

Ferroelectric ice

Steven T. Bramwell

Water molecules are dipolar, and while tumbling in the liquid state can be partly aligned by an electric field (Fig. 1). In ice, however, although the molecules are essentially static, there is no overall alignment (Fig. 2). A question that has long fascinated researchers is whether there is a form of normal ice in which the molecular dipoles have a net orientation towards one direction. Recent papers^{1–3} have revived an old debate about whether such ‘ferroelectric’ ice exists, and if so, what implications its existence would have for our understanding of condensed matter. The groups concerned report definite experimental evidence that at least partial ferroelectric alignment can be induced in normal ice, either by interaction with a substrate^{1,2}, or by doping with impurities³.

The debate dates back to the 1920s and the development of X-ray diffraction. Using this technique, it was established that the oxygen atoms of normal hexagonal ice (ice I_h) form a regular crystal structure in which each oxygen atom is coordinated with respect to four others in a tetrahedral arrangement (Fig. 2). X-rays are insensitive to hydrogen, but in 1933 Bernal and Fowler⁴ argued that each hydrogen must lie along the oxygen–oxygen line of contact, but displaced from the mid-point so as to form one shorter covalent bond and one longer hydrogen bond. To ensure that the structure consists entirely of water molecules, two hydrogens must be positioned closer to, and two others further away from, each oxygen. These ‘ice rules’ allow for many structures, differing in their relative orientations of the water molecules. In most ice structures the orientation of water molecules follows no regular pattern (Fig. 2), but Bernal and Fowler proposed that ice I_h has the simplest ordered arrangement — a form of ferroelectric ice in which the molecules are, on average, aligned.

They were undoubtedly guided in their choice of structure by the third law of thermodynamics, which states that the entropy of a perfect crystal is zero at a temperature of absolute zero (0 K). Entropy is proportional to the logarithm of the number of arrangements or motions available to the system of molecules, and so zero entropy means one arrangement ($\log 1 = 0$). It was suspected at the time (and still is) that the third law arose from a much deeper truth: that for any substance one definite crystal structure is the most stable, and is adopted at 0 K provided that equilibrium is attained. So to postulate a unique structure for ice seemed very reasonable.

It did not, however, prove to be correct. In the same year that Bernal and Fowler’s paper



Figure 1 Polarized water. In a simple experiment, a stream of tap water is deviated by the static electricity of a plastic pen (which has previously been charged by rubbing on wool) because the water molecules are partially aligned in the electric field.

appeared, Giaque and Ashley⁵ definitively demonstrated that ice still had entropy at 0 K. They did this by carefully comparing the ‘spectroscopic’ entropy for gaseous water (calculated from spectroscopic data using a theoretical expression), with the ‘third law’ entropy (estimated from calorimetric measurements by summing the entropy from 0 K upwards, and assuming the third law). The two estimates should be identical, but the third law entropy was $0.82 \pm 0.05 \text{ cal K}^{-1} \text{ mol}^{-1}$ (about 2% of the total) too small. Giaque and Ashley suggested that rotation of the water molecules might account for the discrepancy, but Pauling “consistently objected to” this explanation⁶. In a landmark paper in 1935 (ref. 7) he argued that ice could adopt any one of the huge number of molecular arrangements compatible with the Bernal–Fowler ice rules. He calculated this number and found it to be $(1.5)^N$, where N is the number of molecules — which, for a 1 g crystal of ice, is a number with 6×10^{21} digits! This translates to a residual entropy of $0.81 \text{ cal K}^{-1} \text{ mol}^{-1}$, exactly the value found experimentally (within error). Pauling’s explanation was immediately accepted⁶; but it was not until the advent of neutron diffraction, which can easily locate hydrogen in the form of its isotope deuterium, that the structure was directly confirmed^{8,9}.

It is now accepted that below about 160 K the water molecules of hexagonal ice settle into a random arrangement (Fig. 2), which is always preferred to an aligned one because there are so many more random structures to choose from. But in reality would an aligned structure be more stable? It may be that once ice has adopted a random form at high temperature, relaxation into the preferred state at low temperature is immeasurably slow. An

early report¹⁰ found a maximum in the electrical response of slightly impure ice at 100 K, suggestive of a transition to a ferroelectric state, but this was later ascribed to slow relaxational effects¹¹.

The latest work^{1,2} provides experimental evidence of some net ferroelectric alignment in films of ice grown on ultra-clean platinum surfaces. Ice films deposited at temperatures below about 120 K are amorphous, whereas those deposited at higher temperatures are crystalline, with either the hexagonal structure of the bulk, or a closely related cubic modification to which the Bernal–Fowler ice rules and Pauling’s arguments also apply (see caption to Fig. 2). Iedema *et al.*¹ use potential difference measurements to demonstrate a net polarization in amorphous or cubic ice films of 10^3 – 10^5 monolayers, deposited between 40 and 150 K. They argue that interaction with the substrate during growth aligns a surface layer of molecules, which then influence the orientation of water molecules in the rest of the sample. Only a small proportion (0.2%) of the molecules are actually aligned, but this is sufficient to give the sample a sizeable polarization, and may in fact be relevant to the agglomeration of ice particles in interstellar space¹.

Su *et al.*² show that surface interactions can indeed make ice ferroelectric: ultra-thin

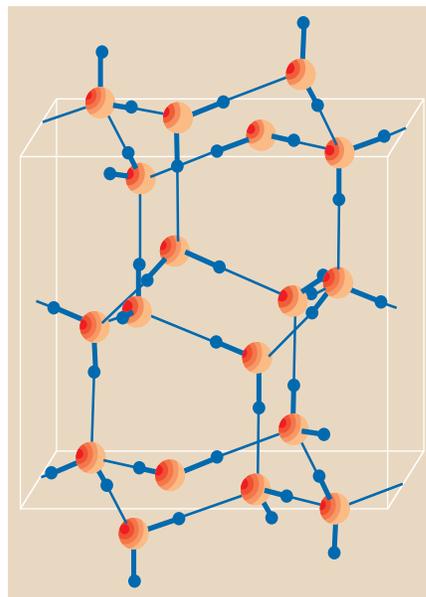


Figure 2 The structure of normal hexagonal ice I_h , showing the arrangement of oxygen atoms and one of the many possible random arrangements of hydrogen atoms (from ref. 9). The cubic modification of ice, I_c , has the same tetrahedral coordination of oxygen atoms, but the six-membered oxygen rings shown in the figure are repeated in a three-layer, rather than a two-layer, stacking sequence. Other high pressure phases of ice have different oxygen lattices and are called $II \dots X$. Three groups^{1–3} have demonstrated the existence of ferroelectric ice in which some of the dipolar water molecules are thought to be aligned.

hexagonal ice films (1–10 monolayers thick) have a net polarization that decays with distance from the substrate. They use ‘sum frequency generation’ to measure polarization in the sample — an ingenious method of overlapping a tunable-frequency infrared laser beam with a fixed-frequency visible laser beam. A vibrational spectrum at the summed frequency results only if the sample medium lacks inversion symmetry, a characteristic of aligned (ferroelectric) but not of random ice. The third approach to ferroelectric ice³ is to dope normal hexagonal ice with a catalytic quantity of hydroxide ions, a process that enhances the alignment (perhaps by enabling relaxation), without significantly disrupting the oxygen structure. Below 72 K this substance, known as ice XI, is suspected to be ferroelectric. Jackson *et al.*³ show that the neutron diffraction of ice XI is consistent with a ferroelectric arrangement, although the exact structure and degree of alignment are not unambiguously determined.

The experimental realization of ferroelectric ice would allow thermodynamic

measurements to establish whether nature really does prefer order at low temperature. However, as Iedema *et al.*¹ write “Over the years there have been many UFI citations (underidentified ferroelectric ices) in the literature”, and it is not yet clear whether one of these elusive objects — a fully hydrogen-ordered ice — has finally fallen to earth. □

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Telomeres

Capping off the ends

Carolyn Price

How many times have you had to deal with a loose end? Whether it be a stray end of hair, a frayed end of rope or the exposed end of a chromosome, ends can pose a problem. Reporting in *Cell*, Steve Schultz and co-workers¹ describe how the ciliate *Oxytricha nova* deals with the ends of its chromosomal DNA (telomeres). They have solved the crystal structure of the telomere end-binding protein (TEBP), which forms a protective cap over the DNA terminus. Their structure illustrates how the TEBP is exquisitely tailored to solve the chromosome-end problem², and also provides insights into how single-stranded (ss) DNA-binding proteins can recognize a particular sequence.

What is the chromosome-end problem? First, because DNA polymerase cannot copy the 5′ end of a linear DNA molecule, chromosome ends must be replicated by some other mechanism. In most eukaryotes this is done by the enzyme telomerase, which adds tandem repeats to the DNA terminus. A second problem is that exposed DNA ends are lethal to cells. Not only do they trigger a DNA-damage response and subsequent cell-cycle arrest but, at chromosome ends, they allow degradation and end-to-end fusion. To avoid such dire events, the chromosome ends exist as DNA–protein complexes³.

The *Oxytricha* TEBP was the first telomere protein to be isolated^{3,4}. It is unusually abundant because *Oxytricha* has around 5×10^7 minichromosomes, and TEBP is found at each of the 1×10^8 telomeres. *Oxytricha*

telomeres consist of exactly 36 nucleotides of G_4T_4 sequence. The first 16 nucleotides protrude to form a single-stranded 3′ $G_4T_4G_4T_4$ overhang, whereas the remainder is double stranded. The TEBP specifically recognizes the 3′ overhang and binds tightly to form a protective complex over the end of the telomeric DNA. The protein is well-suited for its function as a chromosome cap because it binds only to the 3′ terminus of single-stranded G_4T_4 DNA, and forms a very stable DNA–protein complex, protecting the DNA from nuclease digestion⁵. During DNA replication, the TEBP is thought to dissociate from the telomere to allow access to the replication machinery. On rebinding it may regulate the length of the telomere by displacing telomerase⁶.

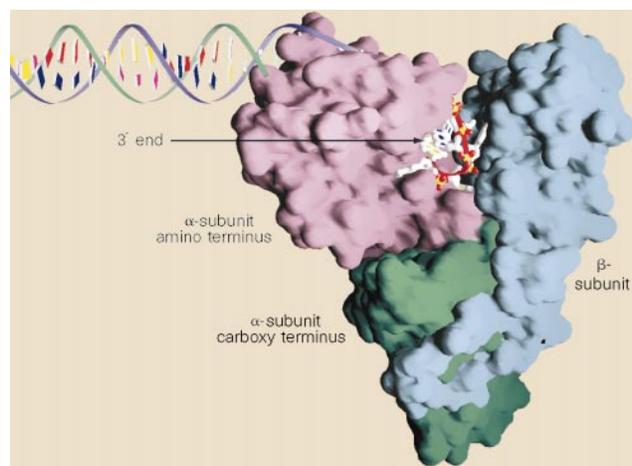


Figure 1 Crystal structure of the *Oxytricha* telomere end-binding protein (TEBP) bound to telomeric DNA. α - and β -subunits form a deep groove in which the single-stranded DNA sits. It seems that the DNA and protein must co-fold as part of the binding process, a new concept that could explain how ssDNA-binding proteins recognize a specific sequence.