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# Externally-applied electric fields up to $1.6\times10^5$ V/m do not affect the homogenous nucleation of ice in supercooled water

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# ABSTRACT

The freezing of water can initiate at electrically-conducting electrodes kept at a high electric potential, or at charged electrically-insulating surfaces. The microscopic mechanisms of these phenomena are unknown, but they must involve interactions between water molecules and electric fields. This paper investigates the effect of uniform electric fields on the homogeneous nucleation of ice in supercooled water. Electric fields were applied across drops of water immersed in a perfluorinated liquid using a parallel-plate capacitor; the drops traveled in a microchannel and were supercooled until they froze due to the homogenous nucleation of ice. The distribution of freezing temperatures of drops depended on the rate of nucleation of ice, and the sensitivity of measurements allowed detection of changes by a factor of 1.5 in the rate of nucleation. Sinusoidal alternation of the electric field at frequencies from 3 to 100 kHz prevented free ions present in water from screening the electric field in the bulk of drops. Uniform electric fields in water with amplitudes up to $1.6 \pm 0.4 \times 10^5$ V/m neither enhanced nor suppressed the homogenous nucleation of ice. Estimations based on thermodynamic models suggest that fields in the range of $10^7$–$10^8$ V/m might cause an observable increase in the rate of nucleation.

## 1. Introduction

The nucleation of ice in water is ubiquitous in nature, and is relevant to phenomena ranging from the formation of atmospheric precipitation[1,2], and ice accretion on the wings of airplanes[3], to the cryopreservation of tissues[4]. Studying ice nucleation under new experimental conditions is relevant both to our fundamental understanding of water and nucleation, and to the discovery of new methods of controlling the nucleation of ice.

Applied electric fields provide one basic experimental condition that we can use to study the nucleation of ice; water is subjected to external electric fields in many naturally-occurring situations. Atmospheric electric fields that exceed $10^5$ V/m can be encountered during thunderstorms[5,6] or near the surface of electrical conductors used in high voltage power transmission lines[7]. A change in the rate of nucleation of ice under these fields could affect the formation of precipitation during thunderstorms[2], and the rate of accretion of ice on high-voltage cables in cold weather[7].

In this paper, we investigated the effect of external electric fields on the homogeneous nucleation of ice in drops of supercooled water. A continuous-flow microfluidic ice nucleation apparatus[8] produced monodisperse drops of water in a carrier phase of liquid fluorocarbon, and transported the drops inside a microchannel through a cooling thermal gradient. While traveling along the channel, the drops supercooled until they froze due to the homogenous nucleation of ice. Across the drops of water, we applied sinusoidal alternating electric fields with frequencies from 3 to 100 kHz and a range of amplitudes. We did not observe changes in the freezing of drops up to field amplitudes of $1.6 \pm 0.4 \times 10^5$ V/m. Electric fields with amplitudes above this value influenced the trajectory and the shape of the drops due to dielectrophoretic forces and made accurate observations of freezing impossible. Based on these experiments, we conclude that the homogeneous nucleation of ice is neither enhanced nor suppressed by electric fields with amplitudes up to $1.6 \pm 0.4 \times 10^5$ V/m.

We studied the effect of electric fields on the nucleation of ice for five reasons: (i) The interaction of molecules of water (which have a permanent electrical dipole) with electric fields is well understood; electric fields change the average orientation of water molecules and the free energy of water becomes dependent on the magnitude of the field. The application of electric fields might therefore provide a conceptually simple and well-controlled way to study the influence of the structure and free energy of water on the nucleation of ice. (ii) Electric fields can be applied remotely and uniformly over the entire sample under investigation, and thus create a homogenous test system. (iii) Previous experimental investigations[9-21] have provided only inconclusive evidence that electric fields affect the homogeneous nucleation of ice. (iv) A new electric-field-based method to control of the nucleation of ice could improve technological processes as freeze-drying[22], cryopreservation[23,24], food manufacture[25], and cold-energy storage[26]. (v) Electric fields are often encountered in water near the surface of particles, molecules, and ions; they might play an important role in the heterogeneous nucleation of ice by impurity particles[9,14,21,27].

What is the magnitude of the electric field at which we might expect to observe an influence of the electric fields on the freezing of water? One hypothesis is that if electric fields become strong enough to align all water molecules along the applied field, the structure of water would change, and water might freeze. Molecular dynamics (MD) simulations investigated this hypothesis and found that the structure of water changed[28,29] as the magnitude of the field reached approximately $2\times10^9$ V/m, but water remained liquid despite the change in its structure. At these fields, simulations predicted the onset of the saturation of the dielectric constant of water[30,31] due to the alignment of water molecules. In MD simulations[29,32], freezing of water induced by electric fields was observed at larger field intensities around $5\times10^9$ V/m.

The field-induced freezing predicted by simulations cannot be investigated in experiments with bulk samples of water, because the magnitude of the electric field exceeds the dielectric breakdown strength of pure water ($\sim10^7$ V/m in millimeter-scale samples[33] and $\sim10^8$ V/m in micron-scale samples[34]). Experimentally, electrically-induced freezing, or an enhanced tendency to nucleate ice, were claimed to be observed at the electrostatically-charged surfaces of conductors[12,15,16,35], polar amino acid crystals[14], and pyroelectric crystals[21]. Water freezing experiments carried on charged surfaces suggested that electric fields much smaller than the predictions of simulations influence the nucleation of ice; nevertheless, careful freezing experiments carried under *external* electric fields[11-13,20] did not observe any effects of the electric field on the nucleation of ice. Therefore, experimental investigations conducted to date have not found conditions under which electric field is the sole cause for inducing the nucleation of ice.

Here we describe an experiment to study the effects of electric fields on the freezing of water. We investigated the simplest case of such effects: pure water freezing by homogeneous nucleation of ice in the presence on an external, and uniform, electric field. Our experimental setup had high sensitivity and allowed us to determine a new experimental value for the highest electric field intensity that does not influence homogenous ice nucleation. We also used a version of the classical nucleation theory that accounts for external electromagnetic fields[36] to estimate the field intensity that might produce observable changes in the rate of nucleation. We interpret the results generated by this theory to indicate that such changes might occur in fields two orders of magnitude smaller than the fields that induce freezing in MD simulations.

## 2. Experimental design

**2.1. Detection of the influence of electric fields through changes in the rate of nucleation.** Although the conditions for field-induced freezing observed in MD simulations cannot be produced in bulk samples of water, the effects of electric fields on freezing might be experimentally observable at much lower fields if freezing can be quantified with high resolution and high accuracy. For example, the complete alignment of water molecules in an electrical field at ambient temperatures requires intensities on the order of $10^9$ V/m[30,31], but partial alignment can be observed in fields with intensities at ~$10^7$ V/m because such alignment causes a measurable change in the dielectric constant of water[33]. Therefore, the objective of our experiment was to detect changes in the probability of freezing of water in the presence of electric fields, rather than to induce freezing.

**2.2. Freezing drops of water though the homogenous nucleation of ice.** Freezing in water that is not in contact with ice is initiated by nucleation of ice in supercooled water. If water is pure and held in a container whose walls do not induce ice nucleation, nucleation occurs homogenously due to thermodynamic fluctuations. The homogenous nucleation of ice is a stochastic process that can be characterized by a homogeneous ice nucleation rate $J_N$, which specifies the probability $P_F$ that a volume of water $V_{drop}$ freezes at a temperature $T$ in a vanishingly small time interval $\delta t$ (eq.1).

$$J_N(T) = \frac{1}{V_{drop}} \frac{1}{\delta t} P_F \qquad \text{Eq. 1}$$

Conditions such as increased pressure, or the presence of a solute in water, change the rate of homogenous nucleation of ice[37,38]. Our objective was to establish the influence of external electric fields on the rate of nucleation. The experimental setup should, therefore, to be able to measure the nucleation rate precisely when supercooled water was subjected to external electric fields that were as large as possible. During these measurements, the measuring devices—especially the electrodes used for the generation of the field—should not contact the water to reduce the possibility of heterogeneous nucleation of ice. To achieve these design goals, we modified a microfluidic apparatus (which we have described previously[8]) made for the study of nucleation of ice in supercooled water; this apparatus can measure nucleation rates reliably and with high accuracy. The modification added a parallel-plate capacitor to generate strong uniform electric fields during measurements.

Figure 1a shows the core of the experimental setup: a flow-focusing generator[39] produced spherical and monodisperse drops of water in liquid fluorocarbon; the drops flowed along the centerline of a microfluidic channel without touching the walls. We sandwiched the channel between two parallel plate electrodes made from thin films of platinum (bottom side, ~200 nm thick) and indium-tin oxide (ITO, top side, ~300 nm thick) deposited on glass slides. The channel, the drop generator, and the plates were part of a microfluidic device made from polydimethylsiloxane (PDMS). The device sat on top of a temperature-controlled plate that cooled a section of the channel to approximately –

40 ºC while keeping the temperature of the rest of the device close to room temperature. The supporting information contains a description of the fabrication of the microfluidic device, and also pictures of the device.

The liquid carrier phase was necessary for the operation of the microfluidic flow-focusing nozzle that made the drops[39], and for the generation of hydrodynamic forces that centered the drops as they traveled in the channel[40,41]; this setup would not function with a gaseous carrier phase. We used a fluorocarbon carrier liquid because fluorocarbons are electrically insulating and compatible with PDMS[42], and they have freezing points lower than that of water. The carrier phase was a mixture of perfluoromethyldecalin (PFMD, 98% purity, F2 Chemicals) with 2% v/v 1H,1H,2H,2H-perfluorooctanol (THPFO, 97% purity, Sigma-Aldrich) as a surfactant. PFMD and THPFO have solubilities in water ($\sim 10^{-12}$ and $\sim 10^{-9}$ mol/L, respectively) that are much lower than the solute concentration ($\sim 10^{-3}$ mol/L) that would produce a measurable change in the rate of nucleation of ice[38].

During operation, the microfluidic flow-focusing generator produced drops at a rate of ~50 drops/s; the drops had a diameter on the order of 100 microns and traveled with a velocity of ~50 mm/s. We chose the rates of flow of water and fluorocarbon such that the separation between drops was ~1 mm during their travel in the channel. This separation was sufficient to ensure that the freezing of one drop did not influence adjacent drops. The temperature of the drops equilibrated with that of the channel by thermal conduction as they traveled down the channel. We set the position of the device and the temperature of the plate such that that a monotonously decreasing temperature gradient formed along the long axis of the channel, and that the drops cooled sufficiently to freeze inside the channel. The detection of freezing was optical, based on the darkening of the drops after freezing due to increased scattering of light by ice crystals. During the experiments, we imaged the drops with a microscope and we recorded movies that contained the freezing events of up to tens of thousands of drops using a fast camera (Phantom V7.3, Vision Research).

The position at which a drop froze indicated the temperature at which the drop froze because a predictable and decreasing thermal gradient existed along the channel. We extracted the distribution of freezing positions from movies of drops freezing using automated image processing. In the ice nucleation apparatus[8], arrays of microfabricated thermometers measured the actual temperature along the channel, and from these temperatures we could calculate the temperature at which each drop froze. In the setup we describe here we could not use thermometers because we used high voltages in places where the thermometers would be placed; these high voltages could damage the sensitive temperature measurement instrument that was connected to the thermometers. We did not measure the freezing temperatures of drops directly in this paper. Instead, we used the distribution of freezing positions to detect changes in the rate of nucleation. Freezing positions have a reproducible distribution in the absence of the electric field. Any change in this distribution when electric fields were applied would indicate that the electric field might have influenced the nucleation of ice.

Without means to measure the temperature at which drops froze, we could not verify that the freezing of drops was due to homogeneous nucleation of ice. Such freezing occurs near –37 ºC in a narrow range of temperatures (1–2 ºC) for drops investigated in our instrument. It was possible, in principle, that the nucleation of ice was initiated heterogeneously by either solid impurities in water, or by surfactant molecules at the interface of drops. We, nevertheless, believe that heterogeneous nucleation was very unlikely because in independent measurements of freezing temperatures in drops of pure water[8] we always recorded a distribution of freezing temperatures that was consistent with homogenous nucleation—and with independent ice nucleation measurements performed on drops of water levitated in air[43]. These freezing temperature measurements were performed in conditions (i.e. water purity, carrier phase composition, nozzle and channel geometry, and the materials used in the device) that were identical to those in experiments with electric fields. We could, therefore, assume safely that in the absence of electric field (i.e. when both electrodes were electrically grounded) all drops froze by homogeneous nucleation of ice.

**2.3. Applying electric fields in bulk water.** In pure water, autoionization of water molecules produces a constant concentration of hydroxide and hydronium ions. These free ions can redistribute to form Debye space charge layers that screen electric fields. Even if all ions were instantaneously removed from water, autoionization would recreate the original concentration of free ions. To apply external electric fields in pure water, we applied temporally-variable electric fields that had a rate of change that is faster than the characteristic rate of charge creation due to autoionization[44], $\omega_{auto}$, (eq. 2) and the rate of formation of the Debye layer, $\omega_{Debye}$ (eq. 3):

$$\omega_{auto} \cong 20\ \text{kHz} \qquad \text{Eq. 2}$$

$$\omega_{Debye} = \frac{e_e n_0 \mu_i}{\varepsilon_w \varepsilon_0} \cong 5\ \text{kHz} \qquad \text{Eq. 3}$$

where $e_e$ is the electron's electrical charge, $n_0$ the equilibrium density of positive or negative ions, $\mu_i$ the electrical mobility of these ions, $\varepsilon_w$ the dielectric constant of water, and $\varepsilon_0$ the permittivity of vacuum. The minimum frequency, $f_{AC}$, of an external sinusoidally-varying electric field that would not be screened is then given by eq. 4:

$$f_{AC} > \frac{\omega_{screen}}{2\pi} \approx 3\,\text{kHz} \qquad \text{Eq. 4}$$

where $\omega_{screen}$ is the faster rate of $\omega_{auto}$ and $\omega_{Debye}$. The numerical values in eqs. 2–4 were estimated at room temperature; since both the autoionization rate and the density of ions decrease as the temperature is lowered[44], the minimum frequency, $f_{AC}$, becomes smaller at lower temperatures. The supporting information contains further information on the derivation of eqs. 2–4.

Time-varying electric fields are necessary to avoid electrostatic screening, but for the study of nucleation such fields can be regarded as static if nucleation happens faster than the rate at which the field varies. In MD simulations[45], the nucleation of ice occurred in less than 100 ns; as long as the frequency of the electric field is less than approximately 1 MHz, ice nucleation practically occurs in a static field. In our experiments we used frequencies between 3 and 100 kHz.

We generated electric fields by applying sinusoidal AC voltages on the top electrode. The electrical setup that produced the electrical field had to be capable of generating AC with variable amplitudes from zero to a high voltage (~1000 V) during an experiment. Such a setup would allow us to test, during a single experiment, different electric fields, and to compare the distribution of freezing positions in the presence of electric field with that in its absence. A high-voltage amplifier (Trek Inc. 30/20A) generated high voltage differences across the electrodes by amplifying the output of a signal generator (Keithley Instruments 3390). A digital oscilloscope (Tektronics TDS 3014) monitored the outputs of the signal generator and of the high-voltage amplifier; a scanning multimeter (Keithley

Instruments 2701) recorded the voltage across the electrodes. Figure S2 in the supporting information contains a schematic diagram of this electrical setup.

Figure 1b displays the construction of the electrical capacitor embedded in the microfluidic device. Rather than putting the electrodes as close to the microfluidic channel as possible, we used dielectric spacers to increase the distance between the electrodes and the drops. The spacers reduced the electrostatic attraction between drops and electrodes, and increased the electric field inside drops; the discussion section contains further details on the design of the spacers. The maximum electrical potential difference that could be applied across the capacitor without electrical breakdown was ~16 kV at a frequency of 1 kHz. For this maximum potential, the magnitude of electric field inside the dielectric spacers was smaller than the dielectric breakdown strength of soda-lime glass[46]. Inside PDMS and the carrier fluid the field was 3–4 times larger than the manufacturer-specified breakdown strength, however[47].

## 3. Results

**3.1. The freezing of drops in the presence of applied electric fields.** Figure 2a shows the freezing positions of 20 600 drops of pure water with a diameter of 70 microns, recorded during an experiment that lasted 420 s. The freezing position was relative to the beginning of the channel. We applied to the top electrode sinusoidal AC voltages with a frequency of 100 kHz and peak voltages from 0 and 800 V, and we modulated the amplitude of the AC voltage with a period of 5 s and 100% modulation depth[48]. The period of the modulation was sufficiently long that the amplitude of the voltage was constant during the freezing of a drop, but much shorter than the period of the small temperature oscillations in the channel that were responsible for the slow drift of freezing positions. We could therefore monitor the presence or absence of any influence of the electric field on freezing by looking for changes in the distribution of freezing positions when the magnitude of the electric field varied. The supporting information (Figure S3) contains the results of three additional measurements made at frequencies of 3, 10, and 30 kHz.

Figure 2 indicates that the voltage had an influence on the freezing of the drops when it crossed a threshold located at approximately 700 V. Figure 2b shows this phenomenon in more detail: when the peak AC voltages during modulation exceeded this threshold, water drops started to freeze significantly earlier (i.e. closer to the beginning of the channel) during their travel. We will refer to this freezing behavior as 'premature freezing' from now on.

During normal operation of the instrument, premature freezing corresponds to higher freezing temperatures. The data shown in figure 2 seem to suggest that electric fields higher than that corresponding to an applied voltage of 700 V make ice nucleation more probable. Despite this apparent correlation, and the suggestion that high voltages catalyze freezing, we will show that these changes in the freezing positions were caused by changes in the hydrodynamic conditions in the channel rather than by a change in the rate of homogenous nucleation due to electric fields.

**3.2. 'Premature freezing' due to destabilization of the flow of drops by electric fields.** We applied high voltages to the drops when the microfluidic device was at room temperature to test the behavior of the microfluidic system under large voltages. Voltages larger than ~700 V destabilized the ordered flow of drops by slowing down the drops, making them collapse with each other, or making them collide with the electrodes and stick to them. The onset of this destabilization was marked by drops moving closer to the walls. At room temperature this change in the position of drops in the channel also resulted in the drops moving more slowly (the velocity of the fluorocarbon carrier was the highest in the center of the channel because the flow of liquid was viscous and pressure-driven[49]). Drops that traveled closer to the walls froze earlier than drops that were centered, because the temperature of the carrier fluid near the walls was lower than that in the center of the channel (Figure 3a); drops therefore cooled faster near the walls.

Figure 3 also illustrates the types of forces that acted on the drops, and the strategies that we used to reduce the effect of electric fields on the movement of the drops. In the absence of external forces, liquid drops migrate to the center of the channel because a hydrodynamic lift force (Figure 3b) develops when they travel off-center[40,41]. For the flow conditions that we used in our experiments, this lift force was strong enough to center drops despite the buoyant force acting on drops of water ($\rho = 1$ g/cm$^3$) immersed in fluorocarbon liquid ($\rho = 2$ g/cm$^3$). If the lift force is also larger than electrostatic forces, the movement of drops is not affected by electric fields and the experiment can produce meaningful data.

Figure 3c illustrates one electrostatic force mechanism that we encountered. External electric fields polarize the drops of water electrically, and the drops develop an induced dipole moment. This induced dipole interacts with a conducting electrode, and this interaction can be modeled as the interaction between the dipole and an 'image' dipole of equal moment located behind the electrode. The interaction between the dipole and its image is attractive, therefore polarized drops will be attracted by a conducting electrode.

As long as the drops is equally far from both electrodes in the system, the attractive forces towards each electrode cancel, but if the drop is not centered, it will be attracted towards the electrode that is closer to the drop. If the intensity of the electrical field exceeds a certain threshold, the electrostatic force becomes larger than the hydrodynamic centering force and the drops collide with the walls of the channel. This electrostatic force is a second-order effect; because we used alternating electric fields, first-order electrostatic forces due to a possible net charge on the drops averaged to zero. The attractive force between the drop and the electrode decreases approximately as the fifth power of the distance between drops and electrode. We had initially investigated the effect of electric fields on ice nucleation using devices that did not have dielectric spacers, and we observed that the drops migrated to the walls of the channel as soon as the electric field became larger than a threshold. We therefore used dielectric spacers, and we chose their thickness such that the electrostatic force between polarized drops and electrodes became negligible compared to the hydrodynamic lift force.

Drops of an electrically-polarizable fluid deform in uniform external electrical fields because the drops develop surface charges and these charges interact with external fields to elongate the drops, as shown in Figure 3d. We can define the deformation of a drop, *D*, as the ratio between the difference between the lengths of the drop along and perpendicular to the field, and the sum of these lengths. In the case of a dielectric drop immersed in a dielectric medium, *D* is given[50] by Eq. 5:

$$D = \frac{9}{16}\frac{r\varepsilon\varepsilon_0 E^2}{\sigma}\frac{(\varepsilon_{drop} - \varepsilon)^2}{(\varepsilon_{drop} + 2\varepsilon)^2} \qquad \text{(Eq.5)}$$

where *r* is the radius of the un-deformed drop, $\varepsilon_0$ is the permittivity of vacuum, $\varepsilon$ and $\varepsilon_{drop}$ the dielectric constants of the medium and the drop, *E* the intensity of the field in the dielectric medium, and $\sigma$ the interfacial surface tension between drops and their surrounding fluid. For a given external field, drops deform less if they are smaller, and if their surface tension is larger.

The electrostatic deformation of drops vanishes if the dielectric constants of the drop and of the surrounding fluid are equal; for drops of water, however, we could not find an electrically insulating carrier fluid that had the same dielectric constant as water and be insoluble in water. The maximum electric field that we could investigate was therefore limited by the onset of electrostatic deformation.

Equation 5 predicts that the maximum fields before deformation occurs are larger for smaller drops. We varied the size of the drops by changing the rate of flow of the continuous phase and by adjusting the temperature of the drop generator[51]. As predicted, we were able to apply larger fields when we froze smaller drops. The data shown in Figure 2 was recorded using the smallest drops (70 microns in diameter) that we could freeze reliably.

Near the threshold field for premature freezing ($E_{PFMD} = 2.9\times10^6$ V/m for $r = 35$ μm) we estimated $D$ ~0.16; this value of D corresponds to drop whose polar radius is elongated from 35 μm to 39 μm. For the estimation of $D$, we used $\varepsilon_{drop,\,-40^\circ C} = 110$ from literature[52] and we extrapolated measurements that we made near room temperature to determine $\varepsilon$ ~2.1 and $\sigma$ ~0.014 N/m at –40 ºC.

**3.3. Calculation of the electric field in bulk water.** In most of the previous work that investigated the freezing of water in the presence of electric fields[9-21], the magnitude of electric field was calculated by dividing the electrical potential difference between electrodes and the distance between electrodes. We will refer to this field as the ‘external’ electric field. The electric field that is most relevant to homogenous nucleation is the electric field that develops in bulk water – the 'internal' electric field. The relation between the intensities of external and internal electric fields depends on the experimental geometry and can vary considerably from case to case. Bulk supercooled water has a high dielectric constant (~100) and the intensity of the internal field could be up to two orders of magnitude smaller than the intensity of the external field. From now on we will use the internal field, $E_{in}$, to characterize the results of our experiments.

The relation between internal and external fields can be calculated analytically for the case of a drop of water immersed in a surrounding medium that fills all space. If a spherical drop of water is placed in a uniform electric field $E_{out}$ and is surrounded by a dielectric material with a dielectric constant $\varepsilon_{out}$, the field inside the drop is given by Equation 6, where $\varepsilon_w$ is the dielectric constant of water[53]:

$$E_{in} = \left( \frac{3\varepsilon_{out}}{\varepsilon_w + 2\varepsilon_{out}} \right) E_{out} \qquad \text{Eq. 6}$$

Eq. 6 predicts that molecules in a drop of water surrounded by air ($\varepsilon_{out} = 1$) experience only a small fraction (0.027) of the electric field outside the drop; this prediction illustrates the difficulty of creating large electric fields inside water without contact with electrodes.

The inner geometry of the parallel-plate capacitor (Fig. 1a) that we used to generate electrical fields is more complicated than that of a drop in an infinite dielectric medium. Therefore, we calculated the electric field inside drops by modeling the electric fields in our system numerically; the supporting information contains a description of the numerical modeling procedure and detailed results. For the data shown in Figure 2, the maximum voltage amplitude for which we did not observe an influence on freezing was

700 V. According to numerical modeling, this potential difference generates a nearly-uniform electrical field $E_{in}$ of $1.6\times10^5$ V/m; the uncertainty in the calculation of $E_{in}$ is $\pm0.4\times10^5$ V/m. This magnitude of electric fields represents the principal result of this work: electrical fields with intensities up to $1.6\pm0.4\times10^5$ V/m do not influence the homogenous nucleation of ice in supercooled water.

## 4. Discussion

**4.1. Comparison with previous work.** To our knowledge, previous work that reported effects of electric fields on freezing of water[9-21] used systems in which freezing was initiated by the heterogeneous nucleation of ice. In the absence of electric fields, the freezing temperatures reported in these experiments were always higher than the temperatures at which homogenous nucleation occurs. In these experiments the systems contained potential ice-nucleating components (solid water containers, exposed electrodes, impurities) which might have been influenced by electric fields themselves. These experiments cannot, therefore, investigate the effect of electric fields on homogenous ice nucleation in bulk water. In contrast, our system is one in which homogenous nucleation occurred reliably in the absence of external fields, therefore providing the necessary conditions for the investigation of the effect of electric fields on homogenous ice nucleation.

For experiments in which there was no direct contact between water and electrodes, the reported magnitude of electric fields must be adjusted before a direct comparison with our results. For example, experiments conducted on drops that fall within the air gap of a capacitor[11,12] could reach maximum external fields on the order of $3\times10^6$ V/m, which is the dielectric breakdown strength of air[54]. According to Eq. 6, however, this external field corresponds to a maximum internal field of $8\times10^4$ V/m. In an experiment reported by Orlowska *et al.*[19], enhanced ice nucleation was observed in external fields up to $6.6\times10^6$ V/m; we calculated that these external fields correspond to internal fields up to $1.1\times10^5$ V/m. The maximum field that we have investigated, $1.6\times10^5$ V/m, is thus higher than that investigated in previous experiments.

**4.2. Thermodynamic estimate of the field that should produce a measurable change in the rate of nucleation.** In the presence of electric fields, the free energy of a substance has an additional electrostatic component. The electrostatic contribution to free energy is different in water and in ice. The free energy barrier for nucleation, $\Delta G$, therefore changes when electric fields are present:

$$\Delta G(n) = \Delta G_0(n) + G_{E,ice}(n) - G_{E,water}(n) \qquad \text{(Eq. 7)}$$

where $\Delta G(n)$ and $\Delta G_0(n)$ are the free energy required to form a nucleus of $n$ molecules in the presence, or absence, of the field. $G_{E,ice}(n)$ and $G_{E,water}(n)$ are the electrostatic free energies of the water sample with and without an ice nucleus. Kashchiev evaluated the change in the rate of nucleation due to electric fields, $J_N$, for nucleation in a spherical drop of metastable material[36]:

$$J_N = J_N^0 \exp\left(-\frac{\Delta G_E}{k_B T}\right) \qquad \text{(Eq. 8)}$$

$$\Delta G_E = G_{E,ice}(n_{crit}) - G_{E,water}(n_{crit}) \qquad \text{(Eq. 9)}$$

where $J_N^0$ is the nucleation rate in the absence of the field, and $\Delta G_E$ is the difference in electrostatic free energies between a critical cluster of ice and a cluster of water molecules, $n_{crit}$ is the number of molecules in the critical cluster, $k_B$ is Boltzmann's constant, and $T$ the absolute temperature. According to Kashchiev, $\Delta G_E$ is given by eq. 10,

$$\Delta G_E = -\frac{1}{2}\varepsilon_0 \varepsilon_{water}\left(1-\frac{\varepsilon_{ice}}{\varepsilon_{water}}\right)\left(2+\frac{\varepsilon_{ice}}{\varepsilon_{water}}\right)V_{crit}E_{in}^{\ 2} \qquad \text{(Eq. 10)}$$

where $\varepsilon_0$ is the permittivity of vacuum, $\varepsilon_{water}$ and $\varepsilon_{ice}$ the dielectric constants of ice and water, $V_{crit}$ is the volume of the critical nucleus, and $E_{in}$ is the intensity of the internal electrical field in water. At the homogeneous freezing temperature (~235 ºK) and a frequency of 100 kHz, the values of the dielectric constants are[52,55] $\varepsilon_{water} = 110$, and $\varepsilon_{ice} = 3.2$.

Our experiment can detect very small changes in the rate of nucleation. We evaluated that the minimum change that we could observe is a factor of 1.5 in the rate of nucleation, factor that is equivalent to a shift of 0.1 ºC in nucleation temperature; the supporting information contains a description of the procedure that we used to evaluate the sensitivity of our measurements. We then calculated the magnitude of the electric field that would produce the same change in the rates of nucleation:

$$\frac{J_N}{J_N^0} = \exp\left(\frac{\Delta G_E}{k_B T}\right) = 1.5 \qquad \text{(Eq. 11)}$$

Combining Eq. 10 with Eq. 11, and using an estimated radius of the spherical critical nucleus[56] of 1.4 nm at 236 ºK, we estimated that an internal electric field, $E_{int}$, of approximately $1.8\times10^7$ V/m would produce an observable change in the rate of nucleation.

The electric fields that we could apply, though having the largest intensities used in homogenous ice nucleation experiments, are still two orders of magnitude too small to observe a change in the rate of nucleation - assuming that Kashchiev's theory of nucleation in electric fields is applicable to the homogeneous nucleation of ice. The main limiting factor that prevented us from applying larger fields was the deformation of drops. Assuming that we could operate the ice nucleation apparatus with surfactant-free drops that have a diameter of one micron or less, Eq. 5 predicts that we could apply fields that are larger by one and a half orders of magnitude than our current limit. Another possibility for reducing the gap between experiment and theory is to improve the sensitivity of our measurements. We estimate that using larger data sets and more sophisticated data processing we might observe changes in the rate of nucleation by a factor of 1.05, corresponding to a minimum observable $\Delta G_E$ nine times smaller than our current sensitivity, and to an internal field of $6\times10^6$ V/m. A microfluidic ice nucleation experiment that uses submicron drops and has higher sensitivity in measuring rates of nucleation could be capable to test Kashchiev's theory.

**4.3. Formation of ferroelectric ice nuclei is unlikely.** The orientations of molecules of water in normal ice (hexagonal ice, ice Ih) are disordered near the melting temperature of ice. Because water molecules are polar, the most stable crystal structure of ice at very low temperature (close to 0 ºK) should be electrically ordered, either ferroelectrically or antiferroelectrically. Pure hexagonal ice remains disordered upon cooling down to 0 ºK because the rate of relaxation of ice is too slow to observe electric ordering experimentally[57]. Impurities such as potassium hydroxide increase the rate of relaxation, however, and KOH-doped ice Ih transforms into ferroelectric ice (ice XI) at 72 ºK[58-60].

Ice XI is unstable in the temperature range in which the nucleation of ice occurs in supercooled water (235–273 ºK), but it might nevertheless play a role in the nucleation of ice. Gavish *et al.* and Croteau *et al.* proposed that ferroelectric ice stabilized by strong electric fields present inside nanocracks in crystals of amino acid[14] and kaolinite[27] cause the heterogeneous nucleation of ice by these crystals. Ferroelectric ice might also play a role in the nucleation of ice in external electric fields. In an increasing electric field, the free energy of a ferroelectric phase aligned with the field decreases faster than that of a disordered phase; therefore, in an external field that is large enough, supercooled water might nucleate to ice XI.

The electric field in which ice XI might nucleate homogenously from supercooled water is at least equal to the field $E_{ferro}$ that lowers the field-dependent free energy of ice IX below the free energy of ice Ih. We estimated $E_{ferro}$ using Equation 12, in which $T_{nucl}$ is the temperature at which ice nucleates homogeneously (235 ºK), $T_{XI\text{-}Ih}$ the temperature of the ferroelectric transition (72 ºK), $\Delta s_{XI-Ih} = k_B \ln(3/2)$ the configurational entropy of ice per molecule[61], and $p_{water}$ the electric dipole moment of water ($6.2\times10^{-30}$ C·m); the supporting information contains the derivation of Eq. 12.

$$E_{f\,erro} = \frac{(T_{nucl} - T_{XI-Ih})\Delta s_{XI-Ih}}{p_{water}} \qquad \text{Eq. 12}$$

Equation 12 predicts that fields larger than $E_{ferro} = 1.5\times10^{8}$ V/m are necessary for the nucleation of ice XI. Such fields are three orders of magnitude larger than the maximum field that we applied, therefore in our experiments ice probably nucleated to an electrically disordered phase. Even if we could subject water to arbitrarily large fields, we might still not form ice XI because according Eqs. 10 and 11 ice might nucleate to a normal phase in fields that are one order of magnitude smaller than $E_{ferro}$.

**4.4. Implications of our results for the freezing of water in the presence of electric fields.** Our experiments show that the homogenous nucleation of ice in drops of water cannot be influenced by external electric fields in air at ambient pressure; upon increasing the strength of the applied field, dielectric breakdown of air will occur before any changes in the rate of nucleation can be observed. Therefore, electric fields in clouds cannot induce the freezing of drops of supercooled water through homogenous nucleation of ice, nor can supercooled raindrops nucleate ice homogenously as they fall through the intense electric field near high-voltage power transmission lines.

In our setup we used large droplets (relative to the size of water molecules) and only a small fraction of water molecules in the droplets were present at the water/fluorocarbon-fluorosurfactant interface. While we expect that water at this interface would have different molecular structure than water in the bulk, the interface did not play a role in the nucleation of ice; we inferred from measurements of the rate of homogenous nucleation of ice in drops of supercooled water[8] that ice does not nucleate at the water-fluorocarbon interface in the absence of electric field. Since the interface was also subjected to external electric fields, our experiment provided a limit for the magnitude below which electric fields do not induce the nucleation of ice at the interface. We could not calculate accurately the magnitude of the electrical field at the interface because the dielectric constant of water at the interface is not known. For the limiting cases in which the dielectric constant is equal to 80 (bulk water) and 2 (surrounding fluid) the magnitude of the electric field is $1.6\times10^5$ V/m, respectively $3\times10^6$ V/m. These magnitudes are at least one order of magnitude smaller than the calculated field inside interfacial water in experiments that observed electrically-enhanced nucleation of ice[15,21].

## 5. Conclusions

We investigated the freezing of water in the presence of electric fields for three reasons. i) Previous experiments suggested that electrical phenomena (fields, currents, or discharges) can cause freezing, but the exact mechanism in which electric field might influence the nucleation of ice remains unclear. We therefore focused on the case of homogenous nucleation in external fields—a case that can be modeled theoretically and numerically. ii) We saw the opportunity to use a microscale system to apply electric fields using relatively small electrical potentials. While we succeeded in applying larger fields than in many other electrofreezing experiments, we were only partially successful in generating large fields inside the drops of water because of its large dielectric constant. iii) We could set up this experiment using a very reliable and ice nucleation instrument with high accuracy. We took advantage of these qualities to produce a useful quantitative conclusion: electrical fields with amplitudes up to $1.6\pm0.4\times10^5$ V/m change the rate of homogeneous nucleation of ice by less than a factor of 1.5.

Given that the electric fields that induce freezing in pure water in MD simulations ($\sim10^9$ V/m) is larger than the dielectric breakdown of water, it is important to investigate whether there are other ice nucleation mechanisms or models that might be sensitive to smaller electric fields. We used a thermodynamic model (a version of the classical nucleation theory that takes into account the electrostatic free energy) to arrive at an estimate suggesting that an enhancement of the ice nucleation rate might be observable for field intensities on the order of $10^7$ V/m. Larger intensities on the order of $10^8$ V/m might enhance the nucleation of ice through a mechanism that involves the nucleation of ferroelectric ice XI. Although we could not test these predictions using our setup, we also estimated that running a higher-sensitivity experiment with micron-sized drops might be sufficient to observe the effect of electric fields on the order of $10^6$ V/m on the nucleation of ice.

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**Supporting information available:** i) construction of microfluidic devices, ii) the derivation of equations 2, 3, 4, and 12 in the manuscript, iii) a description of the electrical circuit used in this work, iv) the results of three measurements of nucleation in the presence of electric fields oscillating frequencies of 3, 10 and 30 kHz, v) description and results of the numerical modeling of electric fields, and vi) the procedure used the sensitivity of measurements of the rate of nucleation. This information is available free of charge via the Internet at http://pubs.acs.org.

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**Figure 1.** Setup for the investigation of the effects of electric fields on the nucleation of ice in supercooled water. a) Experiment schematic. Small drops of water traveled in a microfluidic channel where they cooled until they froze. Two parallel plate electrodes produced uniform electric fields in the channel. b) The structure of the microfluidic device in the volume between electrodes, and the room-temperature electrical permittivities of its materials. Two dielectric spacers made from glass enhanced the electric fields inside drops and increased the dielectric strength of the device.

**Figure 1.**

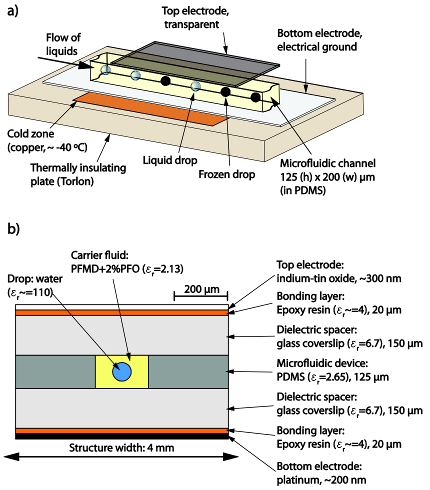

**Figure 2.** Homogeneous freezing of water in the presence of electric fields. The freezing positions of large numbers of drops were recorded while AC voltages of varying amplitude were applied on the electrodes. a) Freezing positions and voltage amplitudes during a full experiment. The distribution of freezing positions was not affected by electric fields when their amplitude was low, but drops froze closer to the beginning of the channel once a threshold amplitude was exceeded. b) Selection of the data showing the influence of the electric field for field ramps that cross or do not cross the threshold. The running average was calculated by averaging the freezing positions of 100 drops.

**Figure 2.**

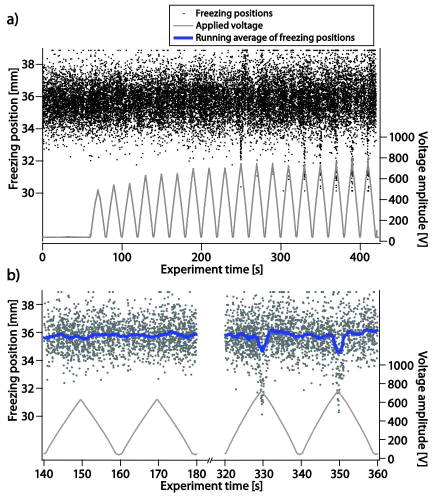

**Figure 3.** ‘Premature freezing’ mechanism due to electrostatic forces acting on drops. a) Typical distribution of temperatures inside the channel in the plane that is perpendicular to the direction of flow of drops. The dashed-line circle indicates the position of drops in the absence of electric fields. Hydrodynamic lift forces (b) center the drops in the channel, while electrostatic interactions (c) push drops towards the walls of the channel. By applying alternating fields and by incorporating dielectric layers, the wall-directed force becomes negligible; however we could not avoid the electrostatic deformation of drops (d).

**Figure 3.**