Dynamic Nucleation of Ice Induced by a Single Stable Cavitation Bubble

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Abstract

Dynamic nucleation of ice induced by a cavitation bubble in undercooked water is observed using an acoustic levitation technique. The observation indicates that a high pressure pulse associated with a collapsing bubble is indeed responsible for the nucleation of a high pressure phase of ice. Both the non-luminescing and luminescing cavitation bubbles require the minimum undercooking, 5 K, to initiate the ice formation. This is attributed to the temperature rise due to the heat associated with compression ardor the undercooking required for normal ice to nucleate on the high pressure phase.

Circumstantial evidence for "dynamically induced nucleation" of a solid in an undercooled liquid exists in the form of observations which reveal the sudden onset of solidification coinciding with the imposition of mechanical disturbances such as stirring and ultrasonic irradiation onto the undercook liquid [1]. Although these disturbances generate both fluid flows and pressure waves, it is generally viewed as improbable that the spatial and temporal scales of the fluid flow fields would extend down to the levels of molecular or atomic solid embryos [2] relevant to nucleation dynamics [3]. On the other hand, thermodynamics shows that a high pressure pulse associated with the acoustic cavitation generated by the pressure waves can induce solidification in undercooked liquids [4,5]. In a cavitation event, a bubble that is expanded during the negative pressure cycle collapses violently in the positive pressure cycle and generates a high pressure pulse. The undercooked liquid exposed to this high pressure pulse experiences the melting point shift which is related to the pressure change by the Clausius-Clapeyron equation. If the melting point shift increases the undercooking level of the liquid, the nucleation rate of the solid nuclei also increases to a degree at which the onset of solidification may be observed within a short time period.

Until recent years, cavitation-induced nucleation studies involved the multiple transient cavitation bubbles generated at the vicinity of an immersed transducer in undercooked liquids. Due to multiple nucleation events associated with the transient cavitation bubbles, detailed observations of the individual nucleation induced by a bubble were very difficult, if not impossible. It was also difficult to evaluate the effect of the liquid/transducer interface on the cavitation bubbles. These difficulties can be circumvented now because of the discovery of a technique which can generate and maintain an isolated single stable cavitation bubble for an extended duration [6]. The technique involves levitation of a bubble in a host fluid by an ultrasonic field which also drives the bubble in a large amplitude volume oscillation mode. This technique has been used to greatly advance the study of the single bubble sonoluminescence observed in some liquids when the bubble is driven into large amplitude volume oscillation [7]. In this letter, we report an application of this technique to study the nucleation of ice induced by a single cavitation bubble in the undercooked water. For successful observations, it is essential to eliminate premature nucleation of ice originated from other nucleation sites such as the container wall. An effective way to improve the undercooking level of water is to reduce the volume. However, this cannot be realized using existing methods because the experimental parameter range within which the single stable cavitation bubble can be generated is very narrow, and happens to require a large amount of water. The amount of water used in the typical bubble oscillation studies is on the order of several hundred cm^3, which is very difficult to undercool more than a few degrees. We have, therefore, developed a novel technique which keeps water around the cavitation bubble, but replaces the majority of the acoustic propagation medium with a fluid mixture which remains in the liquid state below O ‘C. The water and mixture are physically separated by a thin wall.

Figure 1 shows the schematic diagram of the apparatus used in the present study. The levitation cell is filled with a fluid mixture in which a stationary acoustic wave is excited at around 21 kHz by the transducer. The mixture consists of water (75 % by volume) and ethylene glycol (anti-freeze fluid) (25 %), which remains in the liquid state down to -13 “C. The cavitation cell is made from a thin wall plastic tube closed at the bottom. The cavitation cell is filled with distilled water which has been passed through a 5 mm filter. Since the thin wall is essentially transparent to the acoustic wave, a bubble can be trapped inside of the tube without any disturbance from the wall. The cooling of the cells is accomplished by circulating chilled fluid through the copper tubing. The mixture temperature is monitored by a thermocouple placed close to the cavitation cell at the level of the bubble position. Both the mixture and water are well degassed before use in order to prevent undesirable cavitation. The behavior of the bubble is monitored and recorded with a video camera equipped with a telescopic lens.

The experimental procedure is as follows: First, the mixture is precooled to a predetermined temperature below O °C and maintained at this temperature. Next, the cavitation cell filled with water whose temperature is initially above O ‘C, is immersed into the mixture. The amount of the water is approximately 3 cm^3. Then, a bubble is immediately deployed in the water using a syringe with a hypodermic needle. A preliminary experimental run indicated that the water temperature was brought within 0.5 K of the mixture temperature in less than a few minutes. The power input to the transducer is adjusted to generate a desired bubble oscillation mode. The oscillation mode changes from shape oscillation to non-luminescing volume oscillation and then luminescing volume oscillation as the input power is increased [6]. Since nucleation is a kinetic process which may not occur within a certain time period, especially at small undercooking levels, the maximum monitoring duration is set at 30 minutes. After the observation of nucleation or the 30 minute duration, the cavitation cell is removed from the mixture and immersed in a warm water to bring the water temperature back above O "C. The procedure is then repeated for another observation.

The general observation of the bubble behavior is as follows: The bubble can be initially deployed either in the shape oscillation or the volume oscillation mode depending on the acoustic power input level. After the adjustment of the power level, the bubble is generally stable during the thermal transient stage where the water temperature approaches the mixture temperature. The time required for the onset of solidification varies widely for each observation, but the general trend is that the required time becomes shorter as the mixture temperature decreases. The onset of solidification starts with the sudden disappearance of the bubble followed by the appearance of ice in the dendritic form and the growth of the dendrite. A close examination of the onset with the recorded video images run frame by frame reveals that the bubble disappearance is due to ejection of the bubble from its stable oscillation position and subsequent shattering. For most of the cases, the ejection is strong enough to throw the bubble to the cavitation cell wall. Then, the ice immediately starts growing from the wall where the bubble hit and shattered. In several instances, however, the bubble remains near the stable oscillation position and ice starts growing at the same position. The observations are performed with the mixture temperature ranging between O "C and -12 "C to examine the bubble behavior at different undercooking levels. The oscillation mode of the bubble is set either to the non-luminescing or the luminescing mode. We have observed no apparent difference in the sequence of the ice formation between the non-luminescing and luminescing cavitation bubbles. The highest water temperature at which solidification is observed is -5 “C. The time interval between bubble ejection and the first appearance of ice becomes shorter as the temperature decreases. The growth rate of ice in the dendritic form increases as the temperature decreases.

Figure 2 shows an example of the onset of solidification which starts near the stable bubble oscillation position. The sequence is as follows: (a) The bubble is oscillating in the non-luminescing volume mode. The cyclic variation of the bubble radius is seen as a halo around the dark core due to back lighting. The radius at maximum bubble expansion is approximately 45 μm. The inserted image at the bottom corner is for a better visualization of the cavitation bubble. (b) The bubble seems to be distorted judging from the non-spherical halo. (c) The bubble is ejected from the original stable bubble position and moved toward the six o’clock direction. (d) The bubble completely disappears. It is presumed to be shattered. (e) The ice in the dendritic form appears. (f) The dendrite grows at approximately 0.4 cm/sec [8]. Although it cannot be seen, we speculate that the ice nucleus already exists in (a) and the distortion in (b) is caused by the ice nucleus which has grown larger than several μm in the linear dimension. This speculation is based on the several unintended observations in which the cavitation bubble trapped an impurity of several μm in linear dimension, but remained stable without being distorted. The ice nucleus must be a pre-dendritic form, probably a perturbed disk, because the beginning of the dendritic growth is only traced back to at between (d) and (e) according to the measured growth velocity,

The sequence shown in Fig. 2 unambiguously demonstrates that the nucleation of ice is indeed induced by a cavitation bubble without help of the cell wall, supporting the long standing notion of dynamic nucleation as a result of the melting point shift due to the high pressure pulse. However, for water whose specific volume increases on solidification, there is an unsettled argument about the path of the ice nucleation. In a cavitation event, a collapse of the bubble generates a high pressure pulse which consists of the positive period and the negative period. Hickling argued that the positive pulse period was responsible for the nucleation of a high pressure phase of ice which then catalyzed the nucleation of normal ice when the pressure returned to atmospheric pressure [4]. On the other hand, Hunt and Jackson argued that the negative pulse period was responsible for the nucleation of normal ice directly from the undercooked water [9]. As shown in the following section, the present study appears to argue in favor of Hickling's stand.

We observed that the water (approximately 3 cm^3) in the cavitation cell remained in the liquid state down to -12 ‘C when the cavitation bubble was not present. The water could be undercooked further down if the apparatus limitation could be eliminated. However, ice would be eventually and most probably nucleated at the cell wall because a solid surface was generally a preferential location for the heterogeneous nucleation. For ice nucleation away from the wall to occur, further undercooling would be required, whether it was homogeneous nucleation or heterogeneous nucleation assisted by impurities in the water. Since the actual undercooling limit of the water could not determined, we take -12 °C as the highest temperature at which the nucleation of ice occurs in the 3 cm^3 water at a position away from the cell wall. Next, we estimate the highest temperature at which the nucleation of ice can occur in the water exposed to the high pressure pulse. The temporal extent of the high pressure pulse is very limited near the interface of the collapsing bubble, so we assume that water within **5 pm** radius from the center of the bubble is exposed to the high pressure. Then, the amount of the water exposed to the high pressure is on the order of 10^{-13} cm^3. Acceding to classical nucleation theory, the nucleation rate typically increases 6 fold when the liquid temperature decreases by 1 K. Since the highest temperature of the 3

cm^3 water is assumed to be -12°C, the additional undercooking, AT, necessary for the 10^{-13} cm^3 water is estimated by $(3/10^{-13}) = (6)^{\Delta T}$. The result is AT -13 K. Therefore, in order to observe the onset of solidification induced by the cavitation bubble, the undercooking level of the 10^{-13} cm^3 water must be larger than 25 K. There is no estimate of the magnitude of the negative pressure pulse; however, it cannot exceed the tensile strength of water. An available experimental tension value is -140 MPa which is very close to the value required for homogeneous nucleation of a vapor bubble [10]. Figure 3 shows the pressure-temperature diagram of water. According to the diagram, the negative pressure of-140 MPa increases the melting point by 8 K. Then, the effective undercooking level of the water at -5*C at -140 MPa increases to 13 K; however, it is still significantly smaller than 25 K required for the onset of solidification. Therefore, the negative pressure pulse cannot be responsible for the nucleation of ice.

Since the negative pressure pulse is unlikely to induce the nucleation of ice, the positive pulse must be responsible for that. We go on to estimate the pressure level required for the onset of solidification using Fig. 3. When the bubble is compressed, the gases in the bubble are heated up. The temperature rise of the water near the gas/water interface due to the compression of the gas in the bubble under the adiabatic condition calculated by Hickling is shown in Fig. 3. The diagram shows that the positive pressure pulse must be at least in the order of GPa to achieve a sufficient undercooling level for observing the onset of solidification. The other extreme condition, i.e., isothermal condition significantly increases the undercooking level comparing that of the adiabatic condition at the same pressure level. Since the last stage of the collapsing bubble especially the luminescing bubble is not fully understood, the estimate of the magnitude of the positive pressure pulse varies depending on the models used to describe the cavitation mechanism. Among these, the model based on Rayleigh-Plesset equation seems to serve well for describing the radius-time curve of the cavitation bubble [11,12]. According to this model, the maximum pressure generated at the end of implosion is approximately 1 GPa, which is at least the right order and may be sufficient under the isothermal condition.

Finally, the observed minimum undercooling, 5 K necessary for the onset of solidification could be rationalized as follows: The water exposed to the high pressure pulse is heated up by 5 K due to the gas compression; therefore, minimum undercooking is necessary to bring the local temperature down below O ‘C. Alternatively, 5 K could be the
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minimum undercooling required for normal ice to heterogeneously nucleate on the high pressure phase of ice since they have different structures, normal ice cannot grow epitaxially on the high pressure phase.

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References

[1] B. Chalmers, Principles of Solidification (Robert E. Krieger Publishing Co., 1982), p. 86.

[2] Embryos are referred to the solid clusters whose size are smaller than the critical size defined by classical nucleation theory. The embryos are unstable and subjected to dissolution by detaching atoms or molecules. Beyond the critical size, the clusters which are now called the nuclei, spontaneously grow to the macroscopic phases.

[3] W. Kurz and D. J. Fisher, Fundamentals of Solidification (Trans Tech Publications, 1984), p. 184.

[4] R. Hickling, Nature 206, 915 (1965); 207, 742 (1965), Phys. Rev. Lett. 73, 2853 (1994).

[5] C. P. Lee and T. G. Wang, J. Appl. Phys. 71,5721 (1992).

[6] D. F. Gaitan, L. A, Crum, C. C. Church, and R. A, Roy, J. Acoust. Sot. Am. **91**, 3166 (1991).

[7] For a review, see L. A. Crum, Physics Today, Sep. 1994, p. 22.

[8] This value is comparable with the values in the literature, 0.54 cm/sec [S. H. Tirmizi and W. N. Gill, J. Cryst. Growth 8S , 488 (1987)] and 0.39 cm/sec [J. P. Kallungal and A. J. Barduhn, AIChE J. 23, 294 (1977)].

[9] J. D. Hunt and K. A. Jackson, J. Appl. Phys. 37, 254 (1966); Nature 211, 1080 (1966).

[10] Q. Zheng, D. J. Durben, G. H. Wolf, and G. A. Angel], Science 254,829 (1991).

[11] B. P. Barber and S. Putterman, Phys. Rev. Lett. 69,3839 (1992), R. Lofstedt, B. P. Barber, and S. Putterman, Phys. Fluids AS, 2911 (1993).

[12] T. Lepoint, D. DePauw, F. Lepoint-Mullie, M. Goldman, and A. Goldman, J. Acoust. Sot. Am. **101,2012** (1997).

Captions

Figure 1. Schematic diagram of the experimental apparatus.

Figure 2. Sequence of the onset of solidification induced by the cavitation bubble. The water temperature is -5 ‘C and the bubble is oscillating in the non-luminescing volume mode. The time interval between the two consecutive frames is 1/30 sec.

Figure 3. The melting point shift of water as a function of pressure. The melting points of the phases are adopted from the CRC Handbooks. The melting point of normal ice (Icc I) decreases as the pressure increases. The negative pressure side is the extrapolation from the positive side. The melting points of the high pressure phases of ice increase as the pressure increases. The adiabatic heating of the water originated from -5 ‘C (dotted line) at atmospheric pressure is adopted from the Hickling calculation [4].

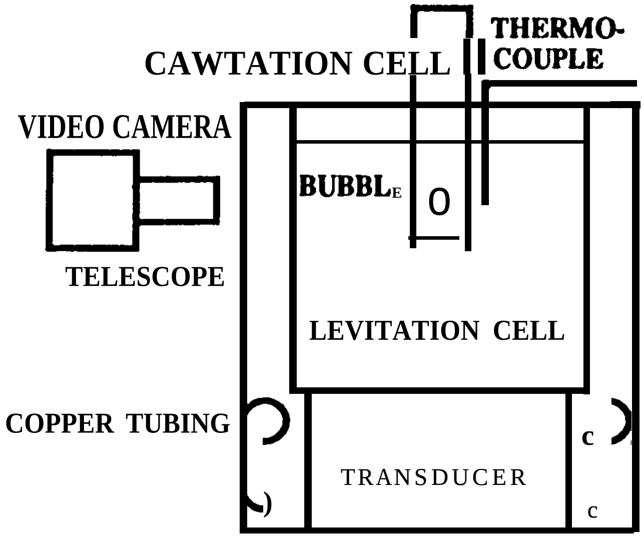
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Figure 1

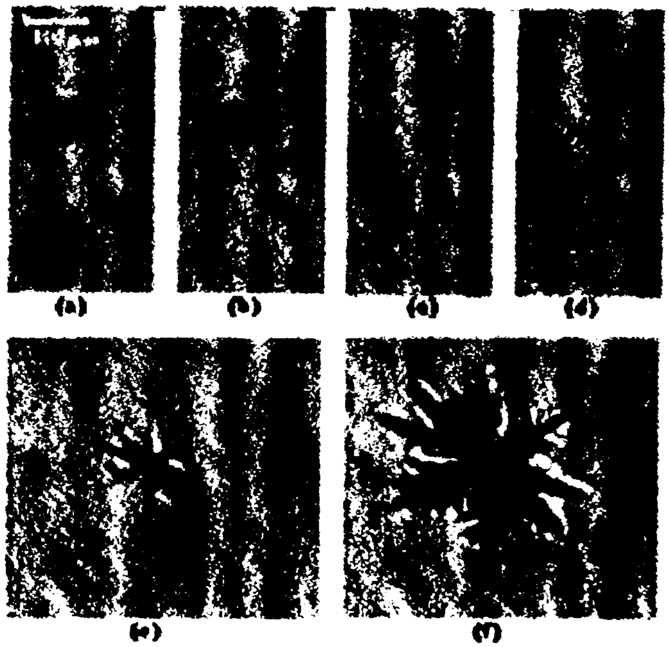

Figure 2

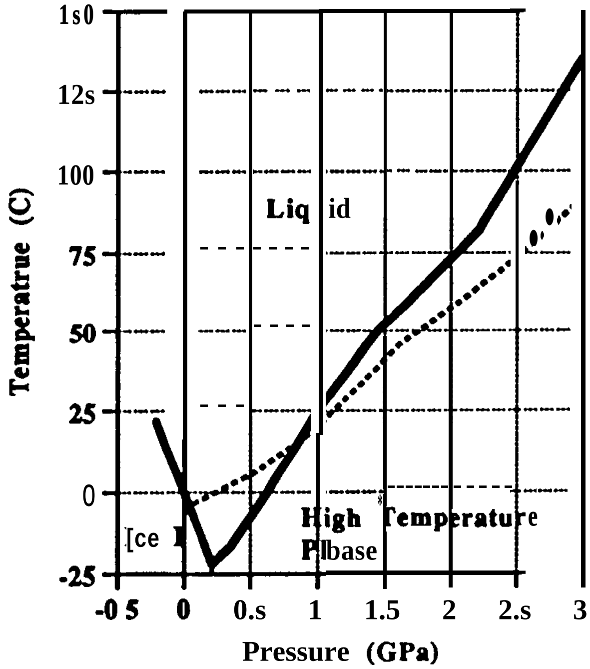
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Figure 3