Expanding to the limit

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Liquid water expands when heated — or cooled — away from a particular temperature that increases when the fluid is stretched. Experiments on water under extreme tension now enable tracking of this distinctive behaviour well into the negative-pressure domain. One of the most interesting manifestations of cohesive forces in matter is the ability of liquids to withstand negative pressures, or tension. When a liquid is under tension it pulls, rather than pushes, on confining surfaces such as the walls of a container. The tensile strength of liquids is appreciable: according to the venerable vander Waals equation[1], a liquid can withstand a maximum tension equal in magnitude to 27 times its critical pressure. Now, writing in *Nature Physics*, Mouna El Mekki Azouzi and colleagues[2] have mapped as-yet uncharted regions of the phase diagram for water — reporting on cavitation experiments that boast tensions higher than 1 kbar.

Liquids under tension are intrinsically metastable: at fixed temperature and volume, they will spontaneously undergo cavitation, forming a vapour cavity, which leads to coexisting vapour and liquid phases[3]. This metastability notwithstanding, the tensile strength of liquids is put to ingenious use in nature — as illustrated by the ascent of sap in plants, and by spore dispersal in ferns[5]. Fluid inclusions in minerals are another excellent example. Formed as a result of crystal growth, fracture and healing in the presence of a fluid medium, such inclusions are the basis[7] of the experiments performed by El Mekki Azouzi *et al.*, and can often persist under metastable conditions, including tension, over geological timescales. Research aimed at harnessing liquids under tension for practical purposes has produced intriguing ideas, including a 'synthetic tree'[8]. Such concepts have yet to be implemented in commercial applications.

As the fluid medium in most known or proposed applications of negative pressure in liquids, the physical properties of water and aqueous solutions under negative pressure are of obvious interest. Furthermore, water, the most ubiquitous of liquids, possesses distinctive properties that render it anomalous in comparison with most other liquids[3]. How negative pressures influence water's anomalies is certainly a question worth probing.

One of water's best-known peculiarities is its ability to expand when cooled. At

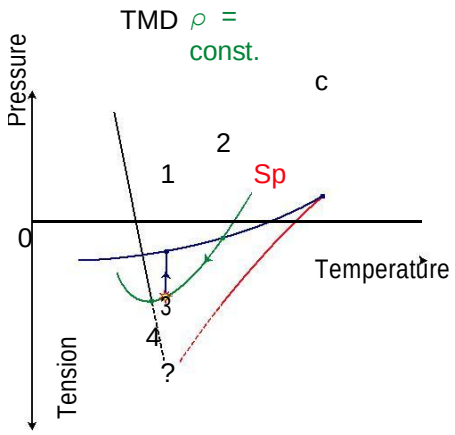

Figure 1: Schematic representation of a cavitation experiment. A quartz inclusion containing liquid water and a vapour bubble (1) is heated until the bubble disappears (2). The liquid-filled inclusion is cooled at constant density and cavitates at tensions of around 1.2 kbar (3). TMD is the locus of maximum densities, and (4) is the new point along this locus estimated by El Mekki Azouzi and colleagues[2]. Line (1, 2, c) is the boiling curve, terminating at the critical point c. Sp is the spinodal curve, where the liquid becomes unstable with respect to the vapour. The intersection, or lack thereof, of the spinodal and TMD lines under high tension has important implications for the global phase behaviour of metastable water. atmospheric pressure, liquid water's density reaches a maximum with respect to temperature at 4 °C, expanding both when heated above 4 °C (normal behaviour) and when cooled below this temperature (anomalous behaviour). The higher the pressure, the lower this temperature of maximum density (TMD).

An important question is therefore whether the TMD will continue to increase as water is stretched, or whether this trend will reverse and the TMD locus will eventually head in the direction of lower temperatures. Each of these scenarios has important implications for the thermodynamic properties of water over broad ranges of temperature and pressure[9]. El Mekki Azouzi *et al.*[2] studied water sealed in a quartz inclusion (Fig. 1). When cooled, their sample followed a path of constant density, leading to a pronounced decrease in pressure. The sample, thus placed under tension, eventually cavitated to relieve the tension. Subsequent heating caused the liquid to expand, once again filling the entire volume. By repeating this cycle many times, they were able to collect statistics on the fraction of runs that do not cavitate during cooling at a fixed rate down to a given temperature.

Their data was consistent with cavitation occurring by homogeneous nucleation — that is to say, the vapour cavity was formed within the bulk liquid, rather than on the quartz surface. Furthermore, the data could be quantitatively described by classical nucleation theory, after allowance was made for the dependence of water's surface tension on the radius of curvature of the liquid/ vapour interface. An interesting methodological advance introduced by El Mekki Azouzi and colleagues[2] is the statistical analysis of cavitation data obtained from a single inclusion. Used in conjunction with fundamental nucleation theory[10], this technique enabled the authors to extract valuable information about the free-energy barriers to cavitation, and the critical volume of the bubble that triggers macroscopic cavitation. El Mekki Azouzi and co-workers measured the temperature of their stretched water and used an equation of state to calculate the pressure. They estimated attaining maximum tensions of 1.2 kbar in these experiments, and located a point on the TMD line at highly negative pressure, close to 300 K and 0.92 g cm^{-3}. Tracing the evolution of the TMD locus to even higher tensions will require additional experiments using lower-density samples. The measurements of El Mekki Azouzi *et al.*[2], as well as those reported in earlier work by Angell and co-workers, represent the deepest systematic penetration into the negative-pressure region of water's phase diagram. The new point identified on the TMD locus[2] suggests that this line is on a collision course with the spinodal curve along which the liquid becomes unstable with respect to the vapour[3]. If such a collision is avoided, the necessary sharp turn in the direction of the TMD must occur at tensions even larger than those attained in this work.

Magnetic frustration in spin ice[1] leads to the apparent disintegration of local dipole moments into 'magnetic monopoles'[2] — freely moving quasiparticles carrying effective magnetic charge 1). Monopole hunters have unearthed compelling evidence for their existence in the principle spin-ice materials3–5, at least down to the 1 K temperature range. Now, writing in Nature Physics, Halle Revell and colleagues6 have presented results showing that the low-temperature magnetic relaxation dynamics of the spin-ice material dysprosium titanate can be successfully explained in terms of the monopole picture if extrinsic effects such as surfaces and impurities are taken into account. Existing on the pyrochlore lattice of corner-sharing tetrahedra, low-temperature spin-ice states satisfy a topological constraint involving two spins pointing into, and two out of, every tetrahedron. Such states provide an unusual kind of vacuum as spin-flip excitations that break these ice rules introduce pairs of freely moving topological defects (Fig. 1). The beauty of spin ice is that, thanks to long-range dipolar interactions, the topological charge is also magnetic charge, so the low-energy theory is that of a magnetic Coulomb gas in the grand canonical ensemble.

Magnetic relaxation measurements have previously been interpreted in terms of the diffusive dynamics of free monopole particles[3]. More microscopically, their movement has been tracked through the identification of classical 'Dirac strings'

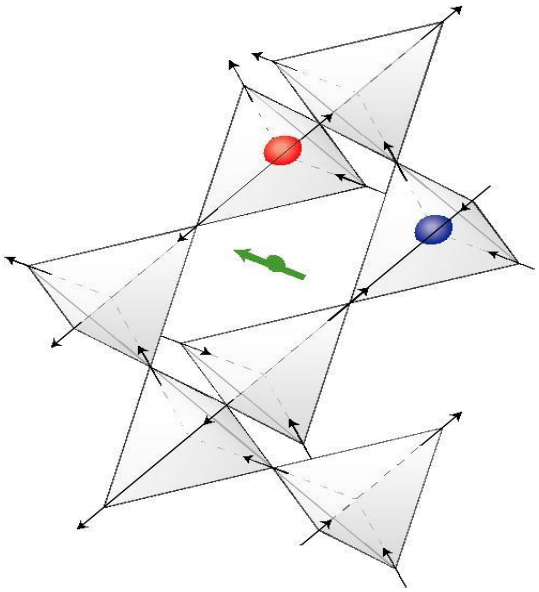

Figure 1 Monopoles in spin ice. Breaking the ice rules deposits a pole at the centre of a tetrahedron, which is free to move via subsequent low-energy spin flips. Stuffed impurities (green) and boundaries give extrinsic resistance to monopole movement. Over turned magnetic moments, which act as tracers of their random walk[4], or from the broadening of the 'pinch-point' features in neutron-scattering patterns characteristic of the low-energy configurations from which monopoles are excited[5]. 'Magnetricity'[9], the magnetic equivalent of electricity, therefore seems like an exciting possibility for spin ice, at least down to the 1 K temperature range.

However, experiments conducted at sub-kelvin temperatures have provided a sterner test for this idealized picture: the characteristic relaxation time increases at a faster rate[10,11] than that predicted by the simplest stochastic dynamics[3], and muon spin resonance experiments focusing on the conductivity of weak electrolytes have suffered controversy. These issues, together with factors such as incomplete screening of the dipole interactions[13], impurities, surfaces and other physical and chemical defects, makes one wonder if the monopole picture will survive the intense scrutiny of high-precision measurement at low temperature.

The results of Revell *et al.*[6] introduce a potential link between intermediate temperatures and this more exacting low- temperature world. In doing so they provide evidence that, just as in the electrical case, extrinsic resistance coming from impurities and boundaries is crucial in interpreting measurements of real systems. In crossing the 1 K threshold, Revell *et al.*[6] exposed three characteristics of the magnetic relaxation: a stretched exponential form, indicative of a hierarchy of decay times, an additional long-time tail, and mean decay time scaling as $\tau = \tau_0 \exp(E/k_B T)$, where $E/k_B \sim 9$ K, none of which appears in the simplest model for dynamics of the Coulomb gas. Through numerical simulation Revell *et al.*[6] showed that the stretched exponential decay can be generated by changing the oft-used periodic boundary.

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