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Stimulation of ice crystallisation with ultrasonic cavitation microscopic studies

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Abstract : While the capability of ultrasonic waves to stimulate crystallisation in various liquids has been known for over 70 years, controlled experiments on the crystallisation of water are almost unknown, as are reports on the direct visualisation of the processes involved. The difficulty of setting up the experiments has been the major factor in the failure to date to identify the mechanisms involved in the sonocrystallisation of water. This report describes the first direct observations of the influence of ultrasonic cavitation on the production of secondary nuclei of ice from dendritic crystals. It has been achieved using a novel microscope measurement stage that not only permits controlled heating and cooling of the specimen, but also its simultaneous excitation with alternating pressures in the ultrasonic frequency range. Three distinct new phenomena have been observed to date. Firstly, there is a tendency for cavitation bubbles to form at the grain boundaries between the (hexagonal) crystals in the ice. Secondly, there is a process whereby the bubbles appear to eat their way into the ice, melting it as they progress, and thirdly, the dendritic structures are fragmented, thus multiplying the number of crystal nuclei in solution (secondary crystallisation).

Keywords : Crystallisation, ice, ultrasonics, microscopy.

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1. Introduction

The phase diagram for ice that indicates the conditions under which ice may crystallize from pure water, is very unusual [1]. As the applied pressure increases up to about 2 kbar, the highest temperature at which freezing can occur steadily decreases (to about –20°C). Furthermore, depending upon the ambient conditions of temperature and pressure, eight different phases of ice are known, five of which may be crystallized directly from water. The birth (or 'nucleation') of an ice crystal starts with the production of a microscopic crystal nucleus. This process may occur in one of two ways : *primary* nucleation, in which crystal nuclei are formed in the liquid containing no pre-existing crystals, and *secondary* nucleation, which involves pre-existing crystals which either act as templates for the formation of new crystal nuclei, or which can be fragmented to increase the number of nucleation sites. The present work is concerned with processes occurring in relation to secondary nucleation.

The presence of an ultrasonic wave in a liquid creates regions where the local pressure is raised or lowered relative to the ambient pressure. It is not surprising therefore, that various reports over the last 70 years have indicated that the nucleation of solid crystals from liquids (varying from organic fluids to molten metals) is influenced by the presence of an ultrasonic wave [2,3]. While a range of effects has been reported for sonocrystallisation in different liquids, to date it appears that for pure water only the initiation of primary nucleation at lower supercooling values has been

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identified experimentally [4,5]. Secondary nucleation processes can be studied by examining the effect of an ultrasonic field on ice dendrites at a microscopic level, however experiments to examine the effect under controlled conditions and at a microscopic level has been difficult to achieve; to the authors' knowledge there has been no experimental work published before, in this area.

The first work in the field was that of Chalmers in 1964, 1965 [6,7], who proposed the original mechanisms which are most widely accepted for the sonocrystallisation of ice. Over the years, these have been debated in great detail [5–12]; however there have been no accepted conclusions, largely due to the experimental difficulties encountered. One of the complexities of the problem is that the main experimental reports in the field [4–6,11–16] give results obtained under conditions in which the ultrasound was generating cavitation in the water. No attempt appears to have been made to characterize the ultrasonic field, while only two of the latest reports [15,16] attempt to quantify the cavitation intensity. Indeed, the latter remains a contemporary problem [17]. Thus, it is still not clear whether or not sonocrystallisation can occur in a non-cavitating field. Independent of this question, the extent to which ultrasound may influence the nucleation of ice is also little understood.

The primary difficulty in these experimental investigations is that of observing them under controlled and reproducible conditions. In order to try and achieve this, a novel microscope stage has been designed and constructed which not only permits controlled heating and cooling in a liquid specimen, but also the simultaneous application of a controlled oscillating pressure at ultrasonic frequencies. Using this cell, the production of secondary nuclei has for the first time, been directly observed in the sonocrystallisation of ice from pure water, and forms the essence of the present report.

2. Experimental arrangement

The overall measurement arrangement is shown in Figure 1. The waveform generator excites the ultrasonic pressure in the measurement cell *via* an amplifier. The excitation and pressure sensed in the cell may be monitored on an oscilloscope. The microscope stage sits underneath the (light) microscope, its temperature being controlled and monitored by the Linkam pump and temperature measurement system. In addition to the binocular eyepiece on the microscope, events in the cell can be recorded using a video camera and viewed on a television screen or captured on a PC. During experiment, the operator must select the following : (i) the ultrasonic frequency and voltage to be applied to the actuator (which determine the applied pressure); (ii) the thermal conditions : the heating or cooling rate (°C/min), the temperature limit, and the hold time; and (iii) the image

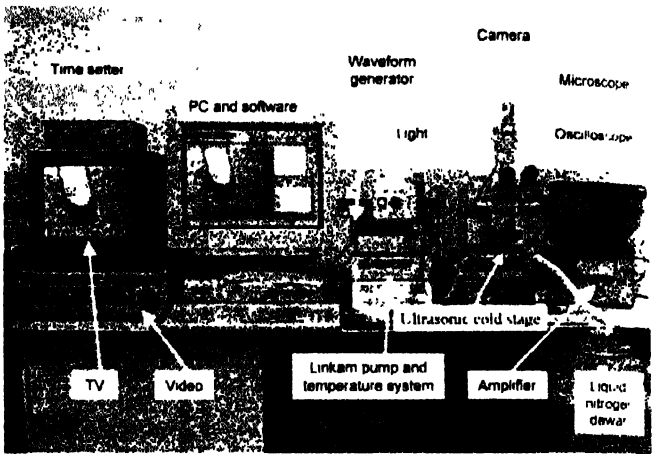

Figure 1. Overall experimental arrangement.

registration method: video or PC (instantaneous, time interval or temperature interval). The three elements of the measurement stage are outlined below.

2.1. Measurement cell :

A schematic cross section of the cell is shown in Figure 2. It is circular in shape and is incorporated into a purpose-built temperature-controlled microscope stage (see Section 2.2). The sample in the cell is subjected to an alternating pressure (in the frequency range 20 kHz to 200 kHz) applied by a ring shaped piezoelectric transducer. The pressure

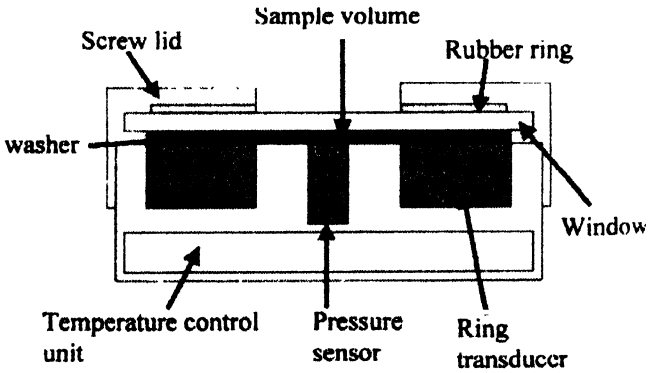

Figure 2. Schematic cross section of the measurement cell.

amplitude is controlled by the voltage applied to the actuator The upper surface of the actuator bears on a stainless steel washer which in turn, contacts (and vibrates) an optically transparent window. The optical window is held in place by a stainless steel ring and screwed lid. A rubber ring under the lid allows the sample volume (and thus the pressure) to be varied when the actuator is energized.

The sample is contained in a volume between the upper surface of the body of the cell and the lower surface of the optical window. The spacing of these is determined by the

thickness of the stainless steel washer. Laterally, the sample is bounded by the washer. The sample can be injected into or removed from the cell *via* the filling tubes incorporated into the body of the stage, and a syringe system.

In the centre of the base of the cell there is a piezoelectric sensor that can, in principle, be calibrated to determine the alternating pressure levels generated in the cell.

2.2. *Temperature control :*

Temperature control is achieved by constructing the body of a good conductor (copper), keeping dimensions as small as possible, and incorporating a labyrinth into the body to permit heating (with warm air) or cooling (with liquid nitrogen). The cell temperature is monitored (at a frequency up to thrice per second) using a platinum resistance thermometer with an accuracy of better than 0.1°C. The control system is a standard system (Linkam TMS 93) which is limited to the range from –50°C to 125°C. The heating/cooling rate can be varied from 0.1°C to 30°C per minute, and the holding time from 0 to 9999 minutes. Control may be automatic (*via* software on a PC) or manual.

2.3. *Observation and recording :*

Imaging is achieved using a video camera with a shutter speed of as little as 1/2000 sec to optimize the capture of fast moving events such as cavitation bubbles. The output from the camera can either be viewed on a television monitor (and recorded on video tape), or transferred by an S-video link to the PC. In addition to the display of a single image, a gallery of successive images (*e.g.* taken at preset temperature or time intervals) can be recorded in order to follow a particular phenomenon. The main limitation at present is that the images can be captured at only 25 frames per second on the videotape, and one frame per second on the PC.

3. Results

Initial results have shown that the ultrasonic cold stage can be used to demonstrate a number of phenomena which have hitherto not been reported. In all cases, double-distilled water (milliQ grade) with a specific conductivity of 18.2 megaohm (25°C) was used. The effects of ultrasound at 69.9 kHz and a driving voltage of 12 Vrms were recorded using the x10 microscope objective lens and video facility. The results presented are highly selected since it is difficult adequately to show a dynamic process in a few still images.

Figure 3 comprises four images. The sample of continuous ice was produced by supercooling the sample from room temperature to –20°C to produce a continuous ice phase. The sample was then heated rapidly to –0.2°C ± 0.1°C and held at this temperature for the experiment. At first, the hexagonal structure of the ice crystals without ultrasound is clearly seen (Figure 3a). One second after switching on the ultrasound, cavitation bubbles appeared at the 'grain' boundaries between the crystals (Figure 3b). Two seconds later, there were many more bubbles and some of them appeared to be eating their way into the crystals, melting the ice as they progressed (Figure 3c). This process appeared to be quite rapid as their progress a further half second later reveals (Figure 3d). The bubbles involved in this process appeared to be stable, at least over time scales of several seconds.

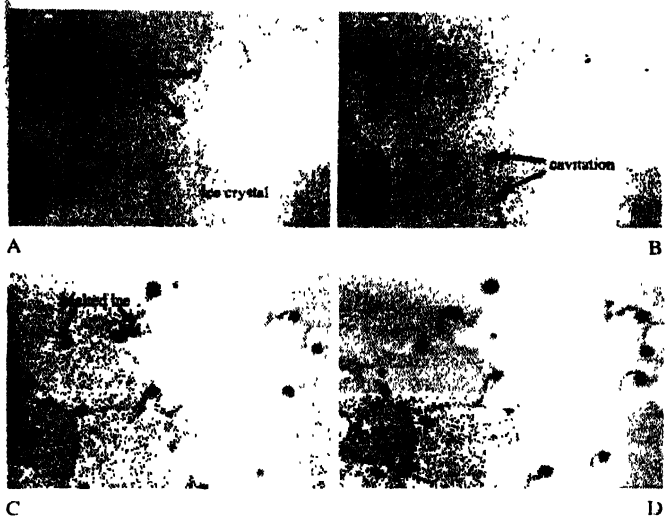

Figure 3. The effect of ultrasound on ice crystals : (a) hexagonal ice crystals before ultrasound, (b) ultrasound induced cavitation bubbles appearing at the crystal boundaries, (c) bubbles eating their way into the ice crystals, (d) further melting of the ice by the bubbles (half a second after (c)). Image width = 0.96 mm

Figure 4 shows a similar series of images related to dendritic ice crystals (Figure 4a) taken before the ultrasound was switched on). The continuous ice phase was produced as described above. In order to produce individual ice crystals, the temperature was held at the melting temperature until discrete ice crystals and a continuous liquid phase could be observed. At this point, the temperature was decreased (30°C per min) to –0.2°C ± 0.1°C. The rapid cooling rate increased the formation of surface instabilities around the spherical ice crystal and the growth of spindles of dendritic ice. When the ultrasound was applied, cavitation was immediately evident (Figure 4b). One tenth of a second later, a crack was seen to develop in a dendrite (Figure 4c), and a further tenth of a second later the tip of the dendrite detached itself from its root (Figure 4d). At this point, enhanced cavitation activity was seen including bubbles at the edges of the break. In subsequent images, two further processes were observed. The first was the rotation and

translation of the severed crystal (presumably under the influence of the streaming processes which must have been set up in the liquid), and the second was the melting of both severed crystal and stump by cavitation bubbles in the manner described in Figure 3.

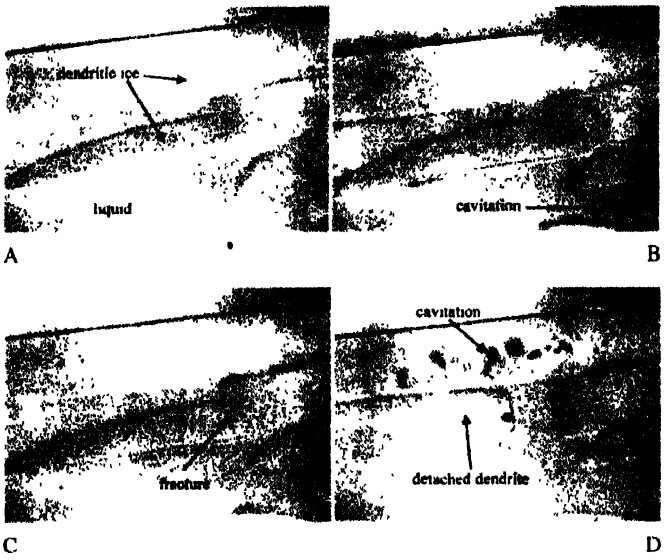

Figure 4. Secondary nucleation of ice crystals with ultrasound : (a) dendritic ice crystal, (b) application of the ultrasound stimulates the appearance of many cavitation bubbles, (c) crack appearing after application of ultrasound, (d) detachment of dendrite tip, with cavitation bubbles appearing on both the tip and the stump. Image width = 0.96 mm.

4. Conclusions

Using a novel measurement cell, it has been possible to obtain direct evidence for some of the mechanisms involved in the sonocrystallisation of water. The discovery of the process whereby a cavitation bubble (apparently stable) steadily melts its way into the ice (Figure 3) deserves more detailed analysis. It might be expected that the ice crystal boundaries would act as nucleating sites for cavitation, and the varying temperatures and pressures associated with the oscillation of a bubble in an ultrasonic field provide mechanisms whereby the melting could take place. However, analysis of the dynamics of the process could provide valuable insights.

Figure 4 provides the first reported evidence for the involvement of ultrasound in the production of secondary nuclei by the fragmentation of dendritic structures. Again, it may be expected that cavitation activity would focus on the boundaries of the ice, once they have been formed, but it is not clear from the results obtained so far, whether or not cavitation was directly involved in the initial fracture.

The cell, in its present or a modified form, should permit further quantitative investigation of the mechanisms by which the ultrasonic pressure in water and other liquids affects crystallisation processes. In particular, it should prove possible directly to investigate the question of whether cavitation is an essential element in the nucleation of ice or whether nucleation may occur at sub-cavitational intensities. Further aspects that invite attention, are the reproducibility of the ultrasonic field conditions and the calibration of the pressures used. In addition to studies on the crystallisation of water, it is anticipated that the cell should prove a valuable tool in the study of well known ultrasonic phenomena (often involving cavitation) such as : depolymerisation, degradation of chemical compounds, mineralisation, lysis of cells and bacteria, emulsification, and the synthesis of new materials.

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