Observations on the nucleation of ice VII in compressed water

Samuel J. P. Stafford, David J. Chapman, Simon N. Bland, and Daniel E. Eakins

Citation: AIP Conference Proceedings **1793**, 130005 (2017); doi: 10.1063/1.4971716
View online: https://doi.org/10.1063/1.4971716
View Table of Contents: http://aip.scitation.org/toc/apc/1793/1
Published by the American Institute of Physics

Articles you may be interested in

Free energy models for ice VII and liquid water derived from pressure, entropy, and heat capacity relations
The Journal of Chemical Physics **147**, 084505 (2017); 10.1063/1.4989582

Onset of ice VII phase during ps laser pulse propagation through liquid water
AIP Conference Proceedings **1793**, 090001 (2017); 10.1063/1.4971620

Nanosecond freezing of water under multiple shock wave compression: Continuum modeling and wave profile measurements
The Journal of Chemical Physics **123**, 064702 (2005); 10.1063/1.1993556

Nanosecond freezing of water under multiple shock wave compression: Optical transmission and imaging measurements
The Journal of Chemical Physics **121**, 9050 (2004); 10.1063/1.1805499

A time-dependent Ginzburg-Landau phase field formalism for shock-induced phase transitions
AIP Conference Proceedings **1793**, 130003 (2017); 10.1063/1.4971714

Experimental investigation of the shock response of bismuth under one-dimensional shock-loading
AIP Conference Proceedings **1793**, 130001 (2017); 10.1063/1.4971712

Observations on the Nucleation of Ice VII in Compressed Water

Samuel J.P. Stafford[a)], David J. Chapman, Simon N. Bland and Daniel E. Eakins

Institute of Shock Physics, Blackett Laboratory, Imperial College London, SW7 2BW, UK

[a)]Samuel.Stafford09@imperial.ac.uk

Abstract. Water can freeze upon multiple shock compression, but the window material determines the pressure of the phase transition. Several plate impact experiments were conducted with liquid targets on a single-stage gas gun, diagnosed simultaneously using photonic doppler velocimetry (PDV) and high speed imaging through the water. The experiments investigated why silica windows instigate freezing above 2.5 GPa whilst sapphire windows do not until 7 GPa. We find that the nucleation of ice occurs on the surfaces of windows and can be affected by the surface coating suggesting the surface energy of fused silica, likely due to hydroxyl groups, encourages nucleation of ice VII crystallites. Aluminium coatings prevent nucleation and sapphire surfaces do not nucleate until approximately 6.5 GPa. This is believed to be the threshold pressure for the homogeneous nucleation of water.

INTRODUCTION

The principal shock Hugoniot of water lies close to phase boundary of solid ice VII. Between 2.2–8 GPa the Hugoniot approaches the phase but does not pass the boundary [1]. Due to the relatively high compressibility of water, the isentrope deviates measurably from the Hugoniot in this regime, crossing the ice VII phase boundary [1]. Experimentally compressing with no change in entropy is unrealistic, but quasi-isentropic compression is possible using a ring-up target geometry. Using this method water compressed above 2.2 GPa has been shown to freeze. The phase change is accompanied by a small volume decrease and a scattering of incident light that results in a loss of optical transmission.

Ice VII can form above 2.2 GPa. In an experiment, after exceeding this pressure there is an incubation time before the crystallisation is detected. The phase change takes on the order of ~100 ns to complete. The surfaces of the water container appear to play a deciding role. Experiments with *z-cut* quartz and fused silica have shown reliable indications of freezing whilst *a-cut* sapphire show no signs until compressed past 7 GPa [2]. Our experiments investigated what can cause the silica to promote ice VII and why this is absent from sapphire.

METHOD

Several experiments were conducted at the Imperial College plate impact facility using its 100 mm bore single stage gas gun. Experimental targets consisted of a thin layer of water, sealed between two windows (see Figure 1). With this 'ring-up' geometry a shockwave entering the water would reflect back and forth from the higher impedance windows. The reverberating shock meant the water accessed a lower temperature states than with a single shock to the same pressure. Each target had three liquid cells, sealed between the windows using a PTFE gasket. All three liquids saw an identical loading allowing for direct comparison of the PDV and image data.

The impactor was a 10 mm thick aluminium 6061-T6 flyer. To avoid early radial release it impinged on a 120 mm diameter front window 5–6.35 mm thick. The three rear windows were 10 mm thick x 25 mm diameter. Either Spectrosil® fused silica or *c-cut* sapphire windows were used. The water was diagnosed using frequency upshifted Photonic Doppler Velocimetry (PDV) probing the rear surface of the water cell. Non-upshifted PDV measured impact tilt, shock breakout and the flyer velocity.

A framing camera imaged one of three cell using a diffuse xenon flash lamp to illuminate through the water. In one experiment, as well as mirroring the impact surface of the imaged water cell, the rear window was coated with a

Shock Compression of Condensed Matter - 2015
AIP Conf. Proc. 1793, 130005-1–130005-5; doi: 10.1063/1.4971716
Published by AIP Publishing. 978-0-7354-1457-0/$30.00

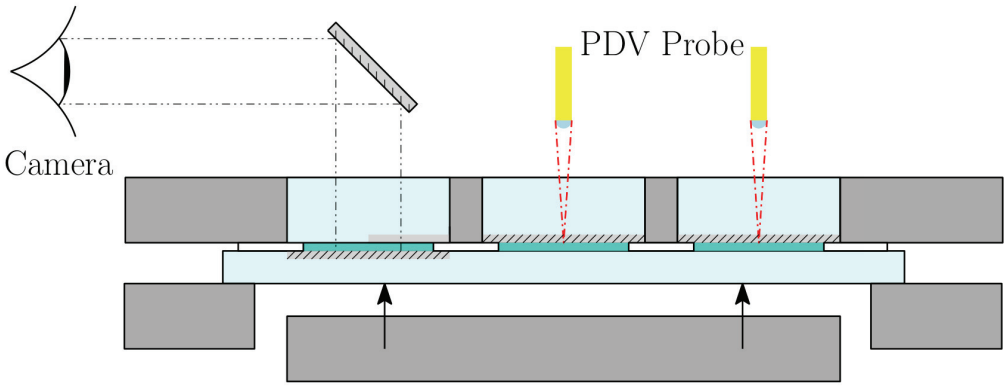

FIGURE 1. Representative drawing of the shot configuration, not to scale. The camera (left) imaged through the water (turquoise) to the impact surface. In one case, a thin translucent aluminium layer coated half of the imaging window (pictured as grey line). The other two cells used PDV reflected from the rear window. Liquid was sealed between two windows using a PTFE gasket (white) and secured onto an aluminium ring. The flyer impacts from below. In the actual experiment, all 3 cells were equidistant from the centre.

thin translucent aluminium layer across half of the face. The water in this half had no silica surfaces because of the aluminium coatings, but was still visible through the rear coating. The water in the other half was in contact with the silica window (see Figure 1).

RESULTS

To verify that freezing could be achieved, water was impacted between fused silica to a peak pressure of 3.9 GPa. The fused silica windows at this pressure have a nonlinear elastic soundspeed that spreads the shockwave into a ramp [3]. Figure 2a shows data from 250 μm of either ethanol or water. The ethanol was used as a control since it has no phase changes at this pressure range. The kinks in the incoming wave are from the first and third reflections of the reverberating ring-up. The two liquids are compressed at different times due to the lower compressibility of ethanol [4], but the peak state reached is the same for both liquids. The water shows a noticeable decline in velocity relative to the ethanol over several hundred nanoseconds, indicative of a small volume decrease and characteristic of a phase change to ice VII. Other experiments reversed the coatings, and exhibited markedly different PDV signals, confirming the observations are largely confined to the surfaces.

Images from an identically arranged experiment are shown in Figure 2b. The partial aluminium coating described earlier was present. The images show a loss of transmission, but with a marked difference between the surface coatings. The water at the silica surface (lower half) exhibits a rapid and even extinction, whilst the water at the aluminium surfaces displays a coarser structure and appears delayed relative to that at the silica. Despite appearances the two water regions lose transmission at a similar rate but are delayed. The aluminised surface is 10% reflective which reduces the dynamic range of the transmitted light in that hemicircle.

Figure 3 shows data from an experiment using *c-cut* sapphire windows approaching ~5.2 GPa peak pressure and still within the Ice VII regime. It did not show any comparable volume change, nor loss of transmission when imaged. A commercial SiO_2 coating was deposited onto the sapphire by reactive magnetron sputtering. This showed a perturbation which coincided with a brief loss of light to the PDV probe, which introduced artefacts. Because of the higher sound speed in sapphire a release wave can be seen converging. Figure 4 shows an experiment with sapphire windows impacted at 730 ms^{-1}. This did show a volume decrease upon reaching their third step corresponding to ~6.6 GPa in the water. The images taken during this time in Figure 4b do not show any obvious change in transmission.

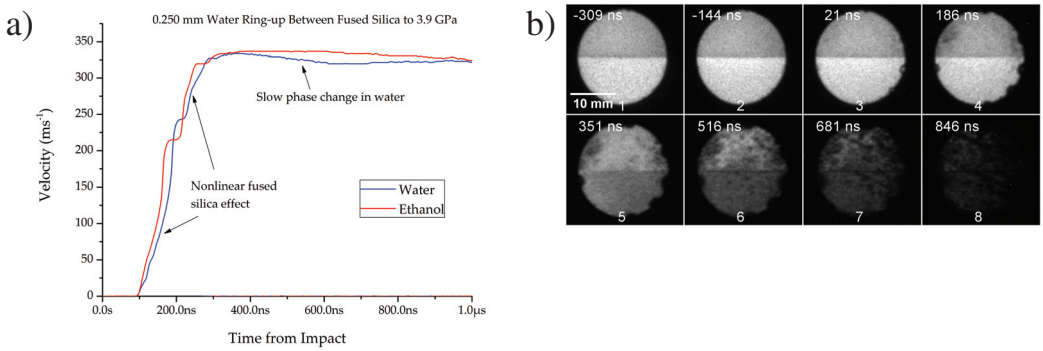

FIGURE 2. Shots using fused silica windows. Time is given from the shock entering the water, and all velocites have relevant window corrections and adjustments for tilt. **a)** PDV from two cells after impact at 588 ms^{-1}. After the ring-up has reached the peak 3.9 GPa the water velocity pulls back indicating the phase change whilst the ethanol control does not. **b)** Images from a similar 599 ms^{-1} impact taken through water reaching 4 GPa. 165 ns exposure and interframe. A sudden loss of transmission occurs from frame 5 onwards. The silica surface (bottom half) extinguishes sooner than the water behind the coating (upper half).

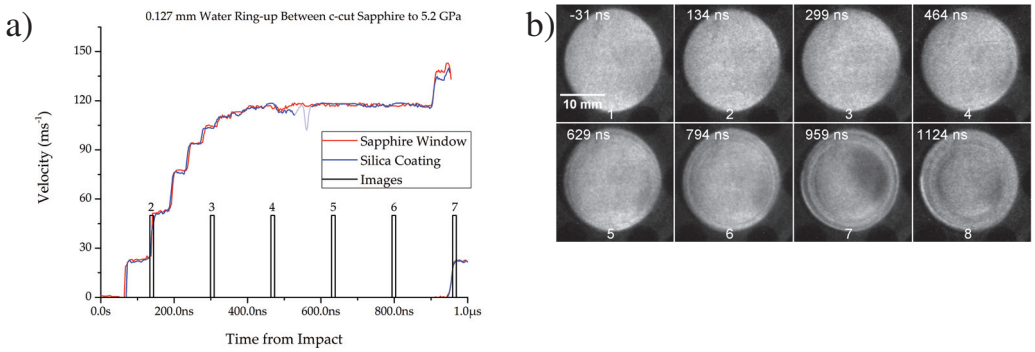

FIGURE 3. Shot data using sapphire windows. **a)** PDV from two sapphire cells containing water impacted at 449 ms^{-1}. One cell had a silica coating deposited on the sapphire window face. At peak velocity there is no obvious decline in either cell. The PDV probes suffered a loss of reflected light causing an artefact in the PDV analysis around 475–575 ns. The uncertain data have been faded. **b)** Images from a) looking through an uncoated sapphire window. 10 ns exposure and 165 ns interframe. No obvious loss of light occurs across the centre. Radial release can be seen converging from the edges and rear-surface release occurs in frame 7.

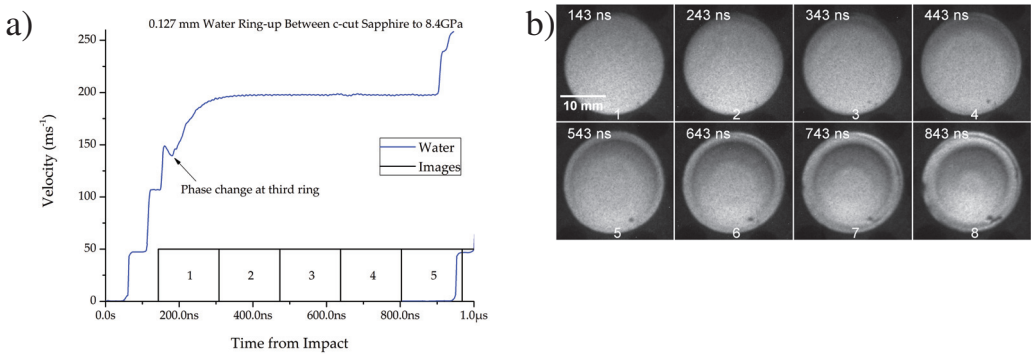

FIGURE 4. Shot data using sapphire windows impacted at 730 ms^{-1} to 8.4 GPa peak pressure. **a)** PDV from the water rear surface. At the third step, the water pulls back sharply indicative of a volume decrease from a phase change. **b)** Images from a). 100 ns exposure and interframe. No obvious loss of transmission can be seen, despite the phase change seen in a). Radial release appears more pronounced than in 3b) due to a longer exposure per frame and can be measured at approximately 11 kms^{-1}.

DISCUSSION

The fused silica data show clear signs of freezing at pressures around 4 GPa. Figure 2a shows the water undergoes a volume decrease over several hundreds of nanoseconds, consistent with previous work[1]. The images in Figure 2b show delayed a loss of transmission over these timescales. The effect of a thin coating of aluminium seems to extend the incubation period. This suggests the ice VII crystallites nucleate easily and more densely on the fused silica and hence have a shorter incubation time, but struggle to nucleate on the aluminium oxide layer. The coarse structures seen growing across the aluminium surface suggest ice VII does nucleate eventually, but given the thickness of the aluminium was approximately 12 nm and since then we have come to believe the coating was 'islanded' and that gaps existed onto the silica beneath.

The sapphire data show no clear signs of freezing at pressures around 5.2 GPa. The constant velocity indicates no volume change and images show no loss of transmission, and the sapphire surface is not sufficient to nucleate ice VII. The imaging includes a fully mirrored surface, so this result also confirms that aluminium mirrors are not capable of nucleation. This further suggests the observations of Figure 2b are the result of gaps in the coating. The suggestion from Figure 3a is that even with a silica coating applied to the window surface, no volume change was detected. This counter-intuitive result suggests merely the presence of silica is not enough for the nucleation, and that some additional surface chemistry occurs.

Surface hydroxyl groups play an important role in the adhesion of water to substrates by contributions to the surface energy. Silica surfaces often have silanol (Si-O-H) functional groups present which form strong hydrogen bonds with water [5]. They are also thought to promote ice-VII-like structures at pressure [6]. Our silica coating was a 92 nm thick layer, commercially deposited using reactive magnetron sputtering. The surface energy was not measured, but a lack of hydrogen during the deposition process may have prevented the formation of silanol groups in favour of siloxane (Si-O-Si), resulting in a different surface energy compared to bulk fused silica. We suggest that silanol groups are required in order to nucleate ice VII on silica. Similarly we suggest that the sapphire and aluminium coatings showed poor nucleation due to their aluminol (Al-O-H) hydroxyls not providing a sufficient surface energy in order to nucleate ice VII [7].

The sapphire data shows clear signs of a phase change at 6.6 GPa which corresponds approximately to the metastable limit [2] for water. Other similar experiments found this effect closer to 6.5 GPa. At this pressure it is believed the threshold for homogeneous nucleation is overcome and the water spontaneously freezes into ice VII. This would explain why velocity drop in 4a) is more sudden, as there is no incubation period and a higher density of nucleating sites. Freezing occurs at this pressure regardless of the sapphire, since the nuclei do not form crystallites on surfaces but throughout the water volume. However, there is no obvious loss of transmission in Figure 4b over the timescales seen in Figure 4a. This raises questions as to whether structures were formed during the phase change that do not scatter the light, or the scattering was simply not captured. Such homogeneous nucleation under pressure is qualitatively similar to a quench [8]. However, a vitrification should not result in a sharp volume change. It may potentially be forming very small, semi-amorphous polycrystals with properties of both ice VII and a glass. This is an aim for further work.

SUMMARY

In summary, experiments have quasi-isentropically compressed water samples between various window surfaces and coatings from 4–8.4 GPa. At lower pressures fused silica surfaces nucleate ice VII which grow out into the water. This is accompanied by a loss of optical transmission caused by scattering ice crystallites. Aluminium coatings showed no/delayed nucleation, suggesting a lack of nucleation sites. Sapphire windows showed no signs of a phase change at low pressures, supporting a theory that aluminium oxide surfaces are poorer nucleators of ice VII due to their surface energy. Future work could use a variety of coatings to verify this. Above 6.5 GPa a qualitatively different phase change was seen, believed to be the threshold of homogeneous nucleation. There was no observed loss of transmission in the water during this time raising questions as to the ice structures formed. Future work should use time-resolved spectroscopy to better discern the structure of this phase.

ACKNOWLEDGMENTS

The Institute of Shock Physics recognises the continued support of Imperial College London and AWE for the provision of funding for this work. The author would also like to thank the American Physical Society (APS) for awarding a travel scholarship that enabled this work to be presented, as well as Steve Johnson and Dave Pitman of the Imperial Physics Mechanical Instrumentation Workshop for the machining, and Dan Dolan and Tommy Ao of Sandia National Labs for useful discussions.

REFERENCES

[1] D. H. Dolan, J. N. Johnson, and Y. M. Gupta, The Journal of Chemical Physics **123**, 64702 (2005).
[2] D. H. Dolan, M. D. Knudson, C. Hall, and C. Deeney, Nature Physics **3**, 339 (2007).
[3] L. Barker and R. Hollenbach, Journal of Applied Physics **41**, 4208 (1970).
[4] P. A. Schulze, T. W. Ivanov, C. A. Bolme, K. E. Brown, S. D. McGrane, and D. S. Moore, Journal of Applied Physics **115**, 0 (2014).
[5] M. Sulpizi, M. Gaigeot, and M. Sprik, Journal of Chemical Theory and Computation **8**, 1037 (2012).
[6] J. Zhu, Z. Quan, Y.-S. Lin, Y.-B. Jiang, Z. Wang, J. Zhang, C. Jin, Y. Zhao, Z. Liu, C. J. Brinker, and H. Xu, Nano letters (2014).
[7] M.-P. Gaigeot, M. Sprik, and M. Sulpizi, Journal of Physics: Condensed Matter **24**, 124106 (2012).
[8] M. Bastea, S. Bastea, J. Reaugh, and D. Reisman, Physical Review B **75**, 1 (2007).