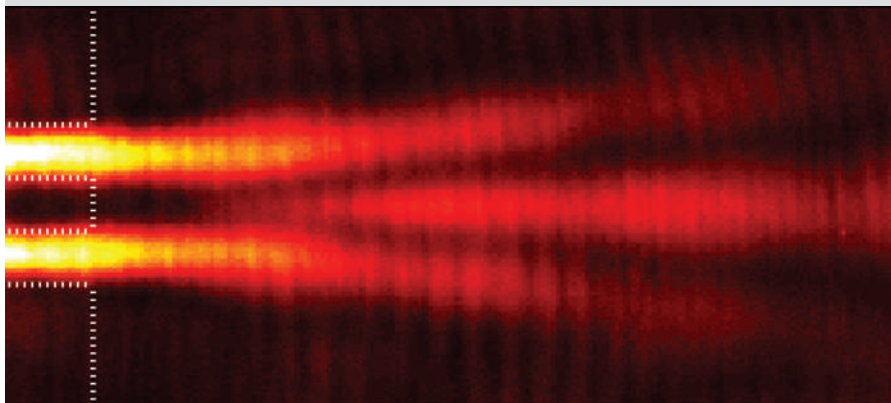


PLASMONICS

New first for double slits



The double-slit experiment has a long and distinguished history in physics and optics that can be traced back to the work of Thomas Young in 1805. This venerable experiment has now been performed with objects that are part-light, part-electron. On page 426 of this issue Rashid Zia and Mark Brongersma of Stanford University report that they have observed the diffraction and interference of surface plasmon polaritons (SPPs) — electromagnetic waves that are coupled to the free electrons in a metal — for the first time (*Nature Nanotech.* **2**, 426–429; 2007).

In its simplest form the double-slit experiment involves sending waves

through two slits in a screen and observing the interference pattern they create on another screen. This pattern is not a simple shadow of the two slits but a series of bright and dark fringes: if the waves from the two slits are in phase when they arrive at the second screen, constructive interference produces a bright fringe; however, if they are out of phase, they cancel each other out, resulting in a dark fringe.

Interference patterns can also be observed when particles are used instead of waves, thus demonstrating the well-known wave-particle duality of quantum mechanics. Over the

years these demonstrations have been performed with larger and larger particles, including atoms and molecules. Moreover, interference patterns have been observed when there was just one photon or particle in the apparatus at a given time, confirming that it is the two possible paths — rather than the photons or particles themselves — that actually interfere, as predicted by quantum theory.

Zia and Brongersma used electron-beam lithography to pattern a 48-nm-thick gold film on a glass surface so that it contained two 2- μm -wide slits that were 2 μm apart. The SPPs were excited on one side of the slits with a laser, and a photon scanning tunnelling microscope probed their intensity on the other side (see Fig. 1a on page 427). The image above shows the near-field intensity measured by the microscope as the SPPs travel from left to right through the slits and then diffract and interfere to form a three-peaked distribution (yellow corresponds to the highest intensities). The results agree with theory if it is assumed that SPPs are only supported by metal stripes with widths above a certain minimum value. The existence or otherwise of such a diffraction limit for SPPs has been the subject of controversy for a number of years.

Peter Rodgers

THERMODYNAMICS

Highs and lows in the density of water

Water contracts when it is cooled but, unlike other liquids, it then starts to expand at temperatures a few degrees above the melting point of ice. However, a new experimental study suggests that normal behaviour returns if the water is supercooled to low enough temperatures.

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Among the many unusual properties of water, the most famous is probably the fact that its density reaches a maximum a few degrees above

the melting point of ice. On cooling to 4 °C, water stops contracting and starts to expand, whereas most liquids contract continuously when they are cooled. This anomalous behaviour persists even when water is supercooled — that is, cooled below the temperature at which, under equilibrium conditions, it would form ice.

Ice crystals typically nucleate near defects, such as cracks or dust particles, but bulk samples of extremely clean

water can be supercooled to just below –31 °C at 1 atm (smaller, 2 μm droplets can be cooled to just below –40 °C). Below this temperature, known as the homogeneous nucleation temperature of water, T_h , it becomes nearly impossible to avoid crystallization and freezing occurs spectacularly fast, with ice needles shooting through the liquid faster than the eye can follow. Indeed, only high pressures or huge quenching rates ($>10^5$ degrees per

second) can prevent crystallization, and under these conditions, cold liquid water forms a glass.

The temperature domain between $-40\text{ }^{\circ}\text{C}$ and $-120\text{ }^{\circ}\text{C}$ (the temperature at which the glass formed by hyperquenching will crystallize when it is reheated) has therefore been called an experimental ‘no man’s land’¹ and has only been explored in simulations, which typically are carried out on timescales that are too short for nucleation to occur. Approaching T_h , the physical properties of water are found to be both extraordinary and provocative², and understanding them is widely held to be crucial to the understanding of water as a whole.

The ability to supercool water well below T_h by confining it in nanoscopic pores can therefore provide a useful loophole. Chung-Yuan Mou of the National Taiwan University in Taipei has refined the fabrication of silica nanotube assemblies, similar to those used as catalysts for cracking hydrocarbons, to reduce their diameters to 1.5 nm. Using these nanotubes as sample containers that suppress the freezing of water, Mou, Sow-Hsin Chen of the Massachusetts Institute of Technology and co-workers³ have been able to explore several properties of deeply supercooled water.

Building on this work, Mou, Chen, Peter Poole of St Francis Xavier University in Canada and co-workers report in the *Proceedings of the National Academy of Sciences USA* that they have taken the extra step needed to measure the density of supercooled liquid water. Using a clever neutron scattering method and analysis⁴, they find a minimum in the density of heavy water (D_2O) at $-63\text{ }^{\circ}\text{C}$, which was used in place of regular water because of its neutron scattering properties. Their finding adds another item to the long list of experimental anomalies associated with supercooled water, and also provides experimental evidence for the existence of a second critical point in liquid water.

Water exhibits a well-known critical point at 647 K, 22 atm and 0.322 g cm^{-3} where the liquid and gas phases become indistinguishable. The predicted second critical point in supercooled water describes the pressure and temperature where two distinct liquid phases — the high-density liquid and low-density liquid phases — become identical. On one side of the critical point, the high-density and low-density phases can coexist, and on the other side, there is a line of continuous transitions between the two (known as a Widom line).

Thermodynamic properties, such as the heat capacity and compressibility,

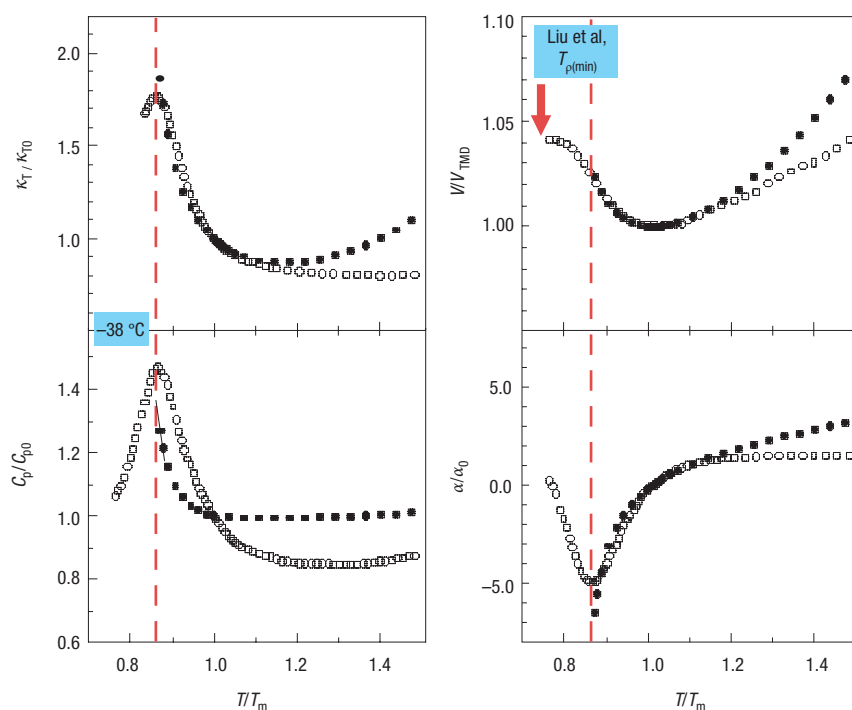


Figure 1 Comparison of the thermodynamic properties of supercooled liquid water and supercooled tellurium. The temperature scale is normalized to the respective melting points, T_m , of liquid water ($T_m = 0\text{ }^{\circ}\text{C}$, closed symbols) and tellurium ($449.5\text{ }^{\circ}\text{C}$, open symbols). The isothermal compressibility (top left), isobaric heat capacity (bottom left) and isothermal expansivity (bottom right) are scaled to their values at T_m ; the volume (top right) is scaled to its value at the volume minimum (density maximum). The dashed red lines coincide with the extrema in the compressibility, heat capacity and expansivity and an inflection point in the volume, and indicate the crossing of a Widom line ($-38\text{ }^{\circ}\text{C}$ for supercooled water). The scaled minimum density temperature determined by Liu *et al.* for nanoconfined water⁴ (indicated by the large red arrow) appears slightly below that of tellurium. Although water and tellurium are structurally different materials, the fact that their thermodynamic properties exhibit the same critical behaviour suggests that we may use similar models to describe them. Reproduced with permission from ref. 10. Copyright (2001) ACS.

are maximal along this line, and diverge at the critical point. Similarly, the density (or inverse of the volume per molecule) will exhibit an inflection point on crossing the Widom line, similar to the behaviour shown in the top right of Fig. 1. As Mou, Chen and co-workers point out, their observation of a density minimum is consistent with crossing the Widom line midway between the temperatures associated with the density minimum and maximum.

The prediction of a second critical point in water is based on molecular dynamics simulations, for example the ‘TIP5P’ and ‘ST2’ models for the water–water interaction potentials. These models also predict the density minimum and qualitative temperature dependence seen in the latest work^{5,6}. Where exactly the liquid–liquid critical point of bulk water lies, however, is a subject of controversy. There is broad agreement on the temperature (-60 to $-40\text{ }^{\circ}\text{C}$

(refs 2,5,7)), but not on the pressure. Opinions range from 3,900 atm for the TIP5P model, to 1,000 atm deduced from melting experiments involving metastable emulsified ice², down to 320 atm, given as a limiting high value consistent with critical point scaling requirements⁷, all the way to negative pressures (and the suggestion that the second critical point may not exist)⁸.

The agreement between the latest work and the simulations with the TIP5P potential provoke two classes of question. In the first, we examine to what extent the behaviour of water, when confined to a nanoscale volume, actually represents the properties that bulk water would exhibit if we could somehow prevent it from nucleating ice. This may smack of metaphysics, but it is of interest because one wants to know what the correct physical description of the bulk phase is, implied by the grossly anomalous behaviour. In the second class of question,

we explore other examples of liquids that exhibit density minima, and ask what their behaviour can tell us about water.

Regarding the first question, reports on the nuclear spin relaxation time for water in nanopores make it obvious that structuring of bulk water during cooling occurs much more rapidly than when it is confined in a nanoporous material⁹. This means that the critical pressure in bulk water must be less than the 3,900 atm from the TIP5P model, and hence of nanoconfined water. How much lower is the interesting question.

Turning to the second area of questioning, we can compare the observation of a density minimum in nanoconfined water with similar effects in two other liquids: BeF₂, which is structurally similar to water, and supercooled liquid tellurium, which is not.

BeF₂ is a tetrahedral network liquid like water, which also exhibits a barely detectable glass transition. BeF₂ expands weakly in its liquid state — at least at temperatures that can be observed in the laboratory — and behaves similarly to the confined water below its density minimum that Mou, Chen and co-workers studied. But if computer simulations are to be believed, BeF₂ also has a density minimum just beyond the highest experimentally accessible temperature,

a density maximum at a somewhat higher temperature, and a heat capacity maximum between the two (ref. 10 and P. H. Poole, private communication). The remarkable difference between BeF₂ and water, though, is that the density extrema in BeF₂ occur not in the supercooled liquid state, but far above the melting point! Exactly what it is that determines the positions in temperature relative to melting remains a challenge for future workers.

Liquid tellurium, on the other hand, has a structure quite different from that of water, yet the thermodynamic properties of these two liquids in the supercooled state are surprisingly similar¹¹ (see Fig. 1). Indeed, when scaled by the temperatures of maximum density or melting point, the thermodynamic properties for these two materials fall on top of one another. A nearby critical point, as in water, could account for the similar behaviour.


Tellurium is not known as a network liquid. It can, however, be characterized by two possible length scales: the Te–Te covalent bond and a second longer distance. A two-length scale model (the Jagla model) has also recently been used to explore the second critical point behaviour similar to that found in water¹². The comparison between the continuous

compressibility, heat capacity and expansivity of tellurium in Fig. 1 (without resorting to nanoconfinement) and now for water in nanoconfinement⁴ suggests that the continuous behaviour of water in nanoconfinement could be supplanted by more extreme behaviour in the case of bulk water at ambient pressure.

The problem of understanding water will no doubt remain a challenge for some time but new insights and stimulations like those provided by the work of Mou, Chen and co-workers will help keep the problem alive, and our understanding of it, improving.

References

1. Stanley, H. E. & DeBenedetti, P. G. *Phys. Today* **56**, 40–46 (June 2003).
2. Mishima, O. & Stanley, H. E. *Nature* **396**, 329–335 (1998).
3. Faraone, A., Liu, L., Mou, C.-Y., Yen C.-W. & Chen, S.-H. *J. Chem. Phys.* **121**, 10843 (2004).
4. Liu, D. *et al. Proc. Natl Acad. Sci. USA* **104**, 9570–9574 (2007).
5. Paschek, D. *Phys. Rev. Lett.* **94**, 217802 (2005).
6. Poole, P.H., Saika-Voivod, I. & Sciortino, F. *J. Phys. Condens. Mat.* **17**, L431–L437 (2005).
7. Fuentesvilla, D. A. & Anisimov, M. A. *Phys. Rev. Lett.* **97**, 195702 (2006).
8. Speedy, R. J. *J. Phys. Chem.* **86**, 982 (1982).
9. Rault, J., Neffati, R. & Judenstein, P. *Eur. Phys. J. B* **36**, 627–637 (2003).
10. Hemmati, M., Moynihan, C. T. & Angell, C. A. *J. Phys. Chem. B* **115**, 6663–6671 (2001).
11. Kanno, H., Yokoyama, H. & Yoshimura, Y. *J. Phys. Chem. B* **105**, 2019 (2001).
12. Xu, L., Ehrenberg, I., Buldyrev, S. V. & Stanley, H. E. *J. Phys. Condens. Mat.* **18**, S2239–S2246 (2006).



The image shows the cover of the journal *Nature Nanotechnology*. The cover features a vibrant, multi-colored molecular structure (likely a nanocrystal) against a dark background. The text on the cover includes the journal title "nature nanotechnology", the date "10 JULY 2007", the website "www.nature.com/naturenanotechnology", and several article highlights: "NANOMETROLOGY: Going beyond Moore's law", "DRUG DELIVERY: Nanotubes hit the target", and "NANOMATERIALS: Self-assembled ceramics". At the bottom, it says "Cutting edge for nanocrystals".

News & Views contributions

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