LIQUID PHYSICS

Still waters run still deeper

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WATER expands upon freezing (one of only a handful of substances to do so), its liquid state has a temperature of maximum density (along with only SiO_2), uniquely when cold its viscosity decreases upon addition of pressure, and it has anomalously high melting and boiling points, specific heat and dielectric constant. Water and its solutions are the most far reaching of solvents. And, of course, it is the grand mediator of the biochemistry that allows us to live and so to contemplate its marvels. The challenge is to explain its macroscopic nature from the microscopic character of the single molecule. Rising to this challenge on page 324 of this issue[1], Poole *et al.* not only propose a new explanation for water's wonders, but deepen them too.

Qualitatively, the source of water's properties can be traced to two fundamental properties of the molecule: its ability to self associate through hydrogen bonding; and its space-filling tetrahedral geometry. Comparison with the hydrides of oxygen's neighbours in the periodic table readily demonstrates this. H_2S, H_2Se and H_2Te are tetrahedral but do not hydrogen bond well; they are relatively simple liquids with low freezing and boiling points. NH_3 and HF form good hydrogen bonds, but the associated structure in the liquid is not space filling. H_2O, however, can both accept and donate two protons, giving a total of four hydrogen bonds to form a tetrahedral arrangement which allows the condensed phases to fill space with a low-density, four-coordinated mesh of molecules. With this microscopic picture, many of the properties of water can be qualitatively explained. For instance, as the temperature falls, weak hydrogen bonds stabilize, so forcing the molecules apart into the fourfold arrangement. This is why ice is less dense than liquid water, and shows that the liquid temperature of maximum density is the anticipation of the solid phase.

So it was until the early 1970s, when some people began asking 'what if' one were to supercool water below its freezing point. In a classic paper, Speedy and Angell[2] showed that a wide variety of thermodynamic and transport properties of water all appear to diverge as the temperature is lowered into the supercooled regime (Fig. 1). Remarkably, the extrapolated point of divergence was at −45 °C for every parameter studied.

Explanations were proposed. All invoked large fluctuations in density and entropy caused by the self-associating nature of water. These fluctuations are the fundamental cause of water's special heat capacity, expansivity and compressibility. But why should they come about? One reasonably successful proposal, the stability-limit conjecture[3], was that supercooled water approaches a spinodal, the metastable limit line of second-order phase transitions beyond which no physically realizable states exist, and along which fluctuations and their concomitant susceptibilities diverge (Fig. 2). Furthermore, the conjecture proposed that the lower branch of the liquid–vapour spinodal (curve CS in Fig. 2) turns around to appear in the metastable region of the liquid–solid transition. Supercooling the liquid would bring one close to this spinodal, which would be at −45 °C for one atmosphere of pressure, so giving the divergent behaviour observed.

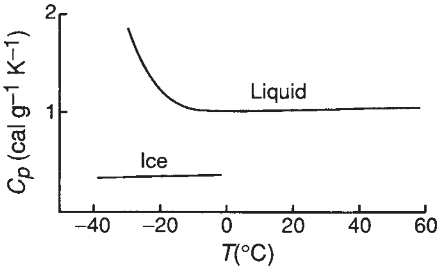

FIG. 1 Divergence in water. Specific-heat measurements at constant pressure as a function of temperature[5] reveal strong changes below −20 °C.

Poole *et al.* have simulated water on a computer. The advantage is that metastable regimes can be explored in depth without the real-world limitation of nucleation from the liquid to the solid state. The disadvantage is, of course, not knowing how well the computer represents real water. Poole *et al.* find that for computer water, at least, the 're-entrant' behaviour of the spinodal does not occur — the stability-limit conjecture does not hold. So what is the source of the anomalous supercooled behaviour? A

Nuclear age reaches half century

IMAGE UNAVAILABLE FOR COPYRIGHT REASONS

University of Chicago/Chicago Historical Society

ON 2 December, the nuclear world will have been with us for 50 years. Shortly before 3.30 p.m. on that day in 1942, Enrico Fermi instructed George Weil to withdraw a manual cadmium control rod a crucial 12 inches from their experimental nuclear pile, and watched the neutron flux steadily increase. Within minutes it became clear that the reactor had reached criticality — the nuclear fission reactions were self-sustaining. The moment was later recaptured in this painting by Gary Sheahan, showing Fermi (bald, to the rear, seated before the instrument panel), Weil (below, by the pile), the "suicide squad" (right corner) — delegated to pour cadmium sulphate solution over the pile if all went wrong — and 37 other members of the Manhattan Project. The construction of the pile, comprising 400 tons of graphite bricks and 50 tons of uranium metal and uranium oxide, had started just over two weeks earlier in the now renowned squash court beneath the west stands of the University of Chicago's football stadium. The pile completed, the experiments started on the morning of 2 December, with Weil withdrawing the control rod 6 inches at a time while the reactor characteristics were checked. The scientists returned after lunch, certain of reaching criticality, which they duly did. The reactor was allowed to run for half an hour before Fermi called a halt. Eugene Wigner (seated, facing us) produced a bottle of chianti which he had been concealing all day, and the experiment was toasted. Fermi later commented on the lack of drama that day: "no fuses burned, no lights flashed. But to us it meant that release of atomic energy on a large scale would be only a matter of time".

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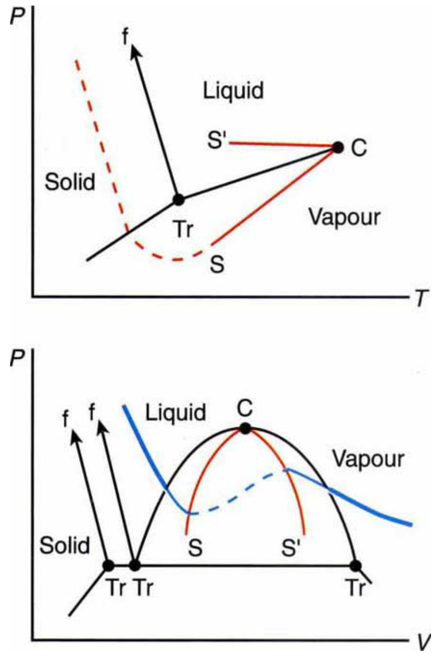

FIG. 2 The concept of a spinodal comes from the van der Waals theory of the liquid–vapour transition. This figure shows two perspectives of a van der Waals gas-phase diagram with a liquid–solid transition (f) added. Black rules mark phase boundaries. In the pressure–volume (*P–V*) perspective, the inverted parabola marks the liquid–vapour coexistence line; depressurizing the liquid brings the system down an isotherm (solid blue line) to the coexistence line, at which point the liquid will boil, and the curve continues on the right of the diagram. (C marks the critical point, where liquid turns to vapour continuously.) The fine blue line marks the metastable state. Points of zero slope for the isotherms correspond to infinite compressibility. These points are on the spinodal (red), the limit of stability (so that the broken blue line is inaccessible). In the pressure–temperature (*P–T*) perspective, these spinodal lines project above and below the liquid–vapour coexistence line. The stability-limit conjecture is that the spinodal, when extended to lower temperature, curves up (broken curve) around the triple point Tr, missing the solid–vapour coexistence curve, to run roughly parallel to the freezing line, f.

new second-order transition in the supercooled regime. A critical point between the two known phases of amorphous ice, the high- and low-density phases, would do the trick. Although, like the spinodal, this critical point could not be reached experimentally, its associated fluctuations would influence metastable states in its vicinity. (I have yet to hear of another material in which two solid phases could have a critical point — another plus for water. The low symmetry of the two amorphous phases allows this possibility.)

The stability-limit conjecture should not be passed off lightly. The conjecture does a remarkable job of correlating an extensive set of thermodynamic data. An attractive feature of the conjecture is in the interplay of the liquid temperature of maximum density (TMD) and the spinodal. As pressure is decreased, the TMD increases, inscribing a line on the phase diagram. One can prove a thermodynamic necessity that the TMD line, if it intersects the spinodal, will do so at a point where the spinodal has zero slope. It is known that the TMD line has negative slope in the pressure–temperature phase diagram and reasonable extrapolation implies an intersection with the spinodal. Hence the spinodal having a positive slope (curve CS, Fig. 2) at high temperature would pass through zero slope at the intersection and then presumably have a negative slope at lower temperature, causing it to be re-entrant.

Experimentally, Angell and coworkers[4] trapped water in microscopic inclusions in quartz. With proper thermal processing, they achieved extreme tension — that is, negative pressure — in the trapped water and mapped out the homogeneous nucleation curve for water near the spinodal curve. Although the re-entrant spinodal could not be observed directly, they did establish the validity of an equation of state extrapolated far from its data base, an equation that predicts a re-entrant spinodal so supporting the stability-limit conjecture. For now, perhaps, it's a matter of taste: do you prefer extrapolations or simulations?

Given the results of Poole *et al.*, what should be our physical picture of water? Certainly, self-association and low-density tetrahedral arrangements are still the key microscopic properties. But deep in the experimentally inaccessible supercooled regime, the two known phases of amorphous ice can coexist, just as liquid and vapour can coexist in equilibrium regimes. And this coexistence is terminated at a critical point where the two amorphous phases become identical, and where large fluctuations and the concomitant critical phenomena of divergent thermodynamic and transport properties occur. Although never attainable in a real experiment, this distant critical point would send out its influence into the attainable regimes, perturbing the thermodynamic landscape and creating a most remarkable liquid. ☐

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DAEDALUS

Hyperfine print

THE human eye is ill-adapted to sustained reading. Some of us have very bad close vision anyway, and we all get long-sighted as age advances. Reading glasses are sold in huge numbers. Daedalus has been looking at the problem from the other end. What sort of print, he wonders, would look sharp and clear when seen out of focus? In principle, the answer is simple. A black letter on a white background would need its outside edge to be blacker than black, while the paper just bordering the letter would have to be whiter than white. Defocused imaging would then reduce this heightened contrast back to normal. The letter would appear a consistent black on a consistent white background.

A whiter-than-white border presents no great problem. Many fluorescent pigments absorb invisible ultraviolet and reradiate its energy in the visible spectrum, thus seeming brighter than the incident light. A well-judged mixture of such fluorescent pigments should give a neutral hyper-white. Blacker-than-black seems a more serious challenge. But Daedalus points out that all conventional black pigments reflect a few per cent of light from their surface. A black pigment that reflected, say, 0.01 per cent of the light, would bear the same relationship to ordinary black ink as that black does to white paper.

This hyper-black ink will exploit the principle of the anechoic chamber. Such a chamber is lined with many protruding fingers of sound-damping material. Impinging sound is repeatedly reflected between them until it is totally absorbed. A surface anechoic to light would need much finer fibres, like a sort of small-scale black velvet (whose blackness derives from just this effect). DREADCO's pigment technologists are seeking an ink that dries in the form of innumerable protruding black microfibres — the ultimate in crackle-finish paints. It may not be too difficult; such surfaces are formed spontaneously by magnetic liquids in a field applied normal to the surface.

When perfected, DREADCO's 'Autofocus Print' will be wonderfully easy on the imperfect eye. Thanks to the hyper-black borders of the letters, and the hyper-white paper around them, it will seem sharp and clear to the most long-sighted reader. Normal readers will see it just as clearly. Focusing by automatic reflex on the most intelligible image, they will simply focus in front of or behind the paper. The amazing result will be standard black-on-white letters, apparently suspended in space. Daedalus intended his invention for the elderly and distinguished readership of scientific journals, but the ad-men may well take it over. David Jones