Freezing of supercooled water drops on cold solid substrates: initiation and mechanism

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Introduction. –The process of cooling a liquid below its melting point without phase change, supercooling, followed by solidification is of paramount interest for many engineering applications and in nature. In most of the liquid solidification research, particularly for water, phase change is assumed to occur at the equilibrium freezing temperature; however, this is not the case. Even, homogenous nucleation of supercooled water drops at -30 °C has been reported[1]. When the supercooling of a liquid exceeds few °C, solidification kinetics differs substantially from simple solidification at the melting point. The process of freezing for subcooled liquids splits into 4 distinct stages (fig. 1): i) droplet cooling, ii) recalescence, iii) main freezing (followed by cusp formation for water[2]), and iv) ice cooling[3-5]. During recalescence, supercooling drives rapid kinetic crystal growth from crystal nuclei. During this stage, 7 to 18wt% of the water, depending on degree of supercooling, is found to get solidified by using a Nuclear Magnetic Resonance (NMR) technique[6]. This stage ceases when the supercooling is exhausted and the droplet has reached its equilibrium melting temperature. Percolation of the hydrogen-bonded water network, with no supporting evidence, was presented as an explanation of this ultrafast temperature rise during recalescence[7]. However, the recalescence stage is still not well understood in terms of initiation mechanism.

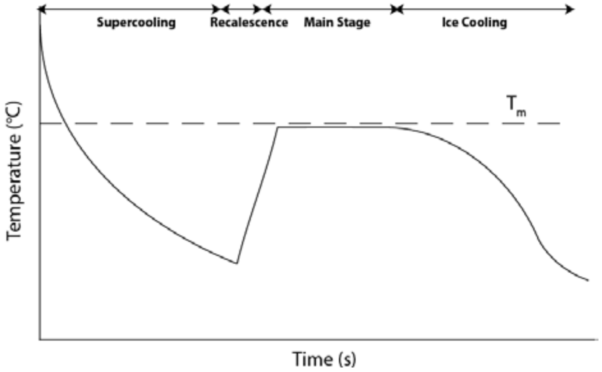

Fig. 1: A sketch of the cooling stages of the supercooled drops[3-5].

There have been many studies on ice nucleation of subcooled melt, mostly motivated by the formation of snow crystals, and commonly revolve around the dynamics of crystal growth from the gaseous phase[8]. These studies usually concern droplets suspended in air[9] or attached to a solid[3,10]. The location of the recalescence initiation has been a subject of debate. For the case of recalescence of water droplets on a solid substrate, some experiments show that nucleation occurs preferentially at the point of trijunction, supporting energetic arguments that ice nucleai at the contact line leads to a reduction in the nucleation barrier energy[11,12]. Most recently, a study over nearly 200 freezing-water events on a homogenous silicon substrate, concludes that there is no preference for nucleation at the trijunction[10]. Avoiding substrate cooling and using low cooling rate eliminates temperature variations in the drop. The air is used to cool the drop and the substrate inside of an isothermal container. Ice nucleation and freezing of acoustically levitated drops are analyzed[9] and it is asserted that ice nucleation from the surface is dominant. Further understanding of recalescence stage for undercooled liquid, in terms of dynamics and structure, can possibly unveil a strong influence of this stage on solidification of static or spreading drops. Furthermore, in many fluids-mechanical research and experimental studies on freezing supercooled drops, whether static[13] or dynamic[14], the recalescence stage has not been considered.

Experimental Section. – In our experiments, glass slides with dimensions of 50×24×0.15 mm^3 (VWR microcover glass) are rinsed successively in acetone, methanol and DI water. The slides are situated on top of a Peltier element which is capable of reaching temperatures as low as -30 °C. Liquid drops are positioned on top of Peltier element using a motorized injection needle. Afterwards, water drops ranging from 3.9 to 6.8mm, are cooled by the Peltier element. A camera (Phantom IV series) is used to view events from the side and the top. The camera is capable of recording events with maximum speed of 1000 frames per seconds. From recording images, we can locate the temporal and spatial origin and propagation of a freezing front. The main stage, on which the Peltier element and glass substrate are situated, can be moved in x, y, and z directions. To monitor surface temperatures of freezing static drops, K-type thermocouples are immersed at the tip of the water drops. Data collection rates are set to 10 ms to capture temperature evolution during recalescence. Solidification of the supercooled water drops is recorded using a camera with recording speed of 89fps, viewing two distinct solidification stages. When the drop is being cooled by the cold solid substrate substantially below melting point, recalescence occurs and a shell-like structure forms throughout the drop. After recalescence, a slower solidification step driven by the heat conduction toward the solid-liquid interface ensues until solidification completion. When the last fraction of liquid turns into ice, a singular tip develops spontaneously due to expansion of water upon freezing and trijuction conditions[13,15]. The water drop solidification followed by cusp formation were also clearly shown, excluding recalescence, experimentally[16,17] and numerically[16,18].

A new set of experiments was arranged to look closely into location of this kinetics-driven phase change (recalescence) and the recalescence front speed. For this, different sizes of water drops are positioned on either hydrophobic (coated cover glass with WX2100^{TM} spray) or hydrophilic substrates (cover glass) and cooled by a Peltier element to temperatures ranging from 0 to -25 °C. It should be mentioned that the water drops and substrate are cooled simultaneously from 25 °C to designated temperatures, as opposed to the other common case of cooling, when 25 °C water drops are deposited on a cold Peltier element. In most of the cases, recalescence starts when the substrate temperature reaches -20 °C. Recalescence renders the drop fully opaque without any further noticeable light transmittance; therefore, the recalescence front can be accurately located during its propagation

Figure 2 shows the progression of the recalescence front from top and side views for two water drops on a clean hydrophilic glass substrate. During recalescence, the liquid drops are pinned down and base diameters remain unchanged; however, there is a 8.62% increase in drop volume after recalescence. This volume expansion is measured by superimposing before and after recalescence picture frames using ImageJ software. This expansion of drops outline corroborates the partial solidification of liquid drop by the recalescence stage, as freezing of water is accompanied by volume expansion in an open hexagonal form.

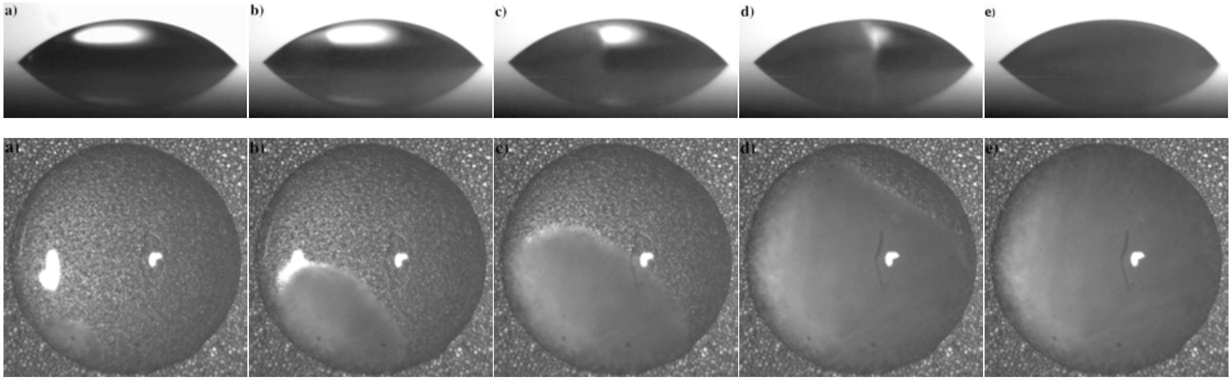

Fig. 2: Recalescence front progression from side and top view (a-f). From both side and top view images, recalescence started from a trijunction point. Drop sizes for side and top views are 3.2 and 4.7mm, respectively.

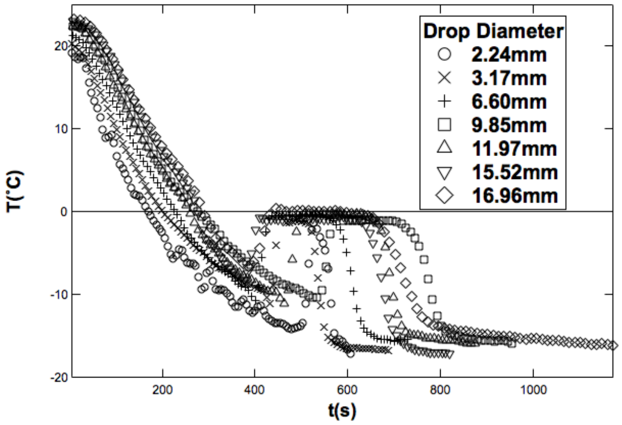

Fig. 3: Evolution of the surface temperature of cooling water drops versus time on a hydrophobic surface (WX2100^{TM} spray on cover glass) measured by a K-type thermocouple for multiple drop sizes.

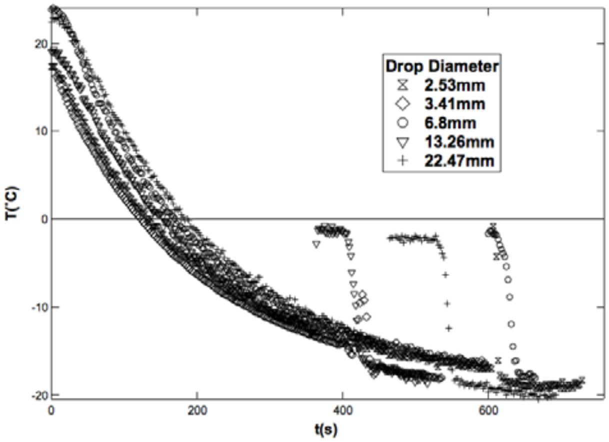

Fig. 4: Evolution of the surface temperature of cooling water drops versus time on a hydrophilic surface measured by a K-type thermocouple for multiple drop sizes.

In our experiments, the cooled drops on both hydrophilic and hydrophobic surfaces undergo four well-known cooling stages (figs. 3 and 4). Smaller drops get cooled faster until recalescence initiation. The recalescence stage duration is less than 20 ms, in which the drop becomes completely opaque. During recalescence, drop temperatures rapidly return to the solid-liquid equilibrium temperature. The main stage starts with rise of an ice sheet from the basal plane and finishes after cusp formation on top of the ice and is strongly dependent on drop size. Larger drop footprints yielded longer solidification times ranging from 27s to 217s for a drop diameter of 2.27mm to 15.52mm on hydrophobic surfaces, respectively. At this stage, droplet temperature would be independent of time. Right after cusp formation, the ice droplet cooling starts and lasts longer for bigger drops, ranging from 38.55s to 135.23s. In addition, main solidification stage lasts longer on hydrophobic surfaces with respect to hydrophilic ones, mostly evident for around 6mm droplets. Most importantly, no conclusive relationship can be made regarding the duration of the supercooling stage with drop size and the surface hydrophobicity.

FLIR® A600-series infrared camera was used as a complementary thermal mapping technique to explore the parameters dictating the supercooling stage duration. As like for previous experiments, water drops were deposited on cold solid substrates and cooled to temperatures below melting point of water. The IR camera was situated 10cm above the substrate surface and emissivity of the camera was set to 0.95. Atmosphere humidity induces formation of micro drop condensation around the main deposited drops on the glass substrate. In larger areas, recalescence of condensed micro-drops surrounding the main drop manifests itself in a wave-like “front” movement. This front seems fairly straight with some instability-induced bumps. The moment at which the wave reaches the main drop circumference, recalescence is triggered in the drop, and propagates through the drop. In return the main drop’s recalescence, after the completion of the main drop’s recalescence, sets off recalescence of surrounding drops close to the drop which continues to move away radially from the main drop. This clearly explains the data inconsistency of elapsed time to recalescence initiation in figs. 3 and 4, as condensed drops wave-like recalescence motion govern the main drop's nucleation initiation. More importantly, this observation could possibly undermine the popular belief that hydrophobic surfaces postpone the solidification initiation[19,20].

Conclusion. We study the freezing of supercooled liquids by cold solid hydrophilic and hydrophobic substrates. Using a high-speed camera, we observe a well-known intermittent kinetics-driven stage (recalescence) prior to the main freezing whose freezing speed is in the range of 50-150 mm/s. This is also confirmed from the temperature measurements acquired by the k-thermocouple and the IR camera, at which cooled drops reached zero degrees °C in less than 20ms and maintained that value until the main solidification interface fully covers the drop from the bottom plane to the top. In all of our 76 experiments, the nucleation fronts initiate from a point on the trijunction and propagate into the drop volume with different structural morphologies determined by temperatures and surface hydrophobicity of the substrate. The morphology of the recalescence structure varies from planar to dendritic growth depending heavily on the substrate temperatures whereas, on hydrophobic surfaces, the recalescence interface maintains a convex front. After completion of the main solidification, cooling of ice begins at relatively constant rate. Both the main solidification and ice cooling duration are highly dependent on drop size. However, no conclusive relationship can be made regarding the duration of the supercooling stage with the drop size and the surface hydrophobicity. The duration of supercooling stage is dictated by the collective recalescence of condensed micro-drops surrounding the main drop that manifests itself in a wave-like "front" movement. This front seems fairly straight with some instability-induced bumps. The moment at which the recalescence wave reaches the main drop circumference, recalescence is triggered in the main drop.

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