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Anti-icing potential of superhydrophobic coatings

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The advantages of superhydrophobic coatings as a new method for protection against atmospheric icing are considered. The basic physicochemical mechanisms determining the anti-icing performance of superhydrophobic surfaces and the problems of decreasing the efficiency of superhydrophobic materials are analyzed.

Ice formation and accumulation hinders the operation and impairs the efficiency of infrastructural components, mechanisms and machines, including aircraft, ships, offshore oil platforms, wind turbines, dams, electrical power plants, power transmission lines and telecoms equipment, heat pumps, refrigerators and air conditioners. In recent decades, an effort has been made to attain a more detailed understanding of the physicochemical phenomena governing the icing processes and to develop more efficient systems for the prevention of icing and/or the mitigation of its consequences.

The most popular current strategies of de-icing are generally power-consuming and not always efficient and environmentally safe. For example, mechanical and electrothermal methods are used to combat the factors that adversely affect the operation of overhead transmission lines under rime conditions. The efficiency of these methods in protection from pickup of wet snow, icing and accumulation of freezing drizzle or frost was repeatedly discussed in the literature.[1–6] The mechanical impact on an overhead transmission line creates conditions disturbing the normal operation of a section being treated. Furthermore, the majority of mechanical methods create additional mechanical stress in the line. This stress can cause failure in some cases.[1] Furthermore, the application of mechanical methods for combating the icing of power lines generally requires access to the line and direct handling of wires and power transmission towers.[7,8]

Electrothermal methods are based on the utilisation of Joule heat evolved upon the passage of current through an object being protected from icing. In recent years, many electrothermal methods were suggested for the prevention of ice formation or accelerated ice melting on structural parts that were subjected to icing. However, these methods require additional power consumption and expensive equipment. The use of electrothermal methods in the transportation of electrical power is either accompanied by redistribution of electric flows in the networks and, in some cases, by a temporary blackout of some consumers, or a more complicated network configuration is required that allows the network scheme or parameters of electromagnetic wave propagation to be modified. Thus, the application of electrothermal methods results in a considerable appreciation of manufacture and operation of an object being protected from icing. In certain cases, the use of such methods results in adverse effects such as reduction in the operating life of an object and an automatic system that monitors its state.

One of the most popular chemical methods involves the use of liquids whose aqueous solutions have much lower crystallization temperatures than that of water. This approach is widely adopted in aviation to reduce the icing of airplanes, helicopters and runways, as well as in road management to remove ice crust from sidewalks and roads. On the other hand, the use of such liquids is inefficient in electric power transportation. This is mainly due to the short duration of this kind of icing protection and the necessity of repeated laborious treatment of extended surfaces. Furthermore, the currently available commercial ‘nonfreezing liquids’ contain either salts that initiate corrosion processes and shift the salt balance in the environment or glycols.[9–11] In the latter case, the extensive usage of such liquids may cause a decrease in the oxygen content of natural water bodies. New reagents recently developed to decrease the crystallisation temperature of aqueous media,[9] *e.g.* sugars of plant origin, demonstrate much lower ecological toxicity and corrosivity. Furthermore, the application frequency of such additives can be considerably reduced by using coatings obtained by a sol-gel technology.[12,13] The main purpose of such coatings that encapsulate an active components is to increase the

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consumption efficiency of nonfreezing liquid components. However, the high cost of these chemicals and technologies considerably limits their applicability.

The efficiency of mechanical, electrothermal and chemical methods currently used to reduce ice accumulation under atmospheric icing conditions is insufficient in some cases. Furthermore, all of these methods require the permanent active involvement of personnel and the consumption of energy or chemical reagents; in some cases, they are ecologically harmful.

Icing reduction by means of passive protection using icephobic surfaces is of considerable current interest. Icephobic surfaces are such surfaces that, due to their physicochemical properties, facilitate a decrease in ice, snow and freezing drizzle accumulation on materials operating under atmospheric conditions and regularly contacting atmospheric precipitation. On the one hand, the efficiency of this approach depends on water-repelling surface properties, which minimize the surface accumulation of water. On the other hand, icephobic surfaces are characterised by low adhesion of already formed ice, freezing drizzle or wet snow. The latter effect leads to the spontaneous removal of snow, ice or freezing drizzle under their own weight or due to wind force. One of the most promising approaches to the creation of icephobic surfaces involves the development and preparation of superhydrophobic coatings on the surfaces of protected materials.

Physicochemical mechanisms providing the anti-icing properties of superhydrophobic surfaces. Let us consider in more detail the main physicochemical mechanisms that ensure the anti-icing properties of surfaces with superhydrophobic properties. Superhydrophobic coatings are such coatings that are simultaneously characterized by a water contact angle greater than 150° and a low wetting hysteresis.[†]

The recent strategy of the purposeful preparation of such coatings involves the solution of three problems.[14–16] First, decreasing the surface energy of a material by treatment of the surface with hydrophobic agents;[14–16] second, increasing the local contact angle of a textured surface by choosing an appropriate shape of textural elements;[17] finally, the formation of a texture with multimodal roughness on the surface (by the treatment of a surface layer or by the application of texturing elements from other materials).[14–16] Using this strategy, a superhydrophobic state can be attained on the surface of any material.

Upon solving the above three problems, it becomes possible to ensure that a coated material is wetted by both liquid and solid aqueous media in heterogeneous mode, *i.e.* the mode where air is trapped inside the grooves in the relief of a textured surface. The presence of an air layer manifests itself, *e.g.*, by total internal reflection of light from a water/substrate surface (Figure 1). The aqueous medium only contacts the material at the surface of the protrusion peaks, so the area of real contact between the liquid and the material is characterized by the fraction of the wetted area, which is generally considerably less than 10% for superhydrophobic coatings. The small fraction of real contact between a superhydrophobic surface and a liquid wetting that surface in heterogeneous regime is among the main factors determining the following icephobicity mechanisms:

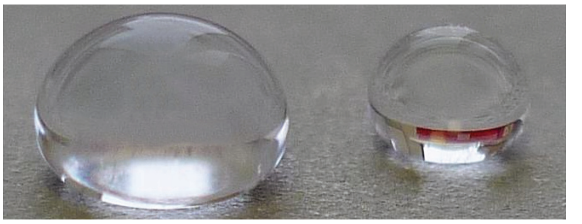

Figure 1 Water drops on a superhydrophobic surface. Due to the formation of air gaps between the drop base and the substrate, the phenomenon of total internal reflection at water/air interface causes a mirror-like appearance of the contact area.

(1) Removal of water drops that contact a material surface with a negative temperature before these drops crystallise.

(2) Decreasing heat transfer from a warmer drop to a cold surface that reduces the probability of drop solidification before it rolls off the surface.

(3) Delaying the crystallisation of water drops that contact a superhydrophobic surface.

(4) Shifting the triple point in water layers that contact a superhydrophobic surface toward negative temperatures.

(5) Low adhesion of aqueous media, in both liquid and crystalline states, to superhydrophobic surfaces.

In order to favour the manifestation of the anti-icing properties of superhydrophobic coatings due to the specified mechanisms, it is necessary to determine the operation conditions of the coatings where the heterogeneous wetting regime will be maintained.

Since we deal with a superhydrophobic surface, the local contact angle in the three-phase aqueous phase/substrate/vapour phase contact zone, which is known as the Young contact angle θ_Y, should be more than 90°. In case of the most efficient fluorine-containing agents that form a dense monolayer on the surface of texture elements, θ_Y on planar surfaces can reach 120°.[14] Even higher Young angles are attained by using texture elements with a high surface curvature.[17] If vapour is condensed in a capillary-porous system (in our case, micro- and nanorelief grooves) with such contact angles, then, in accordance with Kelvin's law, an excess pressure (in comparison with the vapour and bulk liquid phases) is formed in the condensed phase. Thermodynamically, such a process can occur spontaneously only provided that there is an oversaturation in the vapour phase, the extent of which is determined by the relationship[18]

$$p = p_\mathrm{sat}\exp\left(\frac{-\sigma_{\alpha\mathrm{v}} v_\alpha K}{RT}\right), \qquad (1)$$

where p and p_sat correspond to the vapour pressure and saturated vapour pressure at the given temperature, respectively; $\sigma_{\alpha\mathrm{v}}$ is the surface energy of the α/v boundary; v_α is the molar volume of phase α; α = w, i depending on whether the condensed phase is in a liquid or solid state; indices w, v, i correspond to the aqueous, vapour or ice phase, respectively; K is the meniscus curvature of the capillary-condensed phase depending on the contact angle formed by the condensed phase at the coating texture elements, which is negative for nonwettable walls and positive for wettable ones;[‡] R is the gas constant; and T is the temperature. Thus, to enable condensation on a superhydrophobic surface accompanied by filling the surface grooves and transition of wetting from heterogeneous to homogeneous regime, vapour supersaturation is required, which is the higher, the higher the Young contact angle and the smaller the characteristic pore size of the textured surface. However, calculations using equation (1) show that acceptable oversaturation related to the hydrophobicity of a rough

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[†] Both of the specified conditions are prerequisites for establishing a superhydrophobic state, in which surface wetting occurs in heterogeneous regime. Surfaces characterized by an advancing contact angle above 150° and high hysteresis of the contact angle preventing the roll-off of drops from a slanted surface cannot be attributed to superhydrophobic surfaces since, in this case, the heterogeneous wetting regime is violated when the liquid front recedes. As a result of confusion on this issue in the literature, surfaces with large advancing contact angles but with high adhesion to water, *i.e.* homogeneous wetting regime of liquid receding, are wrongly attributed to superhydrophobic surfaces in some papers.

[‡] For example, the meniscus curvature for cylindrical pores with radius r is determined by the relationship $K = 2\cos\theta/r$, and the sign of $\cos\theta$ defines the sign of the curvature.

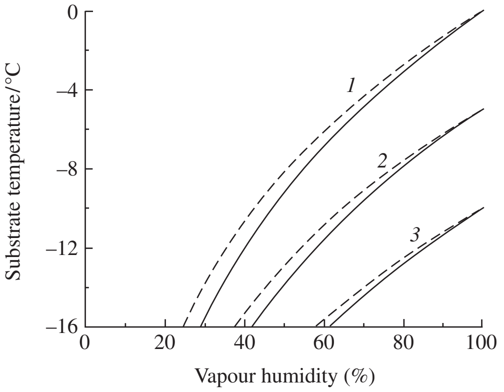

Figure 2 The vapour humidity dependences of minimal temperature of a superhydrophobic surface, at which no condensation of supercooled liquid water (solid lines) or frost (dashed lines) will take place from water vapours, having temperatures of (*1*) 0, (*2*) –5 and (*3*) –10 °C. The data for pressures of water vapours in equilibrium with supercooled water and ice were taken from handbook.[19]

surface is very small for many reliefs typical of superhydrophobic coatings. A considerable shift of acceptable vapour humidity to the oversaturation range such that condensation does not yet take place only occurs for reliefs with nanometer-range characteristic pore sizes. On the other hand, if the substrate temperature is lower than the environment temperature or if a drop of warm water is placed on a cold substrate, a considerable vapour oversaturation can occur (Figure 2). The former situation often occurs in laboratory experiments where a superhydrophobic substrate cooled to negative temperatures by a Peltier element is located under laboratory conditions at room temperature. For water vapour at temperature T, it is easy to calculate the minimum substrate temperature $T_0^{\min}$, such that the superhydrophobicity of the substrate still does prevent the condensation of vapour in relief grooves at a given atmosphere humidity (Figure 2). Since the pressure of vapour that is in equilibrium with ice at $T_0^{\min}$ is lower than the vapour pressure over supercooled water, we computed the relationships $T_0^{\min} = f(p/p_s)$ for the condensation of supercooled water (Figure 2, solid lines) and frost (dashed lines).

The second situation occurs when a warm drop is placed on a colder support under conditions that are close to saturation in a vapour phase with a temperature equal to that of the substrate. In this case, the local pressure of vapours that emerge near the three-phase contact zone is higher than the pressure of vapours that are in equilibrium with a substrate with the same temperature, and condensation into the relief grooves near the drop is possible. It follows from Figure 2 that vapour overheating (or substrate supercooling) is a serious problem in the operation of superhydrophobic coatings at high atmosphere humidity resulting in the loss of superhydrophobic properties due to transition to the homogeneous wetting regime.

The above situations are dangerous for the ground infrastructure in case of ‘freezing rain’/‘freezing drizzle’ and for aviation when warmer atmospheric layers with high humidity are located above cold near-surface layers. However, the condensation problem can be solved in these cases using superhydrophobic coatings in combination with surface heating by a few degrees. Thus, in many practical applications of superhydrophobic coatings, such as aviation and electric power industry, it is possible to prevent capillary condensation and crystallisation of water contacting a superhydrophobic surface.

Let us consider each mechanism of superhydrophobic coating icephobicity listed above in more detail.

Removal of water drops from a material surface before crystallisation. The main factors determining the wetting hysteresis are the chemical inhomogeneity and the roughness of the interface between a wetted material and a wetting liquid. In heterogeneous wetting regime with a large contact angle, the liquid mainly contacts the air phase and, only to an insignificant extent characterized by the fraction of wetted surface f, the solid surface the wetting hysteresis on which is usually high. The liquid/gas interface is characterized by near-zero hysteresis since it is rather smooth and chemically homogeneous. Thus, the heterogeneous wetting regime on superhydrophobic coatings favours a decrease in hysteresis for the surface as a whole. In this case, the smaller the fraction of the wetted surface, the lower the hysteresis.

The wetting hysteresis determines the force preventing the sliding of liquid drops along the surface. The lower the hysteresis, the more efficiently the drops are removed from a horizontal surface of a coating under a wind force or air stream pressure. If a surface is slanted with respect to the horizon, the work of gravitational forces is consumed to change the shape of a drop sitting on the surface. The advancing and receding contact angles θ_{adv} and θ_{rec} are established in the advancing and receding fronts of a drop, respectively. When the work of gravitational forces reaches an amount sufficient to perform the work of adhesion that involves separating the contact between the drop and the substrate in the receding meniscus and establishing the contact in the advancing meniscus, movement of the drop along the substrate occurs. Irrespective of the character of drop movement, *i.e.* forward motion of the centre of mass (drop slide-off) or translational rotational motion (drop roll-down from the substrate), the wetting hysteresis is the main physical mechanism that retains a drop on a material surface. As a first approximation, the surface slope angle α, starting from which a drop is removed from the surface by sliding/rolling down from the surface, can be calculated by the relationship[20]

$$mg\sin\alpha = \omega\sigma_{\text{LV}}(\cos\theta_{\text{rec}} - \cos\theta_{\text{adv}}), \qquad (2)$$

where m and ω are the drop mass and width, respectively, and σ_{LV} is the surface tension of the liquid. It follows from relationship (2) that, for drops of the same size, the rolling angle on superhydrophobic coatings characterized by equal hysteresis but different advancing contact angles θ_{adv} is the smaller the larger θ_{adv} (Figure 3). Furthermore, since the rolling angle of a drop depends on the drop mass, the efficiency of drop removal from the surface of the same superhydrophobic coating is the higher the

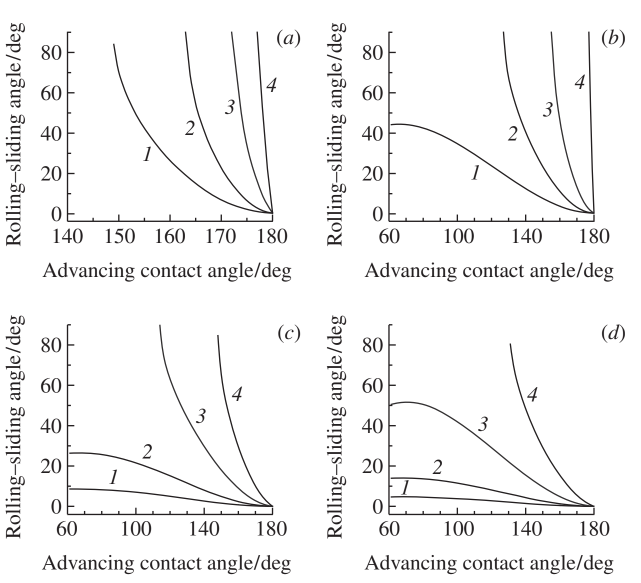

Figure 3 Dependences of rolling/sliding angles on the advancing contact angle for water drops with volume of (*a*) 50 nl, (*b*) 1 μl, (*c*) 10 μl and (*d*) 25 μl at fixed magnitudes of contact angle hysteresis: (*1*) 1°, (*2*) 3°, (*3*) 10° and (*4*) 25°.

larger the water drop size. Note that, under the most dangerous atmospheric icing conditions, the volume of water drops varies within the range 6×10^{-5}–5×10^{-2} μl in the case of 'freezing drizzle' or 5×10^{-2}–50 μl in the case of 'freezing rain'.[21] Figure 3 shows that drops with a small volume are attached to a slanted substrate even at very low wetting hysteresis. Thus, it is impossible to prevent completely ice formation on superhydrophobic substrates contacting a water aerosol with a broad range of sizes. In this case, the superhydrophobic surface acts as a filter that favours the removal of drops larger than microliters but traps nanolitre-sized drops. This filtration of precipitated drops under conditions of their crystallisation on a superhydrophobic surface favours a decrease in ice accumulation and predefines a very loose structure of the ice aggregates formed.

A secondary effect favouring the removal of a considerable fraction of drops without crystallisation arises due to reduction of heat transfer from the warmer drop to the cold surface. Again, the heat insulating properties are owing to a considerable number of air bubbles trapped in the relief grooves. Furthermore, the polymerisation of hydrophobic agent molecules on the texture surface also favours a decrease in the heat flux through a superhydrophobic coating. A decrease in heat transfer through superhydrophobic coatings was found experimentally.[22–24] However, it was also noted that, though the probability that a drop solidifies before it rolls off a surface decreases due to the heat insulating properties of a coating, the delay in crystallisation resulting from reduction of heat transfer through a coating is as small as tens of seconds.

Delay in the frost formation and crystallisation of water drops on superhydrophobic surfaces. The problem of slowing down the crystallisation under fixed supercooling of water drops and decreasing the rate of frost formation on superhydrophobic substrates was repeatedly discussed.[21–30] This problem is closely related to bulk water supercooling. It is well known that the triple point of water is near 0 °C. On the other hand, bulk water freed from external crystallisation centres can be easily supercooled to –41–42 °C, *i.e.*, the temperature corresponding to the limiting temperature of homogeneous nucleation.[31–34] The main supercooling mechanism is associated with the existence of an energy barrier for nucleation, which can be determined as a maximum work for the formation of a crystalline phase nucleus in the bulk liquid phase without changing the thermodynamic state of the latter.[35] Analysis of ice heterogeneous nucleation, where a solid phase nucleus is formed at the interface between the bulk liquid phase and the external phase, *e.g.* a substrate or a gaseous phase, was performed.[35,36] The results show that in the case of heterogeneous nucleation, the energy barrier can be much lower than that in the case of homogeneous nucleation, which lowers the probability of deep supercooling of water drops on substrates. As shown by a thorough analysis,[35] the maximum work for the formation of a nucleus of phase B at an interface between bulk phase A and substrate S can be calculated from the relationship

$$W^*_{\text{hetero}} = \frac{16\pi\sigma^3_{\text{AB}}\upsilon^2_{\text{B}}}{3\Delta\mu^2_{\text{AB}}}\varphi(\theta) = W^*_{\text{homo}}\varphi(\theta), \tag{3}$$

where

$$\varphi(\theta) = \frac{(1-\cos\theta)^2}{4}(1+\cos\theta). \tag{4}$$

Here W^*_{hetero} and W^*_{homo} indicate the maximum work for the formation of a nucleus of phase B in bulk phase A in case of heterogeneous and homogeneous nucleation, respectively; σ_{AB} is the interfacial energy of the A/B interface; υ_{B} is the molar volume of phase B; $\Delta\mu_{\text{AB}} = \upsilon_{\text{B}}(p_{\text{A}} - p_{\text{B}})$ is the difference between the chemical potentials of molecules in phases A and B if the thermodynamic state of phase A remains unchanged during nucleation; and $(p_{\text{A}} - p_{\text{B}})$ is the capillary pressure in a nucleus of phase B, which equals the pressure difference between phases A and B existing in equilibrium. Finally, the coefficient $\varphi(\theta)$, which is determined by competitive contact angle $\theta_{\text{BS(A)}}$ of substrate S wetting by phase B in ambient phase A, reflects the degree of decrease in the nucleation energy barrier on the substrate in comparison with nucleation in bulk phase A. The dependence of coefficient φ on the corresponding contact angle θ presented in Figure 4 allows one to conclude that $\lim\limits_{\theta\to 0}\varphi(\theta) \to 0$, *i.e.*, by improving substrate wetting by phase B that is formed from phase A, it is possible to reach the almost barrier-free formation of phase B nuclei on the substrate. And *vice versa*, the energy barrier in heterogeneous nucleation tends to the barrier characteristic of homogeneous nucleation at $\theta_{\text{BS(A)}} \to 180°$. Relationship (3) is easily transformed into corresponding relationships for the formation of an ice nucleus from an aqueous phase on a substrate

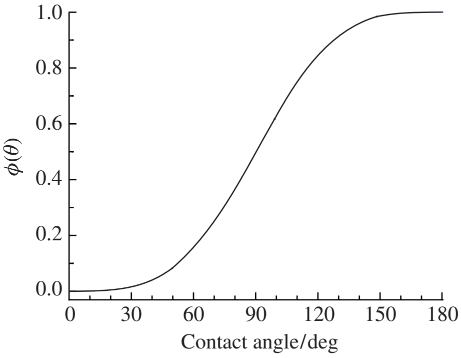

Figure 4 Factor of decrease in the energy barrier for heterogeneous nucleation on a substrate, characterized by the angle of competitive wettability *θ*, compared to the energy barrier for homogeneous nucleation within bulk liquid phase.

$$W^*_{\text{hetero}} = \frac{16\pi\sigma^3_{\text{wi}}\upsilon^2_{\text{i}}T_0^2}{3\Delta H^2_{\text{wi}}(T_0 - T)^2}\varphi(\theta_{\text{is(w)}}), \tag{5}$$

and the formation of frost nuclei from supersaturated vapour

$$W^*_{\text{hetero}} = \frac{16\pi\sigma^3_{\text{iv}}\upsilon^2_{\text{i}}}{3[RT\ln(p/p_{\text{sat}})]^2}\varphi(\theta_{\text{is(v)}}). \tag{6}$$

Here $(T_0 - T)$ is the amount of water supercooling with respect to the temperature of bulk phase transition T_0 at a given pressure of the bulk phase where the nuclei are formed; the indices w, v and i correspond to the aqueous, vapour and ice phases, respectively. The values of ΔH_{wi} and υ_{i} correspond to the mean ice enthalpy of melting and molar volume over the overcooling range; p and p_{sat} correspond to the vapour pressure in the bulk phase from which the nuclei are formed and the saturated vapour pressure at a given temperature, respectively. Angles $\theta_{\text{is(w)}}$ and $\theta_{\text{is(v)}}$ correspond to the angles formed by the ice phase on the substrate in overcooled water or supersaturated vapour environments, respectively.

Note that the decrease in the barrier for ice nucleation from water on substrates with various wettability, and hence the delay in crystallisation of water drops contacting such substrates, is determined by the angle of competitive wetting of the substrate with ice in water, $\theta_{\text{is(w)}}$, rather than the angle of substrate wetting with water in a vapour environment, as it was intuitively assumed in a number of studies. As for $\theta_{\text{is(w)}}$, it is traditionally assumed that $\theta_{\text{is(w)}} \approx 90°$ owing to the similar physicochemical characteristics of ice and water.[30] In this case, the nucleation barrier would be two times smaller than the homogeneous nucleation barrier, for both superhydrophobic and hydrophilic substrates. In other words, crystallisation would slow down, but the delay would be of the same order of magnitude, irrespective of the contact angle of the substrate with water. Moreover, the heterogeneous nucleation mechanism would prevail for drops on substrates, as it was observed previously.[28,37]

However, the assumption that $\theta_{\mathrm{is(w)}} \approx 90°$ is not justified and seems to be not quite valid. This is due to the fact that the contact angle is governed by surface forces acting in a three-phase system.[17,38] These are primarily van der Waals forces and the ion-electrostatic component of the disjoining pressure. The van der Waals forces in air/ice/substrate systems differ considerably from those in the air/water/substrate system due to differences in the spectra of dynamic dielectric permittivity of ice and water.[39] Furthermore, depending on the chemical structure of the substrate surface, the charge densities on the ice/substrate and water/substrate interfaces can differ considerably to result in changes in electrostatic forces on a transition from ice films to water films. Thus, theoretical analysis of the energy barrier for heterogeneous ice nucleation based on relationship (4) and the corresponding delay in liquid crystallisation on a substrate remains an open issue. Obviously, additional experimental studies are needed, based on which it would be possible to predict the contact angle of substrate wetting with ice in water, $\theta_{\mathrm{is(w)}}$, depending on the chemical structure of the substrate surface.

On the other hand, the results of experimental studies on the delay in crystallisation of water drops on substrates with various wettability are available. A considerable delay in the crystallisation of water drops on superhydrophobic substrates that exceeded considerably the delays typical of hydrophilic and hydrophobic coatings was noted.[22,26] These studies were carried out at very low[22] or moderate[26] vapour humidity. The greatest increase in the time period before the start of drop crystallisation on superhydrophobic substrates in comparison with hydrophilic ones was observed[22] at much higher temperatures than that corresponding to the homogeneous nucleation limit. However, the results on the determination of a delay in drop crystallisation on hydrophilic and hydrophobic substrates under conditions of considerable atmosphere undersaturation may be distorted owing to differences in the drop shape determined by the surface wettability. The necessity of maintaining a vapour-saturated atmosphere follows from the fact that a drop in an undersaturated atmosphere would have a lower temperature than the ambient vapour phase[40] due to evaporation of the liquid. The temperature decrease depends on both the relative humidity and the drop surface area, and it can reach tens of degrees.[40] In our laboratory, we also studied the times of drop crystallisation on hydrophilic and superhydrophobic substrates at various overcoolings. Unlike studies reported in the above citations, these studies were carried out in saturated vapours at all of the temperatures used. In agreement with published data,[22] the results demonstrate the greatest deviation in crystallisation times on superhydrophobic and hydrophilic substrates at system temperatures from 0 to 10 °C. The smaller differences at lower temperatures result from the fact that the probability of homogeneous nucleation increases as the homogeneous limit threshold is approached. This makes the trend that the energy barrier for heterogeneous nucleation grows for superhydrophobic surfaces less significant for drop crystallisation. However, differences in crystallisation delay times on substrates with various wettabilities are obvious even at –30 °C (Figure 5).

It should be emphasised that, although a conclusion on the slow-down of drop crystallisation on substrates is noted by all researchers who performed studies in this field, doubts are raised in refs. 27, 28 that delay in crystallisation on superhydrophobic surfaces is more significant than that in the case of hydrophilic substrates. What is more, the results[27,28] made it possible to conclude that the crystallisation delay times on hydrophilic substrates exceeded the corresponding values on superhydrophobic surfaces. Without going into experimental details, note that the humidity in the chambers differed from 100% in both studies. For example, a low temperature of the support with the drops was achieved by fast cooling of the substrate in a supersaturated atmosphere.[28] In this case, the heat of condensation released in the drops would raise the local temperature of a drop the more strongly, the larger its surface area (at a given volume) and hence the smaller its contact angle. Condensation processes would result in a lower temperature of the start of drop crystallisation for a hydrophilic substrate in comparison with a superhydrophobic one.

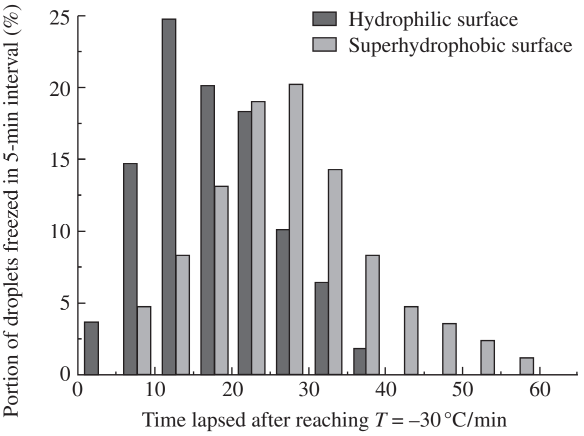

Figure 5 Distribution of the fraction of droplets crystallized on a hydrophilic and superhydrophobic surfaces of an aluminium plate over the time elapsed after establishing a temperature of –30 °C in a climate chamber.

Let us analyse the frost formation rate on substrates with various wettability. Relationship (6) predicts a barrier-free mechanism of frost nucleation on superhydrophilic substrates with $\theta_{\mathrm{is(v)}} = 0°$ and an increase in the barrier to a value typical of homogeneous nucleation in case of complete non-wetting. Hence, frost formation would be delayed to the greatest extent at non-zero supersaturations in case of superhydrophobic surfaces. Indeed, experimental data[24,25,41,42] confirm this theoretical estimate.

Thus, the analysis carried out here shows that the crystallisation of water drops is delayed considerably on superhydrophobic substrates. This delay can reach a few hours at moderately cold temperatures and 100% atmosphere humidity. As an example, Figure 6 presents an optical image of drops at –15 °C on aluminium with a superhydrophobic coating characterized by a contact angle of 167°. Only two of five drops crystallized after 155 min. As concerns the hindrance of frost formation on superhydrophobic substrates, visible formation of frost was blocked for 55 min at 40% humidity (the humidity of vapours was determined at room temperature) and a surface temperature of –10 °C.[41] Such long delays of water crystallisation and frost formation make it possible to reduce considerably the accumulation of ice and frost on superhydrophobic surfaces, and in some cases, *e.g.*, if an aircraft resides in an atmosphere with high humidity for a short time, completely prevent the icing of surfaces.

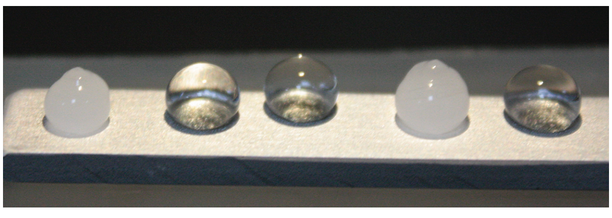

Figure 6 Photograph of sessile water droplets on an aluminum sample with superhydrophobic coating after 155 min exposition in the climate chamber at the temperature of –15 °C.

Phenomena that favour a decrease in the adhesion of crystalline aqueous phases to superhydrophobic surfaces. Let us consider the phenomena that simplify considerably the removal of the already formed ice and frost from superhydrophobic surfaces. It is assumed that crystallisation occurred under conditions that did not cause capillary condensation into the relief grooves.

If, for some reasons, a layer of ice or frost has still formed on a superhydrophobic surface with retention of heterogeneous wetting regime, the removal of such precipitates does not require large amounts of energy and, in some cases, can occur under wind force, gravity or air stream pressure. Below we discuss two mechanisms responsible for the low adhesion strength of the crystalline aqueous phase / superhydrophobic substrate contact.

The first mechanism is related to the shift of the water triple point at the ice/vapour and ice/solid surface interfaces towards low (negative) temperatures and leads to the existence of a water layer at negative temperatures, either on the ice surface or between ice and a substrate. This phenomenon, which is called ice premelting in the literature, was noted a long time back by Faraday.[42] Later, it was studied by various real[44–54] and numerical[55] experimental methods. Note that, though published data on the thickness of a liquid layer at various negative temperatures differ, it was unanimously demonstrated that a polymolecular water layer is formed, which is tens of nanometers thick at temperatures above –1 °C and a few nanometers thick at temperatures of about –20 °C. According to reported data,[50] the liquid layer disappears completely at $T < -28$ °C. A theoretical explanation of the triple point shift at phase boundaries and in spatially confined systems, and the ice pre-melting phenomenon in particular, was provided in our studies.[18,56] We have shown that the surface layer structure changes when affected by a field of surface forces acting near the interface. This, in turn, changes the density of the surface phase and the components of the pressure tensor, providing a shift of triple point T^* in the intermediate layer at an interface of two media. Depending on changes in the above parameters, T^* can shift either towards lower temperatures, which results in pre-melting as is the case of ice, or towards higher temperatures to ensure pre-solidification, as with medium-chain hydrocarbons.

A polymolecular water layer at the ice/vapour phase and ice/hydrophobic surface interfaces acts as a lubricating layer of a liquid anti-adhesive agent and thus makes it possible to decrease considerably the ice–coating adhesion strength under shear load and combined shear conditions. The efficiency of liquid anti-adhesive agents results from the fact that the contact between the surface and crystalline water phase breaks by a cohesion mechanism.[57] Moreover, the movement of internal layers of a liquid relative to each other under shear load occurs without the need to overcome the force of static friction. However, this optimistic picture is generally observed only in those points of heterogeneous ice–coating contact where a water layer separates ice and a vapour phase. On a wetted coating area where ice contacts a solid surface, the surface nanorelief with heights exceeding the water layer thickness creates an energy barrier against ice sliding relative to the coating along a water layer. Thus, by using the heterogeneity of the wetting regime of a superhydrophobic coating and by decreasing the fraction of the wetted surface, it is possible to diminish considerably the value of the experimentally measured adhesive strength of the coating/ice contact. Our study on the loss of adhesive contact between a superhydrophobic coating on aluminium wire and an ice sleeve under shear conditions has shown[58] that, even at very low prolonged shear stress, the sample slowly slides out of the ice sleeve due to successive sliding/melting processes (Figure 7). Note that the abrupt decrease in the thickness of the pre-melted water layer with a decrease in temperature may be among the main reasons for the experimentally observed rise of the adhesive strength of the ice/hydrophobic aluminium contact at more negative temperatures.[58]

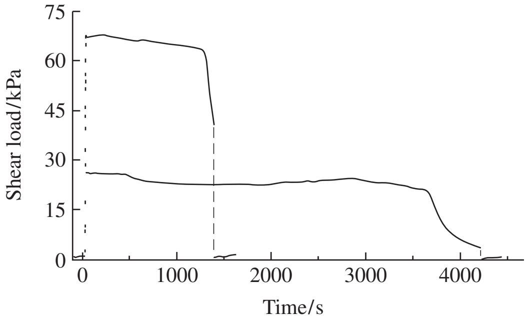

Figure 7 Dependence of shear stress measured by the loading console of an adhesiometer on the time elapsed after the load is applied along the axis of an aluminum cylinder with a superhydrophobic surface, one of the ends of which is frozen in the ice at –8 °C. Two dependences corresponding different values of the initial load are presented. The experimental procedure was described elsewhere.[56]

Let us discuss the second mechanism related to the low adhesive strength of the ‘ice/superhydrophobic coating’ contact. The breakage of a mechanical contact between two solids (as applied to the breakage of the ice/substrate contact) practically cannot occur by an isothermal reversible process. Contact breakage along an interface is characterized by the adhesive strength that equals the force required to break the adhesive bonding per the apparent[§] adhesive contact area. Here, the adhesive strength is determined, to a large extent, by the number of defects in the near-surface layer and the character of deformation in the contacting bodies. Therefore, a direct comparison of adhesive strengths in case of ice contact with different coatings is only possible provided that the roughness of the coating/ice interfaces, the defectness of the structures of the contacting phases, and the specifics of coating deformation are similar. In turn, the differences in the character of adhesion for various kinds of crystalline aqueous media (ice, freezing drizzle and wet snow) on the same coating are caused by the variation in the number of defects in the near-surface layer and differences in the degree of deformation under the same load.

For a long time, hydrophobic anti-adhesive coatings with low surface energy that did not form covalent chemical bonds with the components of an aqueous medium were used to decrease the adhesive strength of ice contact with structural materials. Analysis of both commercial[59,60] anti-adhesive coatings and those synthesised in laboratories[58,61–63] led to the conclusion that the adhesive strength of ice bonding to structural materials and the energy consumed for ice removal from their surfaces using solid anti-adhesives can be reduced.

Recent studies have shown that the adhesion bond strength of ice to superhydrophobic coatings can be considerably lower than that in hydrophobic coatings.[58,64–67] However, a correlation between an increase in the effective contact angle and a decrease in the adhesive strength is only observed for coatings with low hysteresis, *i.e.*, true superhydrophobic coatings.[64,65] To clarify this statement, it should be reminded that, if surface wetting occurs in heterogeneous regime, water/ice partially contact the coating surface and partially the air bubbles trapped in the grooves of the relief. In this case, it is reasonable to characterize adhesion by the actual adhesive strength, *i.e.* the force required to break the adhesive bond per the actual adhesive contact area, which is determined by the product of the wetted area by the roughness

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[§] The apparent area is that of the projection of the actual contact area between two bodies onto the substrate plane.

factor of the wetted area. The breakage of an interphase contact assumes the breakage of intermolecular interactions between water/ice and the coating only along the surface of the real contact with the coating; hence, it is determined by the chemical structure of the coating. Superhydrophobic surfaces are generally characterized by a small fraction of wetted area f and moderate wetted surface roughness r determined by the shape of the texture elements. Thus, due to the small actual contact area, the measured adhesive strength of contact between ice and a superhydrophobic surface is much smaller than that in the case of hydrophobic anti-adhesives with wetted area fraction $f = 1$, whereas the actual adhesive strengths may be similar in these cases.

Considering the adhesive bond strength of ice to coatings with high advancing contact angles $\theta_{\text{adv}} > 150°$ but a large water wetting hysteresis, note that we deal with a highly hydrophobic rather than superhydrophobic state. In this case, the fraction of wetted area is high. Thus, even if the actual adhesive strength is low, a several fold increase in the real contact area would bring about a growth of the experimentally measured adhesion strength of ice to a highly hydrophobic coating, up to values exceeding those on smooth substrates.[62–64]

As noted above, if water crystallisation on a superhydrophobic substrate occurs under conditions of vapour supersaturation with respect to the substrate, a transition from heterogeneous to homogeneous regime of the superhydrophobic coating wetting by the solid aqueous phase is possible. Obviously, in such a case, the adhesion strength to the coating is rather high, and a considerable energy consumption is required to remove the crystalline aqueous phase from the surface. On the other hand, if the wetting regime remains heterogeneous, the weak adhesion of drops to a superhydrophobic coating leads to the spontaneous removal of solid drops from a vertical surface upon shaking.

Thus, the above results allow us to conclude that the small contact area between a superhydrophobic surface and a crystalline aqueous medium due to the heterogeneous wetting regime, on the one hand, and the presence of a liquid water layer on the ice surface or between ice and a substrate, on the other hand, favour the removal of crystalline water phases from the coating surface with a small energy consumption. In some cases, spontaneous ice removal under combined effects of gravity, wind force, vibration or air stream pressure can occur. Furthermore, in order to maintain the anti-adhesive properties of superhydrophobic coatings, it is necessary to prevent condensation into coating relief grooves during water crystallisation or frost formation. For example, maintaining the temperature of a superhydrophobic surface a few degrees above the ambient temperature[¶] usually allows icing to be prevented even at very low temperatures.

Durability of the icephobic properties of superhydrophobic coatings. Recently, researchers[68–70] started to express doubts on the durability of superhydrophobic coatings obtained by a certain method when such coatings are used with regular exposure to weather phenomena such as ‘freezing rain’/‘freezing drizzle’. In particular, it was noted that the icephobicity of coatings decreases considerably after five or six ice freezing/thawing cycles. This phenomenon is particularly characteristic of superhydrophobic coatings obtained by deposition of particles of a filler embedded into a matrix of a hydrophobic polymeric binder. Changes in surface morphology owing to breakage of surface asperities upon crystallisation of water contacting a textured superhydrophobic surface and upon mechanical removal of already formed ice were considered[68–70] as the main reasons for the loss of superhydrophobic and icephobic properties. Furthermore, the hydrolysis of a hydrophobic agent upon prolonged contact of the coating with aqueous media can also result in some degradation of superhydrophobic properties.[71] However, we obtained superhydrophobic coatings on stainless steel and electrotechnical aluminium, which had high stability against periodic crystallisation of water contacting the coating. In 250-h tests, after 100 cycles of freezing/thawing of water into which a test specimen was immersed, the contact angles for both coatings remained above 150°, while the rolling angles for 10 μl drops did not exceed 40° for steel and 52° for aluminium. Scanning electron-microscopic and IR spectroscopic data and the analysis of wetting dynamics for the developed coatings obtained before and after testing in freezing/thawing cycles showed that, though some changes in the surface morphology and hydrolysis of an insignificant number of siloxane bonds in the coating occurred during the initial test stage, steady-state rolling and contact angles, which corresponded both to superhydrophobic and durable icephobic properties, were quickly reached.[4]

In conclusion, note that the main physicochemical mechanisms resulting in the anti-icing properties of superhydrophobic surfaces well complement each other. Their joint effect makes it possible to solve, more reliably and without the active involvement of personnel, the problem of decreasing the amount of snow, ice and frost that are accumulated on the surfaces of materials working in contact with atmospheric precipitations and at low temperatures. The versatility of the icephobic properties of such coatings and the independence from the kind of crystalline water phases from which these coatings are supposed to protect increase considerably the attraction and potential of the use of superhydrophobic coatings for anti-icing purposes. The main problems reducing the efficiency of superhydrophobic materials include the capillary condensation of precipitates arising when vapour oversaturation occurs in the vicinity of superhydrophobic surfaces, the necessity of raising the mechanical durability of the coating texture and the chemical stability of hydrophobic agents against hydrolysis and desorption under operation conditions of an item with a superhydrophobic coating. The former problem can be successfully solved by combining superhydrophobic coatings with surface heating by a few degrees. This kind of heating, *e.g.* in high current power lines, is currently ensured by the operation of the line itself, while in aviation, the heating of the leading wing edge is a widespread protection measure against barrier ice accumulation. As concerns the rest of the above problems, the characteristics of coatings obtained in the laboratory indicate a potential feasibility of creating chemically and mechanically stable superhydrophobic coatings for well defined working conditions.

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