Electrofreezing effect and nucleation of ice crystals in free growth experiments

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Electrofreezing is an effect where an electrostatically charged surface in contact with a supercooled liquid or an externally applied electric field significantly enhances nucleation of the solid phase. The electrofreezing effect has been used as a tool to nucleate ice and heavy ice crystals in free-growth experiments at supercooling greater than 1.5 °C. In order to nucleate ice crystals at smaller supercooling, we describe a device which uses a combination of a thermoelectric cooler and the electrofreezing effect. This system has been used to nucleate crystals at a supercooling down to 0.1 °C, but this figure is only limited by the temperature stability of the growth medium. © *1998 American Institute of Physics.* [S0003-6951(98)03702-4]

Over the last few decades, many studies of the free growth of a crystal from its melt have taken place.[1–4] In those experiments a crystal is injected into a bulk of supercooled melt, usually through a capillary tube. Nucleation in a capillary is started by forced cooling outside the free-growth container.[5] The crystal advances within the capillary to its end, and then grows freely into the supercooled melt. The crystal growth in the capillary can be controlled by blocking the solid with a point heating coil before it reaches the free growth stage. In what follows we introduce an alternative very compact system to induce nucleation of ice in a capillary, based on the electrofreezing effect.

The phenomenon of electrofreezing has been known since 1861.[6] It concerns the enhancement of ice–nucleation by electrostatically charged surfaces or externally applied electric fields. A review of the history of the subject has been given by Pruppacher.[7] Some of the experimental evidence on ice comes from the nucleation of small droplets in air[8] or on polyethylene surfaces.[7] Other experiments relate to freezing in bulk,[9] primarily due to impurities with charged surfaces.[10] It is also known that electric fields have an effect on the melting temperature of helium crystals and have been used to nucleate helium crystals from superfluid.[11,12]

The theory behind electrofreezing is not fully understood and probably the mechanisms in polar and nonpolar materials are quite different. Proposed explanations include acoustic shock,[13] bubble formation,[9] and local dipole–field interaction.[10,14,15] In recent studies by Kusalik and Svishchev,[16,17] they observed, by using a molecular dynamic simulation, that the application of an electric field (of a few tenths of a volt per Ångstrom) could induce crystallization of small samples of supercooled water.

As a specific example of the electrofreezing effect, we found that the application of a brief high-voltage electric pulse to bulk supercooled water induces ice nucleation. The basic experimental system consists of two insulated 0.3 mm diameter copper wires with exposed terminations separated by 0.5 mm inserted into bulk supercooled water. An electric pulse is generated between the two wires, either with a piezoelectric pulse generator or by high-voltage capacitor discharge. The piezoelectric pulser generates an 10 μs pulse of height approximately 10 000 V. When the electric pulse is generated, the supercooled water freezes in the vicinity of the wire terminations, with a temperature-dependent efficiency. For example, at -3 °C one pulse was usually enough to induce nucleation, at -1.5 °C several pulses were required, while at -1 °C even repeated application of pulses was highly unlikely to generate nucleation at all. Shindoh *et al.*[18] have reported somewhat similar results; in their experiments they found that an electric spark was effective in nucleating ice crystals at -0.5 °C.

We also performed experiments to nucleate ice from supercooled water by capacitor discharges; for example, a discharge of a capacitor of 1 nF charged to 2000 V easily induced nucleation in water at -3 °C. In heavy water experiments, an upward shift of approximately 4 °C in the nucleation temperatures was detected, in agreement with the different melting temperatures of water (0 °C) and heavy water (3.8 °C).

The above experiments are qualitatively in agreement with the work of Kusalik and Svishchev,[16,17] since the electric field in the vicinity of the sharp edge of a wire with a curvature of about a micron, under an applied voltage of a few thousands volts, could be of the order of 0.1 V/Å.

We now show how the electrofreezing effect can be implemented as a method for nucleating a single crystal of ice in supercooled water and heavy water, even at very small supercoolings. For nucleation in strongly supercooled liquid (below -1.5 °C in water), the setup described above provides a very simple, compact and flexible way to produce a single ice crystal under controlled conditions. The wires terminate and nucleate the ice within a capillary tube[2] which has a tip sufficiently narrow that only the first crystal to propagate down the tube emerges into the supercooled bulk. The capillary has a 1 mm internal diameter and a 5–100 μm tip. However, nucleation in only slightly supercooled liquid (less then 1.5 °C supercooling) requires the electrofreezing itself to take place at lower temperature. This is attained by an additional cooling element, which is placed near the termination of the wires.

The nucleation device is shown in Fig. 1. It consists of a small ($4\times4\times2$ mm^3) Peltier (thermoelectric) cooler, a small

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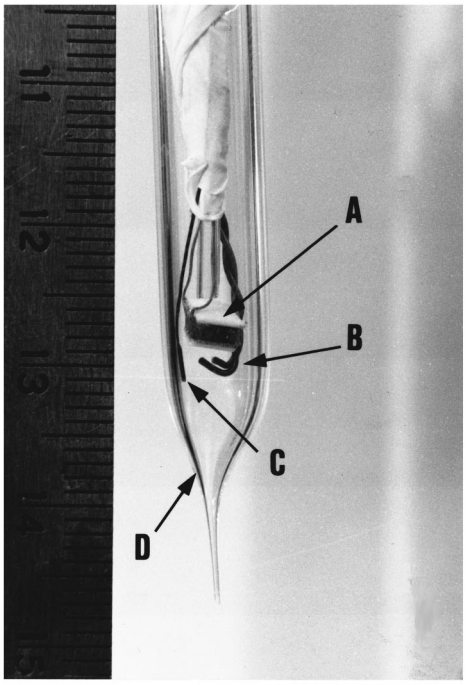

FIG. 1. The nucleation device. (A) Peltier cooler connected to a current supply which cools the vicinity of the electrofreezing wires. (B) Pair of wires connected to a high voltage pulse source. (C) Thermistor. (D) A glass tube with a narrowed tip. The tube with all the components is immersed in supercooled water.

thermistor and a pair of wires connected to a piezoelectric pulser. The thermoelectric cooler is presealed (apart from its free planar surfaces) with silicon glue (RTV) and thus made water resistant. This combination is situated within a glass tube which has a 6 mm internal diameter and a narrow tip. When an electric current flows through the Peltier cooler, its lower surface cools and the upper one heats. The termination of the high-voltage wires is within 1 mm of the cooler surface. For a 100–200 mA cooler current, a few seconds are required to lower the local temperature to the point where electrofreezing can be used efficiently (a few degrees below the surrounding temperature). In that brief duration, only small volumes (the Peltier surface area times a short decay length, or approximately 0.05 cm^3) are heated and cooled, so that the temperature of the bulk is affected negligibly by the cooler operation. In order to control the operation of the nucleation device, the small thermistor is placed near the nucleation wires. Immediately after nucleation, the temperature in the vicinity of the cold surface of the cooler, as a result of the latent heat release (see Fig. 2), jumps to the melting temperature. As soon as the temperature jump associated with nucleation is detected, the Peltier current supply is stopped. The crystal formed then continues to grow within the capillary tube. This device has been used to nucleate crystals at a supercooling of 0.1 °C, when the crystal took 8 h to grow from the nucleation point to the tip of the capillary. In principle, we see no lower limit to the degree of supercooling at which nucleation is possible. However, in order to grow a single crystal at very small supercooling one must take into account the time required for the crystal to emerge from the capillary and the long-term temperature stability of the system.

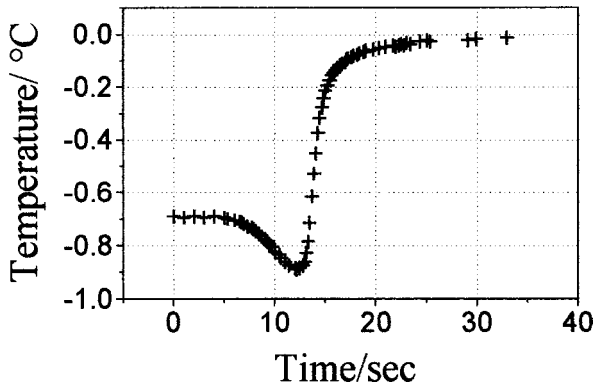

FIG. 2. The time dependence of the temperature in the vicinity of the nucleation device.

The advantages of the electrofreezing method described above are its simplicity, reliability, and compactness, which allow considerable flexibility in designing the capillary tube. In free-growth experiments the geometry and tip size of the tube are critical in determining the character of the emerging crystal. This includes the orientation of the crystal with respect to the vertical and the probability that it is a single crystal. The tip size necessary for a single crystal to emerge is temperature dependent; the lower the temperature, the narrower the tip size needed. For example, at 1 °C, supercooling the tip aperture must be smaller than 300 μm, while at 5 °C supercooling the aperture must be about 5 μm diameter. To control the orientation of the emerging crystal, the end of the capillary can be bent. This takes into account that ice crystals grow fastest normal to the hexagonal axis.[2] Thus if a bend of 60 ° is made near the end of the capillary, there is a high probability that the hexagonal axis of the emergent crystal will be normal to the plane containing the bent tube. Therefore, flexibility in the choice of capillaries and easy replacement of the tubes in the experimental setup is a considerable advantage.

This technique is being used in an interferometric study of the three-dimensional temperature field in the vicinity of dendritic ice crystals in free growth from supercooled water and heavy water.[19] The nucleation device may be used for various other applications, such as the study and characterization of the behavior of the electrofreezing effect itself.

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