

Influences of surface hydrophilicity on frost formation on a vertical cold plate under natural convection conditions

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Abstract

Surface hydrophilicity has a strong influence on frost nucleation according to phase transition theory. To study this effect, a close observation of frost formation and deposition processes on a vertical plate was made under free convection conditions. The formation and shape variation of frost crystals during the initial period are described and the frost thickness variation with time on both hydrophobic and plain copper cold surfaces are presented. The various influencing factors are discussed in depth. The mechanism of surface hydrophilicity influence on frost formation was analyzed theoretically. This revealed that increasing the contact angle can increase the potential barrier and restrain crystal nucleation and growth and thus frost deposition. The experimental results show that the initial water drops formed on a hydrophobic surface are smaller and remain in the liquid state for a longer time compared with ones formed on a plain copper surface. It is also observed that the frost layer deposited on a hydrophobic surface is loose and weak. Though the hydrophobic surface can retard frost formation to a certain extent and causes a looser frost layer, our experimental results show that it does not depress the growth of the frost layer.

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1. Introduction

Frost deposition is a very common phenomenon occurring on cold surfaces in both our daily lives and engineering applications. When water vapor in the surrounding air gets contacted with a heat transfer surface whose temperature is lower than the triple point of water through mass transfer, then frost will inevitably appear on the surface. Frost formation can result in many serious negative effects on cryogenic equipment and systems, including flow passage blockage, poor heat transfer performance, pressure drop increase, low energy efficiency and even system malfunction. Therefore frost deposition control is very important for the equipment and these systems. In order to maintain

their normal operation, defrosting must be carried out regularly. Frost removal not only increases energy consumption, but also decreases effective production time and thus increases production costs.

The factors that influence frost formation on cold surfaces are many. These include cold surface temperature, air velocity, air temperature, air humidity, surface energy etc. Many researchers have studied influences of ambient conditions and cold surface temperature on frost growth, but little research has been done to investigate the effects of surface energy on frost formation. A few studies have shown that changing the surface energy of the cold surface is a very attractive way to modify frost properties and change the process of frost deposition. Nikulshina et al. [1] and Hoke et al. [2] found that a denser frost layer was formed on a lower energy surface than on a higher one, i.e., the frost layer deposited on a hydrophilic surface is

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Nomenclature

G	Gibbs free energy, J	$r_{c,vs}$	critical radius, m
$\Delta G_{c,vs}$	critical potential barrier, J	φ	air relative humidity
k	Boltzmann's constant, J/(K molecule)	θ	contact angle between vapor and solid phases, deg
p	vapor pressure, N/m ²	σ_{vs}	interfacial energy between vapor and solid phases, N/m
p_{vs}	saturated vapor pressure corresponding to T_w , N/m ²	Ω_s	volume of a single molecule, m ³
T_∞	room temperature, °C		
T_w	cold surface temperature, °C		

denser than on a hydrophobic surface. Furthermore, it was postulated that different shapes of frozen droplets on the surfaces with different surface energies are the main reason for the formation of different frost structures. Tao et al. [3], Shin et al. [4] and Hoke et al. [2] predicted that during the initial period of frost formation, the diameter of water droplets formed on a hydrophilic surface before the condensed water droplets turned into ice crystals is larger than that on a hydrophobic surface. Na and Webb [5] provided a detailed analysis of the fundamental factors affecting frost nucleation. They found that a low energy surface requires a much higher supersaturation degree for frost nucleation than a high energy surface and concluded that there is a strong possibility to develop surfaces that delay frost formation on a surface having a lower surface temperature. Forest [6] evaluated the use of polymer coatings to reduce the surface energy. This resulted in a reduced ice adherence force. He concluded that a zero surface energy coating would be the most effective surface for releasing frost particles from the cold surfaces. Wu and Webb [7] studied the possibility of using hydrophobic and hydrophilic surfaces to release frost from cold surfaces. They tried to apply an additional force field to release the frost particles from the cold surface since a zero surface energy surface was impossible for them to achieve. However, their experiments were not successful in removing frost from a hydrophobic surface by additional mechanical vibration. More recently, Lee et al. [8] studied the frost formation on a plate with different surface hydrophilicity experimentally under forced convection conditions and concluded that surface with low dynamic contact angle (DCA) showed lower frost thickness and higher frost density than that with high DCA. But no detailed frost thickness measurement results were presented. They also found that frost structures on surfaces with different DCA were similar.

In this paper, a series of micro-observations of the frost formation process on a vertical cold plate under natural convection conditions were carried out and comparisons were made between the frost deposition phenomenon on a hydrophobic surface and that on a cold plain copper surface. Micro-pictures of the initial liquid drops on the cold plate surface were obtained and the thickness growth of the frost layer on both the hydrophobic surface and the plain copper surface were measured under various ambient

conditions. A mechanism analysis based on homogeneous nucleation is also presented.

2. Experimental apparatus

A thermoelectric cooler was used as a cooling source for the frosting surface. It provided temperatures as low as $-26\text{ }^\circ\text{C}$. A copper plate of $150\text{ mm} \times 52\text{ mm} \times 6\text{ mm}$ was mounted on the cooling unit and the plate was polished by an 800# polishing cloth. During testing, the plate and the data acquisition system were placed in a large enclosure ($2.5\text{ m} \times 2\text{ m} \times 1.5\text{ m}$) in order to maintain natural convection conditions. The plate was placed vertically in all the experiments reported in this paper. The temperature and humidity inside the closure were regulated at the given values by an air-conditioning system and a humidity controller. The surface temperature of the plate was measured by four T -type thermocouples that were buried beneath the test surface 0.5 mm through four holes of 1 mm diameter and 13 mm depth drilled into the plate. Temperature data were recorded by a HP data acquisition system and were finally transferred to a personal computer for further analysis. The cold surface temperature is the average of the temperature readings of the four thermocouples. The thermocouples were all pre-calibrated with a resolution of $0.1\text{ }^\circ\text{C}$. The maximum uncertainty in the plate surface temperature measurements was estimated to be less than $0.5\text{ }^\circ\text{C}$, including the error resulting from position errors and the fact that these thermocouples were not placed exactly at the surface. A microscopic image system that consists of a CCD camera, a microscope and a capture card was used for micro and transient observations of the frost deposition process and measuring the frost layer thickness. The CCD camera and microscope with a maximum magnification of 110 were mounted directly over the cooled surface for taking photographs and observing the frost growth with the help of optical fiber luminescence. The frost deposition process was recorded by the microscopic image system at a speed of 30 f/s and the frost thickness was measured by a micro-measurement system that was integrated into the microscopic image system every 5 min and had an accuracy of $\pm 0.05\text{ mm}$. A thermohygrometer was used to monitor environmental conditions, including temperature and relative humidity. The humidity

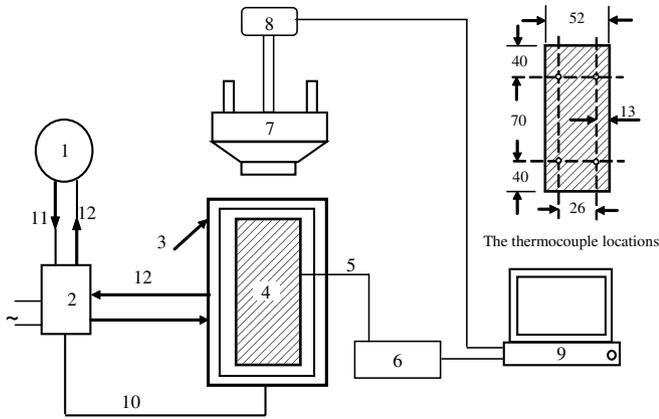


Fig. 1. Experimental system and thermocouple locations: (1) Thermostat bath; (2) power source for thermoelectric cooler; (3) thermoelectric cooler; (4) cold plate; (5) thermocouples; (6) HP data acquisition system; (7) microscope; (8) CCD camera; (9) computer; (10) power supply cable; (11) cooling water in; (12) cooling water out.

was measured by a humidity sensor with an uncertainty of 2%. Fig. 1 shows the experimental system.

3. Experimental results

A hydrophobic surface in this experiment was maintained by coating the cold copper plate with paraffin. In order to make the experimental data reliable and comparable under the exact same conditions, only the left half of the cold plate was coated with paraffin, and the right half of the cold plate of copper was left uncoated. The contact angles of water on these surfaces were measured by a FTA125 contact angle analyzer to test if the surface is hydrophobic or hydrophilic. Fig. 2 shows the measured results: the contact angle of water on the uncoated plain copper surface was 63° and this angle was 133° on the paraffin coated surface, which proves that the paraffin coated surface is hydrophobic compared with the plain copper surface.

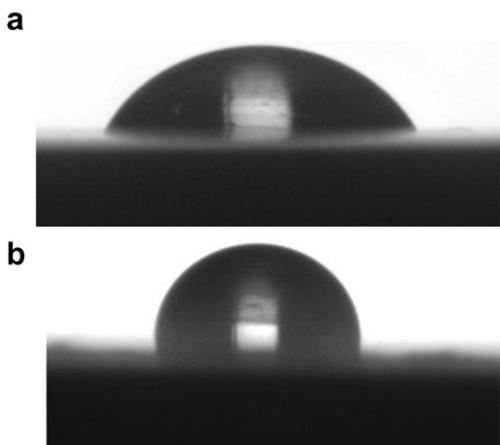


Fig. 2. The contact angles of water on the different surfaces: (a) the plain copper surface: 63° ; and (b) the paraffin coated surface: 133° .

Extensive experimental observations and measurements were carried out for both the coated and uncoated surfaces. Some of the typical results are summarized as follows.

3.1. Observation of the frost formation processes

In order to reveal the differences between the frost formation process on the plain copper surface (a hydrophilic one) and that on the paraffin-coated surface (a hydrophobic one), a close observation was made of frosting phenomena on these two different surfaces. Our observations showed that as the plate was cooling down, water drops would eventually appear. The water drops formed on the hydrophobic surface were small, and, compared with those on the hydrophilic surface, the first observable frost crystal (initial frost crystal) on the hydrophobic surface appeared much later. This is because water on a hydrophobic surface has a large contact angle and therefore the water drops on it have a form that is close to a sphere. Therefore given two water drops of the same volume, the contact area on a hydrophobic surface is much smaller than that on a hydrophilic one. If we further suppose that the heat transfer rate per unit area between the cold surface and the condensed water drop is same for both cases, then comparing the increased heat transfer area of a water drop on a hydrophilic surface with that on a hydrophobic surface predicts that the water drops on the hydrophilic surface will be frozen into frost crystals more quickly than on the hydrophobic surface. Fig. 3 shows a group of typical pictures of condensed water drops and their freezing process on the hydrophobic and on the plain copper surface. In order

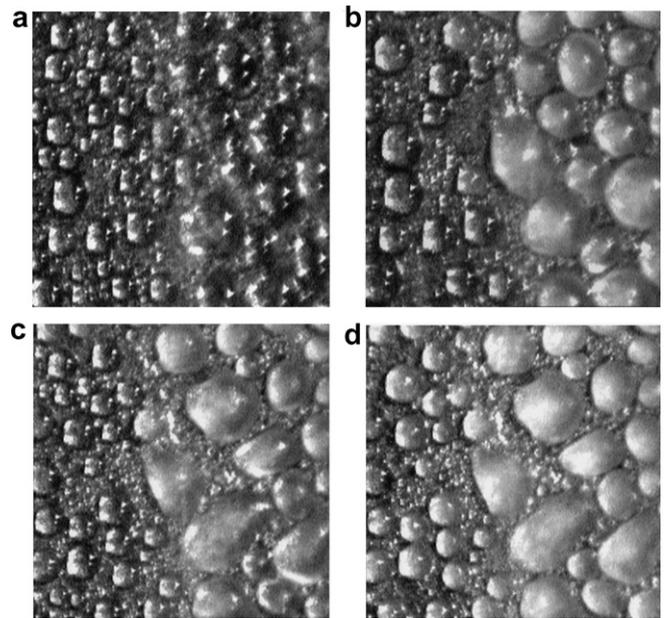


Fig. 3. Condensed water drops and their freezing process on the hydrophobic and on the plain copper surface (magnification: $45\times$): (a) 470 s, both sides unfrozen; (b) 560 s, the right side frozen; (c) 520 s, the right side frozen; and (d) 555 s, both sides frozen.

to observe more clearly the whole process of water drop freezing, the cold plate was cooled down from room temperature and the cold surface was kept in contact with humid air. Therefore the process actually begins from the condensation of water vapor onto the cold surface and then the condensed water is frozen further into frost crystals. Fig. 3(a) and (b) was obtained under the conditions of room temperature $T_{\infty} = 24.0^{\circ}\text{C}$, the cold surface temperature $T_w = -8.0^{\circ}\text{C}$ and the air relative humidity $\phi = 62\%$. Fig. 3(a) shows that there are fewer and smaller water drops on the hydrophobic surface (the left half of the picture) than on the plain copper surface (the right half of the picture). Fig. 3(b) further shows that not only are the water drops on the hydrophobic surface smaller, but also are slower to freeze. The water drops on the hydrophobic surface were still in liquid state while those on the plain copper surface were frozen into solid frost crystals. In this experiment, we found that the water drop freezing time (the time needed for the condensed water drops to be frozen) on the paraffin coated surface was longer than that on the plain copper surface by about 60 s. Under the same conditions of room temperature and air relative humidity as above, but with the cold surface temperature set at -9.4°C instead of -8.0°C , the water drop freezing time on the paraffin coated surface was 35 s longer than that on the plain copper surface, as shown in Fig. 3(c) and (d). Therefore, we may conclude that the difference between the water drop freezing time on the hydrophobic surface and that on the plain copper surface decreases as the cold surface temperature decreases. This may be explained as the following. The lower the surface temperature is, the greater the supercooling, and therefore the smaller the critical nucleate radius. The reduced critical nucleate radius will certainly cause a smaller nucleation potential energy barrier, and therefore the water drops will freeze more quickly. The shortened water drop freezing times then of course make the difference between the water drop freezing time on the hydrophobic surface and that on the plain copper surface smaller. Careful observations of Fig. 3(b) and (d) further reveal that the differences between the sizes of the water drops on the paraffin coated surface and that on the plain copper surface increases as the cold surface temperature decreases.

Fig. 4 presents the pictures of the initial frost layer formed on the hydrophobic surface (the left half of the picture) and the plain copper surface (the right half of the picture) under the conditions of room temperature $T_{\infty} = 23.5^{\circ}\text{C}$, plate temperature $T_w = -12.0^{\circ}\text{C}$ and air relative humidity $\phi = 68\%$ at different times. As we can see from Fig. 4(a) at 460 s, though a continuous ice layer had already formed on the uncoated hydrophilic plain copper surface, on the hydrophobic paraffin coated surface, the condensed water droplets maintained their liquid state in the form of discrete water drops. Even at 530 s, as Fig. 4(b) shows, there are still some unfrozen water drops on the paraffin-coated surface. This agrees with the observations presented by Liu and Chen [9] to a certain extent. However, our close and repeated observations show that large condensed water drops will be formed on the plain copper surface only under the conditions of relatively high cold plate temperature and high air relative humidity. Then these large drops coalesce to form a continuous liquid film and finally are further frozen to produce a continuous ice layer. That is, only under these conditions is the initial frost deposition behavior on a hydrophobic surface significantly different from that on a hydrophilic surface. We also observed that the frost crystal growth on the hydrophobic surface shows a stronger dendritical pattern than on the hydrophilic surface during the initial stage of frost formation. This stronger dendritical growth results in a looser and weaker frost layer structure on the hydrophobic surface, which is in general agreement with the experimental measurement results by Lee et al. [8]. It was also revealed from our experimental observation that the influence on frost formation of the hydrophobicity of a surface is basically limited to the very initial period of frost formation. After a continuous frost layer is formed and therefore the surface is fully covered by the frost layer, the frost formation behavior on a hydrophobic surface and that on a hydrophilic one is the same. Therefore a hydrophobic surface does not actually restrain frost deposition phenomena as effectively as it is expected to. The hydrophobicity of a surface has a very weak influence on the frost deposition process as a whole, especially during the late stages of the process.

3.2. Frost thickness growth

In order to ascertain the effects of the surface hydrophobicity on frost deposition, the frost thickness on both the plain copper and the paraffin-coated surface were measured against time. To make the data comparable, the frost thickness data for both the paraffin-coated and the plain copper surfaces were obtained on the same plate with its left half coated with paraffin. Therefore, each group of frost thickness data for both surfaces was obtained under exactly the same conditions. Fig. 5 presents some of the typical experimental results. From these measurements we found that the frost thickness growth on the hydrophobic (paraffin-coated) surface was smaller than

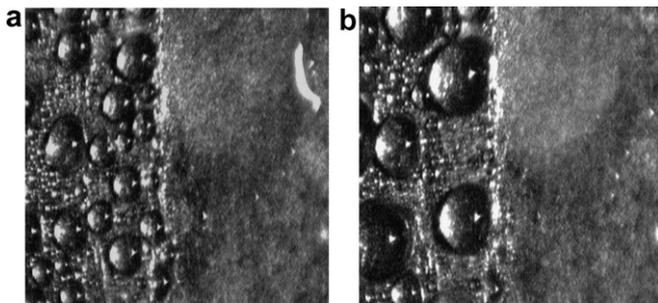


Fig. 4. Initial frost layer comparison (magnification = 45 \times): (a) 460 s; and (b) 530 s.

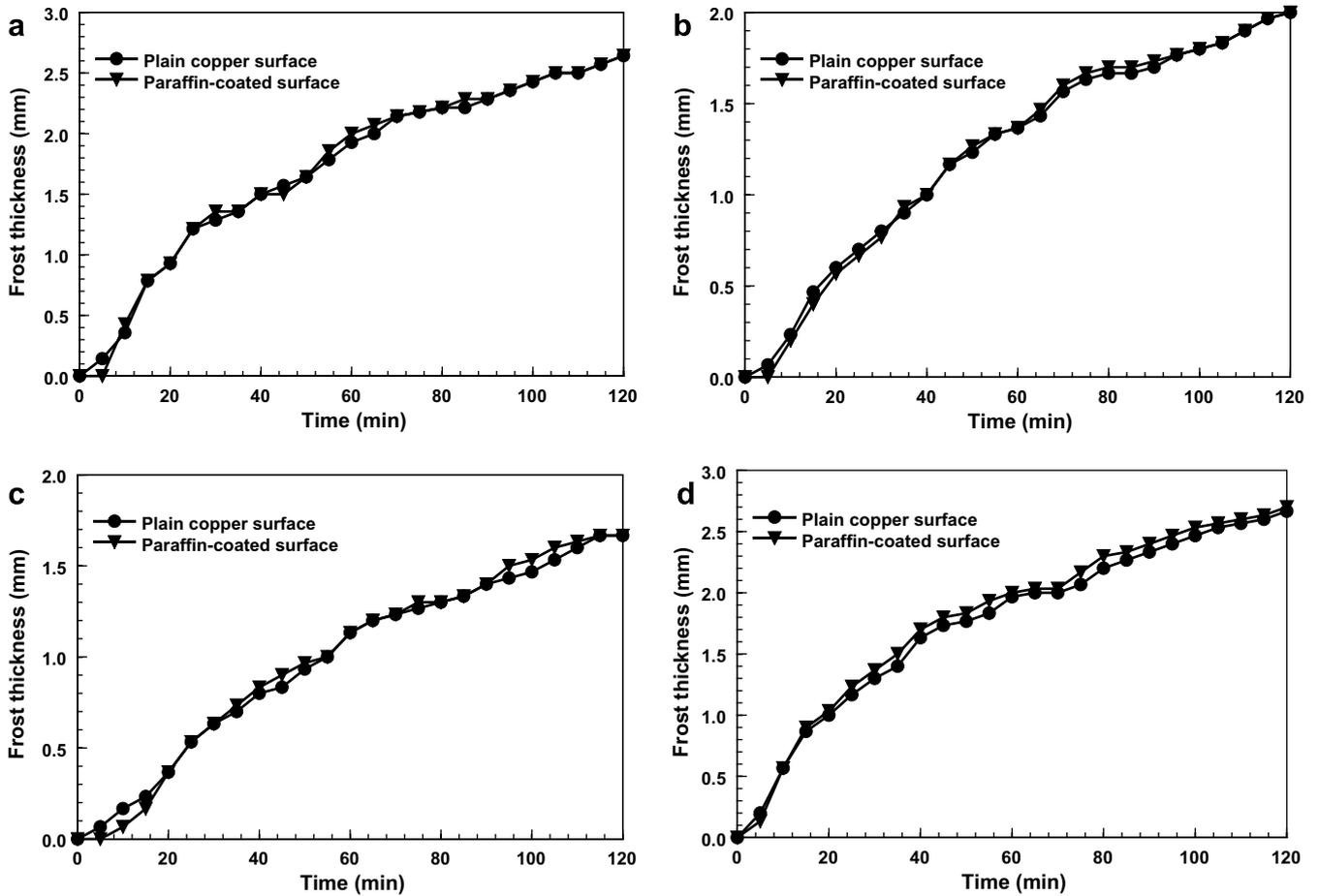


Fig. 5. Comparison of frost thickness growth on the plain copper surface with the paraffin-coated surface under different conditions: (a) $T = 21.0\text{ }^{\circ}\text{C}$, $T_w = -9.4\text{ }^{\circ}\text{C}$, $\phi = 68\%$; (b) $T = 20.4\text{ }^{\circ}\text{C}$, $T_w = -7.1\text{ }^{\circ}\text{C}$, $\phi = 63\%$; (c) $T = 22.6\text{ }^{\circ}\text{C}$, $T_w = -11.0\text{ }^{\circ}\text{C}$, $\phi = 51\%$; and (d) $T = 22.6\text{ }^{\circ}\text{C}$, $T_w = -11.0\text{ }^{\circ}\text{C}$, $\phi = 78\%$.

that on the hydrophilic (plain copper) surface during the early stage of frost deposition. It should also be noted that from Fig. 5(a)–(c) we can see that the hydrophobic surface does show some frost deposition retarding effect, the time for the formation of the first continuous frost layer on the hydrophobic surface is 4–5 min later than on the hydrophilic surface. However, after the cold surface was completely covered by frost crystals, the frost thickness growth on both the hydrophobic and the hydrophilic surfaces was almost the same. Therefore we may conclude from our experimental measurements, that the surface hydrophobicity can only influence the early-stage behavior of frost formation. It will not produce any significant effects on the longer time frost deposition process.

4. Theoretical analysis

Frost formation on a cold surface is a typical crystal growth process, and therefore nucleation will influence the frost growth significantly. According to homogeneous nucleation theory, one of the conditions for a crystal to exist and grow is that its size must be greater than its critical radius. From the thermodynamic theory of phase

transition, we know that the phase transition can happen only if the process will result in a decrease in the Gibbs free energy of the system. If the initial crystal size is bigger than its critical radius, the Gibbs free energy decreases as the crystal grows bigger. Therefore the crystal with a size larger than its critical radius can grow spontaneously [10].

Supersaturated vapor in air is the metastable phase and the frost crystal is the stable phase in the frost formation process. For supersaturated vapor to change from its metastable phase into the stable phase (frost crystal) a so-called potential barrier, i.e., the Gibbs free energy difference ΔG must be overcome. Only when the potential barrier is exceeded, can the new crystal nucleus be formed and grow. If the spherical cap shape is assumed for a frost crystal formed on a flat wall, then the potential barrier that must be overcome [11] is

$$\Delta G_{c,vs} = \left[-\frac{4\pi r_{c,vs}^3 kT_w}{3\Omega_s \ln\left(\frac{p}{p_{vs}}\right)} + 4\pi r_{c,vs}^2 \sigma_{vs} \right] f(\theta) \quad (1)$$

where $\Delta G_{c,vs}$ is the critical potential barrier and $f(\theta)$ is given by the following equation:

$$f(\theta) = (2 - 3 \cos \theta + \cos^3 \theta) / 4 \quad (2)$$

θ is contact angle between vapor and solid phases, σ_{vs} is interfacial energy between vapor and solid phases, Ω_s is volume of a single molecule, $r_{c,vs}$ is the critical radius, k is Boltzmann's constant, T_w is the wall temperature, p is the vapor pressure and p_{vs} is saturated vapor pressure corresponding to T_w .

From Eq. (1) we can see that the value of the function $f(\theta)$ will directly change the potential barrier and $f(\theta)$ is fully determined by the contact angle. Therefore the contact angle, and thus the hydrophobicity of the surface will affect the potential barrier. Hence, the hydrophobicity of the surface influences the frost crystal nucleation.

From Eq. (2) we have,

$$\frac{df}{d\theta} = \frac{3}{4} \sin^3 \theta \quad (3)$$

Since θ is within 0° and 180° and $\sin \theta \geq 0$, therefore,

$$\frac{df}{d\theta} = \frac{3}{4} \sin^3 \theta \geq 0 \quad (4)$$

that is to say, $f(\theta)$ is a monotonously increasing function of contact angle. Hence, increasing the contact angle of a surface will increase the potential barrier, and thus restrain the frost crystal nucleation.

In our experiments, the contact angle of the plain copper surface was 63° and the paraffin-coated surface was 133° . Therefore the potential barrier needed for frost formation on the plain copper surface is smaller than the paraffin-coated surface. So we may conclude that frost nucleation is easier on the plain copper surface than on the paraffin-coated surface. Our experimental observation and measurements confirmed the theory. We found from our experiments that the time needed for a liquid drop to be frozen on the paraffin-coated surface was longer than that on the plain copper surface, and the growth of a frost layer on the hydrophobic surface was slower than that on the plain copper surface during the very early stages of frost deposition. However, as the deposited frost crystals covered the surface and formed a continuous frost layer, the effects of the surface hydrophobicity became weaker and weaker. Therefore, the influence of the surface hydrophobicity on frost formation was only limited to the initial period of the frost deposition process. We also noticed however, that the frost layer formed on the hydrophobic surface during the initial period was much weaker and looser than that on the plain copper surface. This may provide some help for the easy removal of the frost layer.

5. Conclusion

The experimental and theoretical results demonstrate that surface hydrophobicity has a strong influence on frost nucleation and the initial period of the frost deposition process. The water drops condensed on a hydrophobic surface are smaller and present a more spherical shape than that on a hydrophilic surface. It is also revealed from our

experimental observation that the frost layer formed on the hydrophobic surface is loose and weak and can be easily removed, compared with that on the hydrophilic surface. The frost crystal growth on the hydrophobic surface shows a stronger dendritical pattern than on the hydrophilic surface. However, our experimental observation and measurements also show that the influence of surface hydrophobicity is limited to the very initial period of the frost deposition process. After a continuous frost layer formed on the surface, the behavior of frost deposition on both the hydrophobic and the hydrophilic surface shows no significant difference. Actually, our frost thickness measurements on the two different surfaces show that the hydrophobicity has no recognizable influence on the frost thickness growth for long test runs.

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