THE EFFECT

Supercooling Effect Video with Supersonic Jet

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I. Introduction
This video represents one of several made for the Flow Visualization course Team Project 1 at the University of Colorado at Boulder with the purpose of illustrating the supercooling phenomenon. The video not only captures the fluid flow physics of a supercooled liquid, but it also shows the sequence of events leading to the creation of jets formed due to the impact of a heavy object on the fluid surface. This report will discuss both of these physical events taking place in this specific fluid flow, however, it will focus more in detail on the supercooling phenomenon, which was our team's main area of concentration for this project.

II. Setup
This experiment consisted of supercooling water, then dropping a marble into the liquid to start nucleation sites for crystals to start growing with a final output of completely freezing the water. The setup began with cooling the water under its freezing point (0°C) but still keeping it in its disordered metastable state (liquid phase). This first procedure was done by filling up shot glasses with deionized (DI) water and placing these in a bucket of salty ice. The purpose of the salt in the ice was to further lower the cooling temperatures of the ice to then help supercool the DI water. The shot glasses were sealed with paraffin paper to avoid any impurities and prevent any "seeds" from falling into the liquid water that would trigger crystallization. Along with the DI water shot glasses, some tap water shot glasses were placed in the bucket of salty ice as well as used as reference points. Since tap water contains minerals and impurities that act as nucleating sites, the freezing point of tap water occurs at 0°C, which gave our team a reference of approximately the time when the DI water shot glasses would be supercooled enough to handle and move around without disturbing the liquid too much to actually trigger crystallization. Once our reference shot glasses were frozen, the DI water shot glasses were left in the salty ice bath 2-5 minutes longer (a total time of 15-20 min) and then were taken out for experimentation.

Before the DI water was taken out for experimentation, the recording station was already set up because time to conduct tests with supercooled water is limited. The video was shot with an Olympus i-Speed high speed video camera. The camera was set on a tripod about 60 cm from the subject (DI water shot glass) and was lit up with 2 halogen light sources and 1 working light reflector (see Figure 1 for setup schematic). The subject was placed in the center of the light reflections and a few drops of color dye were added to the DI water. These dye drops were not enough to start crystal nucleation sites but were used to highlight the fluid flow effects once the marble was dropped into the glass from a height of about 20 cm.
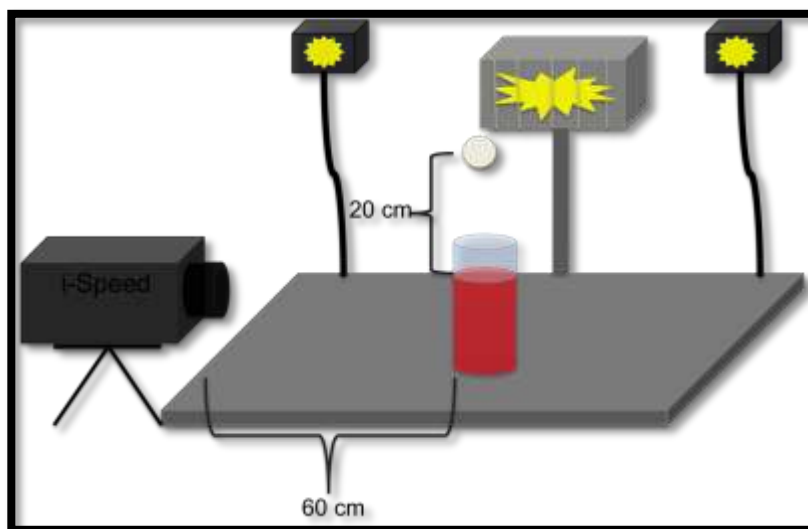

Figure 1: Setup Schematic

III. Film and Editing
The video was filmed at the i-Speed high speed video camera's full resolution of 1,000 fps using a 50mm TV Pentax lens with a full aperture f-stop of 1.4. With a drop from a height of 20 cm from the liquid surface, the ball in theory at a speed of 2 m/s, should take 0.1 s to hit the liquid. However, at this filming speed and a play back of 30 fps the drop of the ball can be seen in a time frame of 3.3 s. The play back of the whole video at 30

fps makes it slow enough for the human eye to capture what in reality just looks like a drop of a ball in the water and then the result of a frozen liquid. The details the camera captures at 1,000 fps are exactly those missed by the human eye. The actual duration of the whole film is of ~ 2 sec capturing ~ 2,000 frames with the i-Speed camera, and it is then played back at 30 fps having a video duration of ~ 1.10 minutes.

This original 1.10 minute video was outputted as an AVI file from the i-Speed camera, and the resulting file was edited using Final Cut Pro. Final Cut Pro places the video in a timeline strip where parts of the beginning and end were cut to take away unneeded footage. Parts of the filmstrip were copied, reverted and added to various parts of the sequence to see the effect in backward and then forward mode. Also, some of these reverted sequences were played back at slower times and some of the original sequence was played at faster times to highlight important details of the fluid dynamics. Finally, after all the editing was finished, the final video was exported into Soundtrack Pro. With this program, sounds were added accordingly to match the effects of the flow. Two liquid drop effects were added at the drop of the ball, two eeriedrone sounds where added to follow the movement of the surface when the bubble comes out of the liquid, and the ambient city tune was played throughout the video to add an ambient feeling to the entire video. Once the soundtrack was matched and edited to the accurate times of the video, the final product was exported as a high quality QuickTime Movie.

IV. Analysis
As previously mentioned, there are two physical phenomenon effects that occur when the marble is dropped into the DI supercooled water. Both of these will be discussed analytically, but the focus will preponderate on the physics of the supercooled liquid.

As the marble falls and strikes the water surface, a complex yet innate fluid flow dynamic begins. The impact of the marble falling on the DI water liquid surface can actually form a series of events leading to the creation of three jets, one of which has been found to be a supersonic jet[1]. In Figure 2, the sequence of fluid dynamics upon the impact of the marble on the liquid surface and then throughout its trajectory into the liquid is depicted. The collapsing splash from the marble falling into the water is the beginning of this fluid dynamics sequence. Upon impact, a thin sheet of liquid, "the crown splash"[1] is thrown upwards (in this case it is thrown sideways since the marble enters the DI water somewhat to the side, hitting the wall of the shot glass) along the rim of the marble, while below the water surface a large cavity forms in the wake of the impactor. As the crater deepens, due to hydrostatic pressure of the surrounding liquid, the cavity immediately starts to collapse and radially pinch in forming an elongated "hourglass" shape with a larger radius at the top and bottom, an elongated thin neck region in the center and a widening exit toward the atmosphere.
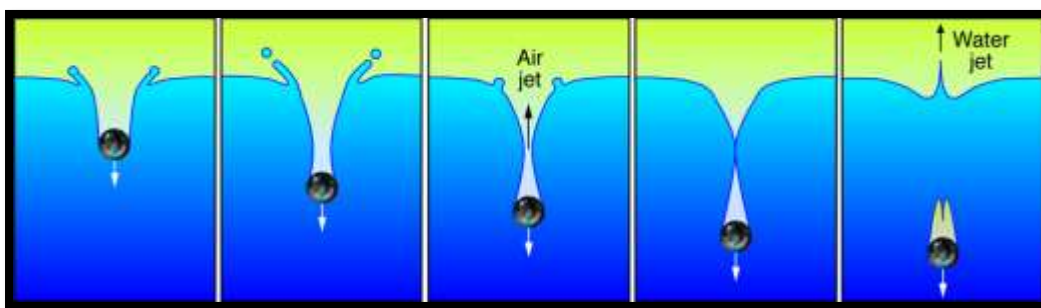

Figure 2: Impact of a marble on a supercooled water fluid surface causes a sequence of events leading to the creation of three jets[2].

Reminiscent of the converging-diverging "de Laval"[1] nozzles known from aerodynamics as the perfect example of supersonic jet engines, this liquid nozzle, formed by the marble's impact, acts just like one. Right before the neck completely collapses, a supersonic air jet escapes (this simulation has been done in previous work and results have shown that not only is the flow, to a good approximation, one dimensional, but it even attains supersonic velocities[1]). Following the impact of the fluid surface on itself at the neck pinch-off, two fluid jets emerge upward and downward from this pinching point. In the video, the upper jet is easily

depicted, again slightly of to the side, due to the way the marble enters the liquid. However, the downward jet is harder to see. The downward jet does form if the video is looked at very closely, but it deforms faster than what you would expect due to the fact that the supercooled water has been disturbed enough to start crystal nucleation and freeze as these other dynamics are taking place.

To determine more precisely at what point the air flow through the neck becomes sonic, other experiments have shown the evolution of the Mach number, $Ma_{neck} = u_{neck}/c$, where u_{neck} is the gas velocity and c is the speed of sound for objects impacting at 1 and 2 m/s. The experiments set up to measure u_{neck} as a function of the neck's radii have found that the speed of sound is attained at cavity radii as large as 0.5mm for the lower impact velocity (1 m/s) and 1.2 mm for the higher impact velocity (2 m/s)[1]. In this case, with a height of 20 cm from where the marble is dropped to where it strikes the liquid surface water, the marble attains a velocity of ~2 m/s and the radius of the collapsing neck reduces to ~ 1 mm. With this close comparison to previous experiments, it can be predicted that the air jet coming out of the collapsing cavity is supersonic.

These jets are the consequence of the local kinetic energy density rapidly rising. These processes involve the interplay of inertia and in some cases surface tension. The root cause, though, of these self-focusing events is that the surface is rapidly changing its topology. When the crater collapses, the surface cleaves from one sheet to another, and in addition, there is a bubble formation. The high velocities and high surface curvatures all occur right around the time of pinch-off[2]. Furthermore, as these high curvature interface regions form and deform the supercooled DI water starts to freeze and the fast formation of crystals start to appear, bringing another whole dimension to the dynamics of this flow.

The phenomenon of supercooling consists of the preservation of a disordered fluid phase in a metastable state while below its known freezing point. It has been known for centuries that pure water, in the absence of any nucleating surface, at atmospheric pressure, can remain in a supercooled liquid state down to temperatures as low as -40°C[3]. The onset of crystallization can be shifted to lower temperatures by reducing the number of nucleation-inducing impurities. In this case, we achieved the reduction of impurities and nucleating sites by using DI water and protecting each filled shot glass from any dust or possible nucleating agents from entering the water by covering the glasses with paraffin sheets. The water was cooled to a few degrees below its freezing point, and then disturbed to observe the liquid-solid phase spontaneous change.

Water's behavior differs from that of normal fluids having more than sixty anomalies[4]. One well known anomaly is that liquid water begins to expand when its temperature drops below 4°C, whereas most liquids contract as temperature decreases and become denser. Furthermore, the irregularities in liquid water become more pronounced in the supercooled region (below 0°C). Supercooled water is known as "metastable", meaning that it is not in the lowest free energy state. In the case of supercooled water, the lowest free energy state (G) is always a crystal lattice. The discrepancy in energy between the crystalline and liquid state increases as the temperature (T) is lowered. Thus, the typical time needed for crystallization decreases as the temperature is lowered.
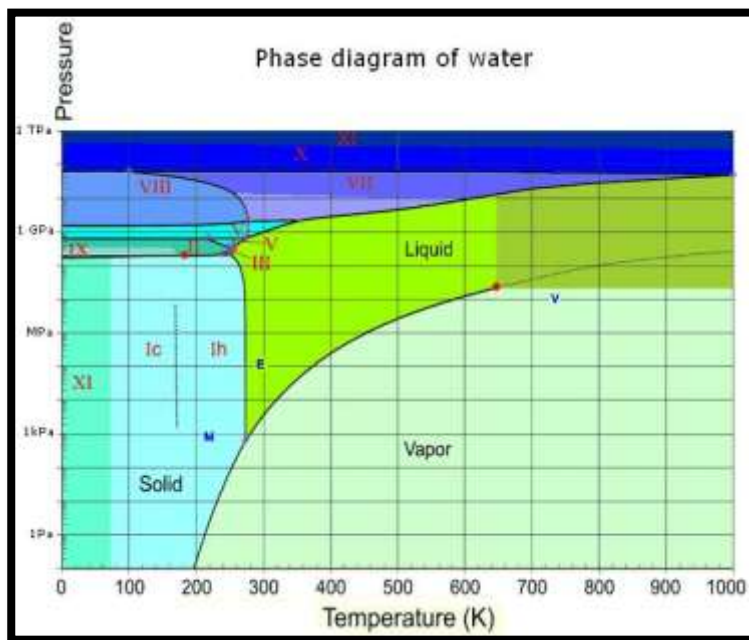

Figure 2: Phase Diagram of Water

A consequence of thermodynamic laws is that substances "seek" to minimize G given a particular T and pressure (P). However, water possesses thermodynamics fluctuations and response functions that diverge from these "normal" laws. The quantity G, called the Gibbs free energy, is defined $G \equiv U - TS + PV$ where U is energy, V is volume and S is entropy. In typical liquids, fluctuations in volume and entropy decrease upon cooling, while the opposite happens in water. Fluctuations in volume and entropy are positively correlated in typical liquids, while in water they become negatively correlated below the temperature of maximum density (4°C at atmospheric pressure)[5]. This means that a volume decrease will increase the entropy and vice versa. This is a consequence of the hydrogen bonding. At supercooled temperatures, the highly ordered, low entropy tetrahedral shapes take up more space than unordered arrangements and as a result increase G (see Figure 3 for water's Phase Diagram).

All these anomalies are usually present in every state of water, however, as previously mentioned, these are more pronounced in the supercooled liquid state. Other experiments have also shown that water's thermodynamic fluctuations and response functions, such as isobaric specific heat, Cp, or the magnitude of isobaric thermal expansion coefficient, αp, increase when T decreases (see equations 1)[6]. The anomalies have been interpreted on the basis of models that propose different scenarios. The scenarios can be divided into two main categories: (a) those scenarios that include the coexistence at low T of two liquids with different densities, and (b) a scenario in which water forms local regions of different densities but does not separate into two phases. Different experiments have been attempted with the purpose of proving these scenarios, however none have come to a defined conclusion of these water's anomalies[6].

$$K_T = -\frac{1}{V}\left(\frac{dV}{dP}\right)_T, \quad C_P = T\left(\frac{dS}{dT}\right)_P, \quad \alpha_P = \frac{1}{V}\left(\frac{dV}{dT}\right)_P,$$

(1)

V. Conclusion

Water can be supercooled at atmospheric pressure to approximately 235 K, at which point it homogeneously nucleates into a crystal regardless of the sample size or purity. In this case, our samples were cooled around -2 to -5 °C, a range much before homogenous crystallization would occur. However, crystallization was initiated by means of disruption or "seed" planting that would create nucleation (in this case dropping the marble in the water). The amount of disruptive energy needed was quite significant considering how spontaneous supercooled water changes phase within any minor crystal formation. However, in this case, it seemed that to start the formation of crystals the amount of energy change needed to lower G was more than just a drop of dye. One may have assumed the dye would have started nucleation, acting as an impurity, but at just a few degrees below the freezing point of DI water, the dye did not act as a seeding site for nucleation to occur.

In regards to the air jet formed in the collapsing neck formed at the pinch-off of the collapsing cavity created by the striking marble into the water, it most likely can be described as a supersonic jet. The characteristics shown in the video and under the parameters tested correlates very closely to previous experiments that measured this air jet to be sonic. Thus, in closing, this video captures dynamic details hidden to the human eye, but yet always occurring under these circumstances. The physics of the flow are clearly highlighted, and it is amazing to be able to see exactly what these dynamics are when an object strikes supercooled liquid.

[1] S. Gekle, I.R., J.M. Gordillo, D. van der Meer, and D. Lohse, Phys. Rev. Lett. 104, 024501 (2010).
[2] D. P. Lathrop, Physics 3, 4 (2010).
[3] S. Hadlington, RSC, Chemistry World News (2010).
<http://www.rsc.org/chemistryworld/News/2010/February/04021002.asp>
[4] G. Franzese, K. Stokely, X. Chu, P. Kumar, M.G. Mazza, S-H Chen and H.E. Stanley, J. Phys. 20, 494219 (2008).
[5] S.R. Becker, Wesleyan University, Dept. of Phys. (2007)
[6] C.A. Angell , J. Shuppert and J.C. Tucker, J. Phys. Chem. 77, 3092 (1973).