DYNAMIC NUCLEATION OF SUPERCOOLED MELTS and MEASUREMENT OF THE SURFACE TENSION AND VISCOSITY

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1. INTRODUCTION

We investigate the phenomenon of acoustic pressure-induced nucleation by using a novel approach involving the large amplitude resonant radial oscillations and collapse of a single bubble intentionally injected into a supercooled liquid. Using a combination of previously developed and proven techniques, the bubble is suspended in a fluid host by an ultrasonic field which supplies both the levitation capability as well as the forcing of the radial oscillations. We observe the effects of an increase in pressure (due to bubble collapse) in a region no larger than 100 μm within the supercooled melt to rigorously probe the hypothesis of pressure-induced nucleation of the solid phase. The use of single bubbles operating in narrow temporal and spatial scales will allow the direct and unambiguous correlation between the origin and location of the generation of the disturbance and the location and timing of the nucleation event. In a companion research effort, we are developing novel techniques for the non-contact measurements of the surface tension and viscosity of highly viscous supercooled liquids. Currently used non-invasive methods of surface tension measurement for the case of undercooled liquids generally rely of the quantitative determination of the resonance frequencies of drop shape oscillations, of the dynamics of surface capillary waves, or of the velocity of streaming flows . These methods become quickly ineffective when the liquid viscosity rises to a significant value. An alternate and accurate method which would be applicable to liquids of significant viscosity is therefore needed. We plan to develop such a capability by measuring the equilibrium shape of levitated undercooled melt droplets as they undergo solid-body rotation. The experimental measurement of the characteristic point of transition (bifurcation point) between axisymmetric and two-lobed shapes will be used to calculate the surface tension of the liquid. Such an approach has already been validated through the experimental verification of numerical modeling results. The experimental approach involves levitation, melting, and solidification of undercooled droplets using a hybrid ultrasonic-electrostatic technique in both a gaseous as well as a vacuum environment. A shape relaxation method will be investigated in order to derive a reliable method to measure the viscosity of undercooled melts. The analysis of the monotonic relaxation to equilibrium shape of a drastically deformed and super-critically damped free drop has been used to derive interfacial tension of immiscible liquid combinations where one of the component has high viscosity. A standard approach uses the initial elongation of a droplet through shear flows, but an equivalent method could involve the initial deformation of a drop levitated in a gas by ultrasonic radiation pressure, electric stresses, or even solid body rotation. The dynamic behavior of the free drop relaxing back to equilibrium shape will be modeled, and its characteristic time dependence should provide a quantitative means to evaluate the liquid viscosity.

2. DYNAMIC NUCLEATION OF SUPERCOOLED WATER

The ability of mechanical disturbances such as pressure waves and high-speed flow to nucleate the solid phase from a supercooled melt has been a subject of controversy for some time. The unambiguous correlation of the nucleation event to the actual mechanicallyinduced disturbance has been difficult to establish because the potential for heterogeneous nucleation cannot be ruled out. Thus, the ability to isolate the melt from container walls by using levitated samples would allow the elimination of one cause for heterogeneous nucleation. The spatial localization of the source of mechanical disturbance within a very small region in the supercooled melt will also allow a more convincing case for ruling out the influence of heterogeneous sites. We have used ultrasonically-trapped and radially oscillating gas bubbles with diameter ranging between 10 and 50 μm to induce pressure waves within a region localized around them. By driving these gas bubbles into the "giant" monopole resonance[1], substantial repeating pressure waves can be generated within the melt immediately outside the bubble wall. At the same time, high velocity motion of the bubble wall during its collapse cycles potentially induce high-speed flows (100-1000 m/s) within a 10 μm wide spatial region.

We have obtained evidence of dynamically-induced nucleation of ice in water supercooled to lower than -5 °C through the large-amplitude radial oscillations of 10 μm-diameter air bubbles. This was accomplished by ultrasonically trapping a gas bubble in a small thin-walled container filled with water placed within another liquid-filled ultrasonic resonator driven at 21 kHz [2]. The experimental procedure consists in introducing the thin-walled cell filled with about 3 cc of distilled and filtered water into the ultrasonic cell maintained at a temperature below 0 °C. Power input to the transducer driving the cell is subsequently adjusted to drive the bubble into large-amplitude radial mode oscillations and into the sonoluminescing region.

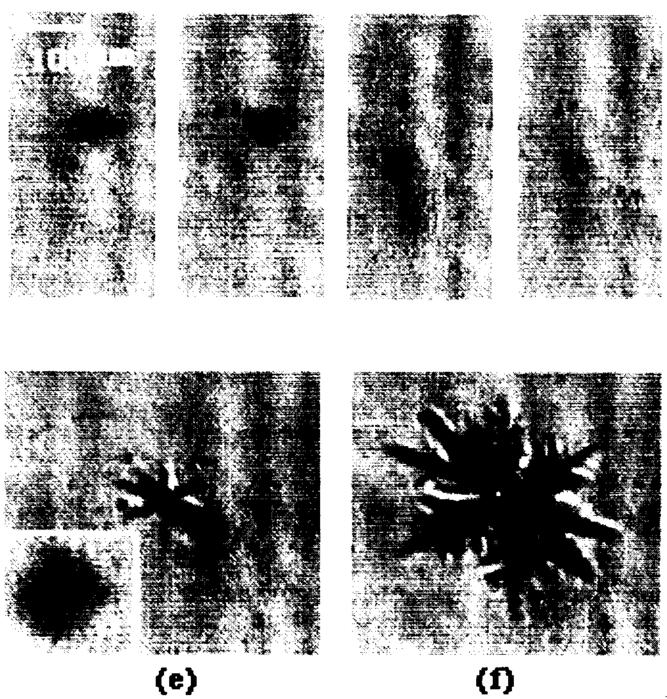

Figure 1. Sequence of the onset of solidification induced by a cavitation bubble. The water temperature is -5 °C and the bubble is oscillating in the non-luminescing volume mode. The time interval between two consecutive frames is 1/30 second.

Figure 1 shows a sequence for the ice formation at -5 °C: (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 of (e) is for a better visualization of the cavitation bubble at the stable state. (b) The bubble seems to be distorted judging from the non-spherical halo. (c) The bubble is ejected from the 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 appears in the dendritic form. (f) The dendrite grows at approximately 0.4 cm/sec. This value is comparable with the values in the literature, 0.54 cm/sec [3] and 0.39 [4] cm/sec.

Although significant velocity flows are generated by the violent bubble oscillations, the time scale of the fluid motion (on the order of microseconds) is still quite long when compared to molecular time constants (tens of picoseconds). The spatial scales of the bubble and its oscillations are also still very large when compared to the size of the fluctuating water molecular clusters described by the classical nucleation processes. Under these circumstances, we believe that pressure waves emitted during the violent periodic bubble collapses are responsible for the ice nucleation. A simple argument based on the water phase diagram and classical nucleation theory concepts suggests that a positive pressure wave up to 10 GPa is capable of nucleating the solid phase[2] because of the freezing point shift.

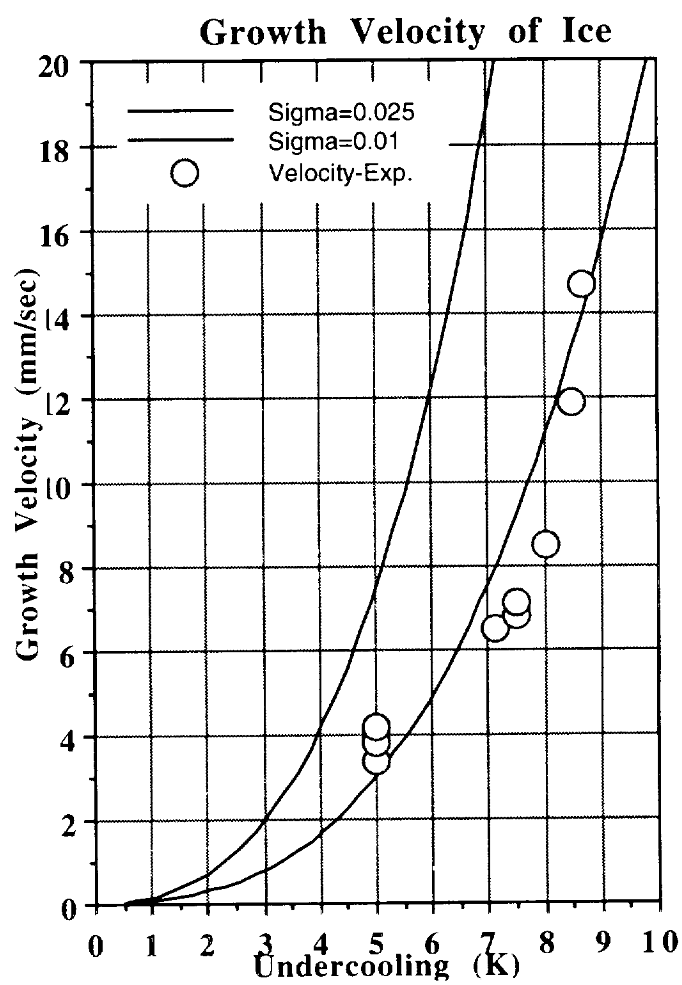

Figure 2. Dendritic growth velocity experimental results and comparison with theory.

Because the initial ice nucleus is generated within the bulk of the liquid without any seed, the dendritic free growth velocity can be measured. Figure 2 presents some preliminary results suggesting that the data can be fitted to the current theory based on a thermal diffusion model [5] with a scaling constant equal to 0.01.

3. MEASUREMENT OF THE SURFACE TENSION AND VISCOSITY

We have first addressed electrically uncharged drops that are ultrasonically levitated in air in 1-G. Due to the necessity to overcome the full impact of gravity on Earth, the high ultrasonic stresses required for the levitation of a drop also distorts its shape into an approximate oblate spheroid [6]. The systematic measurement of the shape of the levitated drop as a function of the acoustic pressure level allows the calculation of the surface tension. This method has the advantage of requiring a single measurement of the aspect ratio of a levitated drop and of the accurate determination of the sound pressure level (SPL). If an absolute measurement of the SPL is not possible, a relative method can be used by measuring the shape parameters of two drops under isothermal conditions: one with known and one with unknown surface tension . When the same acoustic sound pressure is used for levitation in both cases, the unknown surface tension can be calculated.

A second method for the measurement of surface tension for highly viscous liquids involves the accurate measurement of the dependence of the shape parameter of a levitated drop on the rotation rate. When the drop is undergoing axisymmetric solid-body rotation, the precise measurement of the rotation velocity at which the equilibrium drop shape transitions from the axisymmetric to the three-dimensional two-lobed shape (bifurcation velocity) allows the calculation of the surface tension. The bifurcation velocity has been theoretically and experimentally shown to be a unique function of the surface tension and density of the initially *spherical* drop. This bifurcation velocity depends, however, on the initial equilibrium shape of the levitated drop: due to the reduced stability, an initially oblate levitated drop will undergo transition to the two-lobed shape at lower rotation velocity than theoretically predicted for a spherical drop [7]. In order to circumvent this inconvenience, a theory for deriving the bifurcation velocity of non-spherical levitated drops must be made available, or low-gravity measurements are required. Another alternative is the Earth-based levitation and rotation of electrically charged drops using electrostatic fields [8] which yields initially quasi-spherical levitated charged drops. The detailed theoretical analysis of the effects of electric charge and field on the bifurcation velocity is then required. We are pursuing the last of these alternatives by carrying out Earth-based measurement of the bifurcation velocity of levitated drops as a function of the electric charge.

The measurement of the viscosity of super-critically damped liquid droplets could be tackled in a straightforward manner by measuring the relaxation time constant of a drop that is initially distorted from the spherical shape. An alternate approach we are currently investigating involves the shape relaxation of a rotating drop stretched to an equilibrium shape just before the onset of fission. We have thus performed some preliminary experimental measurements of the shape of rotating levitated drops as they spin down from the highly stretched configuration. The procedure involves acoustically rotating a levitated drop past the bifurcation point to a stretched two-lobed shape without inducing fission. The torque is then subsequently and abruptly released, and the drop is left to relax back to the equilibrium axisymmetric equilibrium shape. The time evolution of the relaxation process is accurately measured through video photography and the effects of viscosity through the evolution of differential flow is analyzed. An analytical model of the process is being concurrently developed.

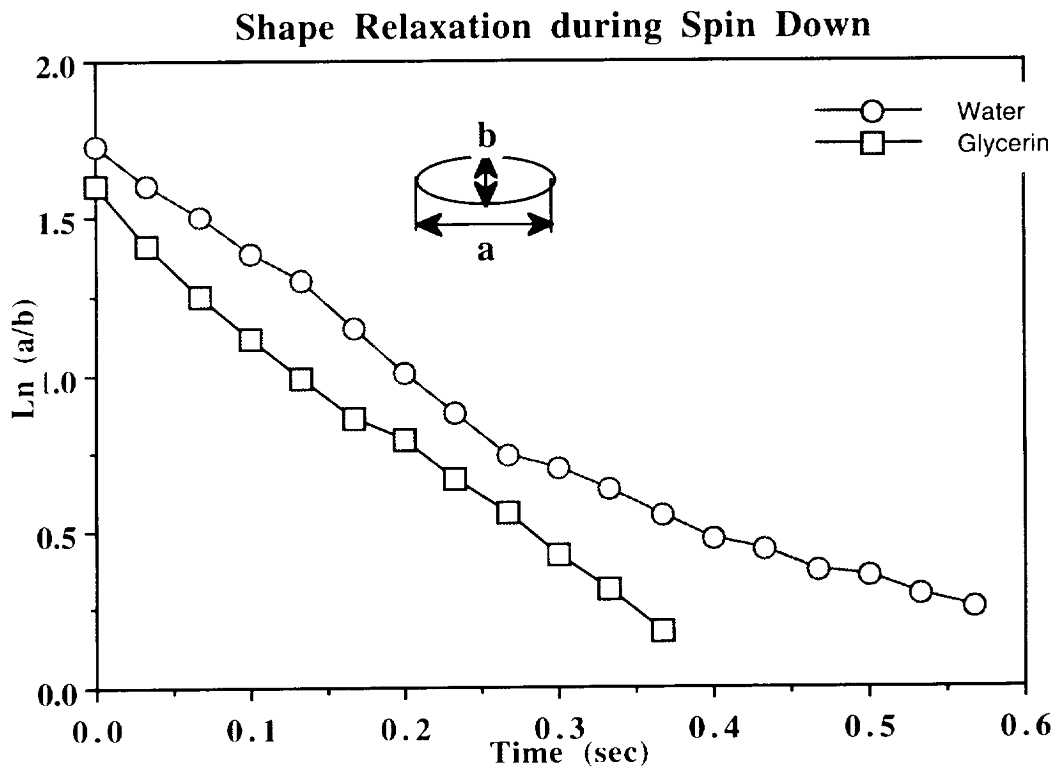

Figure 3. Aspect ratio of levitated drops of water and glycerin as they spin down from the two-lobed stretched configuration.

Figure 3 displays results of the measurement of such relaxation for water (1 cP) and glycerin (850 cP). A significance difference appears to be the double time constant for the water droplet. The sudden transition to a slower relaxation rate for water has been correlated with the transition from negative to positive curvature at the drop midsection. The overall faster relaxation time to axisymmetric shape observed for the higher viscosity liquid is attributed to the absence of differential flows.

4. SUMMARY

We have obtained some strong evidence for the correlation between high pressure pulses and the onset of nucleation of ice in supercooled water. A semi-quantitative analysis based on the effect of pressure on the displacement of the freezing point provides an explanation for such a phenomenon. We are also currently pursuing a number of potentially effective non-invasive measurement methods for the viscosity and surface tension of highly viscous supercooled liquids. Methods based on rotational dynamics appear to be the most scientifically interesting on the point of view of the fluid dynamical processes.

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