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Ice nucleation at the contact line triggered by transient electrowetting fields

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Supercooled water is found to have a significantly enhanced freezing temperature during transient electrowetting with electric fields of order 1 V/μm. High speed imaging reveals that the nucleation occurs randomly at the three-phase contact line (droplet perimeter) and can occur at multiple points during one freezing event. Possible nucleation mechanisms are explored by testing various substrate geometries and materials. Results demonstrate that electric field alone has no detectable effect on ice nucleation, but the moving boundary of the droplet on the substrate due to electrowetting is associated with the triggering of nucleation at a much higher temperature. © 2015 AIP Publishing LLC.
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Nucleation of a solid from a liquid is a problem of broad relevance in many natural systems and technological applications;[1] for example, the nucleation of ice from supercooled liquid water is a critical step in the chain of events leading to precipitation formation in many clouds.[2] Indeed, nucleation of ice is particularly enigmatic and is the subject of active research.[3–5] This paper describes experiments that touch on two aspects of liquid-solid nucleation in general, and water-to-ice nucleation in particular: the influence of an external electric field[1,6,7] and the possibility of preferred crystallization at liquid surfaces or, when a foreign substrate is present, at the three-phase contact line.[8,9]

Early cold stage experiments showed that supercooled water droplets can freeze when an electric field is applied.[10] Since that time, various experiments with bulk water and dispersed water droplets in a supercooled state, with electric field strengths up to approximately 0.1 V/μm, have given conflicting results.[11–18] And yet under some experimental conditions, remarkable electrofreezing of water has been observed.[19] Molecular dynamics simulations suggest that external electric fields significantly promote both homogeneous and heterogeneous ice nucleation when the field strength is larger than 1000 V/μm.[20–22] It is believed that in the high electric field, locally polarized liquid can decrease the critical size of a critical nucleus, thus facilitating ice nucleation. However, such high fields are difficult to achieve in reality because of electric breakdown. Recently, Carpenter and Bahadur[23] generated ultrahigh electric fields up to 80 V/μm using thin dielectric films in an electrowetting geometry[24] and found that interfacial electric fields alone can significantly elevate freezing temperatures by more than 15 °C. These results are consistent with findings from other substances, in which field strengths of 100–1000 V/μm are observed to enhance nucleation rates.[1,7]

Pruppacher[13,14] was apparently the first to note that nucleation induced by an electric field has a tendency to initiate from the contact line formed at a substrate (air-water-substrate line). Since then, similar observations have been reported for freezing in the presence of electric fields.[23,25] Given our group's interest in contact freezing,[9,26–28] we were motivated by these recent studies to further investigate the role of the contact line in ice nucleation induced by electric fields.

Our experiments used a simple electrowetting setup: a single water droplet resting on an electrically insulating substrate, the droplet in contact with a metal electrode and the substrate resting on a conducting plate (see Fig. 1(a), details of the experimental setup are in supplementary material[41]). A rigid piano wire is connected to a DC power supply and a voltage up to 2000 V is applied. The horizontal position of the tip can be controlled by a piezoelectric translation stage. An image of a water droplet taken with the high speed camera is shown in Fig. 1(b).

As a control experiment, a 20 μl droplet rests on the silica glass with no voltage applied; the freezing temperature is observed to be -24.7 ± 0.7 °C for a 2.0 K/min cooling rate. (All experiments are repeated ten times for statistical significance.) Without the electric field, the freezing is always initiated from a single point, randomly distributed on the immersed substrate (not at the electrode, which means the electrode is not a good ice nucleation agent compared with the substrate). To investigate the role of the electric field, we applied three voltages (600 V, 800 V, and 1000 V) between the electrode and the silicon wafer; the voltage was applied with the droplet above 0 °C, and then, the temperature was decreased at 2 K/min. The mean freezing temperatures were -23.7 ± 0.7 °C, -23.3 ± 2.4 °C, and -23.2 ± 1.6 °C for 600 V, 800 V, and 1000 V, respectively. Results show that the mean freezing temperature slightly increases as the voltage increases, but not significantly, and freezing temperatures were always lower than -20 °C. Electric fields for the three voltages are 2.7, 3.6, and 4.5 V/μm. These results confirm the observations of Carpenter and Bahadur[23] that electric fields smaller than 5 V/μm have a small effect on ice nucleation.

However, the observation changes dramatically if we first cool down the temperature to a value above -20 °C, maintain at least 5 min to ensure no freezing occurs, and then turn on the field. In this scenario, ice nucleation is triggered even at much higher temperatures. Experiments were done

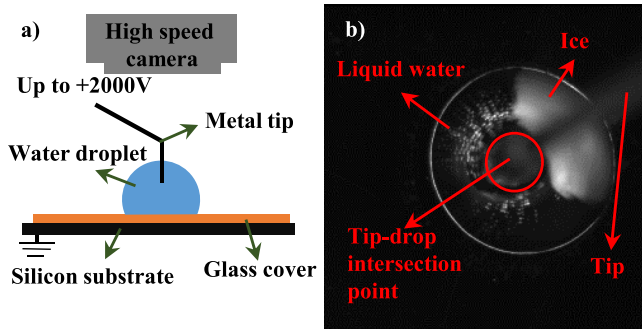a)Author to whom correspondence should be addressed. Email: rashaw@mtu.edu

FIG. 1. (a) Sketch of the experimental setup from the side, illustrating the electrowetting geometry. (b) Top view of a crystallizing droplet from the high speed camera.

between $-3\,°C$ and $-10\,°C$ for the same three voltages. Each case is repeated ten times, and the observed freezing probability is listed in Table I. It can be seen that freezing fraction increases with increasing voltage and with decreasing temperature. It reaches 100% at $-7\,°C$ for 1000 V, at $-9\,°C$ for 800 V, and nearly 100% at $-10\,°C$ for 600 V (only one out of ten does not freeze). From these observations, we conclude that the electric field alone cannot be the reason for this high temperature freezing behavior. At these temperatures and with a static electric field switched on above $0\,°C$, the supercooled droplets can be held for very long time without freezing.

The observation is more surprising if we turn on the field with the droplet above $0\,°C$, cool it down to a value above $-20\,°C$, and then maintain at least 5 min to make sure no freezing occurs; then, when the field is switched off, there still exists a high probability for the droplet to freeze, especially for higher voltage. The freezing fractions for switching off 600 V, 800 V, and 1000 V in droplets at a range of temperatures ($-4\,°C$ to $-10\,°C$) are shown in Table II. Although the freezing fraction for turning off the voltage is usually smaller than that for turning on at the same temperature, it is striking to us that ice nucleation is triggered with 100% probability by turning off the 1000 V voltage for temperatures equal to or below $-8\,°C$.

TABLE I. Mean freezing temperature (T_{freeze}) when turning on field at $T > 0\,°C$ and then cooling down at 2 K/min at three different applied voltages: 600 V, 800 V, and 1000 V. The estimated electric field (**E**) is calculated as the ratio of voltage to the thickness of the glass cover (0.22 mm). The bottom eight rows display the freezing fraction for a droplet at temperatures ranging from -3 to $-10\,°C$, with the voltage switched on at that temperature.

	600 V	800 V	1000 V
E	2.7 V/μm	3.6 V/μm	4.5 V/μm
	Voltage on above $0\,°C$, 2 K/min cooling rate		
T_{freeze}	-23.7 ± 0.7	-23.3 ± 2.4	-23.2 ± 1.6
T	Cool down to T and then turn on the voltage		
$-3\,°C$	0%	0%	0%
$-4\,°C$	0%	0%	30%
$-5\,°C$	0%	0%	70%
$-6\,°C$	0%	10%	80%
$-7\,°C$	40%	60%	100%
$-8\,°C$	70%	80%	100%
$-9\,°C$	70%	100%	100%
$-10\,°C$	90%	100%	100%

TABLE II. Freezing fraction for turning off 600 V, 800 V, and 1000 V at different temperatures.

	600 V	800 V	1000 V
T	Voltage on above $0\,°C$, cool to T, and then turn off		
$-4\,°C$	0%	0%	0%
$-5\,°C$	0%	0%	10%
$-6\,°C$	0%	0%	70%
$-7\,°C$	0%	10%	80%
$-8\,°C$	0%	10%	100%
$-9\,°C$	0%	20%	100%
$-10\,°C$	20%	40%	100%

With the 5 kHz high-speed camera, we find three interesting things about the ice nucleation that occurs when an electric field is turned on. First, when we turn on the field, the droplet will shake and its boundary will expand due to the decrease of contact angle associated with electrowetting.[24] Fig. 2 shows examples of time-resolved images from the high speed camera when turning on the voltage at $-10\,°C$ (see Fig. 2). Boundary movement is more significant at 1000 V, as expected for electrowetting: larger voltage leads to a smaller contact angle. In addition, boundary movement is more obvious at $-10\,°C$ compared with $-15\,°C$ (see supplementary material Fig. S1[41]). This is because the ice propagation speed is faster at lower temperature, so once the edge freezes, it cannot move any more. In addition, we observe that the triple line is distorted (curved) during the expanding process (see supplementary material[41]). This might be due to the pinning effect or the Rayleigh charge instability.[29]

The second interesting observation is that ice always nucleates at the three-phase contact (triple) line, as shown in Fig. 2. From this, we expect that the nucleation mechanism is unlikely due to the changing of the surface charge density because the charge concentration at the edge is only a few percent larger than inside the drop.[24] If the charge concentration can affect ice nucleation, we might reasonably expect that as we increases the voltage we should also see nucleation start away from the triple line; but, ice always forms from the edge even for voltages up to 2000 V. This is consistent with previous finding that surface charge does not affect ice nucleation.[30]

Third, the nucleation sites are randomly distributed along the triple line, and there can be multiple nucleation sites, especially for high voltage. Fig. 2 shows that nucleation starts all around the edge when switching on 1000 V. This is significantly different compared with cooling down the droplet without the electric field, or applying the field above $0\,°C$ and then cooling down the droplet. Under those conditions, the nucleation site is only single point. This implies that the nucleation rate on the edge is extremely large when we turn on the field (waiting time for nucleation events along the perimeter is less than the time for droplet crystallization).

For ice nucleation when turning off the voltage, we still see a slight deformation of the droplet, but not as obvious compared with that when turning on the voltage. This is referred to as the reversibility problem in electrowetting.[31]
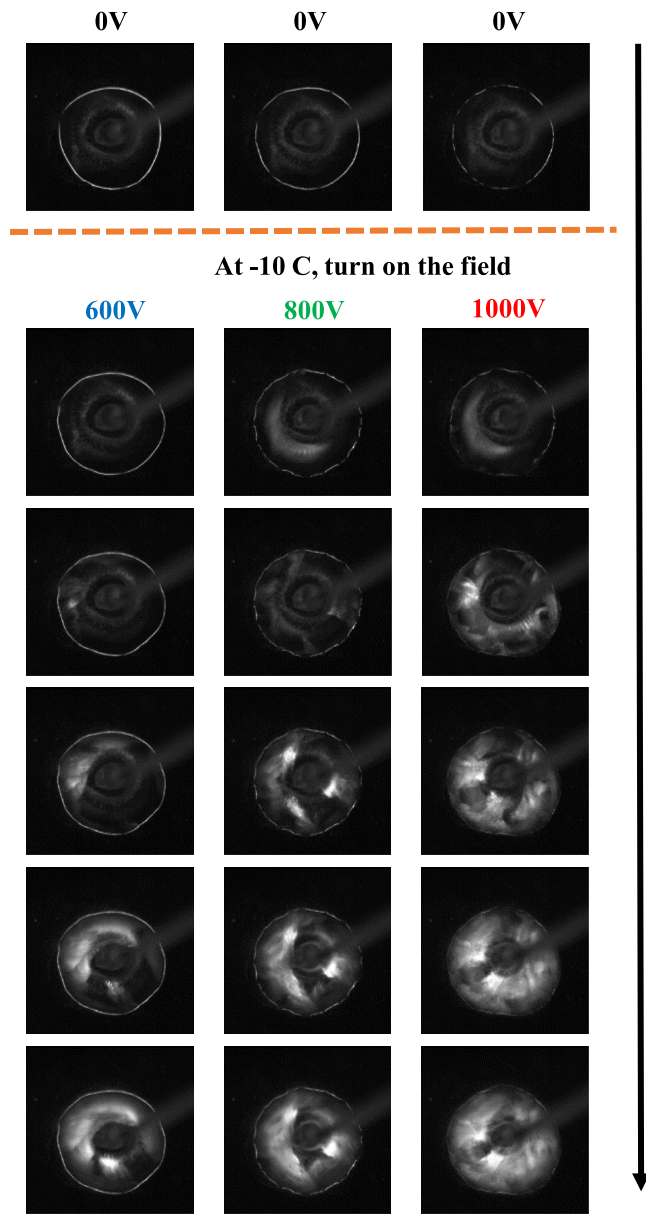
FIG. 2. Time-lapse views of crystallization after switching on three voltages (600 V, 800 V, and 1000 V) at $-10\,^\circ$C. The images are taken with a 5 kHz high speed camera. Each frame in one column is separated by 10 ms. (Multimedia view) [URL: http://dx.doi.org/10.1063/1.4938749.1]

When turning off the voltage, nucleation usually occurs only at one point, and randomly located around the edge. This is quite different compared with ice nucleation when turning on the voltage, which is usually multiple points or even all around the droplets.

From these observations, we conclude that the nucleation mechanism for turning on/off the field is unlikely due to the electric field alone and also is unlikely due to the change of surface charge density. It is more likely that this nucleation is related to the movement of the three-phase contact line. So what is the possible nucleation mechanism? Possibilities include the existence of frost nearby on the substrate, a substrate-specific property, the dynamic boundary movement alone, or the existence of locally high electric fields at the droplet edge. We investigate these possibilities with several additional experiments.

(a) Is there frost on the substrate nearby the droplet?

If so, when the triple line expands due to electrowetting, it might touch the frost and freeze the whole droplet. However, this possibility is ruled out by two experiments: (1) we first cool down the temperature to $-15\,^\circ$C for example, and maintain 5 min, with no freezing occurring. Then, we use the electrode tip (mounted on a piezoelectric translation stage) to drag the droplet across the glass cover. No freezing occurs whether we pull or push the droplet although the displacement is much larger than the boundary movement due to the electrowetting. This experiment also proves that mechanical movement alone cannot trigger ice nucleation. (2) We surround the droplet with oil (Hyvac products, Inc.). Although the air-water-substrate triple line changes to an oil-water-substrate triple line, the contact nucleation efficiency should not be strongly affected.[26] In this way, no frost can form nearby the droplet due to the oil isolation. However, we can still trigger ice nucleation when we apply 1000 V at $-10\,^\circ$C.

(b) Is there a dependence on the substrate?

To test this, we applied voltages up to 2000 V at $-10\,^\circ$C on various substrates: 0.96 mm siliconized glass (Hampton HR3-247), 25 μm polyimide film (McMaster-Carr Kapton Film, 2271K1), 1.0 mm plain glass (Fisherbrand Plain Microscope slides, 12-549-3), and 25 μm mica sheet (Tarheel Mica Co.). Results are shown in Table III. We can trigger ice nucleation on both thick siliconized glass and thin polyimide film, but not on plain glass and mica sheet. However, if we immerse the droplet in oil, we can also trigger ice nucleation on plain glass and mica sheet. With the high speed camera, we find that the droplet only freezes when the boundary is observed to expand when we turn on the field. We can see the boundary movement when we apply the voltage on siliconized glass, polyimide film, plain glass with oil surrounded the droplet, and mica sheet with oil surrounded the droplet, but we cannot see any movement on plain glass and mica sheet with air surrounded even for voltages up to 2000 V. This phenomenon appears to be related to contact angle saturation in electrowetting.[32–34] For plain glass and mica sheet, the water-air contact angles are 9° and 26° separately. The contact angle is sufficiently small that it may already be saturated or does not change significantly when we apply the voltage. But, the water-oil contact angles on both substrates are larger than 40°. In this case, electrowetting can decrease the contact angle efficiently, and thus the boundary will expand. Another possible

TABLE III. Results for applying the voltage up to 2000 V at $-10\,^\circ$C on different substrates. θ is the contact angle of water droplet on the substrate without the electric field.

		Apply voltage up to 2000 V at $-10\,^\circ$C	
Substrate	Θ	Boundary move?	Drop freeze?
0.22 mm siliconized glass	80°	Yes	Yes
0.96 mm siliconized glass	80°	Yes	Yes
25 μm polyimide film	72°	Yes	Yes
1.0 mm plain glass	9°	No	No
1.0 mm plain glass + oil	44°	Yes	Yes
25 μm mica sheet	26°	No	No
25 μm mica sheet + oil	46°	Yes	Yes

explanation is that for clean mica, the substrate is wet by a molecularly thin water layer (e.g., pseudo partial wetting).[29] Therefore, there might be no three phase contact line and strictly a contact angle does not exist.[35] This might explain the absence of boundary movement on the substrate.

From above, we conclude that this freezing phenomenon is related to boundary movement associated with electrowetting. It can occur on different substrates, as long as the contact angle is large enough that electrowetting can affect it. In addition, because the mica sheet is atomically smooth compared with glass or polyimide film, the freezing observed on mica sheet rules out the possibility that nanoscale texture might cause a higher freezing temperature at the three-phase contact line.[9]

(c) What are relative roles of triple-line movement and the changing electric field?

From the experiments described thus far, we know that macroscopic boundary movement alone cannot trigger ice nucleation, but boundary movement due to electrowetting is related to the ice nucleation. To test the relative roles of the triple-line movement and the changing electric field, we modify the glass substrate with a graphene layer and a polymer ring.

Three geometric graphene layers are transferred on the glass cover for comparison: a fully graphene covered glass slide, a half graphene covered glass slide, and a graphene ring with the glass slide exposed in the center. (Substrate preparation is detailed in supplementary material.[41]) Because graphene is a good conductor, no electric field exists at the graphene-water interface, and we therefore do not expect to see freezing start from the graphene substrate. In a last test to explore the possible role of triple-line movement, we constructed a round polymer 'wall' on the glass substrate (using oven-dried glue). The polymer acts as a stiff wall so that the water-glass-polymer triple-line cannot move.

Results show that for the full graphene covered glass substrate, graphene ring with exposed glass in the center, and glass substrate with polymer wall, no boundary movement was observed and freezing did not occur, even for voltages up to 2000 V. No freezing on the graphene ring and the polymer wall substrate indicates that the changing electric field alone without the boundary movement cannot trigger ice nucleation. For the half graphene, half glass substrate, the droplet was observed to freeze when the voltage was switched on. We also observed triple-line movement and nucleation sites all confined to the glass side.

Several additional notes should be mentioned: No changes in results were observed when the direction of the electric field was reversed (negative voltage applied to droplet). There is no steady electric current in the water although a charging current exists when we switch the field on or off. However, electrolysis is unlikely to occur during this process because we did not observe bubbles, and nucleation was not observed at the electrode tip as would be expected.[36–38] Furthermore, no nucleation was observed when a current was run through the droplet on a conducting substrate. Finally, no electrical breakdown was observed.

Our experiments show that ice nucleation probability is strongly enhanced during transient electrowetting. The observed freezing temperature is much higher than that for a static electric field. High speed camera images reveal three phenomena that occur when electric field is switched on: (1) the droplet expands due to electrowetting; (2) nucleation sites are always randomly located around the droplet three-phase contact line; and (3) nucleation occurs at multiple points, especially for higher voltage. To understand the nucleation mechanism, we do experiments on various substrates. Results indicate that this freezing is not a result of macroscopic boundary movement without the electric field (droplet dragged by electrode), or the electric field alone, or the change of electric field alone without triple-line movement, or the transient charging electric current. The nucleation must be related to the boundary movement resulting from electrowetting. One possibility is that locally high electric fields may be formed at the distorted boundary during the transient electrowetting process, leading to electrofreezing.[20–22] Alternatively, ice nucleation may be due to the combination of boundary movement and high electric field. Simulations have shown that oscillatory shear in combination with a static electric field proved to be much more efficient in crystallization than an electric field alone.[39] But both of these possibilities must face our observation that freezing occurs even when the electrowetting field is switched off. The exact mechanism remains unknown, but the observations clearly implicate the triple line and, therefore, suggest a link to the phenomenon of contact nucleation in the atmosphere.[40]

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[41] See supplementary material at http://dx.doi.org/10.1063/1.4938749 for details of experimental setup, droplet freezing at $-15\,°C$ (including multimedia view), and graphene-glass substrate preparation.