Super Cool Supercooled

Team Project 1

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Flow Visualization MCEN 4151
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Introduction

The team's intent was to capture a photo or video of supercooled water freezing. Instead of pouring the supercooled water out to initiate freezing, as is done in most of the videos on YouTube, we intended to drop objects or food coloring into the water. We hoped to capture the objects or dye ceasing to move as they fell through the water when the ice formed around them.

About The Physics

The original set up was based off of several you tube videos of supercooled water experiments, where bottles of water were left in the freezer for several hours to supercool. Our original set up used large glasses of deionized (DI) water in a freezer for several hours. However, ice would form on the surface of the water before the water could be supercooled. We predicted that this was because the freezer was too cold and the glasses were not covered.

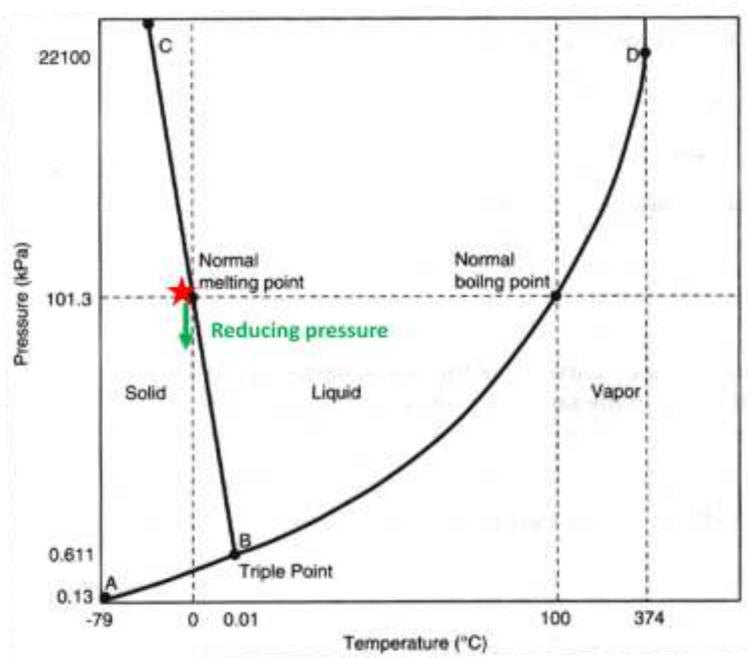
The final set up used small shot glasses instead of large glasses, so that the water could be supercooled in a matter of 15 minutes, rather than hours. Each glass was cleaned thoroughly with soap and tap water, then rinsed with DI water and filled two-thirds full with DI water. The use of DI water insured that there were no particles in the water to act as nucleation sites around which an ice crystal could form. Instead of a freezer, the shot glasses were submerged in a bath of salt and ice water. The water/ice level was brought to just above the level of DI water inside the shot glasses, but not over the rim of the glasses to prevent infiltration of salt water. The shot glasses were also covered in parafilm as a seal to prevent any particles from getting into the DI water and serving as nucleation sites for the formation of ice. One dirty glass filled with tap water was placed in the bath as well to serve as a temperature probe. When this glass had frozen, it meant that the temperature of the water inside the shot glasses was at or below the freezing point; therefore, the DI water in the clean glasses was likely supercooled. This apparatus (pictured above, right) mostly solved the problem of premature freezing. When each shot glass was removed, dye was added to the supercooled water and then a marble was dropped into the glass.

When water is supercooled, it is out of equilibrium in a state called metastable. Thus, small disturbances can cause it to go back to equilibrium and form ice. The most common source of perturbation that starts crystallization is when a particle is introduced that acts as a nucleation site for the crystal. This is the same phenomena that occurs in clouds; recall that even at the right temperature and pressure conditions in the atmosphere, a particle of dust is required to trigger condensation or freezing inside of a cloud. At normal atmospheric pressure, water may be cooled without freezing to temperatures as low as about 231 K, called the "homogeneous nucleation temperature," at which point crystals begin to form homogeneously throughout the water (Debenedetti & Stanley, 2003).

We had predicted that adding a drop of food coloring would be enough to initiate freezing. Dye molecules are large, and thus we had predicted that they would serve as nucleation sites. However, the addition of dye did not start the formation of ice, as can be seen in the first frame of the filmstrip. Furthermore, when the marble was dropped into the DI water without any dye, the ice formed in a very similar fashion. This could possibly have be assisted by the fact that the marble was dirty and introduced nucleation sites. Clearly the addition of the nucleation sites alone was not enough to disturb the water from its metastable state.

In fact, we were surprised by how much perturbation the supercooled water could take before freezing. In the second frame of the photo, the marble has just been dropped into the glass. The water is splashing around substantially, and the formation of ice has not started. Large air bubbles have been introduced into the water. The formation of ice begins as the water is settling after being perturbed.

One possible explanation for why dropping the ball into the water caused ice to form but adding dye did not, is that the ball caused a pressure change in the water. Although the temperature of the supercooled water was not measured, it can be estimated. Obviously the water was below zero degrees Celsius. The ice that was added to the bath was from a freezer at -20 degrees Celsius. Thus the water was somewhere in the range of 253 to 273K, but was probably closer to 273 K because the small amount of tap water which was added to the ice was near 20 degrees Celsius. The pressure that day was about 102.5 kPa (Weather Underground, 2011). The condition of the supercooled water is marked as a red star on the phase diagram for water below (Macgill, 2011). When water freezes it crystallizes. These complex crystal orientations require more room than does liquid water. Thus, lower pressures favor the solid form. The blue line on the phase diagram below represents lowering the pressure of the water while temperature remains constant. This process shifts the water's phase further into the solid region of the phase diagram. Lowering the water's pressure could be enough to shift the water out of its metastable state and begin crystallization.



When the ball is dropped into the water, the water suddenly transitions from being stationary to having some velocity. The energy equation (as presented in Professor Hertzberg's Fluid Mechanics fall 2010 class notes) can be applied to the state of the water before the ball is dropped and the state of the water while the ball is falling through it.

$$Q + W = m(\Delta u + \frac{\Delta P}{\rho} + \frac{1}{2}\Delta\, v^2 + g\Delta z)$$

Some assumptions can be made to simplify this equation. It can be assumed that before the ice begins to form heat transfer, Q, from the ball is negligible. No work, W, is being performed as there are no mechanical components. Because the final state is before the ice has begun to freeze, the change in specific internal energy, Δu, can be assumed to be negligible. Because the system of the shot glass and water remains in place, the change in specific potential energy, $g\Delta z$, can also be assumed to be zero. This simplifies the energy equation down to the very basic Bernoulli principle that a positive change in fluid velocity, $\Delta\, v^2$, results in a negative change in fluid pressure $\frac{\Delta P}{\rho}$. Thus, when the fluid begins to move, its pressure decreases where the fluid is in motion.

This local drop in pressure could be enough to shift the water from its metastable position near its normal freezing point further into the solid region, as shown by the blue line on the phase diagram above. The resulting hypothesis is that the pressure drop is primarily responsible for causing the phase shift in the supercooled water.

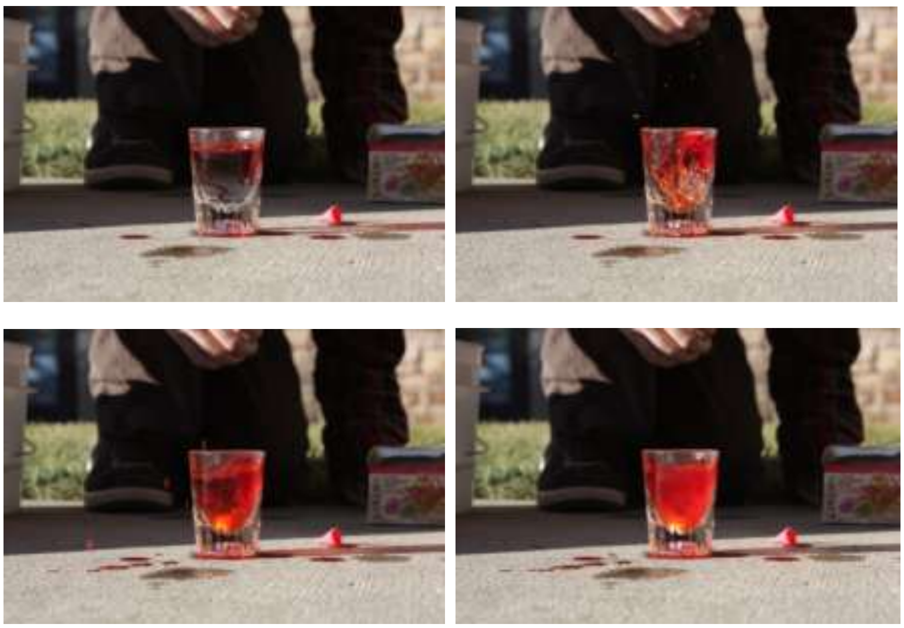
In order to test this hypothesis, acoustic waves from a subwoofer could be used to create high and low pressure waves instead of dropping a ball into water. The same method for supercooling DI water in shot glasses with a salt water and ice bath could be used. Dye would be added to ensure that nucleation sites were present. Then, if the pressure waves from the varying pitch triggered the crystallization of water, it would support the claim that *pressure drop* causes the crystallization. If the sound waves do not trigger crystallization, it might suggest that another mechanism is responsible for freezing. For example, it is possible that when the fluid is mixed up, tiny air bubbles are acting as larger nucleation sites for the formation of crystals.

About The Image

The photos were taken with a Canon Rebel XSi EOS 12.2 megapixel digital camera. The shooting mode was continuous at about 5 frames per second. Thus, there are 0.2 seconds between each of the four individual frames in the filmstrip image. The photos were taken on February 2nd 2011 at 4:29 pm. The lighting is natural sunlight coming from the left in the photos. The camera is located approximately a foot from the shot glass. Each original image is 4272 x 2848 pixels. The final composite image is 3672 x 1896 pixels. The ISO value is 200. The focal length is 55.0 mm. The F-stop value was f/8. The shutter speed was quite fast: 1/200 seconds.

This image is approximately well temporally resolved. The shot glass is about 5 cm tall and the ball was dropped from about 15 cm above the ground. Because the frames are 0.2 seconds apart, the ball must have traveled at least 15 cm in 0.2 seconds, so the fastest velocity in the image was on the order of 1 m/s. This means that in 1/200 seconds or 0.005 seconds that the shutter was open, the fastest moving object would not travel more than about 0.005 m or 5 mm. This would be a substantial amount of motion blur for an image with a frame that is only about 10 cm tall. The ball cannot be seen moving in any of the frames, and little motion blur is visible in any of the frames. This is probably because much of the fluid is moving slower. Some faster moving droplets can be seen in the third frame which have some motion blur. A faster shutter speed would be needed to freeze this flow. The i-speed camera, which used later to capture videos of the ice forming, had good temporal resolution. The depth of field is sufficient for the area that the photo was intended to capture. The background is out of focus, which is ideal because it is not important to the image.

Four successive images were turned into composite filmstrip in Photoshop to visualize the progression of ice formation over time. Each image was cropped to include only the shot glass and the area above where the water splashed. This was achieved using masks and layers. The contrast was increased using the curves tool. “Before” images can be seen below.



Discussion

Even thought the food coloring did not trigger freezing, I think it ended up being important to the visualization the freezing process. I particularly like the choice of red food coloring. I find the choice of using a hot color to visualize a cold fluid flow to be pleasantly unusual and artistically ironic. I liked the videos that were taken with the i-speed camera more so than this composite film strip image. The ice forms so quickly. Thus, the 1000 frame per second shooting rate shows so much more of the physics than does the 5 frame per second film strip. I also would have liked to get a good video of pouring the water to start freezing.

Works Cited

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