2pBAa2. High pressure phase transitions in the fluid region surrounding the collapse point of large single bubbles in water
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Observations from imaging experiments will be presented which have shown persistent, long-lived spherical objects to form in the fluid region surrounding large, single bubbles in highly over-pressured water. Objects have been observed to form in a region of fluid where pressures are first predicted to exceed 0.8 GPa, and to extend radially inward to where fluid pressures are predicted to reach 6 GPa. These pressures bound those requisite for transitions in water to the crystalline phases of Ice-VI and Ice-VII, at 1.1 GPa and 2.1 GPa, respectively. The objects have been observed to behave in a fashion more consistent with a highly viscous fluid. They support and recover from large shape deformations, as well as support fluid flows within them. While water does have phases which are known to exhibit properties of highly viscous fluids, they have only been observed to form at or near cryogenic temperatures, typically via hyperquenching or quasi-static pressurization at low temperatures. Here, we present evidence for a high pressure liquid-liquid phase transition in water surrounding collapsing bubbles at room temperature. [Work supported by Impulse Devices, Inc.]
HIGH PRESSURE PHASE TRANSITIONS IN THE FLUID REGION SURROUNDING THE COLLAPSE POINT OF LARGE SINGLE BUBBLES IN WATER

Bubble collapse phenomena have been studied extensively in recent years due to the extreme conditions of temperature and pressure reached inside, with simulations of some of the highest energy collapses predicting temperatures and pressures in excess of 100000K and 150GPa, respectively [1]. However, as Lord Rayleigh and the British admiral recognized a century ago [2], the pressure in the vicinity of a collapsing bubble can be predicted to reach upwards of 100GPa in a few tens to hundreds of nanoseconds. To that end, it has been speculated that some of the anomalous properties of the resultant sonoluminescence associated with these collapses may be explained a transient phase transition to a high pressure form of ice in the water surrounding the collapsing bubbles [3].

In this paper we present experimental results in support of a high pressure phase transition occurring in the fluid region surrounding the collapse point of large single bubbles in both H2O and D2O. Bubble’s in experiments were nucleated at the center of a high pressure spherical resonator (Impulse Devices, Inc.) using a pulsed Nd:YAg laser [4]. Water used in experiments was filtered to 0.2 microns and degassed by equilibration with air at 120 Torr. Experiments were carried out at room temperature and at ambient fluid pressures of 21 and 26 MPa. Collapse events were monitored using a high speed camera [SIMx8] with 8 CCD elements whose exposure and inter frame times were independently variable.

In a typical experiment, a small nucleus generated by optical breakdown [5] grows into a macroscopic bubble during the tensile phase of the pressure. Bubbles in experiments were measured to grow to a maximum radius of between 0.6 and 1.5 mm before collapsing, and were observed to reach supersonic velocities during the collapse’s final stages. As the pressures in the fluid region surrounding the collapsing bubbles grew, light was refracted away from the camera’s field of view, and a diffuse dark region in images was observed to form. Upon collapse, the high pressure region would travel away from the collapse point and later become the well studied shock wave emitted by a collapsing bubble [6]. As the high pressure region and associated dark region observed in images travelled away from the collapse point, concentric ring structures were revealed which surrounded the collapse point of the bubble and persisted in the fluid for an extended period of time.

Collapse events were typically observed to leave behind two concentric rings whose radii were linearly dependent on the bubble’s maximum radius. The outer ring is apparently the boundary of a spheroidal object, while the inner ring may be the outer boundary of a toroidal vortex, or the inner boundary of the spherical object’s ‘shell’. During collapse events, Rayleigh-Taylor jets were occasionally observed to form, pass through, and exit the spherical objects, resulting in the toroidal vortices within the spheroids as mentioned above. As the Rayleigh-Taylor jets emerged from within the spherical objects into the liquid, turbulent plumes were observed to form at the exit point. In addition, remnants of the Rayleigh-Taylor jets were observed to be ‘frozen’ within the objects boundaries along the path through which they travelled. The presence of these jet remnants, or lack thereof, had no appreciable effect on spheroid size with respect to the bubble maximum radius.

The behavior of these objects, and their interactions with the media around them, are suggestive of a phase transition in the liquid. The objects were observed to persist in the fluid for upwards of 70µs and were not observed to decay away radially, but were rather observed to be destroyed by subsequent bubble collapse events driven by the acoustics. The behavior of the Rayleigh- Taylor jets as they travel through and emerge from the spheroid’s boundary is also suggestive of a change in the fluid. The ‘frozen’ remnants of the jets in the spheroids, which appear as tubular structures travelling from the inner to the outer ring, indicate that as the jet travelled through the spheroid, diffuse motion of the fluid entrained in the jet was constrained by the material surrounding it. In addition, the development of a turbulent plume upon the jet’s emergence is suggestive of a change in transport properties across the boundary of the objects.

Spheroids that were not destroyed by subsequent bubble activity in their vicinity were observed to interact with the bubbles growing around them in another fashion. As bubbles grew in the vicinity of the spheroids, the spheroids were observed to deform in response to fluid forcing resulting from the bubble’s growth. These shape deformations were not observed to destroy the internal features of the spheroids but were instead observed to act on the structure as a whole. Moreover, as the bubbles responsible for deforming the spheroids collapsed, the spheroids were observed to regain their initial shape, which is indicative of a hydrodynamically reversible process typically associated with fluids of different viscosities interacting with one another [7].

The behavior of these objects is suggestive of a phase transition occurring in the liquid, associated with the increase in fluid pressure around the bubble as it collapses. Using the Rayleigh equation [2], the fluid pressure at the location of the rings can be calculated. If we assume that the phase transition is pressure dependent, it follows that a phase transition would begin occurring where the pressure in the fluid first crossed the transition threshold.
Applying this constraint, and plugging in known values of the bubble maximum radius, fluid ambient pressure, and the radius of the rings from experiments, we find that the outer ring of the spheroid forms where the pressure first crosses 0.8 GPa and that the inner ring forms where the pressure first crosses 6 GPa, and that the location of this pressure threshold is linearly dependent on the bubble maximum radius.

While these two pressures do not exactly correspond with the known transition pressures in water, they do bound the transition pressures of the crystalline phase of Ice-VI and Ice-VII at 1.1 and 2.1 GPa, respectively [8]. However, if we assume that there is a time lag for the transition to occur [9], fluid pressure would continue to build both inward and outward as the bubble continued to collapse, expanding the transition region as it did so. As the transition occurred, inward fluid motion, and thereby continued pressurization within, would be arrested, ultimately bringing the transition to a halt as the pressure dipped below the threshold. A transition time lag would account for the growth of the transition region outwards, where pressures are predicted to be lower, as well as for the shell like structure of the spheroids observed.

However, the behavior of the objects is not indicative of a transition to a crystalline solid, but rather an amorphous or liquid state. Water has a number of known amorphous phases which possess characteristics of interest for this study. Particularly, the low-density amorphous (LDA) and very-high-density amorphous (vHDA) phases have been shown to exhibit properties of viscous liquids, with viscosities up to 15 orders of magnitude greater than water [10]. In addition, they have been observed to form at pressures between 0.2 and 1 GPa [11]. While the amorphous phases have a number of properties that would account for many of the observations of the spheroids’ behavior, they have not been observed to form above cryogenic temperatures [12],[13],[14].

In conclusion, we have presented evidence suggestive of a high pressure phase transition in the vicinity of large collapsing bubbles in H2O and D2O water. Objects were observed to persist in the fluid for extended periods of time and to withstand bombardment from subsequent interactions with bubbles around them. Pressure evidence alone would suggest a transition to a crystalline phase of water, however, the behavior of the objects and their interactions with their surroundings are not indicative of a transition to a crystalline solid phase. The spheroids seem to be able to support material flow through them and to recover from large shape deformations in a manner consistent with hydrodynamically reversible processes associated with liquids of different viscosities in contact with one another. While the temperatures at which the observed transition occurs are well above those reported previously for liquid-liquid transitions in water, evidence from these experiments is highly suggestive that this is what was observed. Further investigation is required to shed more light on these objects and to further explain the properties of the objects that lead to the behaviors observed.

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REFERENCES


