Relation between the High Density Phase and the Very-High Density Phase of Amorphous Solid Water

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It has been suggested that high-density amorphous (HDA) ice is a structurally arrested form of high-density liquid (HDL) water, while low-density amorphous ice is a structurally arrested form of low-density liquid (LDL) water. Recent experiments and simulations have been interpreted to support the possibility of a second distinct high-density structural state, named very high-density amorphous (VHDA) ice, questioning the LDL-HDL hypothesis. We test this interpretation using extensive computer simulations and find that VHDA is a more stable form of HDA and that, in fact, VHDA should be considered as the amorphous ice of the quenched HDL.

The most common form of water in the Universe is not a liquid but is a disordered solid named glassy water [1]. Depending on the glass formation route—vapor deposition, hyperquenching of the liquid, pressure (P) induced crystal amorphization—water forms amorphous solids of quite different structures, with the density ρ varying by as much as 40% between the lowest and the highest density forms [2]. The structural and thermodynamical properties of the different amorphous forms of glassy water have been the focus of many recent experimental [3–10], numerical, and theoretical studies [11–13]. However, a clear picture of the phase diagram of glassy water is still missing. This is in part because the properties of glasses change drastically with aging [7,10] and because experiments at high P are difficult to perform. Glassy water can be found in at least two different forms, low-density amorphous (LDA) and high-density amorphous (HDA) ice [14,15]. If a glass is formed by extremely rapid cooling of a liquid, then one can naturally associate the glass with the liquid state. LDA can be obtained experimentally by very fast quenching of low-density liquid (LDL) water at normal P [16]. However, the generation of an HDA glass via high P cooling of the liquid has proved an elusive goal [17]; in fact, HDA is experimentally formed not by quenching but rather by compressing either LDA or crystalline ice [15]. Therefore, the actual relationship of glassy water to the liquid at high P remains unknown. On the other side, computer simulations [18,19] indicate that HDA is a structurally arrested form of high-density liquid (HDL) water, and, therefore, HDA can be obtained by quenching HDL at high P. A second "distinct" high-density structural state, named very high-density amorphous (VHDA) ice has recently been discovered. The ρ of VHDA is 7%–8% higher than the ρ of HDA. VHDA is generated by heating HDA under P. The resulting glass does not convert back to HDA when recovered at ambient P at $T = 77$ K. The possibility of a VHDA

phase in addition to an HDA phase raises many interesting questions [20], such as the relation between VHDA and HDA; this relation is important to elucidate the hypothesis that below a critical T there are two distinct phases of liquid water, LDL and HDL [18]. Which phase, HDA or VHDA, that more closely resembles liquid water at high P is particularly interesting, and it appears that the structural properties of VHDA are closer to liquid water at high P than those of HDA [4,11]. On the other side, the presence of two different high-ρ amorphous ices could imply the existence of more than one form of HDL, as was recently suggested by computer simulations [21].

Computer simulations offer a potentially useful tool to probe the relation among HDA, VHDA, and liquid water, since the time scale of most simulations is sufficiently short that liquid and glassy states can be studied for a wider range of state points than is accessible experimentally. Here we report a set of extensive simulations that suggest that VHDA, not HDA, may be considered as a physical manifestation of the quenched high P liquid. Furthermore, our simulations suggest that VHDA is not a new thermodynamically distinct structure but rather that VHDA results from partial annealing of the HDA structures made possible by the higher annealing T. Hence HDA is not stable but rather is highly metastable, relaxing to VHDA in a fashion analogous to the way that, on slow heating, glasses generated with hyperquenched methods relax to glasses generated with standard cooling rates.

Simulations offer the unique possibility of comparing (i) the glass resulting from the conversion of HDA to VHDA with (ii) the glass generated by isobaric cooling of the liquid. However, a note of caution is in order, since in comparing experiments and simulations for glasses, one must carefully account for the significantly different time scales probed. State-of-the-art simulations probe time scales of 10–100 ns, so when the characteristic relaxation

time becomes comparable to this time, the system glassi-
fies. Since the experimental homogeneous nucleation time
is longer than 100 ns, glass configurations can be generated
in simulations by cooling the liquid both at low and at high
P. We shall exploit this fact in the present study.

We simulate a system of 216 molecules, using the simple
point charge extended (SPC/E) model of water. The long
time required to simulate the glass-glass transitions and the
need of averaging over independent samples restricts the
size of the simulated system to 216 molecules, a small
number with respect to present day simulations in the
liquid state, but consistent with the present day simulations
of "supercooled states." Moreover, size effects have been
stated to be negligible from 1728 down to 216 molecules
[18]. The SPC/E model has been studied extensively, and
the ρ and T dependence of structural and dynamic prop-
erties in equilibrium are known. In particular, the SPC/E
model reproduces the thermodynamic anomalies of
water—e.g., it produces a maximum in ρ [22]. At $\rho =
0.94$ g/cm^3 at low T, the model describes well the LDA
structure. We integrate the equation of motion using a time
step of 1 fs and implement the reaction field method to
account for long range forces. Results are averaged over 16
independent realizations. LDA ice configurations are gen-
erated by cooling to 77 K equilibrium liquid configurations
at $\rho = 0.90$ g/cm^3. We have chosen a glass obtained by
quenching a low-T liquid equilibrium configuration—i.e.,
properly speaking, a hyperquenched glassy water
(HGW)—at $\rho = 0.9$ g/cm^3 as the starting LDA structure
to guarantee that the chosen configuration is a low ρ glass
with an optimized tetrahedral network of hydrogen bonds.
We have also generated independent LDA configurations
by heating at $T \approx 160$ K and $P = 1$ atm HDA configura-
tions, and we have confirmed that the numerical realiza-
tions of the two resulting low ρ glasses are equivalent
within the precision of our calculations. To generate
HDA configurations, we compress LDA at $T = 77$ K to
$P > 1$ GPa at a rate of 5×10^{-5} g/cm^3/ps [13,23]. The
HDA to VHDA transition is studied by heating HDA at
constant P from $T = 77$ K using a heating rate of 30 K/ns.
We use the same heating (cooling) and compression rates
in all our calculations unless they are explicitly indicated.

Figure 1 compares, for a high P isobar, available experi-
mental data [Fig. 1(a)] and simulation results [Fig. 1(b)]. In
Fig. 1(a), $\rho(T)$ for equilibrium liquid water is comple-
mented with the $\rho(T)$ data of Ref. [3] obtained by heating
HDA from 77 K up to 165 K, and then cooling back to
77 K. VHDA is the glass that results from densification of
HDA during heating under high P. VHDA can be cycled, at
constant P, between 77 and 165 K without significant
further ρ changes, leading us to hypothesize that VHDA
is the more stable form of HDA. This hypothesis was
proposed by Mishima who observed that HDA samples
(made by various P-T conditions) heated or annealed to
130–150 K at 1–1.5 GPa were characterized by identical
x-ray patterns [24]. Relaxation of HDA to VHDA and the
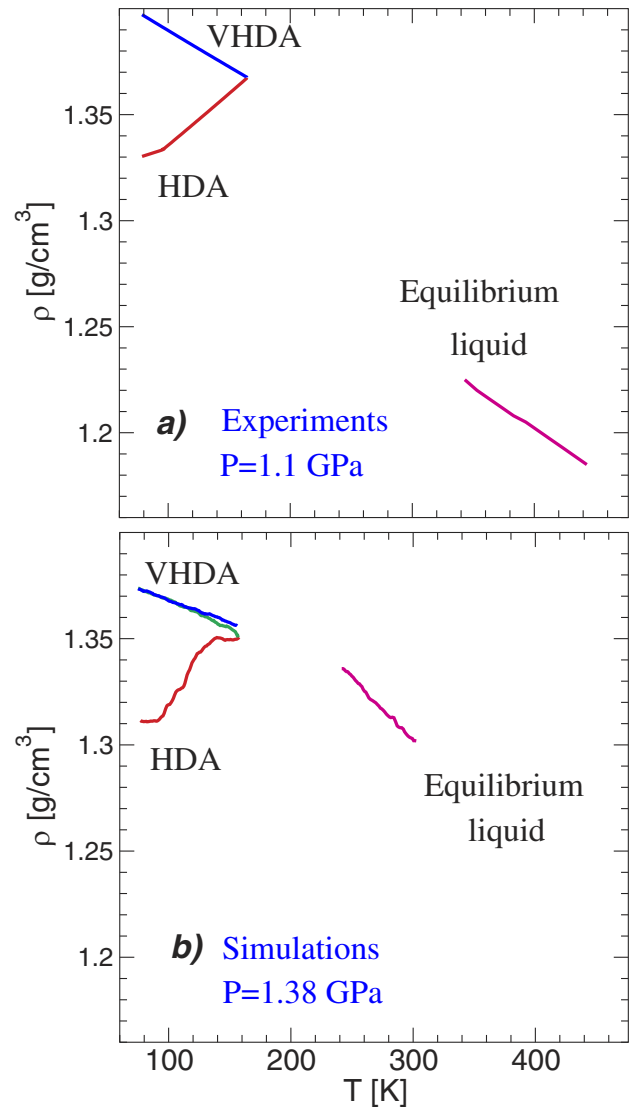irreversibility of such a transformation upon further T

FIG. 1 (color online).   (a) Experimental data (from Ref. [3])
and (b) simulation results for $\rho(T)$ during the conversion of HDA
to VHDA at high P [28] (red line) and for the cycling of VHDA
between 165 and 77 K (green and blue lines). The equilibrium ρ
data in the liquid state (magenta line) from the Haar-Gallagher-
Kell equation of state [29] and for the SPC/E potential are also
shown. Numerical results for different P values are qualitatively
similar to the results shown in the figure for $P = 1.38$ GPa. The
ρ difference between HDA and VHDA decreases on increasing
P. We also find that the ρ dependence of the VHDA recovered at
$T = 77$ K and ambient P varies between 1.22 and 1.28 g/cm^3.

cycling are facts reminiscent of slow heating of hyper-
quenched glasses, so the conversion of HDA to VHDA
can be interpreted as a T-driven partial equilibration of the
sample.

In simulations, HDA is generated—in analogy with the
experimental procedure—by compressing LDA or ice I_h at
77 K [25], while LDA is generated by the cooling of the
liquid at ambient P. Figure 1(b) shows ρ as HDA is heated.
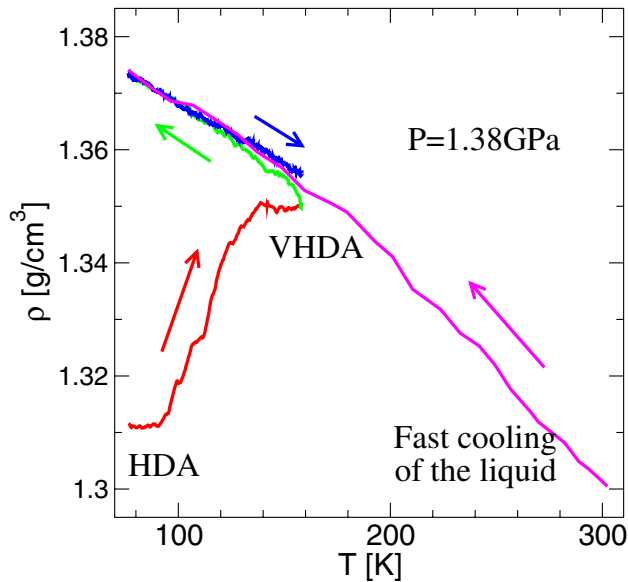At about 100 K, ρ begins to increase, reaching at about

FIG. 2 (color online). Comparison between the $\rho(T)$ of VHDA [from Fig. 1(b)] and $\rho(T)$ during continuous cooling of the liquid to 77 K, at a quenching rate of -10^4 K/ns.
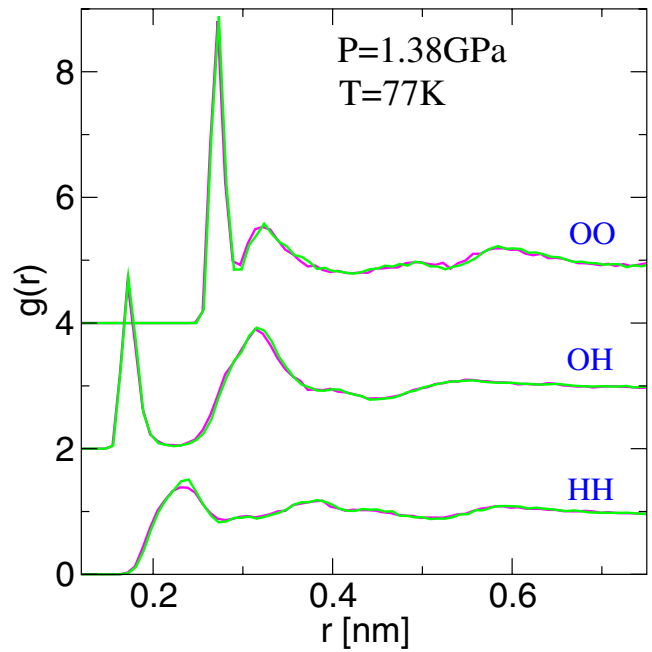

FIG. 3 (color online). Comparison between the structural properties of VHDA (green lines) and the glass obtained by cooling the liquid under P calculated at $T = 77$ K and $P = 1.38$ GPa (magenta lines). Oxygen-oxygen, oxygen-hydrogen, and hydrogen-hydrogen radial distribution functions are shown. Despite the extremely different previous histories, the VHDA structure appears identical to the structure of the liquid cooled under P.

140 K a value 0.04 g/cm^3 larger than the ρ of HDA at 77 K. Decreasing T back to 77 K does not regenerate the ρ of HDA, but instead ρ increases, in agreement with experimental results. The resulting denser material—which we identify with VHDA [26]—can be cycled back and forth without significant changes in ρ.

Next we test the hypothesis that VHDA is the glass that would be generated by cooling the high P liquid. To this end, Fig. 2 compares ρ for isobaric fast cooling of the liquid with ρ for VHDA, two systems generated by *completely different thermal and P histories*. The ρ data display remarkable similarity, supporting the possibility that VHDA is, indeed, the physical realization of the glass generated by fast quenching the liquid. To further support this interpretation, Fig. 3 shows that the radial distribution functions of VHDA and of the glass obtained by isobaric cooling of the liquid are, indeed, indistinguishable. We note that a smaller *heating rate q_h* in the HDA → VHDA transformation generates a denser glass at the final $T = 165$ K. This resulting glass can again be put in a one-to-one correspondence with a cooled liquid by decreasing the cooling rate in the liquid to the VHDA transformation [27].

The results presented in Figs. 2 and 3 indicate that compression of LDA at 77 K generates a system that is kinetically trapped due to the low T. This system relaxes to the more stable VHDA, whose structure is identical to the glass generated by quenching the high P supercooled liquid. In this respect, not HDA and LDA but rather VHDA and LDA should be thought of as the two distinct glassy states arising from the two distinct liquids associated with the hypothesized line of liquid-liquid phase transitions.

If, indeed, HDA is a partially equilibrated glass generated by the compression technique, then one expects that VHDA should not convert to HDA under any transformation which does not involve a different "intermediate" phase (such as LDA or a crystal phase). To confirm this expectation, we recover VHDA at $T = 77$ K and ambient P with $\rho = 1.26$ g/cm^3. Next we isochorically heat this system to 155 K (Fig. 4). We compare the structure of the resulting system with the structure of the VHDA glass recovered at the same ρ at $T = 155$ K. We find that the two glasses, which are generated from two completely different histories, are identical both thermodynamically [Fig. 4(a)] and structurally [Fig. 4(b)], and further we find that no VHDA to HDA transition takes place along the loop. Our conclusion motivates the need for a definitive experimental test that no VHDA → HDA transition occurs. When VHDA is heated isochorically from 77 to 140 K, from a starting P of 0.02 GPa, the width of the x-ray pattern remains narrow like VHDA [8] (and hence does not appear to revert to HDA); however, the position of its first maximum shifts (about 2°) in the direction of HDA (cf. Figs. 1A′, 1B′, and 1D′ of Ref. [3]).

In summary, our simulations support the possibility that (i) VHDA is not a new form of glassy water, but it is the result of annealing HDA upon heating at high P; (ii) VHDA is the glass obtained by fast quenching of high P water, i.e., HDL.
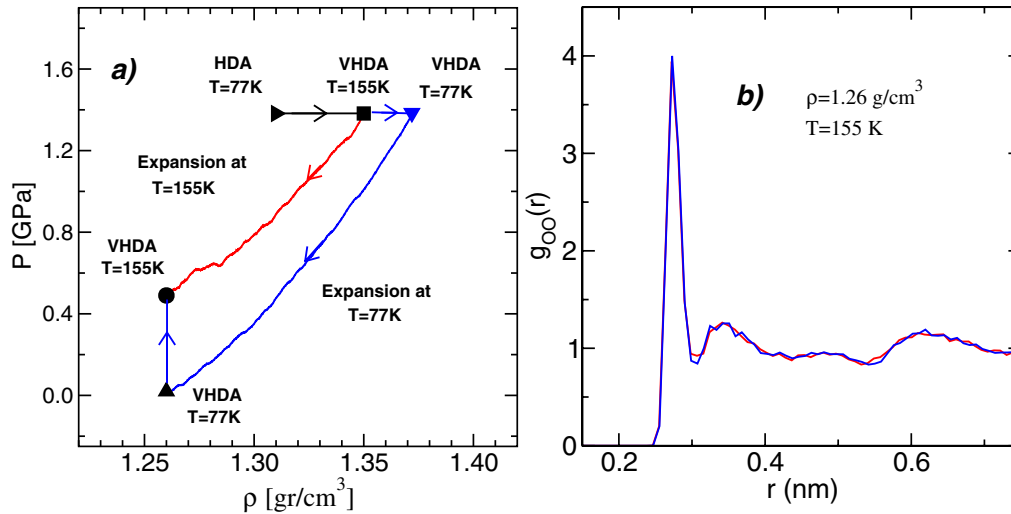
FIG. 4 (color online).   Demonstration that at $T = 155$ K and $\rho = 1.26$ g/cm^3 two glasses, each with completely different histories (red and blue curves), are identical both (a) thermodynamically and (b) structurally. (a) P-ρ diagram. Blue curve: Recovering of the VHDA at ambient P at $T = 77$ K followed by an isochoric heating at density 1.26 g/cm^3 up to $T = 155$ K. Red curve: Isothermal decompression of VHDA at $T = 155$ K to density 1.26 g/cm^3. The final product is independent of the path despite the different histories. The important point is that no transformation from VHDA to HDA is observed. (b) Comparison between the radial distribution function of the two glasses obtained following the blue and the red paths in 4(a).

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