Supercooled water goes supercritical

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figure on page 17, largely jibed with the predictions of stellar evolution models: At its heart, the star is a dense sphere of carbon and oxygen; with increasing radial distance from the center, oxygen levels ramp downward, helium levels ramp up, and carbon levels rise and fall.

It's in the particulars of that profile that the asteroseismology result and stellar evolution theory disagree. In the asteroseismic model, the star's center is more than 85% oxygen—some 15% more than predicted by leading stellar evolution models. The oxygen-to-carbon ratio, averaged over the entire star, is nearly four to one; stellar evolution models predict a two-to-one ratio.

The overabundance of oxygen suggests that somehow the chain of reactions that powered the star during its helium-burning phase progressed further than stellar evolution theory predicts—either because the theory underestimates the carbon-to-oxygen reaction rate or because mixing processes are unexpectedly efficient at replenishing the burning core with fresh helium.

"Stellar evolution theory has to be missing something," says Conny Aerts of the University of Leuven in Belgium. "The theory that for the past 30 years we thought was great is actually not good enough."

An improved understanding of white-dwarf structure could help refine methods for estimating the stars' ages and help astronomers more accurately interpret the light curves of type 1a supernovae, the violent explosions that occur when a matter-accreting white dwarf surpasses a critical mass. But how much can one infer from a single study of a single star?

The question may soon be rendered moot. *Kepler*'s follow-up mission, *K2*, initiated in 2014, is finding pulsating white dwarfs at a furious pace. "*K2* is a gold mine," says Giammichele. "There are already something like 60 white dwarfs that I can analyze. I'm not saying every one of them will give results, but a good portion of them, yes, they're cooperating."

Ashley G. Smart

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Supercooled water goes supercritical

X-ray scattering experiments point the way to water's elusive second critical point.

There's more to water's phase diagram than the simple solid, liquid, and gas of everyday experience. The low-temperature, high-pressure portion of the diagram, for example, contains a spiderweb of solid–solid phase transitions between various stable crystalline structures. And a 25-year-old theory predicts that deep in the supercooled regime, liquid water, too, undergoes a phase transition between two structurally distinct forms. Experiments have hinted at that liquid–liquid phase transition (see, for example, PHYSICS TODAY, December 2013, page 16). But it's never been directly observed.

Now Stockholm University's Anders Nilsson and his colleagues have produced some of the strongest evidence yet in support of the two-liquid theory.[1] The researchers scattered femtosecond x-ray pulses off a stream of water microdroplets that had been evaporatively cooled under vacuum to as low as 227.7 K, or −45.4 °C. From different portions of the scattering curves, they extracted four thermodynamic and correlational quantities. All four peaked at similar temperatures, just above 229 K.

Those previously unseen peaks don't mark the phase transition itself—that would have been characterized by a divergence in the measured quantities, not a simple maximum. But they are a sign of a so-called Widom line, a hallmark of a supercritical fluid. The results support a phase diagram like figure 1, in which the liquid–liquid phase-transition line exists only at high pressures—hundreds of atmospheres—and terminates at a critical point similar to the one that terminates the line separating water's liquid and gaseous phases; the Widom line is an extension of the phase boundary past the critical point and into the supercritical regime. At the same time, the new experiment argues against competing theories in which the phase-transition line either continues all the way to zero pressure or doesn't exist at all.

Into no-man's-land

Experimenters have long known that it's possible to maintain water in its liquid state below 273 K. Freezing at that tem-

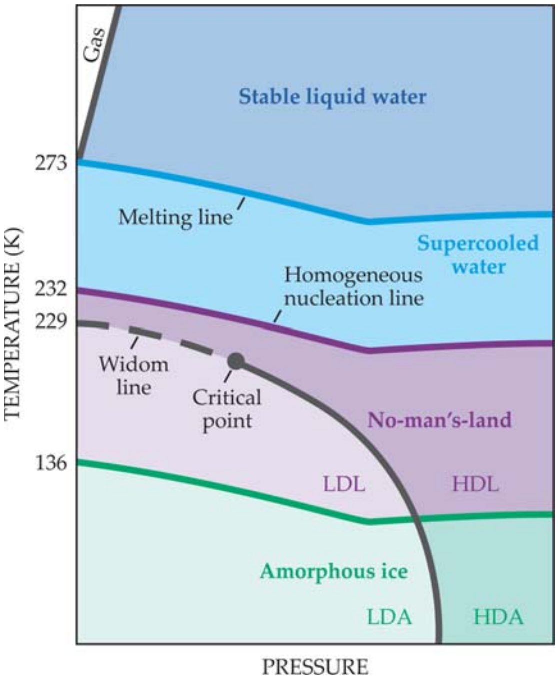

FIGURE 1. A PHASE DIAGRAM of water and its metastable states. Deep in the supercooled regime, water is hypothesized to exist in two distinct liquid phases: high-density liquid (HDL) and low-density liquid (LDL), in analogy to the well-known high-density amorphous (HDA) and low-density amorphous (LDA) ices. New experiments suggest that the liquid–liquid phase boundary ends at a critical point. The Widom line that extends past the critical point is characterized by maxima in the correlation length and several thermodynamic response functions.

perature proceeds by heterogeneous nucleation: The water molecules rely on small impurities—a dust grain or tiny gas bubble, say—to help them over the free-energy barrier that blocks crystallization. Clear the water of those impurities, and heterogeneous nucleation can't happen.

But at a lower temperature, 232 K at atmospheric pressure, the random molecular motion of the water itself is enough to surmount the barrier to crystallization, and even the purest supercooled water, although still technically metastable, inevitably freezes by homogeneous nucleation in just tens of microseconds. For that reason, the swath of the phase diagram between 232 K and water's glass transition temperature of 136 K has been ominously dubbed "no-man's-land."

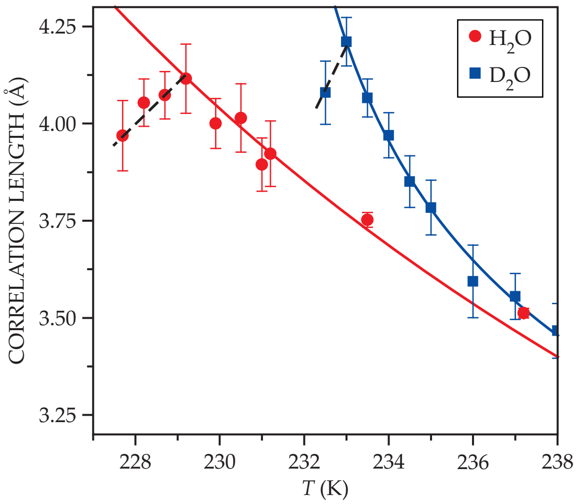

FIGURE 2. CORRELATION LENGTHS, extracted from x-ray scattering data, of supercooled water and deuterated water. The solid red and blue curves are power-law fits of the higher-temperature data; the dashed lines are linear fits to the lower-temperature data. (Adapted from ref. 1.)

Decades of work on the easily reachable part of the supercooled regime have yielded tantalizing results.[2] As water's temperature falls, quantities such as the isothermal compressibility and heat capacity start to skyrocket, and they appear to be heading toward a divergence—a sign of a phase transition or perhaps some other singularity. Frustratingly, however, whatever it is lay just over the homogeneous nucleation line—in no-man's-land.

But no-man's-land isn't inaccessible. A quick enough experiment could, at least in principle, cool water below 232 K and make the necessary measurements in the microseconds before the sample froze. Several groups have been competing in recent years to push the understanding of supercooled water into the heretofore unexplored regime. (See, for example, PHYSICS TODAY, February 2017, page 18.)

Widom's peaks

Nilsson and colleagues settled on x-ray scattering as their technique of choice in 2011. The experiment is elegant in its simplicity. A dispenser shoots a thin jet of water into a vacuum chamber, where it spontaneously breaks up into a stream of equal-sized droplets. As the droplets hurtle toward their intersection with the pulsed x-ray beam, they cool by evaporation. By adjusting the distance between the dispenser and the beam, the researchers can study droplets of different temperatures.

X-ray scattering gives access not only to a measure of a material's local molecular order called the correlation length, whose divergence is the defining feature of a second-order phase transition, but also to the isothermal compressibility and other thermodynamic response functions. Because each of those quantities is extracted from a different part of the scattering curve as a function of scattering angle, they can be regarded almost as independent measurements.

The group's previous efforts with the technique were fraught with experimental difficulties.[3] The water droplets and focused x-ray beam were similar in size, so an x-ray pulse that didn't quite hit the center of its droplet scattered off the droplet's edge instead, giving unusable data. Worse, the x-ray detector had a limited dynamic range, so although the prominent wide-angle x-ray scattering (WAXS) ring was well captured, the small-angle x-ray scattering (SAXS) region was too faint to see—and that's where most of the valuable information is contained.

In the new work, their fourth attempt, the researchers have corrected those problems. They cut down on edge scattering by increasing the droplet size, even though larger droplets cool more slowly and cut down on the accessible temperature regime. And they used a newly developed detector capable of simultaneously recording the WAXS and SAXS regions.

The results are clear. As shown in figure 2, the correlation length of H_2O doesn't diverge; instead, it peaks at a finite value near 229 K, then decreases at lower temperatures. The other quantities Nilsson and colleagues measured did the same. The Widom line is defined as the locus of local maxima in the correlation length, and it's also associated with maxima in other thermodynamic response functions.

To strengthen their case, the researchers repeated their measurements with deuterated water. Again they found four nearly coincident peaks, this time at 233 K instead of 229 K. The temperature difference may be a clue to the origin of some of water's odd behavior. Because they're so light, hydrogen nuclei experience much stronger quantum effects than deuterium nuclei do. Whenever a protonated molecule and its deuterated analogue behave significantly differently—as they do here with the 4 K gap between the Widom lines—it's a sign that those quantum effects are somehow in play.

The first observation of the Widom line in supercooled water strongly suggests that a critical point and a phase transition are lurking at higher pressures in no-man's-land. But a real smoking gun would be the direct observation of the liquid–liquid phase transition. Nilsson and colleagues can't achieve that with their current evaporative-cooling method, which is effective only in vacuum. But they have some ideas—confidential for now—about other ways they might follow the Widom line toward the critical point. They'll try the experiments later this year.

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