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Freezing Characteristics of Water Drop on Different Wettability Surface

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Abstract

In this paper, an experimental system was built to study the freezing characteristics of water droplets on different wettability surfaces, including a hydrophilic titanium alloy surface, a hydrophobic titanium alloy surface, and a superhydrophobic aluminum alloy surface. Using a High-speed camera, we observed that the freezing process of the water droplets on the cold surface, which consists of supercooling process, recalescence (nucleation) process, solidification (freezing) process, and ice-cooling process. The shape features and freezing time evolution of water droplet during each process were demonstrated and analyzed. And the characteristics and regularities of water droplet freezing on surface of various wettability were summarized based on observation and statistics. The present work aimed to provide an insight into freezing characteristics of water droplet.

1 Introduction

In the aircraft flight area, most of the ice forms when supercooled water hits airfoil, where it adheres easily in a short time. Because traditional anti-icing/deicing techniques need lots of energy, investigators have paid attention to superhydrophobic coatings in recent years.

Some research reported superhydrophobic materials could reduce the adhesion of water droplets so that water droplets easily fall off (Mishchenko et al. 2010), delay freezing (Shen et al. 2015), and reduce the ice on aircraft surface effectively. Efforts also have been put on the fundamental of water droplet freezing. For example, Tavakoli et al. (2015) studied freezing process of supercooled water droplets on hydrophilic and hydrophobic surface and observed a well-known process of recalescence. Jung et al. (2011) found homogeneous nucleation took place from the gas-water droplet interface under unsaturated gas flow conditions. Jin and Hu (2012) described the time evolution of water droplets on cold surface by the way of MTT (a lifetime-based molecular tagging thermometry) technique. Chaudhary and Li (2014), Oberli et al. (2013) reported the temperature evolution of cooling and phase change of water droplets. Besides, Anderson et al. (2016), Snoeijer and Brunet (2012) mainly studied the cause of the formation of the tip after the completion of the freezing of water droplets. However, profound studies on water droplet freezing on different wettability are few.

To evaluate wettability of different surface, Contact angle has been defined. On an ideally flat surface in Fig. 1, when the water droplets reach the equilibrium of all three interfacial tensions, the tangent line of gas-liquid interface goes through a point O called as trijunction. The angle θ between this tangent line and the solid-liquid phase interface is defined as contact angle. The contact angle is given by Young's relation:

$$\cos\theta = \frac{\gamma_{SA}-\gamma_{SL}}{\gamma_{LA}} \tag{1}$$

where γ_{SA}, γ_{SL} and γ_{LA} are gas-solid, solid-liquid and gas-liquid interfacial surface tension respectively. When $\theta < 90°$, the solid surface is a hydrophilic surface with high surface free energy. When $\theta > 90°$, the solid surface is a hydrophobic surface with low surface energy. Particularly, when $\theta > 150°$, the solid surface is a superhydrophobic surface.

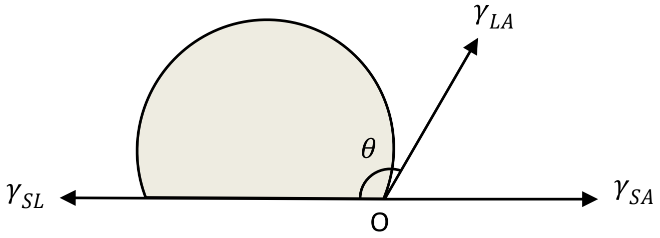
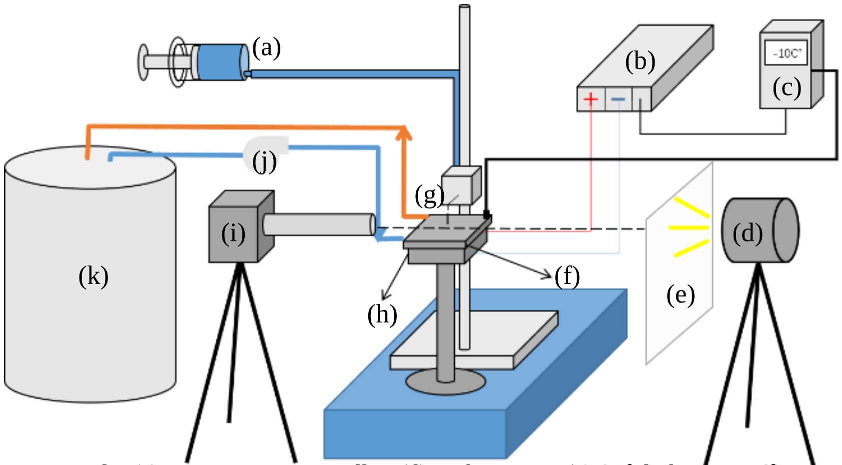


Figure **1**: Schematic representation of a water droplet on smooth solid surface.

2 Experimental Setup

In this experiment as shown in Fig. 2, the deionized water droplets are deposited on the cold test surface by water droplet generator composed of a syringe and a needle. As shown in Fig. 3, the test surfaces with the dimension of 5cm×5cm, consist of a hydrophilic titanium alloy surface, a hydrophobic titanium alloy surface, and a superhydrophobic aluminum alloy surface. With semiconductor cooling, the test surface is capable of reaching temperatures as low as -25℃. The high-speed camera (FASTCAM Mini UX100) with the Navitar microscope Zoom 6000 is used to view the water droplet. The contact angles (Table 1) of water droplets are measured with horizontal light, and the phase change processes of water droplets are observed by semi-backlit lighting method. Experimental data are obtained by MATLAB image processing.



(a) Syringe. (b) Power supply. (c) Temperature controller. (d) Light source. (e) Soft light paper. (f) Test surface. (g) Water droplet generator. (h) Semiconductor plate. (i) High-speed camera. (j) Pump. (k) Water tank.

Figure **2**: Schematic representation of the experimental setup.

(a) hydrophilic surface (b) hydrophobic surface (c) superhydrophobic surface

Figure **3**: Three surfaces of different wettability.

Table **1**: Value of Contact angel

Surface	Hydrophilic	Hydrophobic	Superhydrophobic
Contact angel	84.85°	142.33°	153.43°

3 Results and Discussion

Cooling and freezing process of the water droplets on the cold surface consist of supercooling process, recalescence (nucleation) process, solidification process, and ice-cooling process (Li and Liu 2010).

3.1 Supercooling process

Upon supercooling process, as the temperature of cold surface gradually decreases, the morphology of water droplet changes. The contact angle of water droplet gradually decreases with an increase of solid-liquid contact area. The principle of above observation is that supersaturated water vapor condenses in the vicinity of the three-phase contact line, which changes the solid-gas and the solid-liquid surface tensions. As the surface temperature decreases, the solid surface tends to be more hydrophilic. Although gas-liquid surface tension increased, the contact area between water droplet and surrounding air gradually increases.

3.2 Recalescence (nucleation) process

As shown in Fig. 4, recalescence process starts at the initial moment of nucleation at a certain point on the three-phase contact line until the crystals fill the whole water droplet. Released latent heat results in the increasing of temperature during nucleation. Water droplet changes rapidly from a transparent state to an opaque state in 30ms. Crystal morphologies are different on different wettability surface. On hydrophilic surface, crystals show dendritic growth, planar growth, and half-plane growth. On hydrophobic surface, crystals show a convex structure. However, because of the instability on superhydrophobic surface, crystals develop complex features with dendritic growth, planar growth, and spiral growth.

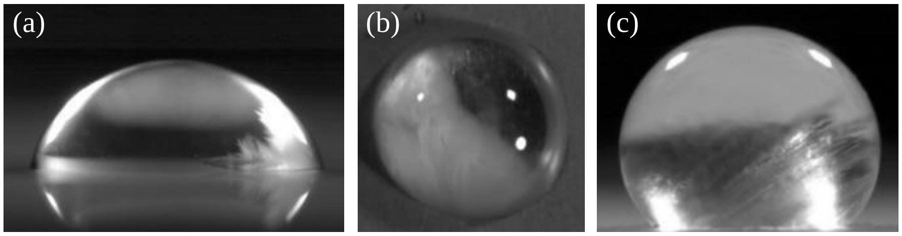
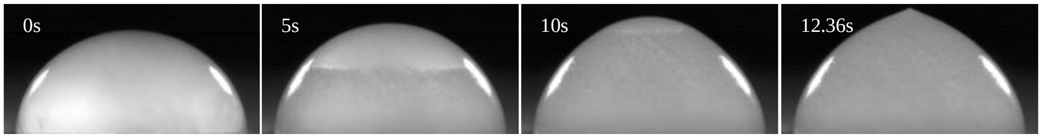


Figure **4**: Recalescence front morphology (a) on hydrophilic surface from side view, (b) on hydrophilic surface from top view, (c) on superhydrophobic surface from side view

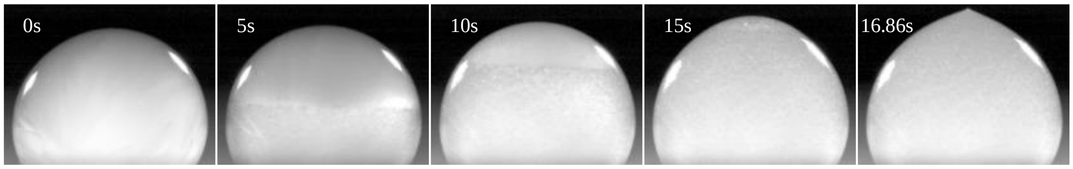
The reason for the loss of transparency of water droplet during nucleation is that the solubility of air in ice is less than the solubility in water (Oberli et al. 2013). Air bubbles release in water droplet, which changes refractive index of light, and the transparency of water droplet loses. Another explanation is that the partially solidification of water droplet leads a solid ice shell because of lower temperature. Then light scattering results in water droplet opaque.

3.3 Freezing (solidification) process

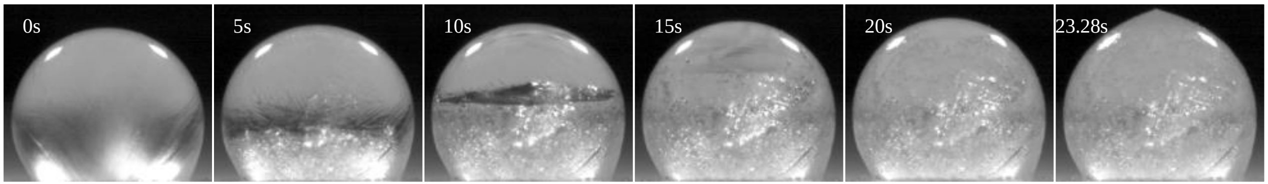
Figure 5 (original images) and Figure 6 show the freezing process that freezing front rises from contact surface to the highest point. Because of different densities of ice and water, the shape of water droplet changes significantly. When the last fraction of liquid solidifies into ice, the shape of water droplet top turns from round to pointy due to expansion of water (Marín et al. 2014). However, water droplet only expands upward with the contact area unchanged. The maximum diameter of water droplet on the hydrophobic surface and the superhydrophobic surface remains unchanged but uplifted. At the final stage of freezing as shown in Fig. 6, water drop height and freezing front increase faster due to rapid expansion of cusp. As shown in Fig. 7, the volume of water droplets and the volume of freezing have the same trends of evolution for the investigated three surfaces with different wettability. Water droplet volume increases equably, but the increasing of freezing volume gradually slows down, which might provide another idea of volume growth instead of height growth (Anderson et al. 2016) to study the shape and freezing rate of water droplets. Supplementary explanation is that Figure 6 and Figure 7 are dimensionless based on the original diameter and volume respectively.



(a) Hydrophilic



(b) Hydrophobic



(c) Superhydrophobic

Figure **5**: Freezing sequence of water droplets on (a) hydrophilic, (b) hydrophobic, and (c) superhydrophobic surface.

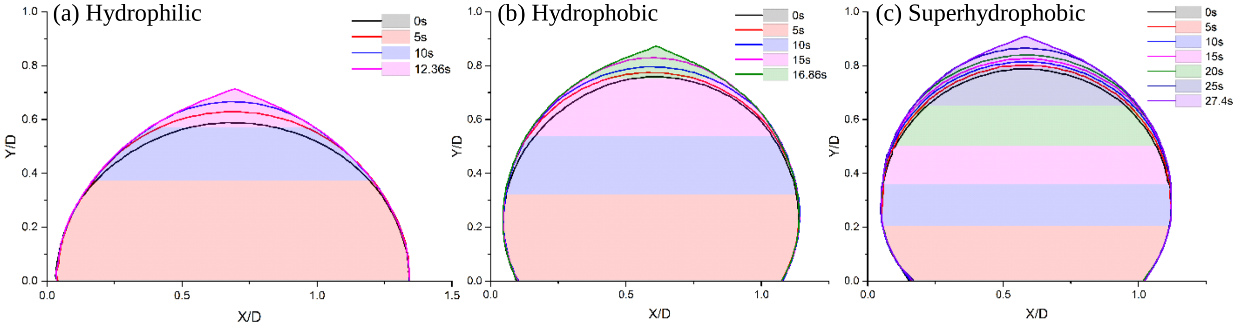


Figure **6**: Changes in morphology of (a) hydrophilic, (b) hydrophobic and (c) superhydrophobic droplets and freezing fronts

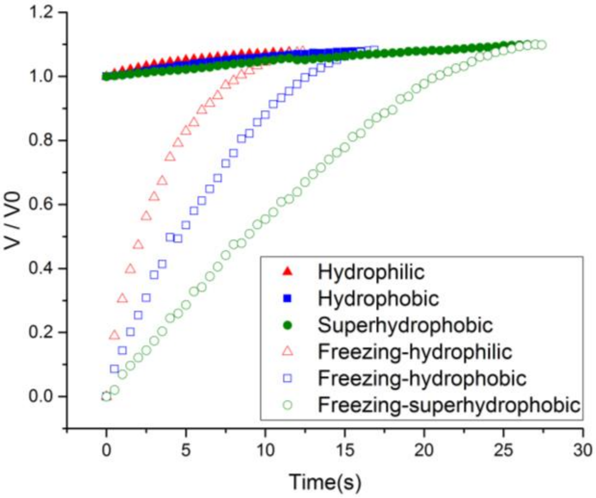


Figure **7**: Changes in water droplet volume and freezing volume

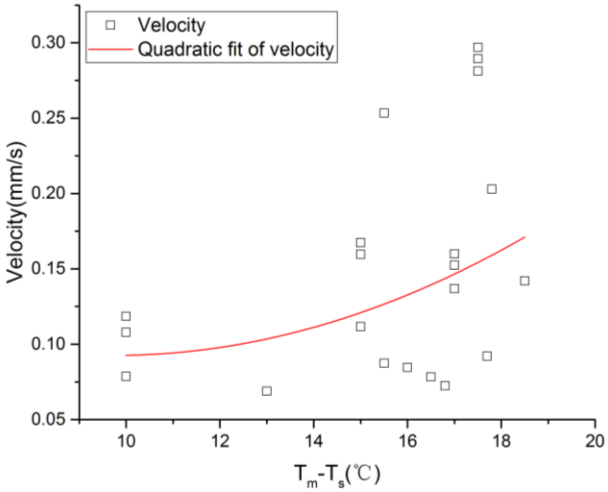


Figure **8**: Freezing front speed versus supercooling temperature for different surface wettability

Freezing process time of water droplet is about 20 seconds. Freezing time on the hydrophobic surface of the titanium alloy is around twice on the hydrophilic surface. Freezing spends a long time due to lower heat conduction rate. The speed of freezing mainly depends on the heat conduction of the cold plate and the air convection in the surrounding environment. The thermal conductivity of the two surfaces can be described by the following equation

$$\mathrm{d}Q/\mathrm{d}t = -hA(T_2 - T_1) \tag{2}$$

where $\mathrm{d}Q/\mathrm{d}t$ = thermal conductivity; h = surface heat transfer coefficient; A = contact area between water droplet and cold surface; T_2 = water droplet temperature; T_1 = cold surface temperature. It describes the heat transfer between cold surface and water droplet and ice-water interface during the freezing process. Thermal conductivity is proportional to contact area. With the same volume of water droplets, contact area on the superhydrophobic surface is smaller than that on the hydrophilic surface. Thus, the complete freezing costs longer on the superhydrophobic surface.

Figure 8 shows the relationship between freezing front speed and supercooling temperature, which illustrates the processing of water droplet freezing is indeed random. Freezing front speed increases as supercooling temperature increases, and the relationship can be expressed by

$$v \propto (T_m - T_s)^2 \tag{3}$$

where v is freezing front speed in mm/s, T_m is melting temperature, and T_s is surface temperature.

3.4 Tip angle of ice droplet

Assume that the angle of the cusp of ice droplet after freezing as shown in Fig. 9 is a constant (Marín et al. 2014) and not affected by cold surface temperature and contact angle of ice droplet, which denotes surface wettability.

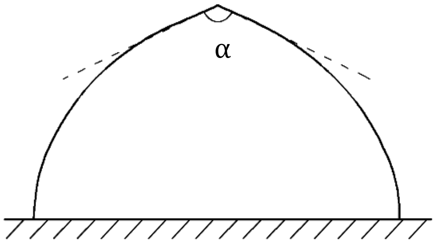


Figure **9**: Schematic representation of the tip angle (α) of ice droplet

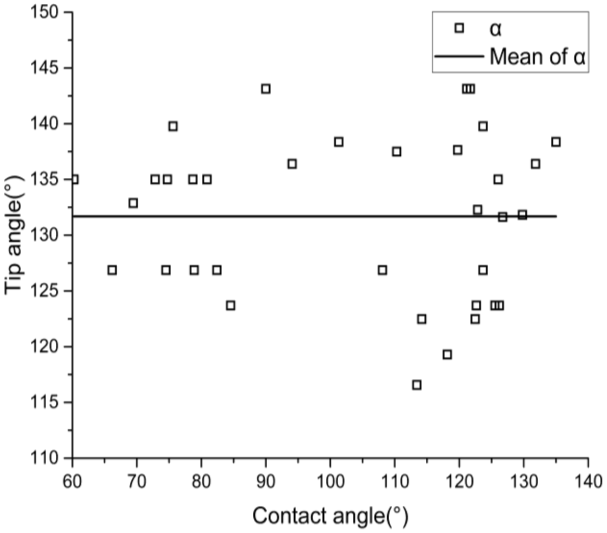


Figure **10**: Scatter plot of tip angles

The average of tip angle is approximately 132° in the result of Fig. 10. Although these data can not prove that the size of cusp has no connection with cold surface temperature and contact angle, it shows that the formation of cusp is irrelevant to the shape of water droplet and the time when water droplet freezes.

4 Conclusion

This experiment observed supercooling process, recalescence (nucleation) process, solidification (freezing) process, and ice-cooling process of water droplets. Water droplet temperature gradually decreases as cold surface temperature decreases, until crystals begin to grow, accompanied by increasing of surface hydrophilicity. Recalescence process is extremely short, when Crystal buds develop rapidly from one point of three-phase contact lines, water droplet becomes opaque and temperature rises sharply. The form of nucleation is related to surface hydrophobicity. During the freezing process, temperature of water droplet remains unchanged. Finally, a cusp appears on the top of water droplet. The time of freezing process increases as the hydrophobicity of surface increases. Freezing front speed is quadratic proportional to the supercooling temperature. The statistics of the tip angle of ice droplets, shows that tip angle is irrelevant to droplet shape and the time of droplet freezing.

In practical application, the anti-icing properties of superhydrophobic materials are not only related to the degree of wettability, but also to the micro- or nano- structures of solid surfaces, chemical stability of super-hydrophobic coatings, and the structural strength of solids. Therefore, in addition to studying the method of enhancing the hydrophobic and anti-icing properties of superhydrophobic surfaces, the durability, chemical stability, and structural strength of solid surfaces are key to the application of superhydrophobic surfaces in practical engineering.

Acknowledgements

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