Dynamic contact of droplet with superhydrophobic surface in conditions favour icing

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Abstract. Flight like droplet impact with superhydrophobic substrate in conditions favour icing is discussed in this work. Test stand with fast camera and equipment eligible to obtain temperatures and humidity at different ranges, lead to results which can prove, that superhydrophobic surface might be good ice repellent substrate. The influence of air humidity on droplet freezing was confirmed.

1. Introduction
The fluid mechanics of drop impact with surfaces is of importance in a variety of different fields. Scientist has been researching the droplet collision with dry or wet substrate since nineteenth century. The precursor of such investigations was Worthington [1]. It is relevant to many industrial applications and has many undesired effects. Droplet collisions have place in agriculture and daily life (processes like spray cooling, coating, painting, ink-jet printing, etc). Erosion at steam turbine blades caused by high-speed impact is one of the undesired effects. Wind-shields, cloths and roofs are examples of things in which repelling water properties have to be enhanced. Recently, application to aircraft anti-icing has been considered. An aircraft during flight has to wrestle with varied flight conditions, which depend on humidity, temperature and pressure. The work of Bobiński [2] has shown that water was not freezing, when experiment has been done in volume filled with waterless nitrogen (the low humidity, around 8%). That is why, this work is focused on results more likewise occurring during flight. Low temperatures and changes of humidity favorable to the ice formation. Such phenomenon is extremely dangerous for all kind of aircrafts and huge amount of money are spent to overcome it. Rapid development of material engineering introduced new type of materials, such as Graphene, textured surfaces coated with different chemical compound, which can be used as a coating of an aircraft wings. Understanding how does the collision of the droplet with aircraft surface in varying conditions may lead to overcome or reduce ice formation during flight.

The main objectives of this thesis were:
- To investigate the droplet behaviour during the impact with surface in flight like conditions - temperature in range from +25°C to -30°C for varying conditions, depending on surface hydrophobicity, humidity and varying temperature.
To investigate the droplet behaviour during impact with varying phases of ice formation
To investigate the supercooled droplet behaviour impact

2. Water properties. Hydrophobicity.
One of the most important factor relevant to droplet impingement is surface upon which it falls. Therefore, the ultimate goal would be to engineer surface in a proper way for certain application, by enhancing or decreasing surface wettability. Recently, the subject of droplet impinging surface is more and more popular because it became possible to produce surfaces with regular, specially designed patterns [3]. What determines whether the surface is hydrophobic or hydrophilic and what does it mean the surface is superhydrophobic? To explain the difference, first it has to be described the nature of surface tension. If we consider a droplet on a perfectly flat, dry and smooth solid surface it may remain as a drop of finite area or it may spread over the surface. Spreading appears if the energy, which is gained in forming unit area, of the solid-liquid interface exceeds that required to form unit area of the liquid-air surface. Hence, spreading will occur if inequality 1 is fulfilled. In case it is not, the drop has finite size and equilibrium contact angle exists. In terms of surface tension one can write

\[ \sum F_x = \gamma_{SL} - \gamma_{SL} \cos(\Theta_E) = 0 \] (1)

\[ \cos(\Theta_E) = \frac{\gamma_{SL} - \gamma_{SL}}{\gamma_{LA}} \] (2)

Rearranging this balance formula yields (1), which describes the droplet’s contact angle and related surfaces free energy. Contact angle is measured as the angle (2), determined by vertex at the three-phase line, where the droplet meets the solid. In the formulas above: \( \Theta_E \) is the contact angle, \( \gamma_{SL} \) denotes the solid/liquid interfacial free energy, \( \gamma_{SA} \) is the solid surface free energy, \( \gamma_{LA} \) is the liquid surface free energy, \( F_x \) is the surface tension. For common smooth surfaces like steel and aluminium plates droplet’s contact angle \( \Theta_E \) is close to 90°. However, there exist surfaces which exhibit other wetting properties. When droplet’s contact angle is lower than 90° the surface is called hydrophilic (Fig. 1a). Surfaces with contact angle higher than 90° are hydrophobic (Fig. 1b). Superhydrophobic surfaces can be characterised by contact angle higher than 150° (Fig. 1c). Any contamination of surface inhibits wetting resulting in higher contact angle in comparison to clean surface. Contact angle can be also affected by the environmental conditions like temperature, relative humidity and surface roughness. More detailed description is given by Cassie [4].

![Figure 1. Surface nomenclature – a)hydrophilic, b)hydrophobic, c)superhydrophobic.](image)

Another important issue devoted to hydrophobic properties is named contact angle hysteresis. Contact angle hysteresis (CAH) is one of the most important and classic elements of wetting of liquid droplets in systems from centimetre to micrometer scales. If the three-phase contact line is in actual motion, the contact angle produced is called a “dynamic” contact angle. In particular, the contact angles formed by expanding and contracting the liquid are referred to as the advancing contact angle \( \Theta_A \) and the receding contact angle \( \Theta_R \), respectively (Fig. 3).

Water has an abnormally high surface tension and surface enthalpy with an abnormally tightly packed surface compared to bulk liquid water. Water molecules at the liquid-gas surface have lost potential hydrogen bonds directed at the gas phase and are pulled towards the underlying bulk liquid water by the remaining stronger hydrogen bonds [5]. Energy is required to increase the surface area (removing a molecule from a well hydrogen bonded interior bulk water to the lesser hydrogen bonded surface), so it is minimized and held under tension. As the forces between the water molecules are
several and relatively large on a per-mass basis, compared to those between most other molecules, and
the water molecules are very small, the surface tension is large. Lowering the temperature greatly
increases the hydrogen bonding in the bulk causing increased surface tension (see Fig. 2).

![Figure 2. Surface tension and surface enthalpy of water at temperature [5].](image1)

![Figure 3. A drop on a vertical surface, stuck at the advancing angle $\theta_A$ and the receding angle $\theta_R$ [6].](image2)

3. Experiment stand.
The stand is designed to enable experiments devoted to dynamic droplet contact with different
surfaces in conditions favour freezing. Physical properties of droplet are recorded with fast camera
Photron FASTCAM SA5. Test chamber is lighted by two LED lamp Cree XM-L T6 1000 lumen. It is
equipped with thermocouples which enable measurement of the temperature of sample and test area.
There is also pyrometer which enables additional measurement of surface temperature. The
construction of stand enables obtaining varying values of velocity, droplet diameter, surface and
surrounding temperatures. Surface can be cooled down with the use of Peltier Cell and water cooling.
Testing space can be cooled by means of heat exchanger connected to liquid nitrogen container. Whole
circuit can be also filled with vapour free nitrogen to obtain vapour free domain or to reduce humidity
inside the chamber. Ambient temperature and probe temperature are measured with DT-8891E
thermometer and humidity inside the test space is measured by A1H Rotronic Hygromer hygrometer.
To get live image from a test area, Logitech Quickcam 9000 Pro was installed. Whole additional
electronic devices and sensors are supplied by 3 Korad KA3005P DC power suppliers.

Measurement range :
- Test surface diameter  150 mm
- Impact velocity       ~ 3-5 m/s
- Droplet diameter      ~ 0.5 – 2 mm
- Surface temperature   ~ -30°C  ~ +25°C
- Ambient temperature   ~ -30°C  ~ +25°C

4. Results
The experiments were carried out to answer question if superhydrophobic materials can prevent icing.
In first part of this work concerned room temperature conditions and it was a referring point when we
tested dynamic contact with surfaces under conditions that favour icing.
Two types of surface were used:
- Polished steel (hydrophilic)
- Silicon wafer with microstructure (superhydrophobic)

Polished steel was used a reference point, since it is a common used substrate, which is
subjected to ice accretion conditions. Silicone substrate was sample with regular, unequivocally
determined micro-structure (Fig.5) was performed. On basis of the results given by Varanasi et al. [7]
height of posts was set to 10µm. It was necessary to provide possibly the largest range of post-to-
width ratio for which Cassie or metastable Cassie states exist. During experiments sample no. 1 was used, which has measured $162^\circ$ wetting angle (static contact angle, which means it was measured in static way). The solid and the dotted lines denote theoretical prediction for Cassie and Wenzel models. Solid circles represent measured values of the WCA – Water contact angle (Fig.4). Micro scale geometry is given by a, b, h, where denote the post width, spacing, and height respectively). The microstructured silicon substrates were hydrophobized in wet chemical process, following the procedure described by Psarski et al [8].

![Figure 4. Static contact angle of 5µL water droplet as a function of b/a ratio (spacing/post width).](image1)

![Figure 5. The model and the SEM image of hydrophobic sample with post array b/a = 0.875.](image2)

4.1.1. Room temperature results
The first part of the research concerned room temperature conditions. Experiments allowed to distinguish (in hydrophobic and other cases) different phases of motion and give a reference point to results obtained for temperatures below 0°C. Both for polished steel and superhydrophobic test cases experiment were carried out in ambient conditions for test volume which means :
- Temperature – 26°C
- Relative humidity – 30%

![Figure 6. Time elapsed images of water droplet impingement polished steel substrate (top) and for superhydrophobic surface (bottom).](image3)

This part of experiments is a reference point for further work with samples exposed on negative temperature. Obtained results show differences in time to reach final diameter for steel (see Fig. 6 top) and superhydrophobic (see Fig. 6 bottom) substrates. It comes from bigger retraction speed at superhydrophobic surface which is directly related to contact angle hysteresis. Another important fact is for such impact velocities may occur some partial bouncing or defragmentation which can be substantial while considering conditions favour icing.

Interesting is fact that for superhydrophobic surface time to reach maximum diameter is shorter than for steel. Table 1 shows exact values of time differences. Such results are different as compared
to e.g. work of Bobiński [2]. Due to the fact such results were not in scope of this work, there was no thorough discussion about, but it is good example for further investigation.

| Table 1. Time differences to reach diameter |
|--------------------------------------------|
| Steel (ms) | Superhydrophobic (ms) |
| Time to reach max diameter | 5 | 1.8 |
| Time to reach final diameter | 44 | 13 |

4.1.2. Negative temperature surface results
This part of the research concerned droplet impacting superhydrophobic surfaces with temperature lower than water freezing point. Anti-icing properties of hydrophobic substrates were confirmed by Wang et al. [9]. It was stated that increasing surface hydrophobicity leads to retardation of ice accumulation (heat transferring capability and water-cooling rate decrease). Important to mention is that, the pure, deionized water was used. The first set of experiments was carried out both for steel and for superhydrophobic surfaces. It is focused on differences for both substrates when icing appears in equal level of humidity (20-24%) and for temperatures: -1°C, -3°C, -7°C, -11°C, -13°C, -15°C.

Such temperatures were obtained by setting constant values of voltage and current at Peltier Cell. The ambient temperature was, room temperature 23°C. To achieve repeatability the sample was blown each time with waterless nitrogen. This was also the way to maintain relative humidity at the same level. The specimen was subjected to water impingement when both temperature and humidity were stable. To remove water from probe between experiments, humid free nitrogen was used. The humidity and temperature just after blow off have increased rapidly, but for experiments it was set as stationary. The last part of results contains additionally carried out experiments with e.g. substrate cooled down for 180sec before impingement or substrate covered by water film of ice. Such test can be better approximation of phenomena appearing on e.g. airfoil during flight.

The second part of work devoted to water (at ambient temperature) contact with cold surfaces shows results for both steel and superhydrophobic substrates. It might be easily said that for obtained conditions, relative humidity around 20-25% and temperatures 0 ~ -25°C, superhydrophobic surface shows perspective results for anti icing application. Results obtained for this part of work acknowledge work of other scientist, but also imply additional issues such as changes of humidity, which may lead to qualitatively different results. For example in work of Bobiński [2], droplet has not froze both on steel and superhydrophobic substrate, but there whole area was fulfilled with non vapor nitrogen ( RH ~ 8%).
In this work droplet does not freeze until reach temperature around -11 ~ -13 °C (see Fig.7). Such results came up across during experiments and may by directly connected saturation pressure which changes for different humidity and temperatures and of course thermodynamic properties of water, steel and silica. Direct comparison steel with silica demonstrates that for ranges till -15°C water does not freeze during impingement on superhydrophobic substrate. Time to reach final diameter is relatively 2 times shorter for superhydrophobic than for steel ( until reaching temperature that freezing occur for steel). Comparing results it can be said that for “smooth” superhydrophobic substrate frost formation is not so rapid and intense as for steel. Interesting fact is that for -19°C at superhydrophobic surface water splashes, reaches maximum diameter and retracts, but much slower than for -15°C (see Fig.8). Water slows rapidly and pretends to freeze but it does not during impingement. Additional “flight like” test cases show how does the water behaves on cold water and ice. Droplet impinged at around 0°C degree water causes wavy structures and some partial defragmentation, but while droplet hit glassy ice at around 0 ~ -1°C it freeze almost immediately. Similar experiment carried out for superhydrophobic substrate partially covered with ice showed that water also froze on surface of ice and retracts at hydrophobic surface. Results from this part of work lead to conclusion that superhydrophobic smooth surface is eligible to be used as a proper anti icing coating. Such results obtained for ambient temperature of water and cold surface may be good approximation what actually happen during icing.

4.1.3. Supercooled droplet result.
As it was mentioned in before, ice repellant in an aircraft application is one the most attractive (and possibly lucrative) application. If we consider superhydrophobic coatings for airfoils it has to be taken into account droplets, which are supercooled. For the experiment, whole system was cooled down by heat exchanger connected to vessel containing liquid nitrogen. Temperature was determined (using thermocouples) in several points of the system. Additionally to tested surface two thermocouples were added – one inside chamber (connected to hygrometer), second one was placed in tube in vicinity of syringe. The obtained temperature was around −10°C. The height of casting was 1.2m to satisfy the conditions for cooling water droplet below 0°C. Startup time of air circulation at heat exchanger was used to obtain different relative humidity values inside circuit. In this section of work test cases were carried out focusing not only on supercooled droplet, but also to provide more possible conditions of icing occurring in real life conditions. Several test cases in range of relative humidity 30% ~ 80%, temperatures of substrate -6 °C ~ -21°C, (temperature around syringe -5 °C ~ -10 °C and temperature inside chamber -7 °C ~ -30 °C were carried out. All test cases were realized in steady conditions, with air circulation switched off. Last part of work is focused on conditions which are highly probable to occur during flight. Changing humidity, supercooled water and various temperatures are variables which can change when e.g. plane flight across clouds. For all obtained results there is no visible ice accretion.
Figure 9. Impingement of supercooled droplet on superhydrophobic substrate. 35% Relative Humidity, -16°C temperature of substrate, temperature in chamber -16°C.

Figure 10. Impingement of supercooled droplet on superhydrophobic substrate. 60% Relative Humidity, -21°C temperature of substrate, temperature in chamber -30°C.

Figure 11. Axis symmetric jetting.

The very first test was carried out at equal temperature of substrate and air (-16°C) and relative humidity 35% (see Fig.9). Higher relative humidity and lower temperatures did not lead to icing on superhydrophobic substrate. Three presented examples have similar solutions for droplet spreading/splashing and then retraction scenarios. Despite the high humidity e.g. 80% there is no frost observed on superhydrophobic substrate which might lead or accelerate icing. For three different values of humidity and different temperatures time to reach final diameter for supercooled droplet is not varying much.

Figure 12. Time to reach final diameter for given temperatures.
Interesting is fact that there might occur some partial jetting of small amount of water in quite different shape (see Fig.11) than known from bibliography. Figure 12 shows times to reach final diameter for all experiments mentioned in work. One of the most interesting fact is for examples with supercooled water and higher relative humidity droplet is not freezing e.g. for -21°C, RH 60%, while for -19°C, RH 20% retraction phase and velocity is slowed down and it tends to freeze. That fact may come from lower surface tension for higher temperature and so called Mpemba effect. At this point of experiments it can be assumed that: for warmer water evaporation reduces mass to be frozen, reduction of water density might suppress the convection currents that cool lower part of the liquid mass and thus colder droplet does not tend to freeze. It can be also concluded that it takes two times longer to reach final diameter for steel than for superhydrophobic substrates, of course not for samples which freeze immediately (see Fig.12, green circle). For lower temperatures time to reach final diameter is smaller, which can be directly connected to dynamic viscosity which is much higher below 0 °C, which affects with no defragmentation and no bouncing. Results mentioned in this conclusion are strictly related to contact angle hysteresis. It is the property which plays important role while considering velocity of retraction. For substrate kept in cold for longer period of time (180 s) before impingement there is no change in time to reach final diameter. That means that frost formation has no meaning for this range of temperatures. Quite interesting is experiment for -21°C which, despite high relative humidity – 60% (see Fig.10) and low temperature in chamber -30°C does not freeze and also takes more time to reach final diameter than other examples.

5. Conclusions
The present paper dealt with investigation of droplet impact on surfaces with different wetting properties and in the icing conditions. The first part consisted of validation of wetting properties of the surfaces in the ambient temperature environment. Second part of experiment related to negative temperature of surface proved ice repellent properties and characteristics temperatures to freeze water at steel substrate were obtained. Interesting is fact that with lowering temperatures time scale is changing, but droplet does not freeze. The main part of the research, presented in this paper, considered the passive anti-icing application of hydrophobic surfaces for various temperatures and humidity. For even high humidity (85%) and low temperatures (-21°C), water does not freeze during impingement on “smooth” silica, superhydrophobic substrate. It seems therefore that, within the range of investigated parameters, the crucial factor for controlling the droplet freezing process is the existence of water vapour in the system and thermodynamic processes which are on going inside and on the surface of water droplet. Some additional interesting behaviours of water were observed during test cases and it is reasonable to carry on further experiments.

References
[1] Worthington A 1876 Proceedings of the Royal Society of London 25 p 261-272
[2] Bobinski T 2014 Droplet impact in icing conditions – the influence of ambient air humidity Arch. of Mech. 66 2
[3] Varanasi K, Deng T, Hsu M and Bhat N 2009 Hierarchical Superhydrophobic Surfaces Resist Water Droplet Impact Tech. Proceedings of the 2009 NSTI Nanotechnology Conference and Expo
[4] Cassie A B D 1948 Discussions of the Faraday Society 3 1116
[5] Hacker P T 1951 Experimental values of the surface tension of supercooled water National Advisory Committee for Aeronautics Technical note 2510
[6] Eral H B, Mannetje D J C M and Oh J M 2012 Contact angle hysteresis: a review of fundamentals and applications
[7] Psarski M, et al 2012 Hydrophobization of epoxy nanocomposite surface with 1H,1H,2H,2H-perfluorooctyltrichlorosilane for superhydrophobic properties Central European J. of Phy. 5 10 p 1197-1201
[8] Wang H, Tang L, Wu X, Dai W and Qui Y 2007 Applied Surface Science 253 22 p 8818–8824

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