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High-Speed Imaging of Freezing Drops: Still No Preference for the Contact Line

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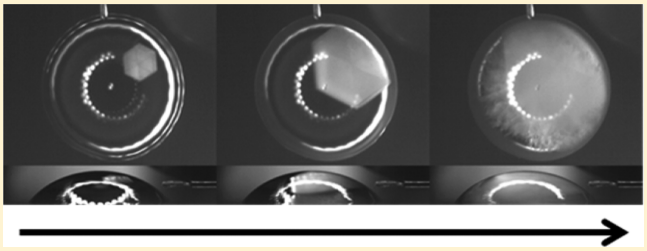
Supporting Information

ABSTRACT: Recent experiments by Suzuki et al. (*Chem. Phys. Lett.* **2007**, *445*, 37−41) and Gurganus et al. (*J. Phys. Chem. Lett.* **2011**, *2*, 1449−1454) on liquid−solid nucleation arrived at conflicting results regarding a preferred status of the triple line between water, air, and an ice-catalyzing substrate. Temperature nonuniformity within drops and substrate-dependent contact angles have been suggested as culprits in a recent review by Sear (*Int. Mater. Rev.* **2012**, *57*, 328−356). To that end, we redesigned our earlier experiment to allow substrate-induced cooling and a side view with a second high-speed camera. The two camera views pinpoint the spatial location of nucleation sites in both the vertical and horizontal directions. Here we report such nucleation positioning results measured within drops freezing on a substrate. The role of thermal gradients was explored in three ways: (i) implementing direct cooling of the substrate; (ii) mimicking (higher) cooling rates used by Suzuki et al.; and (iii) varying the drop−substrate contact angle. No influence of thermal gradients on the preference for freezing at the triple line has been observed. Thermal simulations of the drop−substrate system confirm that horizontal temperature gradients are extremely small. Furthermore, treatment of the substrate to obtain a range of contact angles also yielded no preference for freezing at the triple line. The combined top and side views of the freezing drops suggest that apparent triple-line nucleation can be a spurious result of the viewing geometry.



INTRODUCTION

Heterogeneous nucleation in clouds converts water to ice, thereby affecting weather and climate. Probably, the least understood heterogeneous nucleation pathway is the contact mode, where a catalyst particle causes freezing by contact with a supercooled droplet.[4] Recent laboratory experiments with 10−100 μm particles have indicated that contact promotes nucleation even when the catalyst resides within the liquid drop but in the immediate vicinity of the air−water interface.[5−7] In an attempt to interpret these experimental results, thermodynamic arguments[8] and computational studies[9] have suggested that nucleation may be preferred near the three-phase interface or triple line.

To examine the role of the triple line enhancement, Gurganus et al.[2] distilled the problem into a simple, drop-on-substrate geometry so that the spatial distribution of nucleation sites could be pinpointed. Contrary to expectations, in our first study no preference for the triple line was observed. This is in contrast to a similar experiment by Suzuki et al.,[1] who did observe preferential nucleation at the triple line. The apparent discrepancy between the two experiments has been highlighted in a recent review by Sear,[3] where attention was drawn to differences in drop−substrate contact angle and possible thermal biases induced by different cooling methods. Specifically, Sear suggested that "A set of experiments in which a parameter (cooling rate?...) is varied and the system goes from nucleation at the contact line to nucleation away from this line, would be very helpful".[3] To that end, we have carried out a set of follow-up experiments where we changed the method and rate of cooling and varied drop−substrate contact angles.

The two experiments[1,2] differ in the method of cooling employed, in the water volume studied, and in the form of monitoring the drop freezing. In our prior study we took extreme care to minimize thermal gradients or biases by indirectly cooling the nearly isothermal volume at a very gradual rate of <0.5 K/min. As is commonly done in other studies,[5−7,10] Suzuki et al.[1] employed a substrate cooling technique with a rate of approximately 5 K/min. Such rates can occur in the atmosphere within strong updrafts. It has been suggested that prior studies may have shown a bias in favor of surface crystallization because such high cooling rates will lead to development of a steady state thermal gradient across the droplet.[2] If this gradient exists across the droplet−substrate interface then we might expect to see preferential nucleation at the periphery where the thermal load is reduced (in spherical cap geometry). Finally, in our prior experiment the droplet crystallization was monitored with a camera located above the water drop, whereas in the Suzuki et al. study a side-viewing camera was used. In this work we have introduced substrate

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cooling at comparably high rates as are typical in other experiments, and we have added a second, side-viewing camera to further pinpoint the nucleation location and to continuously measure the drop−substrate contact angle.

EXPERIMENTAL TECHNIQUES

The basic experimental approach is similar to our prior study; namely, the location of an ice nucleation event is identified by observing the initial freezing of a water drop with a high-speed camera: when the freezing movie is played in reverse, eventually the point of origin of the ice crystal can be determined, including whether the point lies at the substrate−water interface or along the substrate−water−air contact line (the triple line). To simplify the interfacial geometry, we utilize homogeneous and atomically smooth 50 mm test grade silicon substrates for our nucleation medium. Using an atomic force microscope, we record root mean squared (RMS) surface roughness values of <10 nm for both new and cleaned (acetone and isopropyl alcohol (IPA) then dried with a nitrogen spray) wafers. Similar to our prior study,[2] in these experiments 30 μL water droplets (distilled, deionized, UV-irradiated) are placed on the substrate with a syringe.

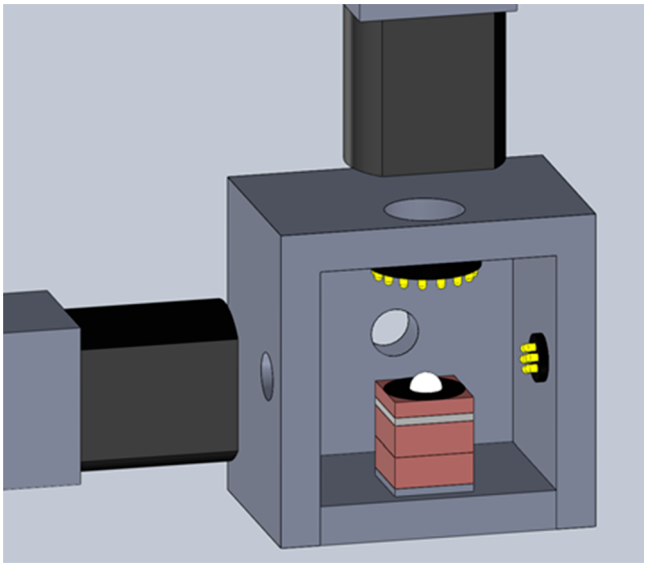

Figure 1. Schematic of the new thermal chamber. Continuing the geometry of refs 1 and 2, this study examines supercooled droplets in contact with an atomically smooth Si substrate. Unlike our prior study, the substrate is placed in thermal contact with a Peltier cooling element (white) to achieve high cooling rates (5 K/min). The droplet and cooling element are contained in an isothermal chamber with positive pressure from a dry air line. Optical ports on the top and sides of the chamber allow for simultaneous imaging of the droplet in the horizontal and vertical planes.

For this study, a larger test chamber was built, with optical ports on the top and side to allow for simultaneous imaging of the top and side of the droplet with a synchronized pair of Photron SA2 cameras. Sufficient lighting for 5−10 kHz sampling is provided by arrays of blue-white LED arrays above and behind the droplet, which contribute negligibly to droplet heating.[2] The overall geometry is shown schematically in Figure 1. The cameras continuously record the droplet during the cooling cycle through a 10 s ring buffer. An IR thermocouple monitors the droplet surface temperature and is used to trigger a transfer of the camera buffer when a latent heat spike is observed. This technique[2] allows us to record the entire freezing event and to isolate the position of each nucleation site with ImageJ image analysis software, in both the top and side views as shown in Figure 2.

In an attempt to maximize the possible role of thermal gradients in the droplet we selected a large drop size (30 μL) and a cooling rate (5 K/min), both similar to the experimental conditions of Suzuki et al.[1] The increased cooling rate was achieved by the addition of a solid state cooling element (Peltier element) in the center of the test chamber (Figure 1). The chamber is maintained at a steady temperature (to within ±0.1 K) by circulation of a chilled glycol solution with a Neslab RE 140 chiller. The temperature of the substrate is set with the Peltier chiller through a PID interface with an RTD probe underneath the substrate.

In a typical experiment, each droplet in the chamber is frozen and thawed 10−20 times as part of a ∼30 min automated cooling and heating cycle. After the droplet melts, the camera buffers are triggered to begin recording again, and the cooling cycle repeats. To prevent icing of the chamber walls, a positive pressure is maintained in the chamber volume with a dry air supply at 2−5 L/min. Because the chamber air is subsaturated, the droplet will continuously evaporate on the substrate, typically losing half of its mass over the duration of the experiment. To better compare the location of nucleation sites between different drops, the droplet diameter is measured after each freeze to normalize the radial position of the nucleation site. During this evaporation process, the drop−substrate contact angle slowly decreases because of drop pinning, and this contact angle is measured with the side-view camera. Furthermore, the contact angle was changed over a larger range by using clean silicon wafers in one set of experiments and silanized silicon wafers in another set of experiments. The resulting variation allows the possible dependence of freezing position on contact angle to be investigated.

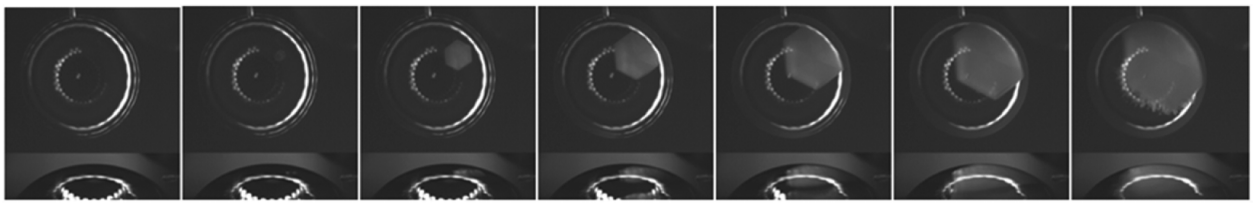

Figure 2. Pair of high-speed Photron SA2 cameras allows us to pinpoint nucleation sites and measure the droplet contact angle. In this film strip each frame represents a time step of 2 ms, or every 20th frame at a sample rate of 10 kHz. The nucleation site is evident at the center of the hexagonal crystal when the film is viewed in reverse.

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RESULTS

The top-view movie of each freezing event was used to determine the nucleation site on the substrate, and the side-view movie was used to determine the contact angle of the droplet. Because the droplet acts as a liquid lens, the exact determination of the freezing site is complicated, especially in the case of the side view (see Supporting Information). In some data runs a small dust particle or Si wafer defect that cannot be resolved will induce nucleation preferentially at one location. We do not believe that these defects are significant in many experiments, as typical surface roughness values of clean and used wafers have both been shown to have surface roughness values of ∼10 nm. Such consecutive nucleation events at the same site are removed from further processing. We also note that the side view shows no evidence of nucleation occurring above the substrate, and this is further confirmed by consistently horizontal (parallel to substrate) orientation of growing ice crystals.

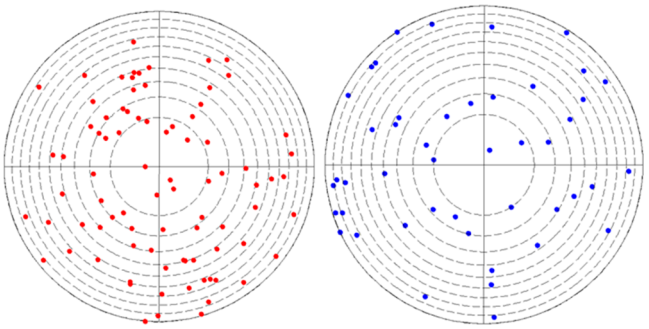

Figure 3. From Image analysis of the top-view movies, we can determine the nucleation site at the droplet−substrate interface. In the left panel, nucleation sites for a droplet with low contact angles on a clean silicon wafer are displayed in red. In the right panel, nucleation sites for a droplet with higher contact angles on a silanized wafer are displayed in blue. The dashed lines separate regions of equal area (10%).[2] Both distributions appear uniformly random in agreement with our previous observations.

The spatial distribution of freezing sites for droplets on the clean Si wafer cooled through the substrate at a rate of approximately 5 K/min is shown in the left panel of Figure 3. As in the prior results,[2] no preference for the triple line is observed. This observation was somewhat surprising, given our initial expectations about the role of thermal gradients. The same holds true when the water drop is placed on a silanized Si wafer, resulting in a steeper contact angle, as shown in the right panel of Figure 3. Despite increasing the cooling rate by an order of magnitude, we see no apparent change in the distribution of freezing sites from our prior study.[2] This would suggest that any thermal bias in the experiment does not play a significant role in nucleation.

The role of contact angle can be further studied. The twin imaging technique allows us to correlate the radial position of a nucleation germ site with corresponding contact angle of the

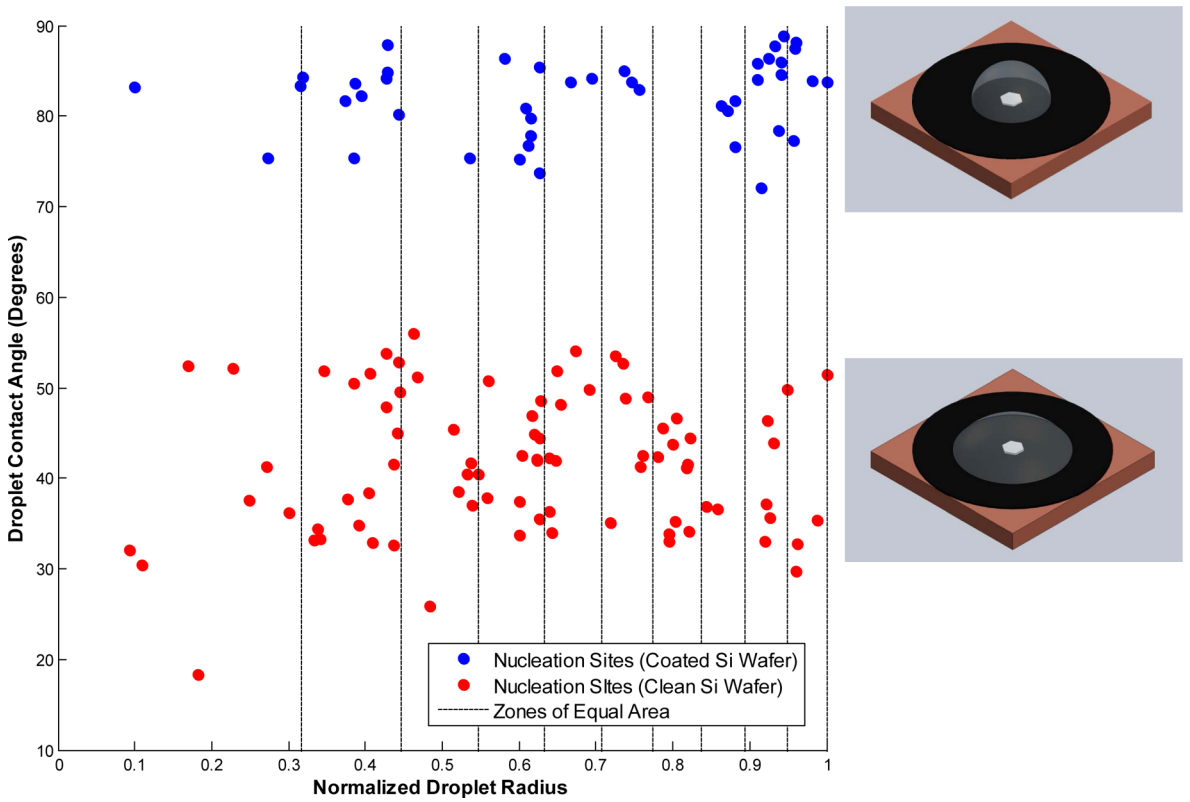

Figure 4. Image analysis from the side-view camera allows us to determine the contact angle of each droplet at the initiation of freezing. The red points indicate observed nucleation events on a clean Si wafer, while the blue points indicate observed nucleation sites on a silanized Si wafer. As in Figure 3, the dashed lines separate 10 zones on equal area to help guide the eye in the radial distribution of sites. The large variability in the observed contact angles of both sets is caused by pinning at the triple line during slow evaporation of the droplet. The approximate ranges for the observed drop contact angle, perimeter, and height are respectively 30−90°, 10−30 mm, and 1−2.5 mm. There appears to be no difference in the distribution of nucleation sites with contact angle.

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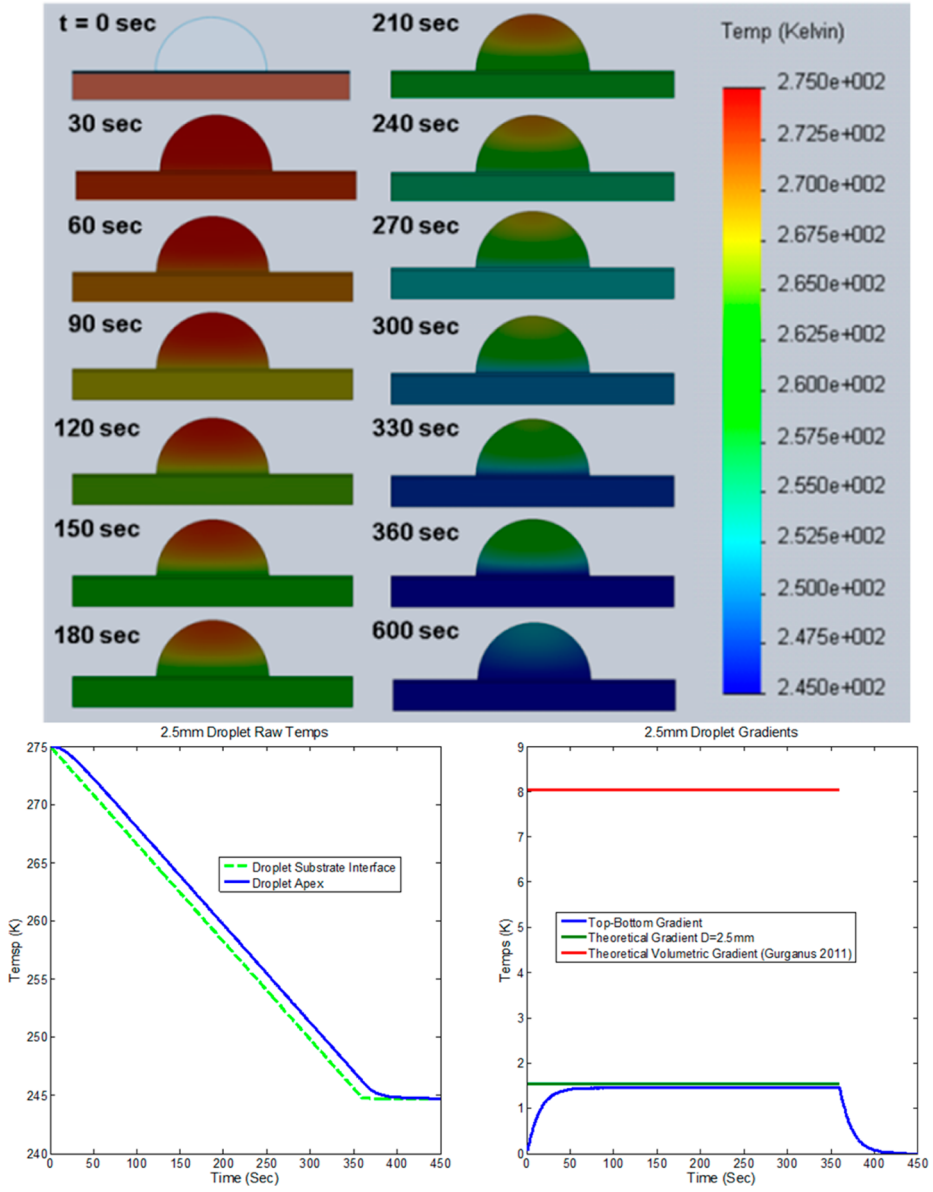

Figure 5. Results of our thermal analysis of this geometry using the Solidworks software package. This simulation mimics our experimental conditions, with the droplet, wafer, and heat sink initially at a stable equilibrium with the isothermal chamber (275 K). At $t = 0$, the temperature of the heat sink is decreased at a rate of 5 K/min for 360 s until it falls to a substrate temperature of 245 K, at which the temperature of the heat sink is held constant until the droplet comes into equilibrium. The bottom panels represent data from nodes at the top and bottom of the droplet. The first node is on the droplet−silicon interface. The selection of this bottom node is arbitrary because we observe no thermal gradient at the droplet−substrate interface. The second node is located at the apex of the droplet 2.5 mm above the interface. The left panel displays the raw temperature at both nodes during the cooling cycle. The right panel displays the thermal gradient that develops between these two nodes. After an initial transient stage (60 s), a steady state gradient of ∼1.5 K is maintained throughout the cooling cycle. After the active cooling ends (360 s), the droplet relaxes exponentially toward the new equilibrium temperature.

droplet on the test substrate (Figure 4). The large spread in droplet contact angles (30−90°) appears to have no correlation with the radial distribution of freezing sites.

■ DISCUSSION AND CONCLUDING REMARKS

Beginning with Gurganus et al. we developed an experimental approach that disentangles the notion of line tension from the contact and has a simple, symmetric, and clearly defined triple line.[2] Unlike most studies, the experiments address nucleation directly in terms of the spatial distribution of nucleation sites rather than in terms of temperature dependence. Here we have tested the conjectures that differences in drop−substrate contact angle or thermal biases may cause a preference for freezing at the triple line.[2,3] In an attempt to better understand the role of thermal gradients in our system, we have modeled the droplet substrate geometry using the Solidworks thermal simulation software package. In this model a 2.5 mm hemispherical water droplet (30 μL) resting on a 500 μm thick silicon wafer is placed in thermal contact with a 10 mm copper block (Figure 5). An automated meshing algorithm mapped the system and established a nodal spacing of ∼100 μm. To begin, all elements in the system are held at an equilibrium temperature of 275 K. To simulate the effect of the solid state cooling element the temperature of the bottom plane

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of the copper block is decreased uniformly at a rate of 5 K/min, for 360 s. These conditions are similar to those within our chamber.

Several simplifying assumptions are made in the model. First, radiation is neglected due to the relative speed of the cooling process. Second, internal circulation and convection within the drop is neglected. There is no external forcing or oscillation (the droplet is pinned to an interface, and minimal air exchange is used), and the simulated thermal gradients are small: with a water droplet diameter of 2.5 mm and a temperature difference of ΔT = 1.5 K, we obtain a Rayleigh number of $Ra = (g\beta\Delta T H^3)/(\nu\alpha) \sim 10^2$, well below the critical value for the onset of convection (where g is the gravitational acceleration, β is the thermal expansion coefficient of water, ν is the kinematic viscosity of water, α is the thermal diffusivity of water, and H is the drop height). Hence, we can safely model the drop via the heat equation.

The simulation results are shown in Figure 5. The higher thermal diffusivity of copper and silicon allows the substrate to relax quickly to the cooling element, and we see virtually no gradient across this region. Within the droplet volume, we observe a temperature gradient develop in the vertical direction, due to the lower thermal diffusivity of water. The temperature difference scales with the depth of the liquid layer, attaining ~1.5 K between the apex of the droplet and substrate after one droplet relaxation time τ (Figure 5, bottom left). In an earlier publication, we proposed a characteristic thermal variation parameter $\Delta T \approx \lambda\tau$, where λ is the system cooling rate.[2] To compare different experimental geometries, the time scale for diffusion was characterized by the liquid volume for a spherical droplet $\tau \approx V^{2/3}/\alpha$, where α is the thermal diffusivity of water. Using this formulation, the temperature difference across the droplet has the correct order of magnitude but is overestimated ($\Delta T \sim 8$ K) because of the spherical cap geometry (Figure 5, bottom right). Instead, by substituting the depth of the fluid (h) into the equation for thermal relaxation $\tau \approx h^2/\alpha$, the predicted steady state gradient agrees well with the simulation. The important observation for interpretation of the nucleation measurements, however, is that the temperature over the base of the droplet is uniform to within our temperature resolution (10^{-2} K). As noted in our previous work,[2] this value is within the 0.1 K tolerance for uniform nucleation based on the classical nucleation theory.[11] Therefore, a negligible bias in nucleation rate occurs even for relatively strong cooling rates. Furthermore, neither surface tension nor contact angle dependence on temperature is likely to play a significant role under these circumstances.[12]

If cooling rate and contact angle do not shed any light on the contrasting results of Suzuki et al.[1] and Gurganus et al.,[2] is there another possible explanation? The addition of the side-view camera may provide a hint. As can be seen in the accompanying video (Supporting Information), even when the point of nucleation is clearly observed to be far from the triple line in the overhead view of the droplet, the side view gives the impression that the freezing initiates at the triple line. The same difference in perceptions can be seen to some extent in Figure 2. This effect is not to be confused with the reflected image of the ice formation in the top of the drop, which also can be seen in both Figure 2 and the movie. There is no proof that this optical artifact explains the difference in observations, but the results of this study stand on their own, independently: over the ranges studied, variations in drop cooling rate and in drop−substrate geometry do not change the prior reported results.[2] There is still no preference for the triple line.

So what are the implications of these results to the observed "contact" nucleation phenomenon[4,10] and its possible relevance to the atmosphere?[13,14] Indeed a skeptical reader might object that the simple geometry explored here has little to do with an aerosol particle nucleating a supercooled droplet by contact. For example, transiency of contact, microscopic roughness,[15,16] or molecular interactions[17] may play a role. However, this simple geometry was developed precisely to single out and test the following conjecture: Does a triple line formed at the aerosol−droplet−air intersection promote nucleation? To that end, this experiment would suggest no, at least not at macroscopic length scales.

■ ASSOCIATED CONTENT

Supporting Information

These movies represent three freezing events of the same droplet, imaged simultaneously with the top and side cameras. This particular droplet was frozen and thawed 14 times, and these movies were taken during the 2nd, 7th, and 10th nucleation events, respectively. Here, a 5 kHz sample rate corresponds to a time step of 200 μs between frames, with complete droplet surface crystallization in ~10 ms. The nucleation sites are defined by the early growth of a pure crystal, hexagonal or bar. The droplets evaporate slowly during repeated cycles, as evidenced by the position of the droplet with respect to the thermocouple wire. Pinpointing the initial crystal with the top view is hindered by the projected reflection of the crystal on the top surface of the droplet. This "glint" from the lensing inside the droplet makes it virtually impossible to determine the radial position of the nucleation site with the side view. In contrast, from the top view of these videos, it is clear that the initial crystal originates away from the triple line. The side views are ambiguous, and in the latter two movies, the nucleation site could be easily be mistaken for the triple line. These optical distortions may have influenced the observations of nucleation at the three-phase interface in other experiments.[1] This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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