Freezing Transition of Interfacial Water at Room Temperature under Electric Fields

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The freezing of liquid water into ice was studied inside a gap of nanometer spacing under the control of electric fields and gap distance. The interfacial water underwent a sudden, reversible phase transition to ice in electric fields of $10^6$ V m$^{-1}$ at room temperature. The critical field strength for the freezing transition was much weaker than that theoretically predicted for alignment of water dipoles and crystallization into polar cubic ice ($> 10^9$ V m$^{-1}$). This new type of freezing mechanism, occurring in weak electric fields and at room temperature, may have immediate implications for ice formation in diverse natural environments.

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The phase transition of liquid water into ice is a physical phenomenon of abiding scientific interest related to environmental, biological, and technological processes. It has long been conceived that external electric fields may affect the freezing of water, and experiments showed some evidence for this possibility [1–3]. For example, the rate of ice nucleation from vapor phase substantially increases from the normal growth rate in electric fields above $10^4$ V m$^{-1}$ [2]. Gavish et al. [3] carried out a careful study of ice nucleation at the hydrophobic faces of $\alpha$-amino acid single crystals, from which they concluded that the freezing temperature of water is altered by the electric fields within narrow cracks in the crystal in the absence of the substrate promotion effect. Molecular dynamics simulations [4,5] predict that electric fields strong ($> 10^9$ V m$^{-1}$) enough to align the dipoles of water molecules can crystallize liquid water into polar cubic ice. Such strong fields, however, are scarcely attainable in ordinary natural environments and also seem to be incompatible with the conditions of the above experimental observations [1–3]. A large gap between the available experimental evidence and the current theoretical explanation obviously indicates that further investigation is necessary for the freezing phenomena in electric fields. All the above works were carried out at temperatures below 0 °C. In this Letter we report the freezing of liquid water inside a gap of nanometer spacing under the control of external electric fields and gap distance. We observed that the interfacial water froze into ice at room temperature under a rather weak electric field, about $10^3$ times weaker than that required for dipole polarization of water. This new freezing mechanism may have significant implications for ice formation processes in diverse natural environments.

We examined the physical state of water present inside the junction gap of an electrochemical scanning tunneling microscope (STM), which is schematically shown in Fig. 1(a). The electrochemical cell consisted of working (WE), reference (RE), and counter-electrodes (CE), and a tip, all made of gold, immersed in a aqueous solution of NaClO$_4$ or pure water. A narrow gap filled with interfacial water was generated between the Au(111) crystal face of WE and a gold tip, which both had clean and electrochemically well-defined surfaces without specific adsorption of electrolytes under the electrode potentials applied. The electric field within the gap was provided by external bias voltage ($V_b$). The gap distance ($s$) was controlled with the precision of 0.2 Å by moving a tip attached to a piezo driver of known sensitivity with the tunneling current feedback loop disabled. In the experiment, we drove the tip slowly toward the surface of WE to the point of contact, while oscillating the tip back and forth in small amplitudes at high frequency. Along the approach of the tip, the tunneling current ($I_t$), the tunneling current modulation ($dI_t/dz$), and the voltage across the tunneling gap ($V_t$) were measured simultaneously. The tip approach speed was typically 5 nm s$^{-1}$, while the amplitude of oscillatory tip motions was typically ±0.5 Å at $5 \times 10^3$ Hz. Hence the $I_t$ and $dI_t/dz$ signals were well separable by the electronics. The temperature was held at 20 °C.

The first step of the study involved determination of the contact position between a tip and a Au(111) surface, which was necessary for establishing the absolute distance of junction gap ($s$). For this, we measured the variation of tunneling conductance $G_t = I_t/V_t$ along the tip approach toward a Au(111) surface. Both the tunneling current $I_t$ and the actual tunneling voltage $V_t$ were measured, because not only $I_t$ changes with $s$, but $V_t$ also is significantly reduced from the applied bias voltage $V_b$ at close proximity of tip and surface [6]. In the upper panel of Fig. 2, $G_t$ is drawn as a function of $s$ for $V_b = -8$ and $-100$ mV. The linearity of $\ln G_t$ vs $s$ plots is in conformity with the well-known tunneling equation [7], given by

$$G_t = G_0 \exp(-1.025\sqrt{\varphi s}),$$

where $G_0$ is the conductance at the tip-surface point contact, $\varphi$ is the apparent barrier height for tunneling in eV, and $s$ is in Å. When the tip touches the electrode surface, the $\ln G_t$ vs $s$ plot bends sharply upward due to electrical

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contact [6] as indicated by the arrows in Fig. 2. This contact point defines the zero gap distance. The values of contact conductance in both curves, $G_0 = 20 \mu S$ ($1 \text{ siemens} = 1 \text{ } \Omega^{-1}$), agree with $8–20 \mu S$ measured between Au tips and Au(111) surfaces in electrolyte solutions [8] and $20–40 \mu S$ between metal tips and Au(110) surfaces in vacuum [6], confirming that the contact position was correctly assigned. We examined the physical state of water within a junction gap by measuring the mechanical softness of the junction against the oscillatory tip motion in small amplitude. The softness of the interfacial medium within the gap is defined by $ds/dz$, where $dz$ is the change of tip position driven by a piezo actuator and $ds$ is the resulting change of actual gap distance [see Fig. 1(a)], $ds/dz$ is close to unity for a fluid interfacial medium that does not resist the mechanical movements of a tip. On the other hand, when the gap is filled with a stiff, solid material, the gap distance cannot change as much as the tip movement. Instead, the tip pressure is transmitted through the solid interface to cause some elastic deformation of the tip and substrate surfaces, thereby diminishing the value of $ds/dz$ toward zero. We obtain $ds/dz$ from independent measurements of $dI_t/dz$ and $dI_t/ds$ using distance-modulated tunneling spectroscopy [7,9], where $dI_t/dz$ is the modulated tunneling current signal with respect to the $z$ oscillation of tip, and $dI_t/ds$ is the differential tunneling current obtained by numerical differentiation from the $I_t-s$ measurement. $ds/dz$ is given by the ratio of two quantities:

$$\frac{ds}{dz} = \left(\frac{dI_t}{dS}\right)\left(\frac{ds}{dI_t}\right).$$

(2)

The basic idea of the measurement is similar to that of the surface force apparatus experiments [10–13], except that we detect the tunneling current to measure the gap distance change, whereas the latter measures the accompanying force change. The present apparatus offers the additional control of external electric fields, and the employed gold surface is chemically cleaner than the mica surface in the surface force measurements [10–13]. The results of $dI_t/dz$ and $dI_t/ds$ measurements are shown as a function of $s$ in the middle panels of Fig. 2. For $V_b = -8 \text{ mV}$, the $dI_t/dz$ curve varies in fair accordance with the $dI_t/ds$ curve. On the other hand, such synchronous variations of $dI_t/dz$ and $dI_t/ds$ break down at a short gap distance for $V_b = -100 \text{ mV}$. Most strikingly, the $dI_t/dz$ signal drops sharply to zero at $s = 7 \text{ Å}$. The reduction of $dI_t/dz$ occurs by at least 3 orders of magnitude (from 0.4 to a value less than 1/4096 in relative scale, which is beyond the sensitivity range of the instrument) and within shorter distance (<0.5 Å) and time (<10 ms) intervals than we are able to resolve. The $ds/dz$ curves in the lower panels of Fig. 2 show the mechanical properties of interfacial water obtained by Eq. (2). With the tip and WE at a far distance, $ds/dz$ is close to unity, indicating the presence of liquid water between them. For $V_b = -8 \text{ mV}$, $ds/dz$ decreases gradually with decreasing $s$, which reflects the fact that a thinner liquid layer within a gap transmits the tip force more efficiently to the surface [10]. In contrast, $ds/dz$ for $V_b = -100 \text{ mV}$ exhibits a sharp transition from unity to zero.

The abrupt transition of $ds/dz$ to zero at $s = 7 \text{ Å}$ suggests that the interfacial water suddenly transforms into a phase that is solid enough to resist the oscillating tip force. This ability to withstand the large tip pressure without

FIG. 1. (a) Schematic of the electrochemical STM setup and the distance-modulation tunneling spectroscopy. The Au(111) surface of WE is flame annealed, and the gold tip is electrochemically etched and coated with a varnish material except at its apex area of 1–10 $\mu \text{m}^2$. A bipotentiostat controls the electrode potentials within the range of values that avoid specific adsorption of electrolytes at the WE and tip surfaces. As we move the oscillating tip slowly toward the WE surface, we simultaneously measure $I_t$ and $dI_t/dz$ by a current amplifier, the latter signal being extracted via phase-sensitive detection. $V_t$ is measured by a high input-impedance (>1 TΩ) voltage follower (not shown). The labels $z$ and $s$ denote the tip apex position and the gap distance, respectively. The normal to Au(111) surface is defined as the $z$ direction. The approach speed of tip can be varied over the range of 0.5–10 nm s$^{-1}$, and the oscillation frequency, $5 \times 10^4$–$10^6$ Hz, which ensures that the speeds of the linear and oscillatory motions overlap in the limiting conditions. (b) A sketch of water molecules that form an ice structure of within the STM gap. The oxygen and hydrogen atoms are represented by white and black spheres, respectively. The Au(111) surface is negatively biased.
deformation is a fundamental signature of a solid phase, whereas a liquid by definition should show a fluid response. Sharpness of the transition suggests that it is a phase transition from liquid water into ice. The virtually zero value \( ds/dz \) after the freezing signifies that a rigid lattice structure is formed and its effective area is large; the area is estimated \[14\] to be much larger than that of contact made between a metal tip and a metal surface in vacuum. In addition, the phase transition occurs only when the gap distance falls down to a critical value, which is 7 Å in Fig. 2(b). Note that the sharp drop in \( ds/dz \) is not due to the clash of a tip onto the surface of a preformed ice film of the corresponding thickness, because even a tip clash onto a harder metal surface does not change \( ds/dz \) as sharply as observed here \[14\].

We further examined the dependence of the freezing transition on \( V_t \), and the results are summarized in Fig. 3, where the critical gap distance for the formation of ice film is plotted against \( V_t \). Sharp threshold voltages were observed. In 1.0 mM NaClO₄ solution, the interfacial water froze for \( V_t < -2.0 \) mV or \( V_t > 4.0 \) mV. For \(|V_t|\) of smaller magnitude, the freezing did not occur. In pure water, the interfacial water froze for \( V_t < -10 \) mV or \( V_t > 4.0 \) mV. The freezing transition occurred reversibly; upon raising (lowering) the voltage across a threshold, the water froze (melted) again. Asymmetry in the threshold voltages with respect to bias polarity may be due to different work function values of the tip and the surface. Another noticeable feature is that the critical gap distance appeared at 6–8 Å in NaClO₄ solution for large values of \( V_t \). This distance coincides with the thickness of two bilayers (BLs) of ice \[1\]. The critical gap distance increased in pure water up to \( \sim 14 \) Å.

The observed voltage dependence indicates that the freezing transition is driven by the electric fields. The critical electric field strength, which is the threshold voltage divided by the critical gap distance, is estimated to be \( V_t/s = (2-8) \times 10^6 \) V m\(^{-1}\) if we approximate the gap geometry as two parallel plates. Remarkably, this field strength is about \( 10^3 \) times weaker than that required for full alignment of water dipoles and crystallization into polar cubic ice, which is predicted to be \( >1 \times 10^9 \) V m\(^{-1}\) by molecular dynamics simulations \[4,5\]. Conversely, if a dipole-saturated ice film were formed, its internal film voltage would be \( 1/V_l = 16 \) V, which is far greater than the applied bias voltage. Thus, the present ice films may have a negligible degree of dipole polarization. It is noteworthy that water molecules do not directly adsorb on gold surfaces at room temperature and thus cannot be spontaneously aligned, according to electrochemical mea-
The phase transition of interfacial water is characterized by its occurrence in weak electric fields ($10^6 \text{ V m}^{-1}$), in confined geometry, and at room temperature. These features indicate that it may be a new type of freezing transition different from that driven by dipole alignment [4,5]. At present we can propose only a qualitative mechanistic model for this observation, hoping that it will stimulate more rigorous theoretical investigations. Although the electric field at the interface is not strong enough to fully reorient water dipoles, it seems to provide a small perturbation to the water molecules in confined geometry to stimulate the fluctuating hydrogen-bonding network to form an ordered structure. The electric field provides a torque to orient some hydrogen atoms toward the negatively charged electrode surface. This can help the oxygen atoms nearest to the electrode surface to be placed on the same plane, providing a higher probability to form stable lateral hydrogen-bonding networks. At the positively charged surface of a tip, the electric field similarly assists the hydrogen bonding between water molecules. The net electric polarization of the whole film can still be very small or negligible [see, for example, Fig. 1(b)]. The situation is analogous to an Ising model case, in which the lateral couplings (intermolecular hydrogen bonds in the present system) are so strong that a weak external field induces the alignment of the whole spin system.

The room-temperature freezing of interfacial water in moderate electric fields seems to have immediate implications on various ice formation processes in nature, particularly because the necessary field of $10^6 \text{ V m}^{-1}$ is more readily attainable than the strong field for the formation of polar ice. Comparable field strength may be found at the charged interfaces of proteins, clay, electrodes, and within the crevices of amino acid crystals [3] and mineral rocks, as well as in electrified thunderclouds [1]. Also, the phase transition of interfacial water might affect nanolithography with scanning probe tips, which is carried out under conditions similar to the present experiment.

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