocol. This represents the highest temperature reached in literature so far, where the polyamorphic transition was observed in pioneering work as low as 105 K [7,16], deep in the glassy domain, far from the supercooled liquid domain.

Our recent study [22] shows that water's second glass transition is hardly affected by small amounts of LiCl. In pure water, this glass transition pertains to pressure-annealed HDA (also called expanded HDA, or eHDA) and is observed about 20 K below the onset temperature of the polyamorphic transition to LDA (T_{Poly}). The corresponding glass transition temperature is labeled $T_{g,2}$ and was determined to be 116 K at ambient pressure [13,16,21].

We here use a recently developed technique that allows to prepare high-density glasses of solutions with arbitrarily small molar fractions (e.g., $x_{\text{LiCl}} = 0.005$) [22]. This is not possible with most other techniques. The reason is that direct vitrification of such solutions under pressure, also known as pressure vitrification, is experimentally very hard to achieve [55]. Again, very dilute solutions (<3.2 mol %) tend to crystallize and are not easily accessible even when using emulsification [36]. When pressure-induced amorphization is chosen instead, phase separations due to freeze concentration occur during the preparation procedure [23,50]. Our technique is based on driving the hyperquenched glassy solution from low density to high density through compression at 77 K. Since a wide variety of solutions can be vitrified via hyperquenching with different solutes even in small concentrations, this method allows to prepare glassy high-density solutions in almost any composition without phase separations [22]. This way it is possible to make high-density glasses from hyperquenched LiCl solutions, avoiding the above-mentioned procedures afflicted with phase segregation and crystallization.

Using the hyperquenching procedure followed by pressurization, we prepare dilute, homogenous high-density LiCl-H_2O glasses of compositions between 0.5 and 5.8 mol %. By employing pressure annealing we thermally stabilize the high-density glasses.

The preparation of the densified samples in this work follows the optimal procedure described in our recent work [21]. First, ∼100 mg of hyperquenched sample were scratched from the copper substrate and transferred into an indium container with a diameter of ∼7 mm. This container was placed in a piston-cylinder setup while being immersed in liquid nitrogen. At 77 K, a uniaxial force was applied using a material testing machine (Zwick Roell, model BZ100/TL3S) with a rate of 40 $\mathrm{MPa\,min^{-1}}$ until a pressure of 1.9 GPa was reached. This was followed by isobaric heating to 175 K with a rate of 5 $\mathrm{K\,min^{-1}}$ and subsequent recooling to 140 K. At this temperature, the decompression was carried out at a rate of 40 $\mathrm{MPa\,min^{-1}}$ until a pressure of 0.8 GPa was reached. From there on, the decompression rate was decreased to 20 $\mathrm{MPa\,min^{-1}}$. After reaching a pressure of 0.15 GPa, the densified hyperquenched sample was quenched to 77 K and recovered to ambient pressure. This procedure results in the most relaxed form of high-density amorphous ice (eHDA) and similarly in the most relaxed form of high-density amorphous LiCl solution.

C. Characterization using differential scanning calorimetry

Finally, these pressure-annealed high-density (HD) samples were analyzed *ex situ* at ambient pressure using calorimetry. A differential scanning calorimeter (DSC 8000, PerkinElmer), calibrated with indium, adamantane, and cyclopentane for heating and cooling at 10 and 30 $\mathrm{K\,min^{-1}}$ was used. Under liquid nitrogen, about 10 mg sample were taken out of the indium container and placed in an aluminum crucible that was subsequently loaded into the instrument at 93 K. The rate was either 20 or 40 $\mathrm{K\,min^{-1}}$ on heating and 30 $\mathrm{K\,min^{-1}}$ on cooling. For the first heating scan, each sample was heated to 143 K and the data were checked for the exotherm related to the polyamorphic transition to confirm the formation of the low-density (LD) state. Then, the sample was annealed at 128 K for 30 min and cooled to 93 K. To analyze the thermal behavior of the $\mathrm{LD_S}$, it was heated to room temperature. As a reference, the sample was cooled back to 93 K and reheated to room temperature again. Due to the rapid evaporation of liquid nitrogen, determining the sample mass by weighing it is not possible. To determine the sample mass inside the crucible, the enthalpy of melting during the second heating scan was compared with data provided by Monnin *et al.* [25] for LiCl-H_2O.

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J.B. and T.L. designed the study. J.G. prepared the samples with help from J.B. and characterized them using calorimetry. J.G. analyzed the data and calculated viscosities. J.G. and T.L. wrote the manuscript with input from J.B.

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