THERMODYNAMICS OF ICE

Not obeying the rules

The physical properties of ice are governed by its tetrahedral network of hydrogen bonds and the ice rules that determine the distribution of the protons. Deviations from the tetrahedral structure and violations of these rules can lead to surprising phenomena, such as the ferroelectric state now reported for thin films of epitaxial ice.

Ivan A. Ryzhkin

When rules are broken, things sometimes get interesting. This certainly applies to ice, the structure of which is determined by the so-called ice rules, specifying how protons are distributed over the network of hydrogen bonds — intermolecular O–H bonds forming a tetrahedral structure.

The ice rules can be relatively easily illustrated with the most common variant of ice: hexagonal ice. In this form, oxygen ions (shown by large red spheres in Fig. 1a) form a rigid and ordered lattice similar to the carbon lattice in hexagonal diamond, also known as lonsdaleite. In hexagonal ice, protons (shown by small black spheres in Fig. 1a) are distributed over the hydrogen bonds in a semi-random way, but the overall pattern has to be such that there are two protons near each oxygen ion and one proton on each hydrogen bond.

Linus Pauling showed that the number of proton configurations within the tetrahedral hydrogen-bond network of ice satisfying the ice rules grows exponentially with system size and suggested that all such configurations have the same energy. This implies a non-zero entropy per water molecule at zero temperature and the absence of a phase transition of ice into any (including ferroelectric) particular proton configuration. Pauling’s suggestion is very unusual as it contradicts the generally accepted statement about zero entropy at zero temperature — the third law of thermodynamics — and its good agreement with numerous experiments remained a mystery for a long time.

Nowadays, the explanation for Pauling’s suggestion is connected with the concept of frustration, and can be understood in the following way. Let us designate the presence or absence of a proton near an oxygen ion by a pseudo-spin variable, taking the values +1 and –1, respectively (Fig. 1b). In a nearest-neighbour approximation, the Coulomb energy of neighbouring protons is at a minimum when the corresponding pseudo-spin variables have opposite signs. As is clear from Fig. 1b, it is impossible to simultaneously minimize all six inter-bond energies: two of them will always be non-optimal — a case of ‘frustration’.

It is this frustration that leads to the degeneracy of the ground state of the ice proton system. At first glance, it may be expected that the interaction between more distant neighbours should disrupt degeneration and lift the impossibility of a phase transition to an ordered (for example, ferroelectric) state. However, such a conclusion would be wrong: degeneracy persists even when taking into account the long-range nature of the physical properties of ice and the ice rules that determine the distribution of the protons. Deviations from the tetrahedral structure and violations of these rules can lead to surprising phenomena, such as the ferroelectric state now reported for thin films of epitaxial ice.

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Coulomb interaction\textsuperscript{5}. This effect is called the self-screening of the Coulomb interaction.

It is important to point out that the ice rules, the frustrated proton system of ice and the peculiar properties of ice are caused by the regular tetrahedral structure of the hydrogen-bond network of bulk ice. In constrained ice (thin films, nanocapillaries and nanocrystals) and in ice with a distorted hydrogen-bond structure, the ice rules can be violated, leading to drastically changed physical properties. The study of ice with a distorted tetrahedral structure and violated ice rules is a challenging problem, but the altered properties have numerous potential applications in medicine, biology and chemistry. For example, we know that a relatively strong violation of the ice rules at high pressure results in a proton metal (a conductive material where charge is transferred by protons rather than electrons)\textsuperscript{6}, that the interaction of water molecules with walls of nanocapillaries leads to quantum behaviour of the protons\textsuperscript{7}, and that the confinement of water molecules between two graphene sheets induces an ice layer with a square oxygen lattice\textsuperscript{8}.

Writing in Nature Physics, Sugimoto et al.\textsuperscript{9} now report a new important result on distorted ice. The authors studied thin epitaxial films of ice on a Pt substrate and discovered a phase transition to a ferroelectric state. The possibility of such a transition had been discussed for a long time, but all attempts to reveal it by direct measurements of the surface potential have been unsuccessful. A possible explanation for this is insufficient sensitivity of the direct method and/or strong screening of the electric polarization by the electrons of the metal substrate. To overcome these problems, Sugimoto and colleagues\textsuperscript{9} used a new method: phase-sensitive sum-frequency generation (SFG) spectroscopy with heterodyne detection. In this approach, visual and infrared light rays irradiated onto the sample generate a sum-frequency signal that has non-zero values for non-zero spontaneous polarization. Practically, information about the polarization can be extracted from the frequency dependence of the second-order nonlinear susceptibility. By means of this method, Sugimoto et al. found a spontaneous polarization (that is, a ferroelectric state) in an epitaxial film of ice at temperatures below 173 K. This demonstrates that SFG spectroscopy is accurate enough to detect electrical polarization in such systems in spite of the strong screening effect due to the electrons of the substrate, and raises hopes regarding the applicability of this method for studying ice/vapour and ice/water interfaces too. Such studies could provide a better understanding of the liquid-like layer that is responsible for so many of the surface properties of ice\textsuperscript{4}.

In addition, Sugimoto and colleagues\textsuperscript{9} found that the spontaneous polarization has a maximum value at the ice/metal interface and that it decreases with increasing distance from it. This is incompatible with the ice rules\textsuperscript{10}; the decrease of spontaneous polarization implies a high concentration of ice-rule violations and very high proton conductivity. High proton conductivity is very important for the design of new materials such as proton-conductive membranes for fuel cells.

Finally, it is worth emphasizing that the reported ferroelectric transition\textsuperscript{9} occurs at a rather high temperature, underlining the important role of the electrostatic interaction between protons and electrons of the metal substrate. This is relevant for our understanding of ice-adhesion processes, which, in turn, is necessary for the improved design of new hydrophobic materials with a low adhesion to ice.

In conclusion, the results reported by Sugimoto et al.\textsuperscript{9} significantly add to our understanding of the physical processes taking place at the interface between ice and a solid substrate, and provide new perspectives for the study of ice with strong violations of the ice rules.

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References


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