Experiments with Nano-Scaled Helium Bubbles in Water Subjected to Standing Acoustic Fields

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Abstract

Understanding the stability of gas filled bubbles dispersed in water, and the features that due to their presence must be taken into account in multiphase flow research, is amongst the most recent and relevant issue in a number of technological, physical and biological fields. Cavitation experiments were designed and conducted using one high-Q acoustic resonator that is able to oscillate at very well controlled conditions, allowing for the characterization of the effect that helium nanobubbles dispersed in water have on the cavitation activity. An increase in the inertial cavitation activity that correlates directly to the presence of the nanobubbles at the antinode was found. The results seem to indicate that the nanobubbles grow under tension to collapse under the compression phase. By other side, they behave as rigid entities under the influence of standing acoustic fields, moving away from the antinode region.

Keywords: nanobubbles, acoustic cavitation

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1. Introduction

Recent nanotechnological advances have established the existence of gas nanobubbles in water. They have also allowed the development of relatively simple methods for their production with diameters between 70 and 650 nm. Surprising evidences show that water nanobubbles are remarkably stable (Borkent et al., 2007; Agrawal et al., 2005). Theories are being proposed trying to explain why gas molecules in the nanobubbles do not dissolve (Brenner and Lohse, 2008; Weijs and Lohse, 2013) forced by large Laplace pressure in less than one second (Epstein and Plesset, 1950). Some proposed models seem to indicate that their stability relates to the fact that the surface of neutral water is negatively charged, pointing towards possible configurations of water molecules at the interface which are stable at nanoscale dimensions (Chaplin, 2009). This explanation conjecture that there exist certain geometric configurations of water molecules at the bubble interface such that a strong electrostatic barrier is formed in a monolayer molecular shell of extraordinary strength under compression (Prevenslik, 2014).

Nanobubbles in water can be generated attached to walls (i) at imperfections on hydrophobic surfaces in oxygen supersaturated water (Zhang et al., 2014), (ii) by controlled surface electrochemical reactions at the electrodes (Chen et al., 2014) or (iii) unattached by swirling complex turbulent whirls in ambient exposed water (Tsuge, 2014). Statistical production of unattached and stable nanobubbles by turbulent generators is very small. Only a marginal fraction of the produced bubbles have the proper (and unknown) molecular configuration and do not collapse, yielding typical concentrations of $\sim 10^8$ bubbles per milliliter. Unattached nanobubbles are found to behave as nanoparticles in suspension and seem to follow established rules expected for Brownian motion.

Bubbles are known cavitation nuclei in water, because they become active and cavitate when the region of the liquid where they are contained is subjected to a pressure above the cavitation threshold. Therefore, the larger the number of bubbles contained in a water sample, the more susceptible it is to produce cavitation events. It is important for a variety of applications to be able to predict the number of cavitation events that may occur in a water sample under certain conditions. For this reason several models are used to estimate the size and number of bubble nuclei found in a gas containing water sample. This fact is used to design experimental devices able to measure the size and concentration of microscale bubbles called *Cavitation Susceptibility*

Meters (Shen and Gowing, 1985). These models and devices are proved to work for bubble nuclei within the 2 to 200 μm diameter range (Ljunggren and Eriksson, 1997).

Cavitation initiates from nuclei because they are preferential points for the onset of liquid rupture due to the local reduction of the tensile strength of the liquid. Therefore, since the superstability of water nanobubbles can only be explained if surface tension effects are inhibited, cavitation experiments become relevant to help to elucidate their unexpected existence. Controlled cavitation experiments, where nanobubbles are subjected to acoustic fields, test their properties under both, tension and compression conditions. Experimental studies have been reported for surface-attached nanobubbles subjected to pressure pulses from shock waves able to generate drops down to $\approx -6\text{MPa}$, to find that they do not act as cavitation nuclei under such conditions. Here, we present experimental results on the effects that the presence of unattached helium nanobubbles suspended in water have on cavitation activity measured in a high Q acoustic chamber set to generate well characterized and controlled standing pressure waves at resonant conditions.

2. Experimental Methods

2.1 Nanobubble generator

Helium nanobubbles are produced using a AS-MK III generator providing supply of 99.995% helium and recirculating for one hour four liters of ultrapure distilled and deionized water with electrical resistivity of 20 $\text{M}\Omega\cdot\text{cm}$. Before recirculation the water was examined using a Nanoparticle Tracking Analyzer (NTA) LM10 from Malvern, finding zero content of particles or bubbles. After recirculation the nanobubbly water was let to settle for 24 hours and analyzed using the NTA, finding presence of nanobubbles with the size (diameter) distribution shown in Fig. 1, for a total concentration of $7\text{e}+08$ nanobubbles per milliliter.

As shown Fig. 1, the size distribution of nanobubbles shows preferential presence of bubbles with diameters of 110nm, 160nm, 220nm, 365nm, 459nm and 614nm.

No significant changes in the concentration and size distribution of the nanobubbly water was noticed after a one month storage.

2.2 High-Q resonator

The acoustic chamber shown in Fig.2 has been described in detail by Cancelos et al., (2010) and it consists of a PyrexTM glass cylinder wall with 94.5mm in outer diameter, 145.4mm in height and 2.5mm thickness. The glass cylinder is belted at middle height by a piezoelectric ring (PZT) polarized in the radial direction (C5400, Channel Industries, Santa Barbara, CA,USA, shown with a yellow plastic cover in Fig. 2). The PZT has 102mm in outside diameter, 30mm in height and 3mm thickness and was glued to the glass with epoxy StycastTM 1264 (Emerson & Cumming, Billerica, MA, USA). Anodized aluminum flanges at the top and bottom were fixed to the glass cylinder ends with Permatex Sensor Safe Blue RTV Silicone Gasket Maker.

When excited at the resonant frequency (i.e. the frequency of the first resonant mode) a standing acoustic field is generated, with a pressure antinode at its center and nodes at the glass walls and top and bottom aluminum flanges. The Q-factor is a dimensionless parameter used to characterize the quality of a resonant system and relates the power stored to the power dissipated. This acoustic chamber has a Q-factor of 134 which is considered a high value for these type of acoustic experimental set-ups (Cancelos et al., 2005). At the first resonant frequency the chamber generates an acoustic pressure of ~357 KPa in amplitude at its center, with a voltage of 37 Volts applied to the PZT. This pressure value was sufficient to stimulate spontaneous inertial cavitation events in highly degassed water. Cavitation events are typically classified as inertial or non-inertial. Non-inertial events relate to bubble dynamics dominated by pressure forces, however inertial cavitation relate to bubble dynamics dominated by inertial forces in the liquid (Leighton, 2007). Experimentally, inertial events can be distinguished from non-inertial ones because of their effects on the stability of the resonant system.

Two liters of distilled water were filtered (SIMS 6000, Millipore Billerica, MA USA) and placed in a 4 liter flask located at a height just above the chamber in order to later allow for easy filling of the chamber driven by gravity. The water in the flask was sealed and connected to a vacuum

pump above the free surface (8890, Welch, Niles, IL, USA) for 45 minutes while the liquid is magnetically stirred for degassing. The bottom of the flask was connected in a closed loop with the high-Q chamber which holds a vacuum pressure of ~ 13 Pa prior to filling. A valve was located in the close loop, and the chamber was filled by opening it. By following this procedure, it is guaranteed that the liquid filling the chamber was free from air bubbles with an air saturation of $\sim 1\%$ (Cancelos et.al 2010). Once the high-Q chamber was filled with water, the fluid was brought to atmospheric pressure by breaking the vacuum at the top of the filtering flask. A 0.76mm outer diameter capillary tube was introduced in the high-Q chamber through one opening located on the top flange and pushed in until the tip is midway between the top flange and the edge of the PZT ring. This capillary tube was connected to an adapter for 20ml syringes through a three way valve (HV3-3 valve, Hamilton Company, Reno, NV, USA). Care was taken to remove all air from the capillary tube before inserting it.

The PZT was powered using a wave generator (33220A, Agilent, Santa Clara, CA, USA) connected to an audio amplifier (SKP PW-210, SKP Pro Audio, Los Angeles, CA, USA). A 1-10 step-up transformer was made and connected between the audio amplifier and the PZT to match their impedances. The voltage and current on the PZT were measured using a DAQ (USB 3656, National Instruments, Austin, TX, USA) and an oscilloscope (54615B Agilent, Santa Clara CA, USA) with a GPIB interface (GPIB-USB-B _488.2, National Instruments, Austin, TX, USA) connected to a personal computer.

The GPIB interface allowed acquisition of the current and voltage measured on the oscilloscope. It was used to determine the response of the system by measuring the electrical admittance ($|Y| = I/V$) and phase angle (ϕ) between voltage and current as a function of frequency. The electrical conductance was calculated ($|Y|\cos(\phi)$) and the resonant frequency identified at the maximum conductance (Cancelos et.al. 2010) as shown in Fig. 3.

The voltage on the PZT was divided by 74 using high current resistors prior to connecting it to the DAQ. A LabView code was programmed to acquire voltage and current on the PZT.

Temperature changes caused by the cavitation events change the elastic properties of the liquid and therefore, the resonant frequency. In order to keep the system at resonant conditions the phase angle between voltage and current was monitored in the LabView program allowing for manual adjustment of the frequency to keep the phase constant. An increase of about 2 Hz was typically necessary for each degree Celsius increase in temperature. The cavitation events were detected as characteristic disturbances of the voltage using the DAQ at a sampling rate of 1.25MSamples/sec.

3. Results & Discussion

Several series of three experiments were conducted by preparing three 20ml syringes (i) containing degassed water, (ii) filled with non-degassed water and (iii) comprising He nanobubbly water prepared as detailed in section 2.1. The effects occurring by inserting the syringes contents through the capillary were reproduced in all the series of experiments.

Fig. 4, shows a typical set of results. Voltage signal at resonant conditions and slightly above the threshold for cavitation are shown 120 seconds before inserting the syringes contents.

Disturbances in the voltage signal correspond to cavitation events. The events can be inertial or non-inertial and can be easily distinguished in our system with detailed inspection of the disturbance. Under these initial conditions inertial events are detected at a rate of 1-3 events per minute, as seen during the initial 120 seconds of Fig.4A, B and C. Fig. 4.D shows a typical inertial event, it is associated with the nucleation, growth and violent collapse of a bubble and momentarily (~20ms) detunes the resonant condition of the chamber. By other side, Fig. 4.E shows the effect of non-inertial events on the voltage signal due to linear bubble oscillations.

In Fig.4C, the syringe containing 20 ml of degassed water is injected in 30 sec. The insertion is noticed by a little drop in the PZT voltage, corresponding to the increase in pressure generated during the insertion. The phase angle (not shown) increases indicating a small detuned from the resonant frequency while adding the fluid. After ~5 sec the system stabilizes and the PZT voltage returns to the steady value. It is obvious the expected absence of effect in the cavitating activity after the insertion.

In Fig.4B, 20ml of non-degassed water were injected after the steady conditions shown from 0 to 120 sec. The effect of pressure increase is noticed as it happens during the insertion of the degassed water. There are no relevant effects after ~100 sec, however later an increasing activity of non-inertial events is detected. Non inertial events are typical in poorly degassed water. These results show how the gas that was injected dissolved in the water dilutes and diffuses within the chamber in ~100 seconds and is responsible for the non-inertial activity, as it should be expected.

Fig.4A shows what occurs injecting 20ml of non-degassed water containing helium nanobubbles. The initial rate of 3 events per minute of inertial cavitation raises to 7 during the 30 sec injection time. During the 60 sec after the end of the insertion the inertial cavitation activity increases ten-fold up to 30 events. Then, the inertial activity decreases sharply to 5 events per second during the second minute after the injection, returning to the typical 1-3 inertial events per second rate two minutes after the injection. It is noticeable that the non-inertial activity raises ~2 minutes of insertion, as it happened in the case of Fig.4B, and as it should be expected since the injected nanobubbly water was not degassed.

By adding 20 ml of helium nanobubbly water (with a concentration of 7×10^8 bubbles per ml) by the forced jet through the capillary, a uniform concentration of $\sim 3.5 \times 10^5$ nanobubbles per milliliter should be expected by diffusion, if we ignore any motion driven by the acoustic field. If we link the 10-fold increment in cavitation activity with the presence of nanobubbles, the region around the antinode point containing ~30 nanobubbles would have a radius of 200 μ m, what is certainly realistic, considering the accurate design of the chamber and the regime of operation just above the cavitation threshold. However, if diffusion would be the only mechanism for transport of the nanobubbles, the increasing inertial activity would not stop after one minute. Even assuming that the inertial events correspond to growth of the nanobubbles under tension and their destruction during the collapse, surrounding nanobubbles would diffuse in the region replenishing the concentration from the bulk.

If it is considered that nanobubbles move driven by the acoustic field, a migration towards the antinode would be expected, as a supposed compressible entity (Doinikov, 1996). This effect added to diffusion makes the experimental finding presented here more paradoxical, since

nanobubbles should concentrate in the region around the antinode point. However, if the nanobubbles are assumed to be rigid, then the acoustic field would drive them away from the antinode dominating over diffusion transport (Aboobaker, 2005). These would be in agreement with the presented experimental findings.

Since, it is not yet established the reasons for the stability of water nanobubbles, it is here proposed, as the most reasonable explanation for the conducted experiments, that unattached water nanobubbles are indeed rigid under compression. But very likely, they do expand and grow under tension to get destroyed during the collapse.

4. Conclusions

Detailed experiments were designed and conducted to study the influence of He containing nanobubbles in water subjected to a standing acoustic field slightly above the threshold for inertial cavitation.

The experiments show a very direct correlation between the presence of nanobubbles and the occurrence of inertial cavitation events. The results also evidence that nanobubbles move away from the region around the antinode point. A behavior opposite to the expected for compressible elements, which can only be explained for rigid objects.

The experimental work herein reported, seems to indicate that unattached nanobubbles in water behave as rigid entities under compression, but readily expand under tension.

This investigation demonstrates that nanobubbles should be treated differently to traditional approaches used for solid-nanoparticles/liquid and gas/liquid systems in multiphase flow research. Although further work must be conducted to establish firm conclusions.

Acknowledgements

This work was partially supported by the US Nuclear Regulatory Commission (Grant No. 38-10-922), the Office of Naval Research (Grant No. N00014-14-1-0836) and US Department of Energy (Office of Science, Nuclear Physics Program, Grant #: DE-SC0006024) for financial support.

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FIGURE CAPTIONS

Fig. 1. Diameter distribution of helium nanobubbles in water generated as discussed in the text.

Fig. 2. Experimental high-Q resonator

Fig. 3. Electrical conductance and phase angle as a function of frequency measured in the high-Q resonator filled with degassed water. The electrical conductance maximum corresponds to the resonant frequency.

Fig. 4. Voltage on the PZT acquired at 1.25MSamples/sec. The vertical line at 120 seconds indicates the start of 20ml injection of: (A) non degassed water containing helium nanobubbles (B) non degassed water and (C) degassed water. (D) Shows in detail a typical voltage disturbance associated with an inertial cavitation event. (E) Detail of a characteristic voltage disturbance related to a non-inertial cavitation event.

Figure1 eps format

Figure1 in tif format

Figure2 jpg

Figure3 eps format

Figure3 in excel format

Figure3 in tif format

Figure4 eps format

Figure4 in tif format