Revisiting Wetting, Freezing, and Evaporation Mechanisms of Water on Copper

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ABSTRACT: Wetting of metal surfaces plays an important role in fuel cells, corrosion science, and heat-transfer devices. It has been recently stipulated that Cu surface is hydrophobic. In order to address this issue we use high purity (1 1 1) Cu prepared without oxygen, and resistant to oxidation. Using the modern Fringe Projection Phase-Shifting method of surface roughness determination, together with a new cell allowing the vacuum and thermal desorption of samples, we define the relation between the copper surface roughness and water contact angle (WCA). Next by a simple extrapolation, we determine the WCA for the perfectly smooth copper surface (WCA = 34°). Additionally, the kinetics of airborne hydrocarbons adsorption on copper was measured. It is shown for the first time that the presence of surface hydrocarbons strongly affects not only WCA, but also water droplet evaporation and the temperature of water droplet freezing. The different behavior and features of the surfaces were observed once the atmosphere of the experiment was changed from argon to air. The evaporation results are well described by the theoretical framework proposed by Semenov, and the freezing process by the dynamic growth angle model.

KEYWORDS: contact angle, wetting, copper, freezing, evaporation, molecular dynamics

1. INTRODUCTION

Surface hydrophilicity/hydrophobicity plays an important role in everyday life and in many industrial applications, including the clothing, building, and aviation industries, where superhydrophobic, superomniphobic, self-cleaning, and anti-icing surfaces are widely applied. Metal surface wetting is also a very important aspect in fuel cells, in corrosion science, or even in heat-transfer devices. On the other hand, the determination of hydrophilicity/hydrophobicity is not a simple task because it is strongly affected by surface contaminations. For example, airborne hydrocarbons adsorbed on a surface strongly influence the water contact angle (WCA) on Au, PTFE, Si, graphene, and many other surfaces. It was also proven that the mechanism of wetting is strongly related, among other things, to the affinity between a substrate surface to a droplet and to adsorbed hydrocarbons. The residual contact angle value is determined by a simple balance between the work of droplet adhesion to a bare substrate surface and the work of adhesion to a surface covered by adsorbed hydrocarbons.

Among the studies reported in the literature, there are discrepancies in WCA values on copper. For example, it was suggested that the most probable WCA for a smooth copper surface is 52°, although some authors reported smaller values. Recently it has been also postulated that a copper surface is strongly hydrophobic. Therefore, one can expect, similarly like in the case of PTFE, that a simple roughening of a copper surface should lead to the rise in WCA according to the Cassie-Baxter mechanism. In fact, the static WCA for the smooth copper surface was recently reported as close to 99° and, as expected, strongly increased for a surface roughened by using different methods. However, the majority of wetting studies do not consider the presence of airborne hydrocarbons, the authors do not provide the substrate characterization (for example, the roughness factor is not provided, and this has a crucial influence on WCA value), and do not use sufficient surface cleaning.

To settle the issue of whether the WCA on pure copper surface is smaller or larger than 90° one can resort to the literature data reporting water adsorption studies on copper since it is well proven that the shape of water adsorption
isotherm is strongly related to the surface hydrophobicity.\textsuperscript{14} Following the BET/IUPAC adsorption isotherms classification,\textsuperscript{15} if water adsorption isotherm is of the type III and/or V one can expect a small affinity of water to a surface, as it has been observed (for example) for strongly hydrophobic unmodified carbonaceous materials.\textsuperscript{14} The appearance of polar sites, for instance oxygen surface functionalities, on a hydrophobic surface leads to the rise of water-surface affinity at low and intermediate relative pressures. As a result, water adsorption isotherm changes its shape, and type II or IV is observed.\textsuperscript{14} Considering the results reported for copper by Lee and Staehle,\textsuperscript{16} and/or Sharma and Thomas,\textsuperscript{17} one can conclude that water adsorption isotherms on copper are of the II type, thus a pure Cu surface is hydrophilic.

One of the aims of this study was to investigate what is the WCA on a well-characterized (1 1 1) copper surface, possessing strictly defined roughness. To do so, an ultrahigh purity copper was used, and a special cell was constructed, enabling the contact angle measurements in hydrocarbons-free atmosphere and after the long-term vacuum and thermal cleaning of a surface. Applied cleaning procedure eliminates hydrophobic and hydrophilic centers from a copper surface. Using the modern Fringe Projection Phase-Shifting method of surface roughness determination, we define the relation between copper surface roughness and WCA, and next, by a simple extrapolation, we determine the WCA for the perfectly smooth copper surface. Additionally, the kinetics of airborne hydrocarbons adsorption on copper was measured. It is shown for the first time that the presence of surface hydrocarbons has a strong impact not only on the WCA values but also on water droplet evaporation and the temperature of water droplet freezing. To get an insight into the influence of airborne hydrocarbons we support the experimental results by molecular dynamics simulation data, and modern theoretical approaches.

2. MATERIALS AND METHODS

2.1. Copper Samples Preparation and Characterization. As a source of the initial copper, a vacuum gasket made of OFHC (oxygen free high conduct) copper (Artvac, Poland) was applied. This gasket, dedicated to ultrahigh vacuum (UHV) systems, contains the highest purity grade of copper (99.999\%) prepared without oxygen access and possessing very high electric conductivity. What is also important, this copper contains (1 1 1) planes. This is crucial for wetting studies because it is well proven that (1 1 1) copper is resistant to oxidation (in fact, the oxidation of this plane is negligible) and prevents water dissociation. This is crucial for wetting studies because it is well proven that (1 1 1) copper is, among all Cu surfaces the least reactive in reaction with oxygen, and hence the most resistant to oxidation (in fact, the oxidation of this plane is negligible). Cu (1 1 1) surfaces also prevents water dissociation.\textsuperscript{18} This structure is confirmed by XRD spectra shown in Supporting Information (SI) Figure S1. The spectra were obtained using Philips X'pert in a transmission mode over a 5–12° 20 range with the scanning speed equal to 0.05 deg/min using X'Celerator Scientific detector with Cu anode (Malvern Panalytical, Malvern, UK). The diffraction profiles were corrected by linear plotting of background and then by the smoothing cycles. The contribution of K2O was eliminated by the Raschinger method. The established experimental data are in good accordance with the pattern (00–0040–0836). The appeared peaks 43.6°, 50.5°, 74.4°, 90.0°, 95.3°, and 116.8° are coming from the following reflections 111, 200, 220, 311, 222, and 400, respectively (see SI Figure S1). However, the peak at 43.6° shows the 111 reflection and possesses the I equal to 100%.

The initial sample was labeled as Cu-0. From this sample, two additional copper samples were obtained using a sandpaper (Trading - Stolker, Poland) of grit 600 and 2000, and the samples were labeled as Cu-600 and Cu-2000, respectively (to remove the sandpaper residues and Cu dust the samples were cleaned using Ar stream—for the efficiency of this procedure see SI Figure S2).

For data acquisition and analysis, One Attension software was utilized equipped with Attension 3D Topography Module (Biolin Scientific Oy, Espoo, Finland). The advantage of the method is the possibility to determine the apparent and intrinsic contact angle (corrected by roughness). To assess the wettability of the surfaces, the dynamic contact angle measurements were performed. The water droplet (6 μL) was dropped by it from the tip of the needle from the height of 1.5 mm and its behavior was monitored during no more than 1000 s. To distinguish which process occurred, that is, evaporation and/or water wetting, the evolution of following factors were determined: WCA, volume and height of the testing liquid, droplet base and work of adhesion.

2.2. Contact angle in Ar and in Air Atmosphere, Droplet Evaporation, and Freezing. Before WCA measurement in Ar atmosphere each sample was placed separately in the special homemade cell (Figure 1).

Figure 1. An overview of a new homemade cell for the measurement of contact angle in controlled atmosphere (A). The vacuum and Ar valves are shown together with the septa-supported dosing system. The goniometric system (a bright diode and lens) is placed on the optical axis crossing the both sides of two sight glasses. The inset (B) shows the side view and a typical image of WCA on a thermally desorbed under vacuum sample.

Both sides of this cell are equipped with sight glasses enabling observation of three phase contact line using a goniometric system described in details previously.\textsuperscript{8} In short: it contains a camera Grasshopper3 GS3-UM3–3254C–C, 3.2 Mpx connected to the specially designed optical system consisting of perfectly located in the optical axis two elements: Edmund Optics 1.0x Telecentric Lens 55350 and Edmund Optics Telecentric Illuminator Lens 62760 with a bright diode placed in it (MicroBriteSpot/Coaxial Light model: SL223 470 IC, Light wavelength: 470 nm) leading to polarized parallel light. The cell was sealed up using FKM/FPM (Viton) gaskets and connected to two liquid nitrogen cold-trap reinforced vacuum pumps: Edwards E2M0.7 and a turbomolecular pump Leybold Turbovac 50. After placing a sample inside, it was desorbed for 24 h without heating to the pressure smaller than 1.2 × 10\textsuperscript{-3} mbar. After this preliminary desorption, a sample was further desorbed for subsequent 72 h at 673 K, and finally cooled down in a vacuum for 30 min in Ar atmosphere (Argon Premier 99.9992%, Air Products, Poland) at Ar pressure equal to 1 atm. Ar application prevents the introduction of oxygen into the system. The initial sample evacuation without heating is a very important step because in this way we avoid copper surface oxidation. Moreover, long-term heating supported by a sample evacuation eliminates not only hydrophobic but also hydrophilic contaminations, for example, polar gases present in air (CO\textsubscript{2}, adsorbed H\textsubscript{2}O etc.). The presence of hydrophilic centers can
drastically decrease WCA\textsuperscript{18} even to the value equal to zero, as it was proven by White and Drobek.\textsuperscript{19} A stainless steel needle containing deionized and deoxidized water (ion conc. < 6 ppm) was introduced into the system by a silicone septa (Injection Rubber Plug 201-35584, Shimadzu, Japan) and WCA values were measured (at least for three droplets, each was placed by dropping it from the tip of the needle from the height of 1.5 mm) and the results were averaged.

Samples measured in this system are denoted by subscript Vac. Desorbed in the same way samples were removed from a cell and subjected to air atmosphere. Samples measured after that exposure are denoted by subscript Vac-Air. WCA values were determined to check the influence of adsorbed airborne hydrocarbons on copper wetting. In this case, we applied our goniometric system described above. To check the influence of hydrocarbons on droplet evaporation in air (25.0 ± 0.1 °C, relative humidity = 35%) we used Attension Theta Flex Optical Tensiometer (Biolin Scientific Oy, Espoo, Finland). A freshly prepared samples (Cu-0 and Cu-2000) were used. In order to obtain the comprehensive characterization of the systems the droplets were also examined for the occurrence of frozen surfaces. The aim of this experiment was to check how the presence of adsorbed airborne hydrocarbons affects the icephobicity. The freezing experiments were performed in air atmosphere (at the pressure of 1 atm, the relative humidity of 50%). To do so a freshly prepared samples of Cu-2000-Air were used. Droplet freezing (the temperature profile is shown in SI Figure S3) were studied in air, at 25.0 ± 0.1 °C (relative humidity = 50%) using Attension Theta Optical Tensiometer (Biolin Scientific Oy, Espoo, Finland) equipped with DEBEN Coolstage (model AFM Nanosurf by Deben UK, Woolpit, Suffolk, United Kingdom). Droplet at these measurements were also placed by dropping it from the tip of the needle from the height of 1.5 mm.

2.3. Molecular Dynamics Simulation. The details of MD simulation procedure are given in the Supporting Information. Shortly: three Cu surfaces were modeled, namely (1 1 1), (0 0 1), and (1 1 0). The energy parameter ε_{Cu-Cu} was determined empirically by matching the experimental WCA for (1 1 1) surface. We use TIP4P/2005 water model.\textsuperscript{25} To estimate the influence of line tension we simulated spherical and cylindrical nanodroplets. In order to check the influence of airborne hydrocarbons, n-decane model was used with the interaction parameters taken from the OPLS-AA force field.\textsuperscript{21} The electrostatic interactions were evaluated using the Particle Mesh Ewald (PME) method. All simulations were carried out using OpenMM package\textsuperscript{22–24} with a Nose-Hoover thermostat (r = 0.1) at the time step 0.002 ps. The rigidity of water was enforced using SHAKE algorithm.

3. RESULTS AND DISCUSSION

3.1. Cu Surface—Hydrophobic or Hydrophilic? In the materials science, to understand all changes caused by the modification, chemical, or physical, it is crucial to fully characterize the material. First the imaging of the surfaces and the roughness determination was performed. The pristine surface was characterized by homogeneous topography with little voids (Figure 2A1). After the treatment with sandpaper, significant changes have been noticed. Well-defined heterogeneities possessing the same orientations due to the roughening process were observed (Figure 2B1–C2). In the case of sandpaper usage with a grit size 600 (for Cu-600 sample) much rougher material was generated. However, an interesting result was obtained for the copper treated with 2000 sandpaper (Cu-2000 sample). The overall roughness of the latter sample was smaller than the pristine one. The roughness was expressed by the S_{d} (area factor, the ratio between the interfacial and projected areas) (eq 1) and r (roughness ratio) (eq 2) which are roughness parameters according to the ISO 25178 standard. The roughness ratio is defined as the ratio between the actual and projected solid surface area (r = 1 for a smooth surface and r > 1 for a rough surface). The value of r equal to 1.09 for the Cu-2000 sample proved that an almost totally smooth surface was generated.

Figure 2. SEM images of Cu-0 (A1), Cu-600 (B1), Cu-2000 (C1), and surface topography (A2–C2), together with respective roughness parameters S_{d} and r.
In the next step of samples characterization, the roughness was correlated with WCA (Figure 3A). The linear relation between WCA and \( r \) proved the high quality of the roughening processes. The presented excellent correlation was observed for the materials desorbed and kept in the ambient atmosphere of Ar to ensure lack of surface oxidation and adsorbed airborne hydrocarbons. In the Ar atmosphere, the highly hydrophilic character of the copper surfaces was presented. WCA was ranging between 13.0° for Cu-600-Vac and 31.8° Cu-2000-Vac, respectively. The value of contact angle (WCA = 34°) for the totally smooth surface with \( r = 1 \), so-called Young surface, was calculated and added to the plot (Figure 3A). The WCA was determined from the Wenzel eq (eq 3):

\[
\cos \theta_m = r \cos \theta_Y
\]

where \( \theta_m \) is the measured contact angle, \( \theta_Y \) is Young’s contact angle, and \( r \) is the roughness ratio.

When the atmosphere of the experiment was changed from argon to air different behavior and features of the surfaces were observed (Figure 3B). Importantly, the range of WCA switched from a highly hydrophilic to an almost hydrophobic one. Due to the lack of pure ambient atmosphere, the values of WCA were now placed between 50.2° and 82.3° (Figure 3B). Thanks to the implementation of Fringe Projection Phase-Shifting method (see SI Figures S4 and S5), it was possible to obtain the roughness-corrected WCA. The mentioned changes were dictated by the value of the roughness parameters. Namely, the biggest impact was noted for the Cu-600 and the smallest one for Cu-0 (Figure 3B).

Figure 4 collects the changes in the WCA of the samples thermally desorbed as in Figure 3A, but exposed directly to the atmosphere. It can be seen that the WCA increases with the exposure time changing the surface nature to less hydrophilic and even hydrophobic.

To get a deeper insight into the wetting mechanism we show in Figure 5A the results for 3900 TIP4P/2005 water molecules placed in a cylindrical droplet on the top of a perfect (1 1 1) Cu surface (after preemptive energy minimization the drop was equilibrated for 10 ns, and the averages were gathered for up to 40 ns). The solid–fluid interaction parameter was determined by matching the WCA of a cylindrical drop to the
Figure 5. MD simulation results showing the wetting of (1 1 1) Cu surface—simulation of cylindrical (A) and spherical (B) droplet, the influence of adsorbed airborne hydrocarbons on WCA for Cu (1 1 1) (blue points) and Cu (0 0 1) (red crosses) surfaces (C), 2D densities of water on Cu (1 1 1) (C1) and Cu (1 1 1) covered with alkane monolayer (C2), and selected snapshots showing the droplet sitting on c.a. 0.7 (D1, D3) of monolayer and on monolayer (E1, E3) of hydrocarbons carpet on (1 1 1) surface. The snapshots for (0 0 1) are F1, F3, and G1 and G3, respectively. The orientation of hydrocarbons in 0.7 of monolayer and in monolayer is also shown for (1 1 1) (D2 and E2) and (0 0 1) Cu surfaces (F2 and G2). Snapshots were prepared using the VMD, a molecular visualization program.™
experimental value (34°, see Figure 3A), and the value equal to $\varepsilon_{\text{Cu}-\text{Cu}} = 2.747$ kJ/mol was found. The impact of droplet size on the WCA is very small (see the results presented in Figure 5B for the spherical droplet), thus we conclude about the small influence of the line tension on WCA. Figure 5C shows the simulation results of the effect of airborne hydrocarbons on WCA. It is interesting that WCA increases with the surface concentration of airborne hydrocarbons, reaching similar values as observed during the experiment (see Figure 4). We note that once the surface concentration of airborne hydrocarbons gets over the monolayer concentration, the impact of additional n-decane molecules on WCA is quite small. Likewise, insignificant WCA changes can be observed for very small alkane concentrations. Figure 5D,F show the snapshots of water on n-decane covered (1 1 1) and (0 0 1) copper surface evaluated at surface concentration equal to 1 molecules/nm$^2$, what corresponds to ca. 0.7 of hydrocarbon monolayer. The droplet is in so-called “dimple” state, that is, only few or no hydrocarbons under the droplet are observed. Figure 5E,G shows the snapshots of water on n-decane covered (1 1 1) and (0 0 1) copper surface evaluated at surface concentration equal to 1.45 molecules/nm$^2$, what corresponds to a full hydrocarbon monolayer. We find the droplet to be in the so-called “carpet” state. It is worthy to mention, that we also performed simulations for (1 1 0) Cu surfaces. We assessed how different exposed planes affect the WCA values, and to what extent the change in the exposed surface type influences the packing of the adsorbed hydrocarbons (selected representative results are shown in Figure 5C for selected points of (0 0 1) surface). Our simulation data show that the WCA on pure (0 0 1) Cu surface for cylindrical droplet is equal to 44°, that is, this Cu plane is more hydrophobic than (1 1 1) plane. The influence of the airborne hydrocarbons is similar for both surfaces leading to similar WCA values as recorded for (1 1 1) surface (Figure 5C); however, small differences in WCA can be caused by small differences in hydrocarbons packing. Also the orientation of “carpet state” hydrocarbons on both Cu surfaces is the same (Figure 5E2,G2). Hydrocarbons energy minimization is achieved by parallel orientation on Cu surface.

Finally, Figure 6 collects the WCA values plotted as a function of the density of Cu surface atoms. Excellent correlations are recorded, leading to the conclusion that all Cu surfaces are hydrophilic, however, large differences in WCA are recorded. Thus, it can be observed, that predicted by us from MD simulation WCA values can vary for pure Cu in the range 34° (for (1 1 1)) to 52° (for (1 1 0)), with the value of 44° for Cu (0 0 1). This is correlated with the density of the surface atoms.

As the density of surface atoms increases, the rise in the work of droplet adhesion is observed, leading to the decrease in WCA value.

3.2. How Airborne Hydrocarbons Influence Droplet Evaporation on Cu? Figure 7 collects the results of the experiment on droplet evaporation. Generally, one can observe that with the rise in exposure time, the WCA increases due to presence of hydrocarbons (Figure 7A). This presence, however, causes the elongation of the evaporation process (Figure 7A), accompanied by the decrease in baseline length (Figure 7B) and the work of adhesion (SI Figure S6).

According to the current state of art, three stages of evaporation from the sessile water droplet in unsaturated H$_2$O vapor atmosphere can be distinguished: the evaporation at a constant contact area and decreasing contact angle, at a decreasing contact area and constant contact angle, and finally, at both area and angle decreasing.

Because of the short time, the evaporation at the beginning (just after the droplet deposition, during its spreading) can be neglected and this is confirmed by our results (see Figure 7C). However, it is hardly to find the second stage of evaporation (at constant angle and decreasing contact area), excepting the system Cu0 (Figures 7A and 7C).

Therefore, we estimate the kinetics of only first stage of evaporation (constant contact length). For the diffusion controlled evaporation the time changes of droplet volume, $\frac{dV}{dt}$, can be expressed as

$$-\frac{dV}{dt} = \beta F(\theta)L$$

(4)

where $L$ is the contact radius, $\beta$ and $F(\theta)$ are defined as

$$\beta \equiv 2\pi \frac{\text{DM}}{\rho} (c_{\text{sat}}(T_{w}) - c_{\infty})$$

(5)
In our case $\theta$ is always above 0.175 rad, therefore we do not show $F(\theta)$ for $\theta < 0.175$ rad.

In eq 5, $D$, $M$ and $\rho$ are the diffusion coefficient of H$_2$O vapor in air, water molar mass, and liquid density, respectively, $c_{sat}$ is the molar concentration of saturated vapor at the temperature $T_{av}$ which is the average temperature of a surface. Finally, $c_0 = Hc_{sat}(T_{\infty})$ is the molar concentration of vapor, $T_{\infty}$ and $H$ are the temperature and humidity of air far from the surface, respectively.

$$F(\theta) \equiv (0.00008957 + 0.6333\theta + 0.1166\theta^2 - 0.08878\theta^3 + 0.01033\theta^4)/\sin \theta$$

for $\theta \geq 0.175$ rad

(6)

As the droplet volume can be expressed as a function of $L$ and $\theta$,$^{27}$

$$V = L^2 f(\theta), f(\theta) \equiv (1 - \cos \theta)^2(2 + \cos \theta)/\sin^3 \theta$$

definition of $\theta(\theta = 0)$ which give the smallest deviation of $\theta(t)$ obtained by solving eq 8 calculated from the experimental $\theta$, we applied the Nelder–Mead method. The initial period where there are changes of $L$ are excluded from the fitting. Thus, $\theta_0$ is close to the advancing contact angle. The results are presented in SI Table S1 and, for selected systems, on Figure 7C. It can be seen that the data fit is

(7)

$$-\frac{d\theta}{dt} = \frac{\beta V(\theta)}{L^2 f'(\theta)}$$

(8)
reasonably good as indicate the values of the determination coefficient ($R^2$ in the range 0.995–0.9999).

The time dependence of approximated contact angles is slightly more steep than the experimental one. It does not seem to be caused by the decrease in the driving force of evaporation, $X \equiv c_{sat}(T_w) - c_{\infty}$, which in the calculations is assumed to be constant. As the droplet decreases $T_{w}$, should not decrease because the distance between the metal plate and the droplet surface decreases and the heat transport to the surface should be faster. The value of $c_{\infty}$ should be practically constant because the volume of evaporated liquid is very small compared to the compartment where the droplet is deposited. The parameter $\beta$ practically does not depend on the kind of surface on which the droplet was deposited; there is no correlation between $\beta$ and $\theta_0$ or $L$ and the standard deviation does not exceed 5% of the average value of $\beta$. Thus, it confirms that $\beta$ depends only on the driving force of evaporation, $X \equiv c_{sat}(T_w) - c_{\infty}$, and the parameters related to vapor ($D$) and liquid ($M, \rho$). In SI Table S1, $X$ divided by the saturated vapor concentration at the measurement temperature, $c_{sat}(T_m)$ is also shown. The value $c_{sat}(T_m)$ can be treated as the maximum force of evaporation, thus $X/c_{sat}(T_m)$ represents the fraction of that force. Because $T_{w0} < T_m$ and $c_{\infty} > 0$ $X$ is below 50% of the maximum force.

There are correlations observed between $\theta_0$ and $L$ (the higher is $\theta_0$, the lower is $L$). They are obvious considering the fact that the initial volumes of droplets were almost the same. Summing up, the results of droplet evaporation on studied Cu surfaces are described by the model proposed by Semenov et al. very well. Generally, adsorbed hydrocarbons influence the WCA, and prolong the process but do not change the mechanism of droplet evaporation from Cu surface.

**3.3. Droplet Freezing.** The droplet freezing experiment is very informative from the material and application points of view. It is clear that the presence or lack of the adsorbed airborne hydrocarbons have a significant influence on the surface resistance to cooling (Figure 8) and ice formation. For the material that has no contact with the airborne hydrocarbons (time for hydrocarbons exposition, $t_{h\_air} = 0$ min) the lowest contact angle (WCA = 50.1°) as well as the shortest time ($t = 190$ s, start of freezing up, full ice formation after 216 s) required to freeze the materials was observed (Figure 8A). Then after 2 days of exposure ($t_{h\_air} = 48$ h) of the sample on the air 61% of WCA increase was seen (Figure 8A). However, a substantial difference was observed after 2 weeks of contacting air atmosphere ($t_{h\_air} = 336$ h). Due to the formation of a layer of airborne hydrocarbons, the value of the WCA exceeded the hydrophobicity level and was equal to 103.3°. Moreover, in this case the time required for freezing of a droplet on the surface was also prolonged to 259 s (Figure 8A). The results collected in Figure 8B show, that the temperature of the start of ice formation decreases with the time to surface exposure for the atmosphere. It means that the hydrocarbons layer acts as a protective layer due to its own heat capacity.

At the next stage, we used a theoretical model to check the evolution of profiles of frozen droplets. As the Bond number for our droplets is within the range 0.28–0.45 the gravity effect on the droplet shape can be neglected. Although a more advanced description of the freezing of a droplet exists,²⁸ for the fitting of the frozen sessile droplet, we decided to apply a simple model for zero gravity and dynamic growth angle.²⁹ In this approach mass conservation demands that the rate of change of liquid volume is related to the solidification rate ($dH/dt$) via:

$$\frac{dV}{dt} = -\pi R^2 \frac{dH}{dt}$$

(9)

where $H(t)$ is the height of the solid–liquid interface, $V_{SC}$ is the volume of a spherical cap, $\rho = \rho_l / \rho_0$, $\rho_l$, $\rho_0$ are the densities of solid (ice), and liquid water, respectively. The radial coordinate of the trijunction line evolves as

$$\frac{dR}{dt} = -\frac{1}{\tan(\theta - \theta)} \frac{dH}{dt}$$

(10)

where $\theta$ is the apparent contact angle. The dynamic growth angle $\theta_i$ is related to the slip velocity $V_s$ via²⁹

$$\theta_i = \theta - \tan^{-1}\left(\frac{V}{V_s} + \frac{1}{\tan\theta}\right)^{-1}$$

(11)

In the above $V = dH/dt$, and we use

$$V_s(\theta) = \begin{cases} \eta(\theta_k - \theta) / \theta, \theta < \theta_k \\ 0, \theta \geq \theta_k \end{cases}$$

(12)

where $\theta_k$ and $\eta$ are fitting parameters. By setting $\theta_i = 0$ one recovers the fixed contact line model. While the latter model is purely geometrical, that is, the final shape is independent of the...
solidification rate, the former, dynamic growth angle model requires specification of the rate of solidification. Here we assume that

$$\frac{dT}{dt} = \frac{\kappa_S \Delta T}{\rho_S L_S H}$$

where $\kappa_S$ is the thermal conductivity, $L_S$ is the latent heat of solidification, $\rho_S$ is the density of ice, and $\Delta T$ is the difference between the freezing temperature and the temperature of the cold plate.29 Equations 9–13 together with a relation for $V_{SC}$ form a set of differential-algebraic equations that has to be solved numerically. Numerical details of the fits are collected in SI Table S2 and the results are presented in Figure 9. We note that the incorporation of nonzero growth angle significantly improves the quality of the fits. Clearly, eq 13 represents a rather crude approximation to the actual experimental conditions. However, the good quality of the obtained fits suggests that the final shapes of the droplets are insensitive to

![Figure 9](image-url)
the precise details of the solidification front description, at least for the cooling rates used in our experiment (SI Figure S3).31,32

■ CONCLUSIONS
The application of modern Fringe Projection Phase-Shifting method and a new cell allowing the in situ measurement of WCA in a controlled atmosphere after a sample desorption, leads to the conclusion that Cu (1 1 1) surface is hydrophilic with WCA = 34°. This is in accordance with the shapes of water adsorption isotherms reported in the literature. When subjected to atmosphere WCA increases due to adsorption of the airborne hydrocarbons. The application of MD simulations provides the WCA values equal to 52° (for (1 1 0)) and 44° (for Cu (0 0 1)), thus WCA strongly depends on the type of Cu planes. Airborne hydrocarbons strongly influence droplet evaporation and freezing, prolonging the evaporation and decreasing ice-formation temperature. The evaporation process is well described by the model of Semenov,26 whereas the final shapes of frozen sessile droplets are well characterized using the dynamic growth angle model.29

■ ASSOCIATED CONTENT
1 Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.1c09733.

XRD spectra of studied (1 1 1) copper. Fringe projection phase-shifting method. MD simulation details. Water evaporation fitting results (PDF)

■ AUTHOR INFORMATION

Author Contributions
The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes
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